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An open marine record of the Toarcian oceanic anoxic event

D. R. Gröcke¹, R. S. Hori², J. Trabucho-Alexandre¹, D. B. Kemp³, and L. Schwark⁴

¹Dept. of Earth Sciences, Durham University, Science Laboratories, South Road, Durham, DH1 3LE, UK

²Dept. of Earth Sciences, Faculty of Science, Ehime University, Matsuyama 790-8577, Japan

³Dept. of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, UK

⁴Christian-Albrechts-University – Kiel, Institute for Geosciences, Ludewig-Meyn-Str. 10, 24118 Kiel, Germany

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Correspondence to: D. R. Gröcke (d.r.grocke@durham.ac.uk)

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Abstract

Oceanic anoxic events were time intervals in the Mesozoic characterized by widespread distribution of marine organic-rich sediments (black shales) and significant perturbations in the global carbon cycle. The expression of these perturbations is globally recorded in sediments as excursions in the carbon isotope record irrespective of lithology or depositional environment. During the Early Toarcian, black shales were deposited on the epi- and peri-continental shelves of Pangaea and these sedimentary rocks are associated with a pronounced (ca. 7‰) negative (organic) carbon isotope excursion (CIE) which is thought to be the result of a major perturbation in the global carbon cycle. For this reason, the Early Toarcian is thought to represent an oceanic anoxic event (the T-OAE). Associated with this event, there were pronounced perturbations in global weathering rates and seawater temperatures. Although it is commonly asserted that the T-OAE is a global event and that the distribution of black shales is likewise global, an isotopic and/or organic-rich expression of this event has as yet only been recognized on epi- and peri-continental Pangaeen localities. To address this issue, the carbon isotope composition of organic matter ($\delta^{13}\text{C}_{\text{org}}$) of Early Toarcian cherts from Japan that were deposited in the open Panthalassa Ocean was analysed. The results show the presence of a major (>6‰) negative excursion in $\delta^{13}\text{C}_{\text{org}}$ that, based on radiolarian biostratigraphy, is a correlative of the Early Toarcian negative CIE known from European epicontinental strata. Furthermore, a secondary ca. -2‰ excursion in $\delta^{13}\text{C}_{\text{org}}$ is also recognized lower in the studied succession that, within the current biostratigraphical resolution, is likely to represent the excursion that occurs close to the Pliensbachian/Toarcian boundary and which is also recorded in European epicontinental successions. These results from the open ocean realm suggest that, in conjunction with other previously published datasets, these major Early Jurassic carbon cycle perturbations affected all active global reservoirs of the exchangeable carbon cycle (deep marine, shallow marine, atmospheric). An extremely negative $\delta^{13}\text{C}_{\text{org}}$ value (-57‰) during the peak of the T-OAE is also reported, which suggests that the inferred open

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ocean mid-water oxygen minimum layer within which these sediments are thought to have been deposited was highly enriched in methanotrophic bacteria, since these organisms are the only plausible producers of such ^{12}C -enriched organic matter.

1 Introduction

5 Over the past quinquennium there has been an increased effort to unravel the cause(s) and consequences of the Early Toarcian oceanic anoxic event (T-OAE). Of enormous diagnostic significance over this interval is the presence of a pronounced, transient negative carbon isotope ($\delta^{13}\text{C}$) excursion that has been recognized in marine inorganic and organic matter (Jenkyns and Clayton, 1988; Schouten et al., 2000; Kemp et al., 2005; Suan et al., 2008), and terrestrial plant material (Hesselbo et al., 2000; 10 2007). This feature has been postulated to be the result of an increase in ^{12}C in the carbon cycle, perhaps following the dissociation of methane hydrates (Hesselbo et al., 2000; Kemp et al., 2005). Associated with the T-OAE is concomitant evidence for: a sudden rise in seawater palaeotemperatures (Rosales et al., 2004; van de Schootbrugge et al., 2005), a three-fold increase in atmospheric CO_2 levels (McElwain et al., 2005), a major increase in silicate weathering rates (Cohen et al., 2004; Waltham and Gröcke, 2006) and a biotic crisis affecting marine invertebrates and biocalcifying micro-organisms (Little and Benton, 1995; Mattioli et al., 2004; Tremolada et al., 2005).

15 The lithological expression of the T-OAE may be locally very different. The development of anoxic, organic-rich facies was not generalized in the European Neotethyan realm and, where developed, the petrology and organic richness of the sediments is variable. For instance, certain limestones in the *H. falciferum* ammonite Zone of northern Europe (Hallam, 1967) and of the Tethys (Jenkyns, 1985) are pink/red. These differences illustrate the importance of local environmental conditions that are ultimately 20 more important in determining the local lithological expression of an OAE (Trabucho Alexandre et al., 2010). Indeed, available biostratigraphical data indicate that the development and demise of organic-rich facies in Tethyan and Boreal provinces of Europe 25

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are diachronous (Wignall et al., 2005 and references therein): similar to the Cenomanian/Turonian boundary OAE (Tsikos et al., 2004).

