A high-resolution shallow marine record of the Toarcian (Early Jurassic) Oceanic Anoxic Event from the East Midlands Shelf, UK

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A record of the Toarcian (Early Jurassic) Oceanic Anoxic Event from the East Midlands Shelf, Leicestershire

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Abstract

The global deposition of organic rich-mudrocks, a mass extinction, and marked changes in C-, Sr-, O-, Os-, and Mo-isotopes during the early Toarcian indicates a period of extreme environmental change and an oceanic anoxic event. This study investigates the environmental and biotic changes that occurred during the event using sediments that were deposited on the East Midlands Shelf, UK. In particular, we present a new graphic log, geochemical data ($\delta^{13}C_{org}$, total organic carbon, $CaCO_3$, total sulphur and nitrogen), and benthic macroinvertebrate ranges from North Quarry, Holwell, Leicestershire, UK. Similar to other lower Toarcian sections in the world a ~-5‰ $\delta^{13}C_{org}$ excursion occurs.

Comparison of geochemical data and ammonite ranges between the Yorkshire and Leicestershire successions shows that there is a hiatus across the *semicelatum*/*exaratum* subzone boundary in Leicestershire. The *exaratum* Subzone, at Holwell similar to Yorkshire, is dominated by three bivalves, but

their ranges differ significantly between the successions. A diverse micromorphic fauna occurs within the upper *exaratum* Subzone at Holwell and other UK sections. The biotic data indicate that conditions on the East Midlands Shelf were shallower and less inhospitable than in the Cleveland Basin, and may have provided a refuge for some fauna.

Supplementary material: geochemical data, and crossplot showing the stratigraphic correlation of the Leicestershire and Yorkshire sections presented in this study are available at www.geolsoc.org.uk/SUP00000.

Introduction

Geochemical and stratigraphical studies have shown that the early Toarcian (Early Jurassic) was a period of considerable environmental change (e.g. Cohen *et al.* 2007, Hesselbo *et al*. 2007) and that it coincided with the mass extinction of both marine and terrestrial biota (Benton 1995; Little & Benton 1995; Aberhan & Fursich 1996; Hori 1997; Gahr 2005; Bambach 2006; Zakharov *et al.* 2006; Caswell *et al.* 2009). The event is associated with: widespread marine carbon burial (Jenkyns *et al.* 2002; Fig. 1a), and a large negative carbon isotope excursion in marine organic matter ($\delta^{13}C_{org}$) and marine carbonates ($\delta^{13}C_{carb}$) in successions deposited in both the major oceans at that time (Fig. 1a; Tethys Ocean: Hollander *et al.* 1991; Jiménez *et al.* 1996; Hesselbo *et al.* 2000; Jenkyns *et al.* 2001; Röhl *et al.* 2001; Kemp *et al.* 2005; van Breugel *et al.* 2006; Cohen *et al.* 2007; Hesselbo *et al.* 2007; Suan *et al.* 2008; Hermoso *et al.* 2009; Hesselbo & Pienkowski, in press; and Pacific Ocean: Gröcke *et al.* 2003, Gröcke pers. comm., Carathers *et al.* 2010, and Al-Suwaidi *et al.* 2008). Additionally, the negative carbon isotope excursion has been observed within fossilised wood (Hesselbo *et al.* 2000, 2007; McElwain *et al.* 2005) indicating that the event also influenced the atmospheric system. The carbon isotope excursion is synchronous with evidence for higher seawater surface temperatures (7-13°C, McArthur *et al.* 2000; Bailey *et al.* 2003; Gomez *et al.* 2008; Suan *et al.* 2008), enhanced rates of global chemical weathering (Cohen *et al.* 2004), and widespread marine anoxia (Pearce *et al*. 2008).

The event was interpreted to represent an oceanic anoxic event (OAE) by Jenkyns (1988) based on the widespread deposition of organic-rich lithologies (Fig. 1a-b). Geochemical proxy evidence has since shown that the areal extent of marine anoxia increased globally at this time (Pearce *et al.* 2008). The presence of biomarkers from phototrophic anoxygenic marine bacteria during the carbon isotope excursion shows that marine euxinia locally extended into the euphotic zone (Schouten *et al.* 2000; Pancost *et al.* 2002; Schwark & Frimmel 2004; van Breugel *et al.* 2006).

A high-resolution study of the succession deposited in the Cleveland Basin (Fig. 1b) and now exposed in Yorkshire, UK has shown that the negative $\delta^{13}C_{org}$ excursion occurs in four abrupt shifts termed 'A' to 'D' (Kemp *et al.* 2005; Cohen *et al.* 2007). These abrupt shifts have since been reproduced in the Luisitanian Basin, Portugal (Hesselbo *et al.* 2007), and the Paris Basin (Fig. 1b; Hermoso *et al.* 2009).

Lower Toarcian mudrocks are poorly exposed in a number of places in Leicestershire, UK including: a disused railway cutting at Tilton [SK762055] and preserved quarry faces at Harston [SK843305], Browns Hill Quarry [SK472234], Holwell and North Quarry [SK740236], Holwell (Figs 1c and 2). The best preserved faces are those near Holwell. The North Quarry contains a more complete and less weathered succession of the Whitby Mudstone Formation than Browns Hill Quarry and so was chosen for this high-resolution study. The quarries at Holwell are both Regionally Important Geological Sites and are part of a geological SSSI and nature reserve they are managed by the Leicestershire and Rutland Wildlife Trust.

During the Jurassic, Leicestershire was situated on the East Midlands Shelf (Fig. 1b), which covers ~60 000 km^2, and formed a relatively high area on the edge of the London Brabant massif (Fig. 1b). The Cleveland Basin was to the north and the Wessex Basin to the south (Fig. 1b). The Toarcian succession on the East Midlands Shelf represents fairly shallow marine conditions ranging from just below storm-wave base to relatively shallow water depths which facilitated the formation of both iron ooids and occasional carbonate ooids. Ooids of carbonate and iron composition occur within the Marlstone Rock Bed and the *falciferum* Zone at Holwell (Clements pers. comm.; Fig 2), Tilton (Howarth 1980), Harston (Horton *et al*. 1980), Northampton (Howarth 1992), Nettleton, Lincolnshire (Bradshaw & Penney 1982) and twelve borehole sections across the Midlands (Horton *et al*. 1980). Iron ooids are formed in median to distal offshore transition settings and may occur in proximal offshore settings; however iron ooids do not occur in distal offshore settings or the shoreface (Collin *et al*. 2005).

This study presents a new high resolution graphic log, high-resolution total organic carbon (TOC), calcium carbonate ($CaCO_3$), total sulphur (TS) total nitrogen (TN) abundances, and carbon isotope ratios, as well as palaeontological data for the Whitby Mudstone Fm., North Quarry, Holwell. These new geochemical data have been used to interpret the Leicestershire succession and to correlate the section with the Toarcian succession exposed in Yorkshire.

