



MICROBES, MUD AND METHANE: CAUSE AND CONSEQUENCE OF RECURRENT EARLY JURASSIC ANOXIA FOLLOWING THE END-TRIASSIC MASS EXTINCTION

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Abstract: The end-Triassic mass extinction (*c.* 201.6 Ma) was one of the five largest mass-extinction events in the history of animal life. It was also associated with a dramatic, long-lasting change in sedimentation style along the margins of the Tethys Ocean, from generally organic-matter-poor sediments during the Triassic to generally organic-matter-rich black shales during the Jurassic. New core material from Germany provides biomarker evidence of persistent photic-zone euxinia during the Hettangian, the onset of which is associated with a series of both negative and positive carbon isotope excursions. Combined inorganic and organic geochemical and micropalaeontological analyses reveal strong similarities between the Hettangian and the better-known Toarcian anoxic event. These events appear to be the most clearly expressed events within a series of anoxic episodes that also include poorly studied black shale intervals during the Sinemurian and Pliensbachian. Both the Hettangian and

Toarcian events are marked by important changes in phytoplankton assemblages from chromophyte- to chlorophyte-dominated assemblages within the European Epicontinental Seaway. Phytoplankton changes occurred in association with the establishment of photic-zone euxinia, driven by a general increase in salinity stratification and warming of surface waters. For both events, the causes of large negative carbon isotope excursions remain incompletely understood; evidence exists for both variation in the $\delta^{13}\text{C}$ of atmospheric CO_2 and variation in the sources of organic carbon. Regardless of the causes of $\delta^{13}\text{C}$ variability, long-term ocean anoxia during the Early Jurassic can be attributed to greenhouse warming and increased nutrient delivery to the oceans triggered by flood basalt volcanism.

Key words: Jurassic, carbon cycle, anoxic events, phytoplankton.

FOLLOWING the end-Triassic mass-extinction event *c.* 201 Ma, the Early Jurassic was a time of profound change in the atmosphere, geosphere and especially the biosphere (Vermeij 1977, 2008). On land, the Late Triassic extinction of the Archosaurs, including the primitive Rauisuchians, opened the door for the rapid evolution of the theropods and giant sauropods during the Early Jurassic (Sereno 1999). Ongoing break-up of the supercontinent Pangaea triggered widespread flood basalt volcanism, denatation of continental margins and increased flooding of continents. In shallow, well-lit epicontinental seaways, dinoflagellates and coccolithophorids rose to ecological prominence (van de Schootbrugge *et al.* 2005a). Marine predators may have profited from an increased abundance

of algal biomass and a larger diversity in algal sterols: along the Dorset Coast, the remains of innumerable ammonites still litter the beaches at Lyme Regis.

In Germany, the Lower Jurassic is informally known as ‘Schwarzer Jura’ (Black Jurassic), denoting the prevalence of black and dark grey, bituminous sediments overlying Upper Triassic pale sandstones and underlying brownish, iron-rich sediments of Bajocian and Bathonian age, belonging to the so-called Brauner Jura (Brown Jurassic). The term ‘Schwarzer Jura’ was coined by Leopold von Buch in 1837 during a lecture held at the Royal Academy of Sciences in Berlin (cited in Quenstedt 1843, p. 122) and further defined by Friedrich von Quenstedt through a detailed overview of palaeontological findings and

sedimentological observations made in southern Germany (Quenstedt 1843). The deposition of black shales, notably during most of the Hettangian, in the late Sinemurian and part of the Pliensbachian, culminated during the Toarcian with the deposition of the ‘Posidonien Schiefer’ (Posidonia Shales).

The prevalent mode of black shale deposition during the Early Jurassic was not geographically restricted to Germany (see also Fig. 1). The transition from the Lillstock Formation to the Hettangian Blue Lias Formation in England is characterized by the deposition of black shales belonging to the Watchett and Pre-Planorbis Beds (Wignall 2001). Organic-rich sedimentation continued into the latest Sinemurian (Wignall and Hallam 1991) with the deposition of the Black Ven Marls. The overlying Lower Pliensbachian Belemnite Marls are generally paler in colour, but exhibit lime-marl alternations that still contain considerable amounts of organic matter content (Weedon *et al.* 1999). Black shale deposition was only briefly interrupted during the Late Pliensbachian by a sandy ironstone facies before a thick succession of