Hesselbo et al. (2000) suggested that the cause of the negative CIE was the dissociation, release and consequent oxidation of methane derived from continental shelf methane hydrates. More recently, a high-resolution $\delta^{13}\text{C}_{\text{org}}$ record across the T-OAE obtained from mudrocks exposed in northeast England was generated by Kemp et al. (2005). These data show that the negative $\delta^{13}\text{C}$ excursion was not a single event but three rapid events, the timing of which was paced by astronomically forced climate cycles. An alternative hypothesis recently put forward for the cause of the T-OAE is that ^{12}C -enriched thermogenic methane was released into the ocean-atmosphere system due to an igneous intrusion into coaly organic-rich facies in the Karoo Basin, South Africa. (McElwain et al., 2005; Svensen et al., 2007). This mechanism has subsequently been questioned by Gröcke et al. (2009), who showed that both the physical nature of the contacts between intrusions and organic-rich facies and the geochemical pattern within these facies suggest little or no thermogenic methane generation from the Karoo Basin.

A key controversy surrounding the T-OAE is that localities where the negative $\delta^{13}\text{C}$ excursion has been recorded have primarily been restricted to epicontinental sections exposed in Europe. This has prompted speculation that the isotopic perturbation is a feature affecting only the shallow marine environment (i.e. <200 m water depth) and driven by localized phenomena (van de Schootbrugge et al., 2005). Recently, however, Al-Suwaidi et al. (2010) documented evidence for the Early Toarcian negative $\delta^{13}\text{C}$ excursion from strata from the Neuquén Basin, Argentina. This record revealed the onset of the excursion, although the main excursion interval and recovery were not documented owing to the presence of an unconformity that truncates the succession. A further commonly cited issue surrounding the event is the lack of evidence for the negative $\delta^{13}\text{C}$ excursion in belemnite calcite (van de Schootbrugge et al., 2005; Wignall et al., 2006; McArthur et al., 2007). However, Suan et al. (2008) have recently reproduced the negative $\delta^{13}\text{C}$ excursion in brachiopod calcite across the T-OAE from a

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section in Peniche, Portugal. This work thus suggests that belemnites are either: (1) not present during the negative $\delta^{13}\text{C}$ T-OAE, termed the “belemnite gap” by Hesselbo et al. (2007); and/or (2) are shifting habitats and thus sampling different components of the water column thus masking (diluting) the isotopic excursion.

In this study, the specific issue of the global extent of the Early Toarcian negative $\delta^{13}\text{C}$ excursion as well as the expression of the T-OAE in the open ocean are addressed by analysing a deep-sea chert record from Katsuyama, Japan (Fig. 1), which was located in the palaeo-Pacific (Panthalassic Ocean) during the Early Jurassic.

2 Geological setting

The studied samples were obtained from the Inuyama area, Mino Terrane, which is one of the Mesozoic accretionary complexes presently exposed in Japan, extending to the north of Tokyo (Ashio Terrane) and lithologically and stratigraphically corresponding to the Chichibu Terrane (Fig. 1). In Japan, these Mesozoic complexes consist of seamount-related sequences of volcanic rocks, limestones and pelagic sediments (bedded chert and siliceous mudstone) associated with trench-fill sediments. The sediments were deposited on the seafloor of the Izanagi Plate from Carboniferous to Early Cretaceous and were subsequently accreted to the margin of Far East Asia during the Jurassic to Early Cretaceous (Matsuda and Isozaki, 1991).

The stratigraphic section in the Inuyama area mainly consists of bedded cherts spanning the Early Triassic–Early/Middle Jurassic and has been well-constrained using conodont and radiolarian biostratigraphy (e.g., Yao et al., 1982; Hori, 1990, 1993; Mat-suoka, 2004). Since the sedimentary complex of this area formed by accretionary processes at shallow depths (Kimura and Hori, 1993) undergoing extremely low-grade metamorphism (diagenetic zone of illite crystallinity index; Otsuka and Watanabe, 1992), it is considered that the cherts retain a primary record of the Upper Triassic and Lower Jurassic depositional environments.

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The studied pelagic sediments in the Inuyama area are typically distal, open ocean sediments characterized by sedimentation rates of 1 m to 7 m Myr⁻¹ and long sequences (>50 Myr) (Hori et al., 1993; Wignall et al., 2010). Although such sediments are generally considered to be analogous to present-day deep-sea radiolarian ooze (>3 km water depth), similar Mesozoic sequences drilled by the IODP offshore on Pacific seamounts are much shallower (within the mid-water oxygen minimum layer) and have been interpreted as reflecting deposition on seamounts under highly productive surface seawater below the equatorial divergence zone (Wilson et al., 1998; Jenkyns and Wilson, 1999; Robinson et al., 2004).

Palaeomagnetic studies reveal that these cherts contain primary magnetism and record normal and reverse polarity zones during the Triassic (Shibuya and Samejima, 1986; Ando et al., 2001). The data imply that the Inuyama chert sequence was indeed deposited at low Southern Hemisphere latitudes during the Middle Triassic and migrated to the Northern Hemisphere during the Late Triassic–Early Jurassic, crossing the equatorial regions of the palaeo-Pacific (Fujii et al., 1993; Ando et al., 2001).