Lithostratigraphy and biostratigraphy

At the Holwell quarries the lowermost part of the Toarcian is represented by the Marlstone Rock Bed, which comprises a *c.* 1 m of sandstone overlain by *c.* 4.4 m of oolitic ironstone (Clements 1989; Fig. 2). The Marlstone Rock Bed is overlain by *c.* 9 m of dark-grey mudstones which comprise the laterally extensive Whitby Mudstone Formation. The upper Toarcian (*Hildoceras bifrons* Zone and higher) is not preserved, and these facies are thought to have been removed by erosion prior to deposition of the Middle Jurassic (Simms 2004).

Ammonite biostratigraphy for the Toarcian is well established (Howarth 1992 and references therein) and the stratigraphically complete succession in Yorkshire forms the basis for the Upper Pliensbachian and Lower Toarcian stages in NW Europe (Howarth 1992; Fig. 2a). The *exaratum* Subzone of the

Subboreal Province, which is the main interval of interest in the present study, contains a formally recognized succession of ammonite species (Howarth 1992) that have been used to divide the subzone into three informal divisions (Howarth 1992) or formal biohorizons (Page 2003). From the base of the subzone these divisions are *Eleganticeras elegantulum, Cleviceras exaratum*, and *Cleviceras elegans*. The ranges of these important ammonite index species have been used in the correlation presented in this paper (Fig. 2).

The ammonite biostratigraphy at the Holwell quarries has not been studied in detail, but some specimens have been collected by Clements (pers. comm.; Fig. 2d-e), although the position of these is only recorded to the nearest bed. For this reason the ammonite biostratigraphy for the nearby (<7 miles), and lithologically similar, exposures at Tilton railway cutting and Harston Quarry described by Howarth (1980; 1992; Fig. 2b-c) are used to provide further information on the likely relative age of the beds at Holwell. Howarth (1980, 1992) showed that in the Midlands, including at Tilton, that the top 1-3 m of the Marlstone Rock Bed represents the *Dactylioceras tenuicostatum* Zone and the lower 3-6 m represents the *Pleuroceras spinatum* Zone. Therefore, the Pliensbachian-Toarcian stage boundary occurs within the Marlstone Rock Bed rather than within the 'Transition Bed (Fig. 2) as previously believed (Wilson & Crick 1889; Hallam 1955).

At Tilton there is no evidence for the any of the *tenuicostatum* Zone subzones except for the *Dactylioceras semicelatum* Subzone (Fig. 2c). Although at Harston Quarry (Fig. 1c) ammonite evidence shows that the *tenuicostatum Z*one is complete except for the lowermost subzone (Howarth 1980; 1992), however it is relatively condensed (Fig. 2b). At Browns Hill Quarry, Holwell a bed with abundant belemnites occurs at the top of the Marlstone Rock Bed (bed 7, Fig. 2d). This bed most probably represents a hiatus between the Marlstone Rock Bed and the Whitby Mudstone Fm. and is likely to represent the greater part of the *tenuicostatum* Zone (Clements 1989).

Abundant *Tiltoniceras antiquum* occur in the top 0.20 m of the Marlstone Rock Bed at Tilton (Fig. 2c, Howarth 1992) and in the top 0.08 m at Harston (Fig.

2b). This species represents a useful marker species because it has a very limited stratigraphic range in Yorkshire and is only found at one level in the uppermost part of the *semicelatum* Subzone (bed 31; Fig. 2a). This level is 0.27 m below $\delta^{13}C_{org}$ shift 'A' in Yorkshire.

At Tilton, Howarth (1980, 1992; Fig. 2c) did not find any specimens of *E. elegantulum* or *C. exaratum* indicating that the lower and middle horizons of the *exaratum* Subzone, respectively, may be absent. At Tilton, the ammonite *Harpoceras serpentinum* which is found in both the *exaratum* and *elegans* horizons of the *exaratum* Subzone, was found between 1.40 m and 1.90 above the base of the Whitby Mudstone Formation. Its occurrence overlaps with *C. elegans* (1.85 m and 2.00 m above the base of the Whitby Mudstone Fm.) at Tilton (Fig. 2c; Howarth 1980, 1992) suggesting that only the very uppermost part of the *exaratum* horizon and the *elegans* horizon is present. Although Howarth (1980; 1992) did not find *C. exaratum* and *E. elegantulum* at Tilton it is possible that the lowermost 1.30 m of the Whitby Mudstone Fm. from which no ammonites have been recovered yet represents the lower and middle part of the *exaratum* Subzone (Fig. 2c). At Harston Quarry *E. elegantulum* has not been found, and only fragments of *C. cf. exaratum* occur in a bed 0.05 m thick at the base of the Whitby Mudstone Fm. (Howarth 1980; 1992; Fig. 2b). Therefore, all of the *elegantulum* horizon and possibly most of the *exaratum* horizon are also likely to be missing from the Harston section.

At the Holwell quarries, *C. exaratum* occurs in the lower 3 m (beds 10-14; Fig. 2d-e) of the Whitby Mudstone Formation, and *Harpoceras falciferum* occurs from bed 18 upwards (Fig. 2e). To date, *E. elegantulum*, *C. elegans, Hildaites murleyi,* and *H. serpentinum* have not been reported from either Holwell quarry (Clements, pers. comm.). Taking into account, the ammonites recorded from the Holwell quarries as well as those from Tilton and Harston it is probable that at least the lowermost part of the *exaratum* Subzone (*elegantulum* horizon) is absent throughout Leicestershire. It appears that these strata are also missing in Northamptonshire (Howarth 1978). In addition at Holwell the position of the *exaratum-falciferum* subzone boundary is uncertain.

Palaeontology

At both of the Holwell quarries the lowest 1 m of the Whitby Mudstone Fm. (beds 10 and 11; Fig. 3) contains bivalves, ammonites and echinoids (Clements 1989); and concentrated in the basal few centimetres (bed 8; Fig. 3) there are abundant fish remains and occasional insects (Clements 1989). These immediately overlie the belemnite bed (bed 7; Fig. 3) at the top of the Marlstone Rock Bed. In Northamptonshire the Abnormal Fish Bed immediately overlies the Marlstone Rock Bed and is interpreted to represent the middle to upper *exaratum* Subzone (Howarth 1978, Howarth 1992). At the base of the *exaratum* Subzone in Harston and Denton Park Quarries, Lincolnshire, shell beds occur that contain abundant broken bivalve shells, large numbers of belemnites, and large *Tiltoniceras* specimens (Howarth 1980; Fig. 2b). A fish bed (the Saurian Fish Bed) of equivalent age exposed near Ilminster, Somerset contains abundant fish, insects, crustaceans, ammonites, belemnites and teuthoids (Moore 1876).