Toarcian organic-rich sediments belonging to the Whitby Mudstone Formation was laid down, including the famous Jet Rock. In northern Spain, the Pliensbachian contains at least three intervals with black shales (Aurell *et al.* 2003; Rosales *et al.* 2006) that are beautifully exposed along the Asturian coast, for example at Playa de la Vega close to Gijon (Borrego *et al.* 1996). Farther south, the Sinemurian and Pliensbachian successions of the Lusitanian Basin in Portugal record several organic-rich intervals (up to 22 per cent TOC; Duarte *et al.* 2010). In the Grands Causses Basin of southern France, organic-rich sedimentation started only during the late Sinemurian, but continued well into the Aalenian (Harzizim *et al.* 2013). Organic-rich facies of Hettangian age similar to those in the UK and Germany also occur in the Paris Basin (Poujol 1961).

Of the various Lower Jurassic black shale intervals, those of the Lower Toarcian have garnered most attention, starting with seminal publications by Hallam (1967) and particularly Jenkyns (1988), who suggested that black shale deposition and the anoxia were of global extent.

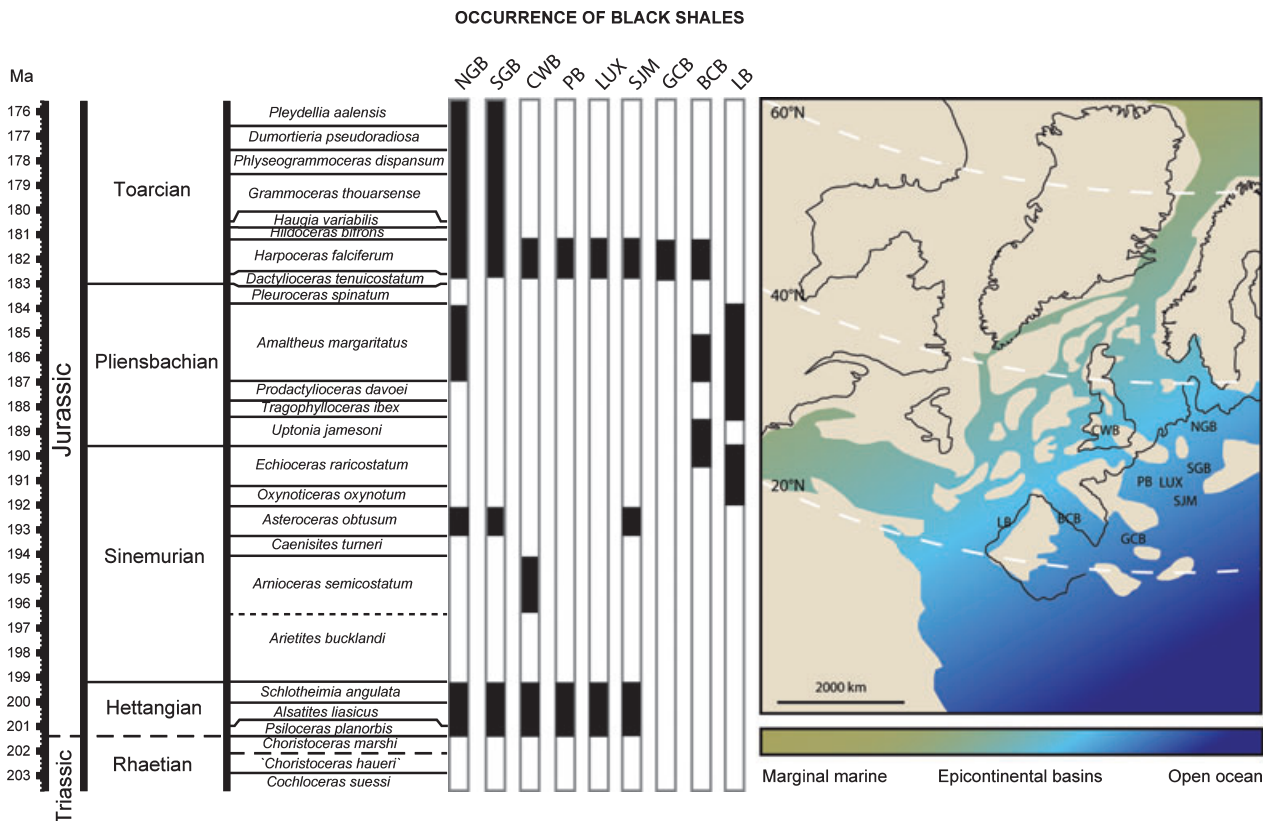


FIG. 1. Distribution of black shale deposits in Europe during the Early Jurassic (partly modified after Fleet *et al.* 1987; timescale created with *Time Scale Creator 5.0*). Timescale was adjusted to account for recently updated time frame for the Triassic–Jurassic boundary interval based on Schaltegger *et al.* (2008) and Ruhl *et al.* (2010). Palaeogeographic map of the European Epicontinental Seaway (modified after Redfern *et al.* 2010) showing main basins and sites mentioned in the text. NGB, north German Basin; SGB, south German Basin; CWB, Cleveland–Wessex Basin; PB, Paris Basin; LUX, Luxembourg; SJM, Swiss Jura Mountains; GCB, Grands Causses Basin; BCB, Basque–Cantabrian Basin; LB, Lusitanian Basin.

The Toarcian oceanic anoxic event (OAE) has been studied intensively with an enormous array of tools and techniques, bringing to light major changes in phytoplankton populations (Bucefalo Palliani *et al.* 2002; Mattioli *et al.* 2008), stable carbon, oxygen, strontium and sulphur isotope records (Hesselbo *et al.* 2000; McArthur *et al.* 2000; Bailey *et al.* 2003; Newton *et al.* 2011), trace elements and their isotopes (Cohen *et al.* 2004), organic geochemistry (Schouten *et al.* 2000), clay minerals (Dera *et al.* 2009a) and sedimentology (Röhl *et al.