2.1 Katsuyama section

The biostratigraphy of the sequence at Katsuyama (Fig. 2), located in the northern part of the Inuyama area, has been well studied (Hori, 1990, 1992, 1997; Takeuchi, 2001; Matsuoka, 2004). The studied sequence consists of a continuous succession of bedded cherts (>100 m thick), which based on radiolarian biostratigraphy (Matsuoka et al., 1994) spans the upper Lower Triassic (Spathian) to lower Middle Jurassic (Aalenian). Over the Lower Jurassic part of the succession, five radiolarian (sub)zones are recognized: the *Parashuum simplum* sSubzones I to IV, and the *Mesosaturnalis hexagonus* (= *Hexasaturnalis hexagonus*) Zone (in ascending order) (Hori, 1990; 1997). A distinct change in palaeontology and lithology is observed within the upper part of the Lower Jurassic succession (Hori, 1997). Here, organic-rich black chert beds suggestive of a dysoxic/anoxic environment occur in the upper part of *Parashuum simplum* Subzone IV (ca. 40 cm, Fig. 2) which is covered by a massive white chert bed and black-white chert

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beds containing MnCO_3 spherules (ca. 200 cm, Fig. 2). White chert (novaculite) may be the product of low-grade metamorphism of siliceous sequences or, alternatively, it may be the product of silicification of volcanoclastic rocks, which, given the geological setting appears to be more likely. The lithologies of this interval differ from the more predominant red cherts found above. Wignall et al. (2010) analysed samples from Katsuyama and suggested the presence of anoxia based on pyrite framboid evidence. The correlation with their published log of the succession with the one presented here is ambiguous.

The samples for the present isotopic study were obtained from the interval spanning the upper part of the *Parashuum simplum* IV (Ps IV) Subzone to the lower part of the *Hexasaturnalis hexagonus* (Hh) Zone, which is composed of a ca. 340 cm thick sequence of bedded chert. This equates to the radiolarian Zones in Carter et al. (2010) of *Eucyrtidiellum nagaiae*-*Praeparvicingula tlellensis* to *Elodium pessagnoii*-*Hexasaturnalis hexagonus* (see Fig. 2). On the basis of a 1 m Myr^{-1} sedimentation rate for the Lower Jurassic cherts of the Inuyama area (Hori et al., 1993), the studied interval is calculated to have lasted a maximum of ca. 3.5 Myr.

Age assignments for the Katsuyama succession can be made based on the available radiolarian biostratigraphy. The Pliensbachian/Toarcian boundary is not well-constrained using radiolarian biostratigraphy although the last occurrence of *Eucyrtidiellum nagaiae* is at ca. -30 cm (Fig. 2). This level is also about 2 m above the first occurrence of *Trillus elkhornensis* in the Katsuyama section. On the basis of radiolarian data from east-central Oregon, North America, *Trillus elkhornensis* makes its first appearance in the Upper Pliensbachian Nicely Formation (*Amaltheus margaritatus*-*Pleuroceras spinatum* ammonite Zones) (Pessagno and Blome, 1980). In addition, the highest occurrence of *Eucyrtidiellum* sp. 2 (= *E.* sp. C2 of Nagai, 1986) has been reported from the Lower Toarcian Hyde Formation overlaying the Nicely Formation (Nagai, 1990).

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There is a significant gap in constraining the radiolarian biostratigraphy between ca. –30 cm and ca. 250 cm due to a lack of diagnostic species (Fig. 2). The lowest occurrence of the genus *Parvincingula* has been recognized in the middle Toarcian Whiteaves Formation (*Hildoceras bifrons* ammonite Zone) from the Queen Charlotte Islands, Canada (Carter et al., 1988) and *Hexasaturnalis hexagonus* is also obtained from the upper/middle to lower/upper Toarcian sequence from the same area. Therefore at ca. 250 cm the first occurrence of *Hexasaturnalis hexagonus* suggests an age equivalent to the *Harpoceras falciferum*/*Hildoceras bifrons* ammonite Zone boundary of NW Europe (see Carter et al. 2010). This interval is also characterized by a remarkable faunal change, termed the Toarcian Radiolarian Event (Hori, 1997) (see Fig. 2). Thus, if the T-OAE is present in the form of CIE then it should occur below ca. 240 cm (Fig. 2).

3 Analytical methodology

Bulk sediment samples were decalcified using 3M HCl in 50 ml centrifuge tubes for 16 h. Stable isotope measurements were performed at Durham University using a Costech elemental analyser (ESC4010) coupled to a ThermoFinnigan Delta V Advantage isotope ratio mass spectrometer. Carbon isotope ratios are corrected for ^{17}O contribution (Craig, 1957) and reported in standard delta (δ) notation in per mil (‰) relative to VPDB. Data accuracy is monitored through routine analyses of international and in-house standards: the latter are stringently calibrated against the international standards. Analytical uncertainty for $\delta^{13}\text{C}_{\text{org}}$ measurements was typically better than $\pm 0.1\text{‰}$ for standards and $< 0.2\text{‰}$ on replicate sample analysis. Total organic carbon (TOC) data was obtained as part of this method. Because of the low TOC contents of the studied chert samples, the tin capsules used contained up to 100–120 mg of powdered chert and the Costech was set to Macro- O_2 . The isotope analyses were done in no dilution mode and all results produced more than 1000 m.