At the Holwell quarries the overlying *c.* 1.5 m of fissile organic-rich mudrocks (beds 10-14; Fig. 3) contain a low diversity fauna of squashed ammonites and bivalves (Clements 1989). The bivalves include the key species, *Bositra radiata* (Goldfuss), *Bositra buchi* (Roemer), and *Pseudomytiloides dubius* (Sowerby), which are found in high abundance in the Whitby exposures (Caswell *et al*. 2009). The stratigraphically equivalent organic-rich mudstones at the base of the *exaratum* Subzone at Tilton also contain the remains of insects (Clements, pers. comm.). The upper part of the North Quarry section (*falciferum* Subzone, beds 16 to 19; Fig. 3) contains a diverse fauna of micro- and macrofossils (Clements pers. comm.). Hylton (2000) studied the foraminifera from Tilton and Browns Hill Quarry and found that the lower and upper *exaratum* Subzone were dominated by a small opportunist *Reinholdella? planiconvexa*. In beds 14 to 15 of the middle *exaratum* Subzone (Fig. 3) foraminifera were absent, and the *falciferum* Subzone contained a low diversity fauna (Hylton 2000). The facies which represent the *falciferum* Zone at Tilton contain abundant ammonites, *P. dubius*, and the gastropod *Coelodiscus minutus* (Schubler) (Hallam 1967a). Additionally, fish scales, insect and teuthoid remains, small brachiopods, echinoid spines and sporadic occurrences of *Nucula* sp., *Astarte* sp., *Meleagrinella substriata* (Münster), and *B. radiata* occur (Hallam 1967a).

A diverse and abundant micromorphic fauna occurs in beds 17 and 19 at North Quarry (Clements, pers. comm.). These micromorphic species include brachiopods, bivalve, echinoids, crinoids, ophiuroids, holothurians, gastropods, and scaphopods (Clements, pers. comm.). Micromorphic faunas of *exaratum* Subzone age have been reported from other contemporaneous sections in the UK. For example, an abundant micromorph fauna of the brachiopods '*Terebratula' globolina* and '*Rhynchonella' pygmaea*, and echinoid spines have been observed within the *exaratum* Subzone at Alderton, Gloucestershire (Buckman 1922). At Ilminster, Somerset the 'Leptaena Clay', which represents the base of the *exaratum* Subzone (Howarth 1992), contains abundant very minute brachiopods (*Stolmorhynchia bouchardii, 'Rhynchonella' pygmaea*, and '*Terebratula' globolina*), and the spines and plates of minute echinoids (Moore 1867; Hallam 1967). Furthermore, one gastropod and 17 bivalve species occur in Ilminster, including *P. dubius* and *B. radiata,* the majority of which are very dwarfed (Moore 1876).

Materials and methods

The Holwell North Quarry succession was cleaned with a trowel and graphically logged using a ladder to reach the upper part of the face. The collection of palaeontological data was limited due to the overgrown nature of the exposure and the limited sampling permitted by the wildlife trust. Using a small pocket knife on the cleaned face mudrock samples were collected every 1.25 cm. The samples were dried at 35^{o}C and crushed using an agate pestle and mortar. A total of 337 samples were analysed for total organic carbon (TOC), calcium carbonate ($CaCO_3$), total sulphur (TS) and total nitrogen (TN) abundance using a CNS-2000 Leco elemental analyser. Analytical precision was better than 0.02 wt% for carbon, 0.11 wt% for sulphur and 0.02% for nitrogen based on inter-run analyses of the in house standard. These samples were collected every 1.25 cm between 0.0625 m and 3.075 m, every 2.5 cm between 3.10 m and 4.63 m, and every 10 cm between 4.65 m and 6.75 m.

One hundred and seventy three samples were analysed for carbon isotopes at a stratigraphic resolution of 2.5 cm between -0.06 m and 2.70 m, a resolution of 5 cm between 2.75 m and 4.00 m, and at a resolution of 10 cm between 4.00 m and 6.75 m (Figs 3 and 4). These samples were decarbonated using 1M HCl, rinsed and dried at 35^{o}C and then analysed using Geo-20-20 mass spectrophotometer with ANCA elemental analyser preparation system (PDZ Europa Scientific). Carbon isotope values are reported relative to the Vienna Peedee belemnite standard (VPDB). Standard in house references were calibrated against the international standard IAEAN$_3$. Analytical precision for carbon isotope analyses was 0.08‰ based on inter-run analyses of an in house standard.

Results

The succession at North Quarry, Holwell, Leicestershire comprises *c.* 9 m of sedimentary deposits which represent the *falciferum* Zone (Fig. 3). Based on the unpublished work of Clements (pers comm.) detailed in the introduction, the lower part of the succession represents part of the *exaratum* Subzone but the exact stratigraphical extent of the *exaratum* Subzone has not been clearly established from the ammonites found to date (Fig. 2). The basal *c.* 1.5 m of the succession comprises yellow and grey mudstones, and this is overlain by *c.* 3.0 m of dark-grey mudstones of varying fissility (Fig. 3). The upper *c.* 4.0 m of the succession consists of medium-grey mudstones. Towards the top of the succession marlstones occur which contain calcium carbonate nodules, carbonate ooids and a small amount of Fe ooids (Fig. 3). The succession contains several iron rich mudstone horizons (Fig. 3).

The Leicestershire facies have relatively high TOC content of up ~10 wt% (Fig. 3). The highly fissile mudstones of the upper part of bed 14 and lower part of bed 15 have the highest TOC (~6-10 wt%; Fig. 3). The fissile mudstone facies either side (lower part of bed 14 and the upper part of bed 15, beds 16 and 17) are also relatively high with values between 4 and 8 wt% TOC. TS, TN, and $CaCO_3$ abundance are also highest between bed 14 and 17 (Fig. 3).

The North Quarry succession records a negative carbon isotope excursion of ~-5‰ within the *exaratum* Subzone. Carbon isotope ratios range from -24.85‰ to -29.98‰ throughout the section (Fig. 3), and are consistently ~1‰ higher than those from the succession in Yorkshire (Fig. 4). The negative carbon isotope excursion is overlain by an interval with fairly constant values of ~-25.93‰ and the upper part of the measured section averages -25.58‰ with slightly more variation (Fig. 3). Between 1.075 m and 1.30 m (Fig. 3) $\delta^{13}C_{org}$ values are anomalously high and highly variable, ranging from -6‰ to -23‰, for marine organic matter. Repeat analyses were performed on these samples, and on samples collected from contemporaneous facies that were spatially separated (~50 m), but anomalous $\delta^{13}C_{org}$ values were also produced. Furthermore, TOC and $CaCO_3$ within this interval are very low and show low amplitude variations (Fig. 3).

The succession is dominated by three epifaunal bivalve species *Bositra buchi*, *Bositra radiata*, and *Pseudomytiloides dubius* (Fig. 3). The infaunal deposit feeding bivalves *Pleuromya* sp., *Palaeonucula hammeri* (Defrance), and a single small (~2 mm) specimen of *Dacryomya ovum* (Sowerby) were also found in the upper part of the succession (Fig. 3). The gastropods *Levipleura blainvillei* (Goldfuss) and *Ptychomphalus expansus* (Sowerby) also occur in low abundance (Fig. 3). Species diversity and abundance are relatively low during the main negative carbon isotope excursion (Fig. 3).