4 Results and discussion

4.1 The Katsuyama T-OAE record

The physical expression of the Early Toarcian OAE in the Katsuyama succession is defined through the presence of organic-rich facies (cf. Wignall et al., 2010). TOC contents through the section range between 0.01–2.75 wt %. Two marked increases in TOC occur at ca. 45 cm and ca. 190 cm, where major lithologic changes are observed in the form of shifts from grey to black cherts (Fig. 3).

The siliceous sediments of the Katsuyama section are here interpreted to have been deposited in an open ocean setting on the seafloor of a volcanic seamount at mid-water depths. The seamount, which was originally emplaced in the Southern Hemisphere (Fujii et al., 1993; Ando et al., 2001) was transported north-westwards to its current position in Far East Asia by seafloor spreading (cf. Wilson et al., 1998). During its journey, the seamount was covered by pelagic sediments and, within the equatorial divergence zone, siliceous black shales were deposited as part of the pelagic sequence. The black shales are organic-rich radiolarian cherts and, therefore, attest to conditions of high productivity in the euphotic zone and of low oxygen at the seafloor. Whereas low oxygen conditions are a characteristic feature of the global oxygen minimum layer in the ocean, underneath the equatorial divergence zone these conditions would have been intensified. Due to the palaeogeographical setting of the Katsuyama section in the Early Jurassic, the T-OAE not only records the global perturbation in the carbon cycle that is characteristic of this time interval and the record of which is known from sections worldwide, but it is also characterized by organic-rich open ocean lithologies.

Indeed, the presence of black shales in open ocean settings needs not necessarily to represent a spread of anoxia in the oceans, but rather the passage of an ideal substrate for the preservation of organic matter through a zone in the ocean which is a priori anoxia-prone. This model helps to reconcile the presence of black shales in open ocean settings with evidence for upwelling in the open marine environment and for enhanced ocean overturning (Kajiwara et al., 1994; Suzuki et al., 1998; Trabucho

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Alexandre et al., 2010) during such events, as well as with high C/S ratios in similar sediments (Suzuki et al., 1998) not easily explained by ocean anoxia and stable stratification.

The $\delta^{13}\text{C}_{\text{org}}$ record reveals two negative shifts – the first occurring between ca. 65 cm to ca. 90 cm; the second occurring between ca. 180 cm to ca. 240 cm. Both shifts broadly coincide with a change in lithology from grey to black cherts. The excursion between ca. 65 cm and ca. 90 cm involves a change in $\delta^{13}\text{C}_{\text{org}}$ of ca. 2‰, whereas the excursion from ca. 180 cm to ca. 240 cm represents a more pronounced perturbation with values shifting from ca. –30‰ to –33‰. Within this negative $\delta^{13}\text{C}_{\text{org}}$ excursion one sample (at ca. 212 cm) records a $\delta^{13}\text{C}_{\text{org}}$ value of –57‰. Extremely negative $\delta^{13}\text{C}_{\text{org}}$ values of < –40‰ have not been recorded in the Phanerozoic, although such values are relative common in anoxic, organic-rich sediments in the Archaean (Rasmussen et al., 2008). At ca. 250 cm, coinciding with the TRE (Fig. 3), $\delta^{13}\text{C}_{\text{org}}$ values markedly increase from ca. –33‰ to ca. –25‰. This increase to less negative values is also coincident with a return to lower TOC values (Fig. 3).

4.2 Correlation of the Pliensbachian/Toarcian and T-OAE $\delta^{13}\text{C}$ curve

The radiolarian biostratigraphy, in combination with the $\delta^{13}\text{C}_{\text{org}}$ record, permits a correlation to be made between the Katsuyama succession and Early Toarcian successions in Europe. Coupling of the age constraints of the Katsuyama succession to the TOC record and $\delta^{13}\text{C}_{\text{org}}$ variations strongly support the inference that the negative CIE occurring between ca. 180 cm and ca. 250 cm height in the succession is the Early Toarcian negative CIE. Similarly, the data (Fig. 4) also supports the inference that the ca. 2‰ negative excursion occurring between ca. 60 cm and ca. 100 cm height represents the excursion found in European sections at the Pliensbachian/Toarcian boundary. Evidence for a Pliensbachian/Toarcian negative CIE from Europe has been documented from sections in Yorkshire (Littler et al., 2009) and Peniche (Hesselbo et al., 2007; Suan et al., 2008) and is also apparent in the Mochras Farm record of Wales (Jenkyns et al., 2001) (Fig. 4).