Discussion

The Early Toarcian palaeoenvironmental change is prominently recorded on the East Midland shelf by changes in lithology, bulk rock geochemistry, a -5‰

change in $\delta^{13}C_{org}$, and changes in the biota. The average TOC content within the North Quarry succession (~4%) is generally lower and the $CaCO_3$ abundance higher than that of the Yorkshire succession (TOC ~8%, Kemp 2006; Fig. 4). The TS abundance within the North Quarry deposits is comparable to those of the Yorkshire section (Kemp 2006). The $\delta^{13}C_{org}$ -5‰ excursion in Holwell North Quarry is of a similar magnitude (~-7‰, Fig. 4; Kemp *et al.* 2005) but varies in detail from that from the Yorkshire succession. This is probably mainly a result of the likely significant hiatus at the *semicelatum/exaratum* Subzone boundary that is discussed in further detail below. The anomalously high $\delta^{13}C_{org}$ values between 1.075 m and 1.30 m (Fig. 3) at North Quarry are interpreted to be the result of a diagenetic overprint and are not discussed further.

Correlation between Leicestershire and Yorkshire

The combined ammonite biostratigraphy from Tilton, Harston, and Holwell in Leicestershire indicate that there is a hiatus representing the top of the *semicelatum* and base of the *exaratum* subzones. This is because, in Leicestershire, the highest strata within the *semicelatum* Subzone strata are at the *T*. *antiquum* level, and the lowest strata in the overlying *exaratum* Subzone contain *C. exaratum* for which the lowest occurrence in the type section in Yorkshire is near the middle of the subzone. In addition, the *C. exaratum* found in the Holwell quarries are only recorded to the nearest bed level. Therefore, based on the ammonite biostratigraphy alone, the oldest level that could be represented by the base of the *exaratum* Subzone in Leicestershire is between the top of the range of *E. elegantulum* and base of the range of *C. exaratum* in Yorkshire within the interval that lacks biostratigraphically useful ammonites (Fig 2a).

Using the ammonite biostratigraphy and ranges discussed above as a framework for correlation of the $\delta^{13}C$ record from Leicestershire and Yorkshire, the $\delta^{13}C$ shifts ‘A’, ‘B’ and ‘C’ recognized in Yorkshire are interpreted to be missing in the hiatus between the *semicelatum* and *exaratum* subzones in Leicestershire. The large $\delta^{13}C_{org}$ shift in the lowermost

0.2 m of the North Quarry section is correlated with $\delta^{13}C_{org}$ shift 'D' of Cohen *et al*. (2007) in Yorkshire (Fig. 4). This correlation is supported by the preceding distinctive rapid increase in carbon isotope variation at both locations (Fig. 4). The identification of carbon isotope shift 'D' allows the correlation to be refined and shows that the hiatus in Leicestershire is represented by the strata between -2.0 to 2.6 m in Yorkshire (Figs 2a and 4). Carbon isotope shift 'D' appears to be 2‰ larger in North Quarry than in Yorkshire, but this may simply be because the North Quarry succession is slightly expanded over this interval, as it is *c.* 11 cm, compared to 2.5 cm in Yorkshire (Fig. 4). In addition, 2.5 cm is the resolution of the sampling over this interval in Yorkshire.

The $\delta^{13}C_{org}$ variation through the 3.7 m of succession at Leicestershire above shift 'D' can be correlated with the 4.1 m of succession in Yorkshire (Fig. 4). It indicates that the *exaratum-falciferum* subzone boundary occurs near the top of bed 15 at North Quarry (Fig. 4). The $\delta^{13}C_{org}$ in North Quarry is offset from Yorkshire by ~ +1‰ and may reflect a greater incorporation of terrestrial organic matter into the sediments that were deposited in the more proximal setting of the East Midlands Shelf. The carbon isotope ratios of fossilised wood from Yorkshire are offset by ~+2‰ from that of organic matter from the same facies (Hesselbo 2000). It should be noted however that variation in the origin of the organic matter alone is insufficient to explain the -5‰ change in $\delta^{13}C_{org}$ in the Leicestershire section.

Biotic and sea–level changes associated with the Toarcian palaeoenvironmental change

The fauna of the Abnormal Fish Bed, the insect remains, belemnite and shell concentrations at the *tenuicostatum-exaratum* subzone boundary in Lincolnshire, Northamptonshire and Leicestershire all indicate extensive current and/or wave activity, together with the mortality of pelagic species. Increased current activity and winnowing of the sediments is likely to be related to the onset of relative sea-level rise due to the thermal expansion of sea-water. This is consistent with the evidence from Mg/Ca ratios and O-isotopes (Bailey *et al.* 2003) for global warming at the start of the Toarcian event together with an increased hydrological cycle indicated by Os- and Sr-isotopes (Cohen *et al.* 2004).

The high abundance of fossilized fish is consistent with the intermittent but widespread development of anoxic and euxinic conditions during carbon isotope shifts ‘A’, ‘B’ and ‘C’ as evidenced by both the Mo isotopes (Pearce *et al*. 2008) and the presence of isorenieratane (Schouten *et al*. 2000; Pancost *et al*. 2002; Schwark & Frimmel 2004; van Breugel *et al*. 2006). The insect remains suggest that insects were unable to adapt to changes in atmospheric composition that is indicated by the $\delta^{13}C$ signature of fossil wood from this interval (Hesselbo *et al.* 2000, 2007; McElwain *et al*. 2005).

Several of the macroinvertebrate species found in the lower Toarcian of North Quarry also occur in Yorkshire, these include *L. blainvillei, P. expansus, D. ovum, B. buchi, B. radiata* and *P. dubius* (Tate & Blake 1876; Little 1996). Similar to the biota of the Yorkshire succession (Caswell *et al*. 2009; Fig. 4), the lower Toarcian facies in North Quarry, Holwell are dominated by *B. buchi*, *B. radiata*, and *P. dubius*. However, in Holwell the benthos of the upper part of the *exaratum* Subzone and the lower part of the *falciferum* Subzone is more diverse than in Yorkshire (Fig. 4), and the local species ranges of the dominant bivalves within the two successions differ considerably. In Holwell North Quarry *P. dubius* is common but is only abundant at the boundary between beds 14 and 15 (Fig. 4). In Yorkshire *P. dubius* occurs in high abundance and completely dominates the benthos during the negative carbon isotope excursion (*exaratum* Subzone; Fig. 4), and lower half of the *falciferum* Subzone (Caswell *et al*. 2009). However, at North Quarry *B. buchi* and *B. radiata* dominate during the carbon isotope excursion.

In Yorkshire the first occurrence of *B. buchi* is later (near the *exaratum-falciferum* subzone boundary; Fig. 4; Caswell *et al*. 2009) than in Leicestershire (Fig. 4), and it occurs abundantly in some horizons within the *falciferum* Subzone in both sections. *B. radiata* only occurs in abundance within the most organic-rich facies within the upper part of the *exaratum* Subzone (bed 14 to bed 15; Fig. 4). At North Quarry, based on the correlation presented herein (Fig. 4), this is coincident with the beginning of the relatively oxygenated interval in Yorkshire (Caswell *et al*. 2009; Fig. 4). In Yorkshire *B. radiata* occurs in two discrete intervals at the beginning and end of the negative carbon isotope excursion (Caswell *et al.* 2009; Fig. 4). *B. radiata* becomes extinct at the *exaratum-falciferum* subzone boundary in Yorkshire (Caswell *et al*. 2009), however it is found slightly later in Holwell just above the subzone boundary (bed 17 Fig. 4) and this occurrence may represent the final occurrence of *B. radiata* in the UK.

The palaeontological data indicate that conditions in Holwell were most inhospitable during the negative carbon isotope excursion (Fig. 4). However, the higher faunal diversity in Leicestershire and the differences in the stratigraphic ranges of *B. buchi*, *B. radiata* and *P. dubius* throughout the negative carbon isotope excursion suggest that conditions were more hospitable than in Yorkshire. The lower TOC of the Leicestershire deposits support this interpretation. The facies of the *exaratum* Subzone of the East Midlands Shelf indicate that they were deposited in shallower water relative to those of the Cleveland Basin and so the water column would have undergone a greater degree of mixing and therefore been better oxygenated and thus relatively more diverse.

Relative sea-level rise in the *exaratum* Subzone of Leicestershire is indicated by the deposition of clay facies (Beds 8 to 13) over the remaine bed (bed 7) across the East Midlands shelf. The higher TOC and $CaCO_3$ abundance in Leicestershire between beds 14 and 17 could indicate decreased dilution by clay minerals due to continued relative sea level rise over the East Midlands Shelf as global temperatures continued to rise.

The return to organic-poor clay facies and the diverse and abundant micromorphic fossil fauna within beds 17 and 19 (Fig. 4) in North Quarry and further afield, indicates that conditions became relatively more oxygenated at the time of deposition of these beds and a more diverse range of fauna were able to settle in the benthos. However, it is likely that the small size of the fauna is a result of the environment remaining relatively inhospitable. These micromorphs may represent juvenile assemblages which were periodically killed off before attaining maturity, or may represent adult organisms with stunted growth due to low dissolved oxygen concentrations.

Modern studies have shown that mobile vertebrates and invertebrates migrate out of hypoxic areas (Diaz & Rosenberg 1995; Diaz 2001; Whitney *et al.* 2007), and the East Midlands Shelf may have been a refugium for these mobile species. The East Midlands Shelf could also have been a refugium for sessile species, such as the bivalves, from which future recruitment could occur once palaeoenvironmental conditions became more favourable.

Conclusions

- Geochemical analyses of the lower Toarcian deposits from North Quarry, Holwell, Leicestershire show that the average TOC content is ~4% and the average $CaCO_3$ content is ~20%. The TOC is ~4% lower and the $CaCO_3$ ~10% higher than in Yorkshire. These data, and the faunal assemblage, are consistent with relatively shallower water deposition.

- A negative $\delta^{13}C_{org}$ excursion of ~-5‰ is evident from the lower Toarcian at North Quarry, and this excursion is of similar magnitude to the negative $\delta^{13}C_{org}$ excursion within the Yorkshire section.

- The ammonite ranges indicate that between Leicestershire and Yorkshire there is a hiatus that spans from the upper part of the *semicelatum* to lower part of the *exaratum* subzones, but that the middle to upper *exaratum* Subzone is present.

- The $\delta^{13}C_{org}$ record allows further refinement of the correlation between the Yorkshire and Leicestershire and indicates that: (i) the base of bed 8 in North Quarry corresponds to near the top of bed 34 in Yorkshire and that

(ii) the *exaratum-falciferum* subzone boundary occurs in bed 15 in North Quarry, Holwell.

- The negative $\delta^{13}C_{org}$ shift 'D' identified from the Yorkshire succession (Kemp *et al*. 2005; Cohen *et al*. 2007) also occurs within the Leicestershire succession, however it is 2‰ greater in magnitude. In Leicestershire $\delta^{13}C_{org}$ is offset by ~+1‰ from Yorkshire, and may represent dilution by terrestrial organic matter.

- The lower *exaratum* Subzone facies deposited in the Midlands contain abundant belemnites, fish remains, and insects which is consistent with an intermittently euxinic water column as shown by biomarkers and Mo-isotope ratios over the interval represented by $\delta^{13}C_{org}$ shifts A to C.

- The benthic macro-invertebrate species composition of the Leicestershire succession is very similar to the Yorkshire succession, and is dominated by the epifaunal opportunists *P. dubius, B. radiata,* and *B. buchi* which are well adapted to oxygen deficiency. However, the *falciferum* Zone in Leicestershire is more diverse than in Yorkshire.

- The local occurrences of *P. dubius*, *B. buchi*, and *B. radiata* are different within the Leicestershire and Yorkshire successions. The main differences were: *P. dubius* occurs in significantly lower abundance and does not dominate during the main negative carbon isotope excursion in Leicestershire, *B. buchi* and *B. radiata* occur in higher abundance and dominate during the negative carbon isotope excursion in Leicestershire. *B. buchi* occurs earlier in Leicestershire and *B. radiata* occurs later.

- Palaeontological data indicate that in beds 16 to 17 in North Quarry Leicestershire a diverse micromorphic fauna occurs which indicates that whilst conditions improved after the end of the negative carbon isotope excursion the environment remained relatively inhospitable at times. Furthermore, it appears that a micromorphic fauna occurs contemporaneously in other UK sections.

- Palaeontological and geochemical data indicate that conditions during the negative carbon isotope excursion in Leicestershire were less inhospitable than in Yorkshire, and that the benthic fauna recovered more quickly in Leicestershire. This is consistent with the deposition of the Leicestershire sediments within shallower water than in Yorkshire. The East Midlands Shelf may also have provided a refuge for some fauna.

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Figure captions

Fig. 1: Palaeogeographical maps for the early Toarcian. (a) Global palaeogeographical map showing distribution of organic-rich facies modified from Cohen *et al.* (2007) and references therein. Inset box shows area of covered by (b). (b) European palaeogeography showing the widespread distribution of organic-rich facies. Modified from Loh *et al*. (1986). Inset box shows area covered by (c); present-day coastline is shown; PH = Pennine High; CM = Cornubian Massif; EMS = East Midlands Shelf; and WB = Wessex Basin. (c) Map of the area around Holwell, Leicestershire showing major roads, the Lower Jurassic outcrop and geological exposures mentioned in the text; A-roads (black) and B-roads (grey).