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In the Argentinean $\delta^{13}\text{C}_{\text{org}}$ record presented by Al-Suwaidi et al. (2010), however, clear evidence for a negative shift at the Pliensbachian/Toarcian boundary was absent. As such, the data from the Katsuyama succession potentially represents the first evidence for the Pliensbachian/Toarcian $\delta^{13}\text{C}_{\text{org}}$ excursion outside Europe and in an open ocean setting, suggesting that the development of organic-rich facies was not restricted to epi- and peri-continental basins and thus more widespread than previously assumed. Interestingly, the rise in TOC occurs prior to the Pliensbachian/Toarcian CIE and thus differs from the T-OAE record, which typically indicates a TOC rise during the most negative part of the CIE (see Hesselbo et al., 2000; Jenkyns et al. 2002; Kemp et al., 2005).

Using the time-scale adopted by Hori et al. (1993), the duration of the negative excursion across the Pliensbachian/Toarcian can be calculated at ca. 200 kyr, with the T-OAE being ca. 535 kyr. The latter value is similar to the recent estimate by Suan et al. (2008), who assigned a value of 600 kyr for the duration of the T-OAE negative excursion. Suan et al. (2008) further suggested that the entire excursion (negative and positive excursion) lasted 900 kyrs. If it is assumed that the end of the T-OAE excursion in Fig. 2 occurs at ca. 300 cm then, indeed, a duration of 991 kyr is estimated. The presence of these CIEs in stratigraphic positions for the Pliensbachian/Toarcian and T-OAE related to radiolarian biostratigraphy and their respective durations that are similar to other similars supports the notion that these major Early Jurassic carbon cycle perturbations affected all active global reservoirs of the exchangeable carbon cycle (deep marine, shallow marine, atmospheric).

4.3 Mechanistic Model for the T-OAE

The new geochemical record of the T-OAE presented in this study represents the first complete record of the excursion outside Europe and also the first open ocean expression of the event. Using the “most” negative $\delta^{13}\text{C}$ segment of the T-OAE as a tie-point, comparison of the record to that from sites in the United Kingdom and Portugal clearly

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shows that the geochemical signature of this OAE is similar between epi- and peri-continental, and open ocean localities (Fig. 4). Moreover, because the Katsuyama succession is truly pelagic and, at the time of deposition, away from land influence, the negative excursion is shown to indeed represent a primary global signal. The T-OAE is therefore defined (and sediments deposited during the T-OAE associated with) by a rapid negative excursion in the carbon isotope record that is recorded globally whatever the physical/lithological expression of the associated facies. In the open ocean, marine Katsuyama succession, the T-OAE interval is characterized by dysoxic, organic-rich facies (Fig. 2), with periodic anoxia and euxinia intervening (see also Wignall et al., 2010).

As noted in the introduction, the seemingly localized nature of the Early Toarcian negative $\delta^{13}\text{C}$ excursion, apparently confined to epicontinental successions of the Neotethyan realm (Europe), has prompted a number of workers to question whether a global mechanism is capable of explaining the Early Toarcian excursion (e.g., Wignall et al., 2006; McArthur et al., 2007). An alternative hypothesis for the event has been offered instead which invokes local overturn of ^{12}C -enriched dissolved CO_2 from deeper waters to the surface, where photoautotrophic uptake of this carbon would consequently lead to a regional negative $\delta^{13}\text{C}$ excursion (Kuspert, 1982; Rohl et al., 2000; Wignall et al., 2006; van de Schootbrugge et al., 2005). The overturn hypothesis was questioned by van Breugel et al. (2006) who analysed isorenieratene abundances and $\delta^{13}\text{C}$ across the event in the Paris Basin, France and concluded that respired CO_2 could not have contributed significantly to the negative CIE. Indeed, in light of the data presented here, and that of the recent Al-Suwaidi et al. (2010) study from Argentina, the overturn scenario is improbable given that it implies that overturn of a large amount of ^{12}C affected the global ocean synchronously.

These results notwithstanding, the purported lack of a negative $\delta^{13}\text{C}$ excursion in records of belemnite calcite has been used by some authors to support the claim that isotopically light carbon did not dominate the ocean-atmosphere system during the T-OAE (Wignall et al., 2006; van de Schootbrugge et al., 2005). Such a claim would

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argue against the methane hydrate and igneous intrusion thermogenic hypotheses. This view is countered by evidence for a synchronous negative CIE in terrestrial plant material (Hesselbo et al., 2000, 2007). This observation, coupled with the results presented here, unequivocally demonstrates that isotopically light carbon dominated the global marine organic (both shallow and deep) and atmospheric reservoirs of carbon. Furthermore, evidence exists for a well-developed negative excursion in carbonate rocks dominated by coccolith fossils (Hermoso et al., 2009) and brachiopods (Suan et al., 2008). This raises the question as to whether belemnites are reliable recorders of the isotopic composition of seawater during environmental perturbations such as those recorded during the T-OAE (cf. Hermoso et al., 2009).

The emplacement of the Karoo-Ferrar large igneous province in the latest Pliensbachian is likely to be of significance in the development of the negative $\delta^{13}\text{C}$ excursion that defines the T-OAE. Long-term injection of volcanic greenhouse gases (primarily CO_2) into the atmosphere associated with the emplacement of large igneous provinces is thought to have led to an increase in global mean temperatures (Pálffy and Smith, 2000). Although the Toarcian palaeotemperature record may have been influenced by a reduction in salinity (freshwater input) and/or latitudinal water flow through the NW European corridor (Bjerrum et al., 2001), belemnite-derived Mg/ca. and $\delta^{18}\text{O}$ palaeotemperature calculations show an increase in seawater temperature through the latest Pliensbachian and Early Toarcian (McArthur et al., 2000; Rosales et al., 2004). In turn, rising temperatures would have led to an intensification of the hydrological cycle, for which there is evidence in the form of a peak in kaolinite abundance, thus indicative of a humid environment during the Toarcian (Ruffell et al., 2002; Dera et al., 2009). Additionally, Cohen et al. (2004) reported an $^{187}\text{Os}/^{188}\text{Os}$ excursion during the T-OAE and inferred it to represent an increase in global weathering on the order of 400–800%. The magnitude of the increase was subsequently reduced by modelling work on a strontium isotope record through the Jurassic by Waltham and Gröcke (2006). McArthur et al. (2007) argued, however, that the strontium isotope profile through the event was an artefact of changing sedimentation rates, rather than a primary climatic

signal. Nevertheless, an increase in both seawater palaeotemperature and weathering rates are in agreement with an increase in atmospheric CO₂.

An increased nutrient flux driven by accelerated continental weathering regimes would have enhanced and promoted surface water productivity and led to algal and bacterial blooms (Watson et al., 2000) in proximal epi- and peri-continental environments. $\delta^{15}\text{N}_{\text{tot}}$ values through the Mesozoic suggest that cyanobacteria were a significant contribution to oceanic productivity, with values fluctuating around 0‰ (Jenkyns et al., 2002). However, modern laboratory experiments have shown that cyanobacteria require five times as much iron over carbon when grown with N₂ (Kustka et al., 2003), thus indicating that iron supply must have been high during the Mesozoic and, in particular, during OAEs. The concurrent input of methane into the oceanic and atmospheric carbon reservoirs, and its subsequent oxidation would have increased CO₂ and decreased O₂ concentrations – potentially in both the ocean and atmosphere (i.e., Dickens, 2000). Also, a subsequent rise in global productivity would also have led to increased consumption of O₂ in the oceanic and atmospheric reservoirs, enhancing organic matter preservation, extinctions in the ocean (Cecca and Macchioni, 2004) and floral radiations in the terrestrial realm (Vakhrameev, 1991). Based on the findings presented here and those of Wignall et al. (2010), these processes clearly not only affected the shallow marine system but also the deeper, open marine environment with enhanced TOC values and evidence of anoxia/euxinia in the Katsuyama cherts (Fig. 3, Wignall et al., 2010).

Submarine mass movements are recorded in Portugal and Spain (Kullberg et al., 2001) and have been dated as coeval to the initiation of the negative $\delta^{13}\text{C}_{\text{org}}$ excursion noted by Hesselbo et al. (2001): *Polymorphum* ammonite Zone, *Semicelatum* ammonite Subzone. The discovery of submarine mass movements concomitant with the T-OAE $\delta^{13}\text{C}$ negative excursion make this event very similar to the Palaeocene-Eocene Thermal Maximum (PETM) clathrate dissociation event (Dickens, 2000). Hence, submarine mass movements and the rise of bottom water temperatures during the *Tenuicostatum* ammonite Zone potentially led to the release of continental

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margin clathrates and the Toarcian $\delta^{13}\text{C}$ negative excursion. Indeed, many of the geochemical features of the T-OAE are readily apparent during the more recent PETM and these similarities have prompted direct comparisons to be made (Cohen et al., 2007). The results presented here further attest to the broad similarities between the two events because a key feature of the PETM is a well-developed expression of carbon isotope changes in the atmosphere, and shallow and deep oceans.

5 Conclusions

The perturbation in the carbon cycle that occurred during the T-OAE was a global phenomenon that affected all carbon reservoirs and is recorded by a negative CIE in terrestrial and marine sediments (both shallow and deep ocean settings). Therefore, the forcing mechanism(s) behind the T-OAE must have been capable of driving global environmental change. These mechanisms may have included: the eruption of the Karoo-Ferrar continental flood basalts; the massive dissociation of continental margin clathrates; an increased hydrological cycle; and a transient greenhouse climate with increased CO_2 concentrations and palaeotemperatures. Apart from the T-OAE CIE, the Pliensbachian/Toarcian CIE is recorded in the Katsuyama cherts suggesting another global carbon isotope excursion. These CIEs are important for understanding the Early Jurassic carbon cycle, as well as a tool for stratigraphic correlation between diverse palaeogeographic realms.

The palaeogeography of black shale depositional environments during OAEs is a matter of discussion. All previously known examples of Toarcian black shales were deposited on epi- and peri-continental shelves in environments proximal to Pangaea. In this study, a distal, truly pelagic, open ocean setting is described. These black shales were deposited on the seafloor of a volcanic seamount due to its passage under the highly productive waters of the equatorial divergence zone of Panthalassa. The shorter export path for organic matter resulting from the presence of a submarine topographical high in association with the expansion of the oxygen minimum layer due to high oxygen

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demand favoured the preservation of organic matter and led to black shale formation. Thus, it appears that the palaeogeographical distribution of black shales during the T-OAE is similar to that of other Mesozoic OAEs and to that of PETM black shales.