Fig. 2: Comparison of the lower Toarcian stratigraphic sections at: (a) Yorkshire, (b) Harston Quarry, (c) Tilton railway cutting, (d) Browns Hill Quarry, Holwell, and (e) North Quarry, Holwell. Ammonite biostratigraphy and bed numbers for Yorkshire are from Howarth (1962; 1973); graphic log is from Kemp (2006); ammonite species ranges are from Howarth (1992; species ranges are only shown for those species which are used to correlate the five sections). Ammonite biostratigraphy, lithology, and ammonite species ranges for Harston and Tilton are from Howarth (1980; 1992). Bed numbers for Tilton are from Clements (pers. comm.), but are also reproduced in Simms (2004) with the permission of Clements. Lithology for Browns Hill Quarry is from Clements (1989); lithology for North Quarry is from the present study (refer to Fig. 3 for the detailed lithology). Ammonite occurrences and bed numbers for Browns Hill and North Quarry, Holwell are from Clements (pers. comm.). Stratigraphic position of the stage boundary and ammonite zonal boundaries at Holwell are uncertain, therefore, the boundaries are approximated (shown as dashed lines) based on the lithology and ammonite biostratigraphy at Tilton. Grey broken horizontal lines represent the correlation between the ammonite biostratigraphy for the five different successions; four grades of broken line are used, and these are as follows proceeding from the base of the succession: *hawskerense-paltum* subzone boundary, occurrence of *T. antiquum*, lowest extent of the range of *C. exaratum*, and the lowest extent of

the range of *H. falciferum* (for the Holwell quarries the biostratigraphic correlation takes into account the carbon isotope correlation presented on Fig. 4 and discussed in the text). Some biostratigraphic correlations are less certain than others and are indicated by '?'. Ammonite subzone abbreviations: *Pl. spinatum* = *Pleuroceras spinatum* (Brugière), *Pl. apy*. = *Pleuroceras apyrenum* (Buckman), *Pl. hawsk.* = *Pleuroceras hawskerense* (Young & Bird), *D. ten*. = *Dactylioceras (Orthodactylites) tenuicostatum* (Young & Bird), *Pr. paltum* = *Protogrammoceras paltum* (Buckman), *D. crosbeyi* = *D. (O.) crosbeyi* (Simpson), *Hi. murleyi* = *Hildaites murleyi* (Moxon), *D. clev.* = *D. (O.) clevelandicum* Howarth, *D. semi.* = *D. (O.) semicelatum* (Simpson), *H. falcif.* = *Harpoceras falciferum* (J. Sowerby), *C. exaratum* = *Cleviceras exaratum* (Young & Bird), *T. antiquum* = *Tiltoniceras antiquum* (Wright), *E. elegantulum* = *Eleganticeras elegantulum* (Young & Bird), *H. serp.* = *Harpoceras serpentinum* (Schlotheim), *C. elegans* = *Cleviceras elegans* (J. Sowerby), and *P. hetero.* = *Phylloceras heterophyllum* (J. Sowerby). Pliens. = Pliensbachian; Fm. = Formation; Mbr. = Member; TB = Transition Bed; MRB Marlstone Rock Bed, Lthostrat. = Lithostratigraphy. Note the Yorkshire section (a) is at a different scale to the other four sections.

Fig. 3: Graphic log for the Whitby Mudstone Formation at North Quarry, Holwell, Leicestershire. Ammonite biostratigraphy and bed numbers are from Clements (pers. comm.). Uncertainty on the stratigraphic position of the *exaratum-falciferum* subzone boundary is represented by the shading. Species range and abundance data are from the present study (diamonds joined by lines). Fossil abundance is number of specimens. $\delta^{13}C_{org}$, $CaCO_3$, TOC, TS and TN are from the present study. Data for $\delta^{13}C_{org}$ between 1.075 m and 1.30 m are not plotted values ranged from -6 to -23.3‰.

Fig. 4: Correlation between the Yorkshire (left side) and Leicestershire successions (right hand side). Graphic log, ammonite biostratigraphy, and bed numbers for North Quarry, Holwell are as for Fig. 3. Graphic log for the Yorkshire succession is from Kemp *et al*. (2005) and Kemp (2006); ammonite biostratigraphy and bed numbers are from Howarth (1962; 1973, 1992). Range data for *B. Buchi, B. radiata,* and *P. dubius* for Yorkshire and the

oxygenated interval are from Caswell *et al.* (2009). *B. Buchi, B. radiata*, and *P. dubius* range data for Leicestershire are from this study; microfaunal interval is based on data from Clements (pers. comm.). $CaCO_3$ (grey) and $\delta^{13}C_{org}$ (black) data for Yorkshire are from Kemp *et al*. (2005) and Kemp (2006), and data for Leicestershire are from the present study; carbon isotope shifts 'A' to 'D' are from Kemp *et al*. (2005) and Cohen *et al*. (2007). Dashed horizontal grey lines and grey shaded regions show the correlation between Yorkshire and Leicestershire, and are based mainly upon variation in $\delta^{13}C_{org}$ with some information from $CaCO_3$ abundance. See also cross plot in the supplementary data. Dashed horizontal black line represents the position of the *exaratum-falciferum* subzone boundary. Key to the lithology and species abundances for the Holwell North Quarry section are as for Fig. 3. Abbreviations: *D. semic. = Dactylioceras semicelatum*; and *D. ten. = D. tenuicostatum*.