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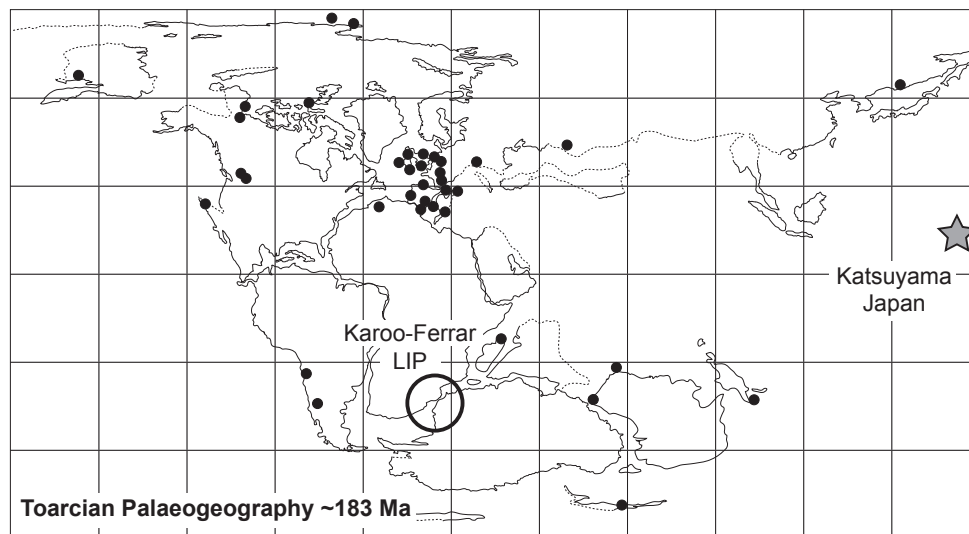


Fig. 1. Palaeogeographic map of the Early Jurassic showing the distribution of organic-rich facies (filled circles) dated as Early Toarcian (modified from Jenkyns et al., 2002). The star indicates the approximate palaeogeographic location of the Katsuyama section, Japan, during the deposition of Toarcian succession. Large circle represents the location of the Karoo-Ferrar large igneous province.

Katsuyama Section, Inuyama, Japan

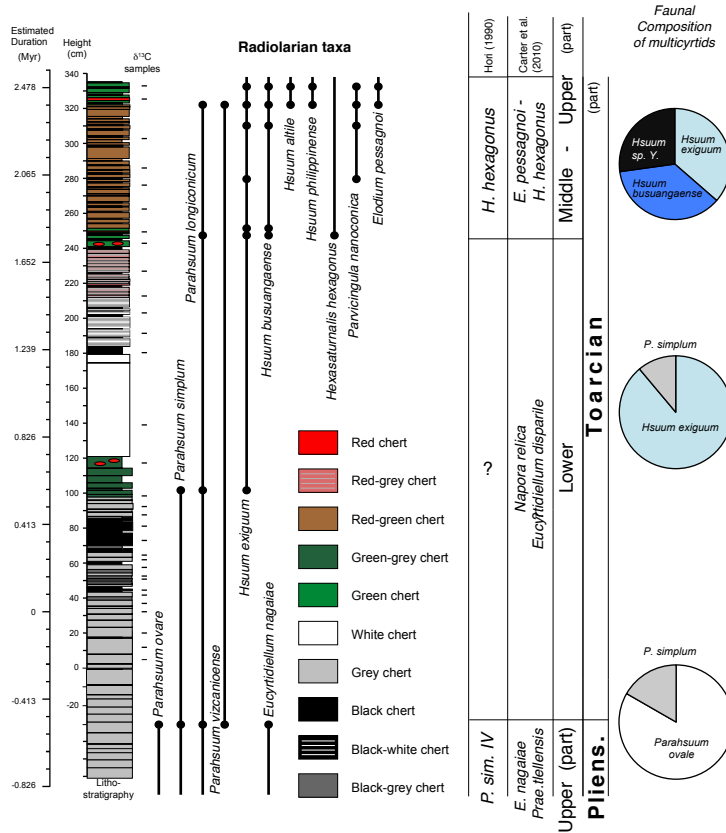


Fig. 2. Detailed lithostratigraphic log and biostratigraphy of the Katsuyama UF Section, Inuyama, Japan. Radiolarian biostratigraphy is from Horii (1997) and modified according to Carter et al. (2010). On the basis of a 1 m Myr⁻¹ sedimentation rate for the Lower Jurassic chert succession at Inuyama, the studied interval is calculated to be ca. 3.5 Myr in duration (see Horii et al., 1993).