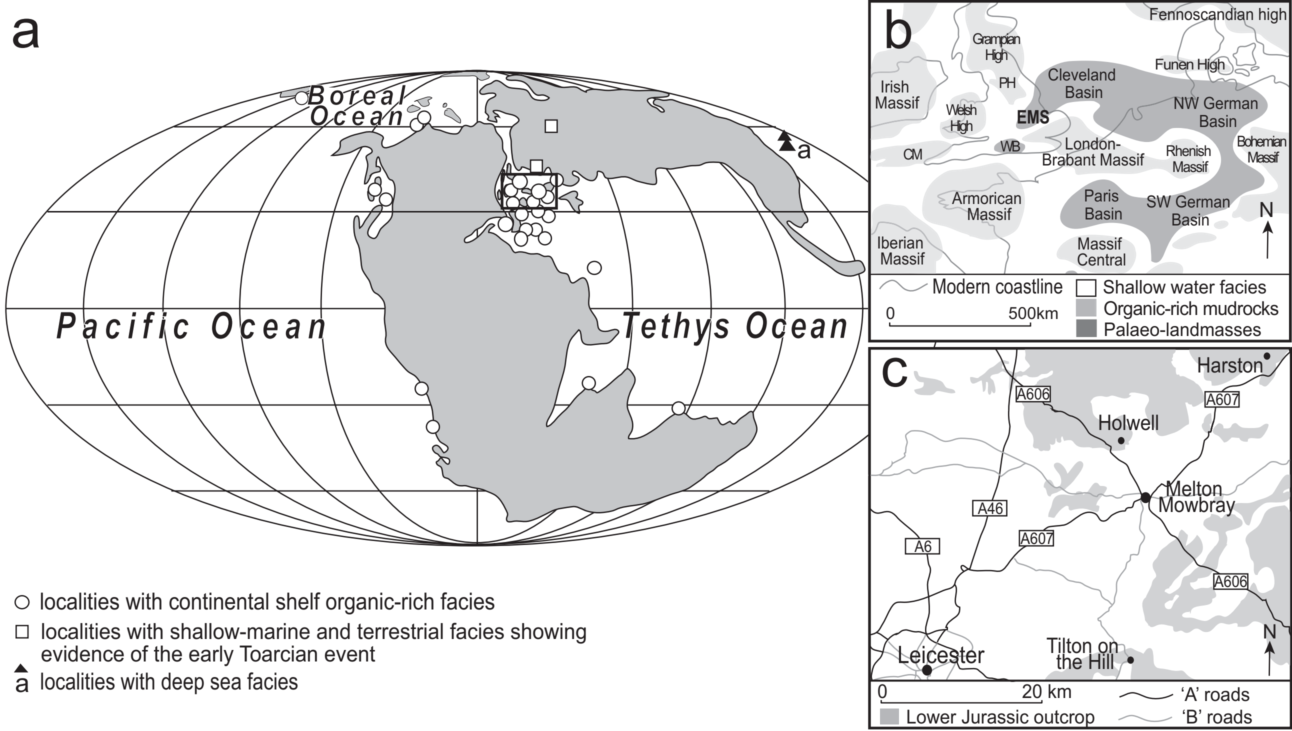
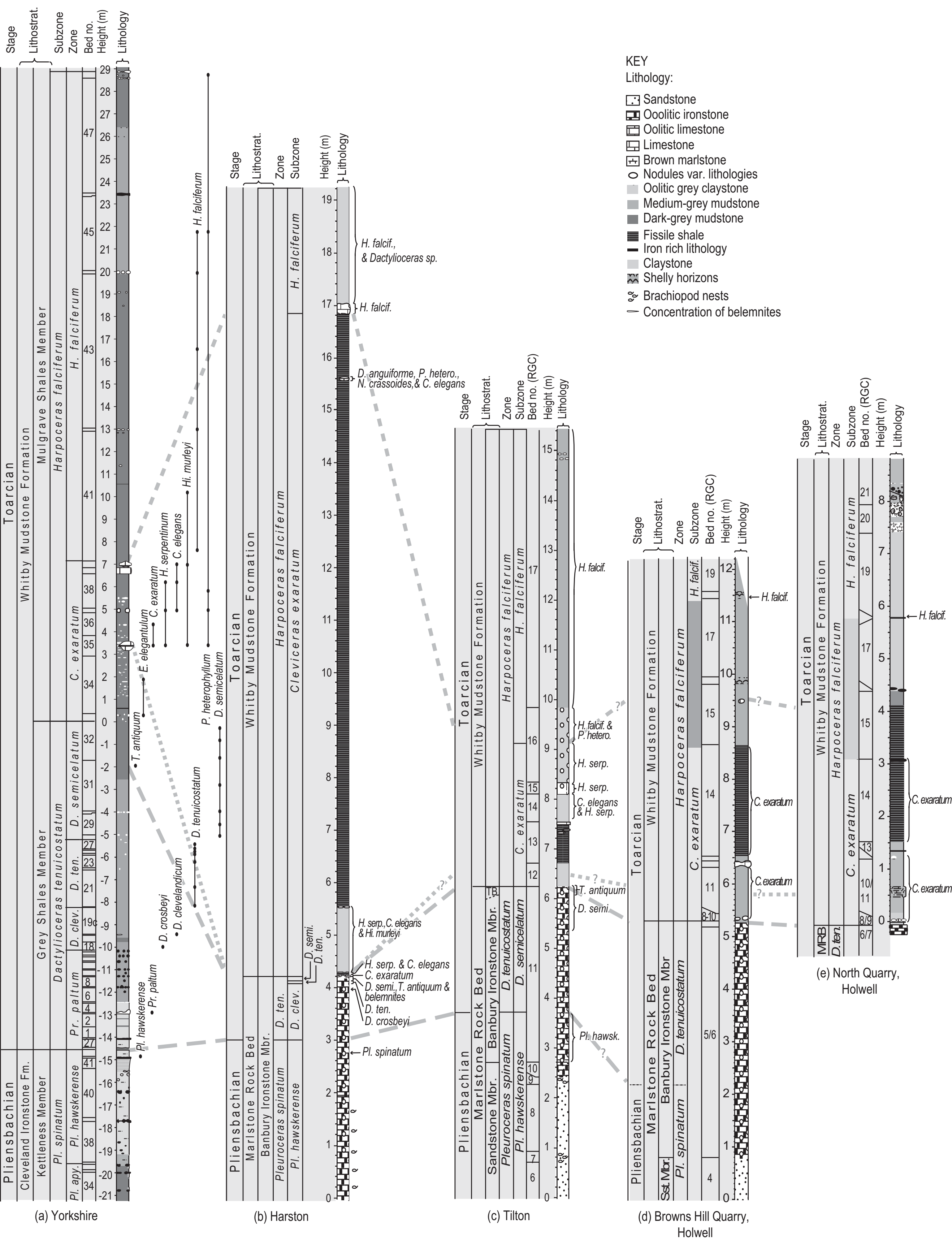


Fig. 1 Caswell & Coe


KEY
Lithology:
Sandstone
Ooolitic ironstone
Oolitic limestone
Limestone
Brown marlstone
Nodules var. lithologies
Oolitic grey claystone
Medium-grey mudstone
Dark-grey mudstone
Fissile shale
Iron rich lithology
Claystone
Shelly horizons
Brachiopod nests
Concentration of belemnites
Stage
Lithostrat.
Subzone
Zone
Bed no.
Height (m)
Lithology
Toarcian
Pliensbachian
Whitby Mudstone Formation
Cleveland Ironstone Fm.
Mulgrave Shales Member
Grey Shales Member
Kettleness Member
Harpoceras falciferum
Dactylioceras tenuicostatum
H. falciferum
C. exaratum
D. semicelatum
D. ten.
D. clev.
Pr. paltum
Pl. hawskerense
Pl. spinatum
Pl. apy.
Marlstone Rock Bed
Banbury Ironstone Mbr.
Sandstone Mbr.
Pleuroceras spinatum
Cleviceras exaratum
Bed no. (RGC)
H. falcif., & Dactylioceras sp.
H. falcif.
D. anguiforme, P. hetero., N. crassoides,& C. elegans
H. serp. C. elegans & Hi. murleyi
H. serp. & C. elegans
C. exaratum
D. semi.,T. antiquum & belemnites
D. ten.
D. crosbeyi
Pl. spinatum
D. semi.
H. falcif. & P. hetero.
H. serp.
C. elegans & H. serp.
T. antiquum
D. semi
Pl. hawsk.
H. falciferum
Hi. murleyi
C. elegans
H. serpentinum
C. exaratum
E. elegantulum
T. antiquum
P. heterophyllum
D. semicelatum
D. tenuicostatum
D. clevelandicum
D. crosbeyi
Pr. paltum
Pl. hawskerense
Sst. Mbr.
MRB
D.ten.
(a) Yorkshire
(b) Harston
(c) Tilton
(d) Browns Hill Quarry, Holwell
(e) North Quarry, Holwell

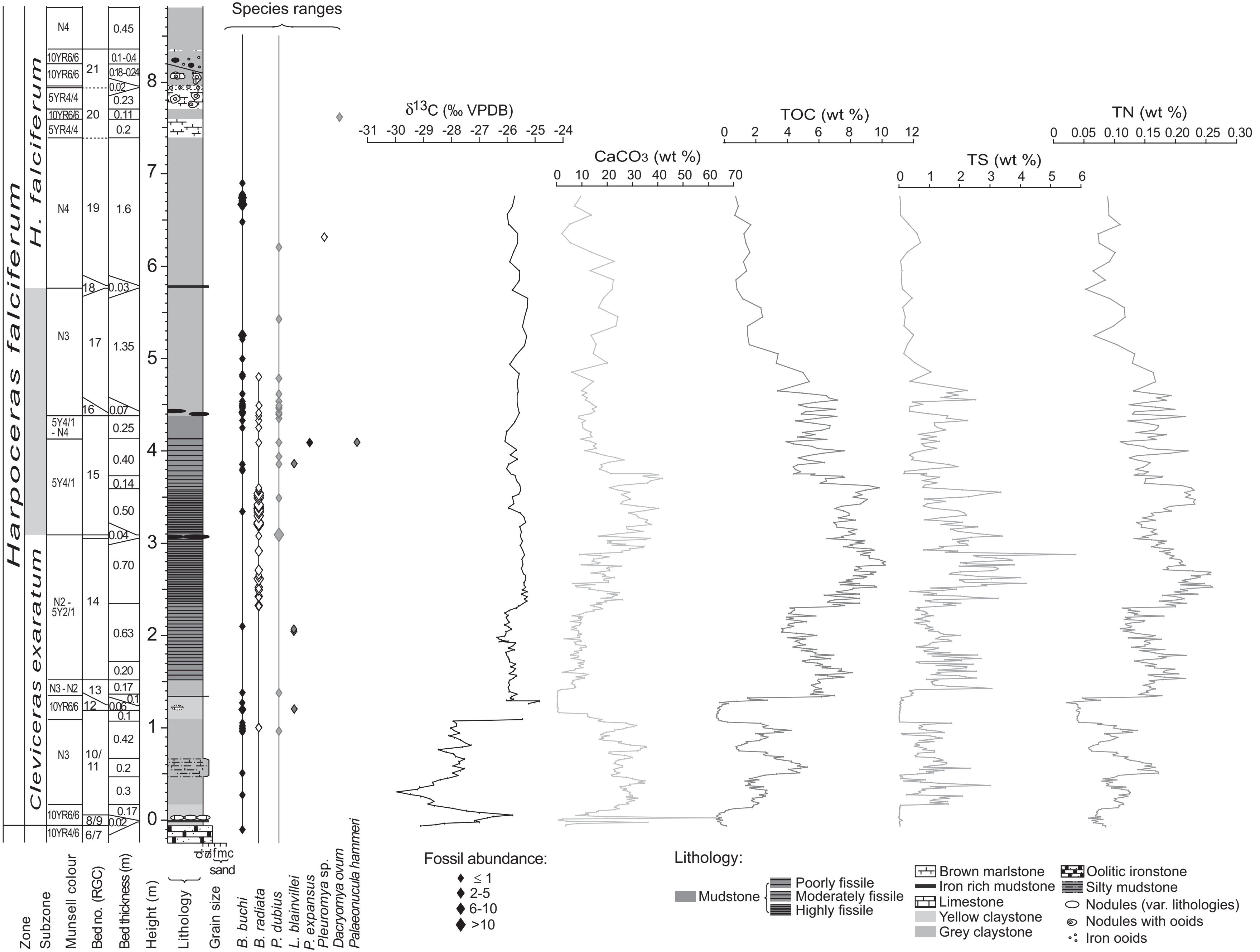


Fig. 3 Caswell & Coe 2010

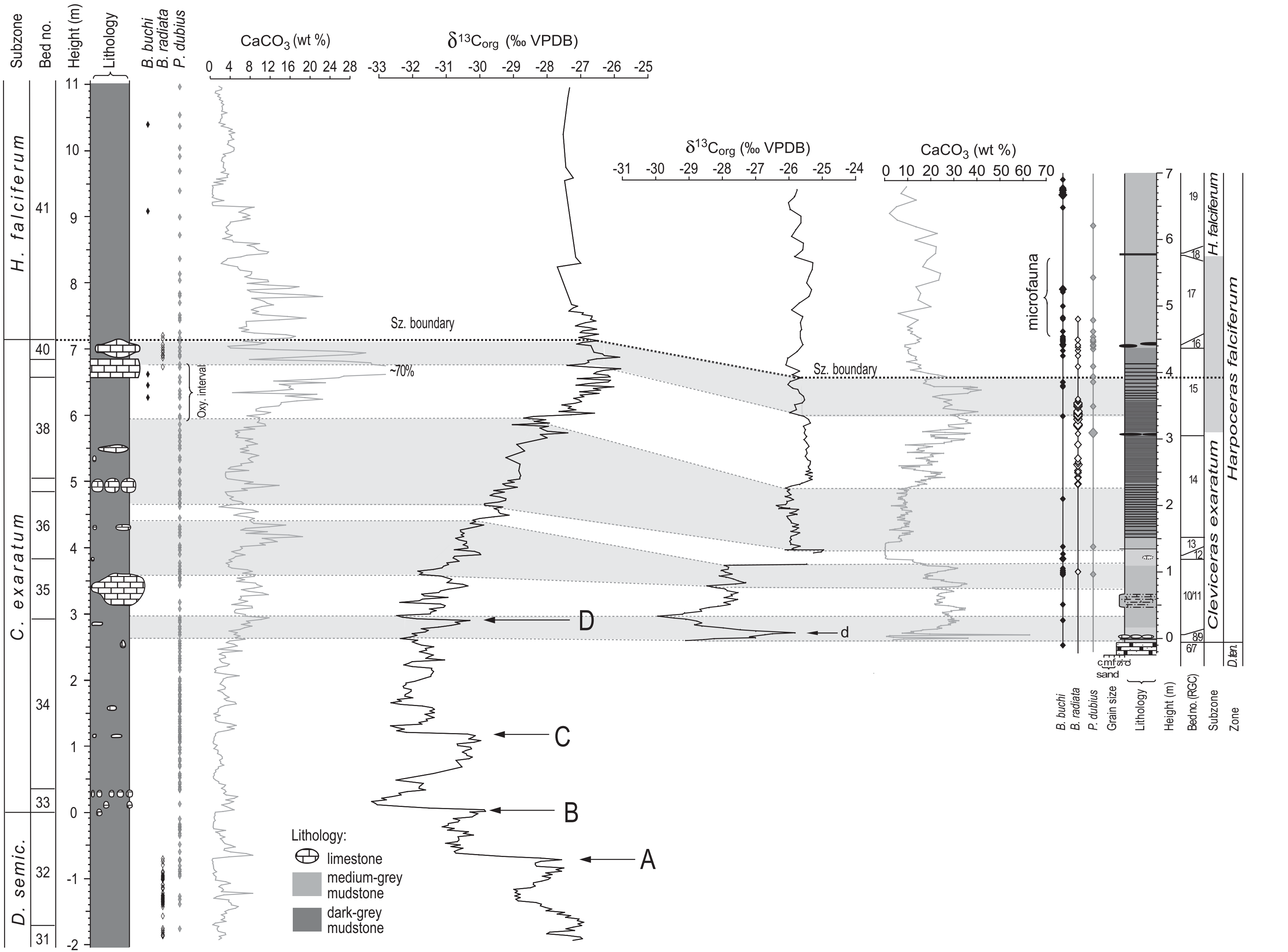


Fig. 4 Caswell & Coe 2010