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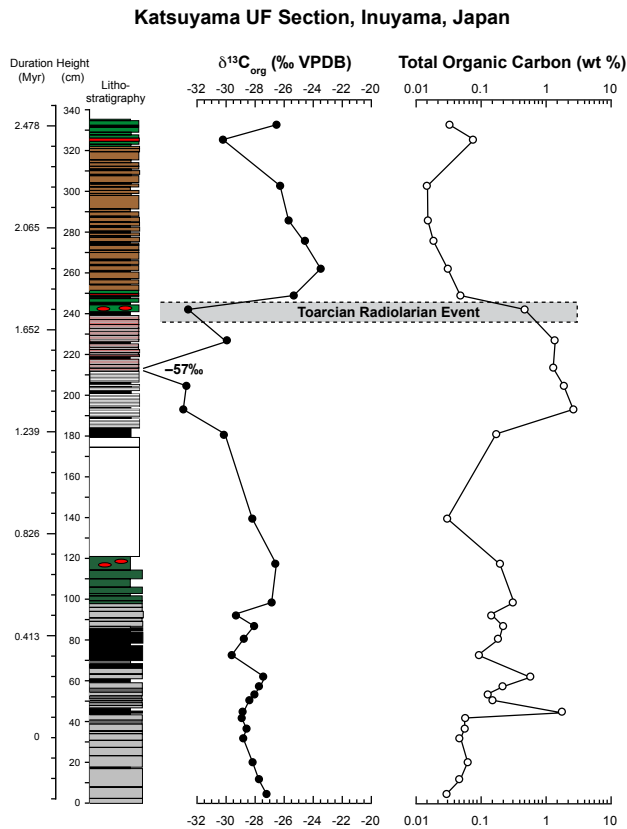


Fig. 3. Organic carbon isotope record ($\delta^{13}\text{C}_{\text{org}}$) of the Katsuyama UF Section, Inuyama, Japan. Total Organic Carbon (TOC) as weight percent (wt%) was determined during stable-isotope measurements. Note that the scale for TOC is logarithmic. The chert sample at ~212 cm has a $\delta^{13}\text{C}_{\text{org}}$ value of -57‰ . The Toarcian Radiolarian Event is also depicted at ~240 cm. See Fig. 2 for lithostratigraphic and biostratigraphic details.

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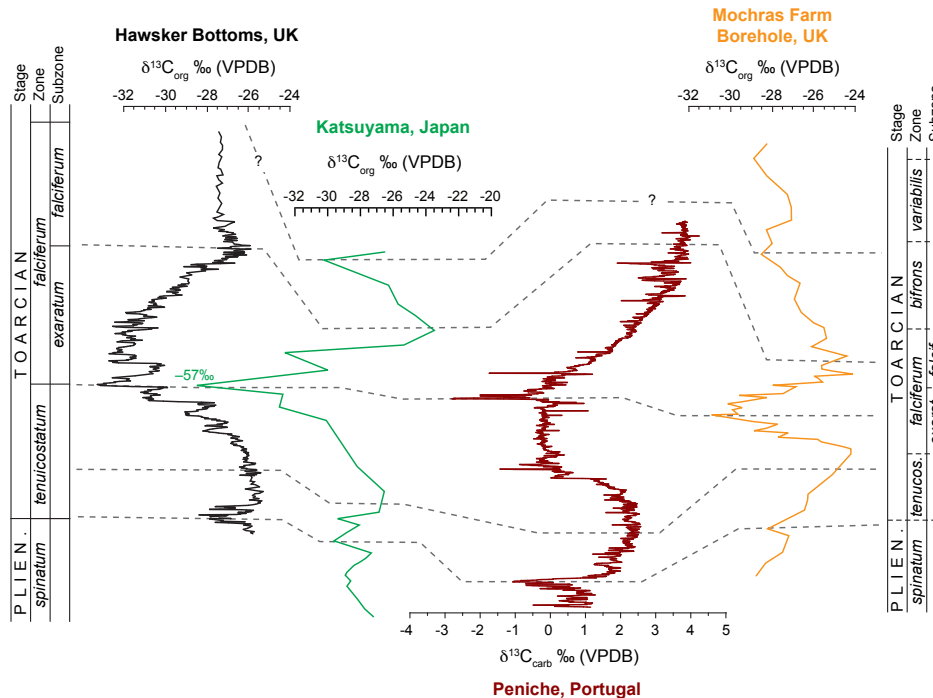


Fig. 4. Comparison of $\delta^{13}\text{C}$ profiles for the Pliensbachian–Toarcian time interval. Bulk-sediment data are compiled from Whitby (dataset is from both Port Mulgrave and Hawsker Bottoms) (Kemp et al., 2005; Littler et al. 2009), Katsuyama (this study), Peniche (Hesselbo et al., 2007) and Mochras Farm Borehole (Jenkyns et al., 2001). The $\delta^{13}\text{C}_{\text{org}}$ profiles have been correlated using the negative excursion at the Pliensbachian/Toarcian boundary, positive values in the Early Toarcian, the maximum negative values in the T-OAE, the subsequent positive excursion after the T-OAE, and finally the negative trend in the Bifrons ammonite Zone between Mochras Farm Borehole and Katsuyama. No data has been adjusted for changing sedimentation rates. Note, that Peniche is the only carbonate carbon isotope record.