* 2001; Wignall and Bond, 2008). None of these studies, however, conclusively show that the deposition of Toarcian black shales was truly a global and synchronous event. Extremely condensed sections with Toarcian black shales have been described from Japan, which presumably recorded open-ocean anoxic conditions (Wignall *et al.* 2010). Recently published studies on successions in Argentina (Al-Suwaidi *et al.* 2010), Japan (Gröcke *et al.* 2011; Izumi *et al.* 2012) and Siberia (Suan *et al.* 2011) indicate that timing and intensity of oxygen depletion depended strongly on local factors. Even in Europe, where Toarcian black shales are widespread, several sections in Portugal (Suan *et al.* 2008) do not show evidence for anoxia. Along the northern margin of Gondwana, black shales are absent also in Morocco (Bodin *et al.* 2010), Oman (Watts 1990; Immenhauser *et al.* 1998) and the Indian Himalayas (Bhargava and Bassi 1998). In fact, TOC-rich black shales increase in prevalence and thickness from south to north along the European Epicontinental Seaway (EES; Baudin *et al.* 1990).

Whereas the deposition of Toarcian black shales was not global, the regional deposition of black shales in the EES was likely caused by global environmental and biological changes. There are currently two primary hypotheses for these changes (Cohen *et al.* 2007), both of which rely heavily on the interpretation of carbon isotope records. The first scenario envisions the destabilization of gas hydrates on the sea floor and consequent release of methane to the atmosphere (Hesselbo *et al.* 2000, 2007), possibly modulated by orbital forcing (Kemp *et al.* 2005). The alternative scenario links Early Toarcian changes to the eruption of flood basalts of the Karoo-Ferrar large igneous province (LIP) (McElwain *et al.* 2005; Svensen *et al.* 2007). Both methane release and volcanic activity have also been implicated in the end-Triassic mass-extinction event (Ruhl and Kürschner 2011; Ruhl *et al.* 2011). Given the coincidence of flood basalt volcanism with anoxia during both the Hettangian and Toarcian, comparative analysis may aid in understanding both events.

In his review of the 'Geochemistry of Oceanic Anoxic Events', Jenkyns (2010) emphasized that the organic matter preserved in black shales is the key to understand OAEs. Microscopic (e.g. palynological) and organic geochemical data can be used to identify the organisms living

in anoxic oceans and the conditions governing black shale deposition during the Phanerozoic. All other (derived) proxy records, such as bulk organic C-isotope, pyrite and carbonate associated S-isotope, or trace element records, can only be deciphered when their relationship with organic matter is taken into account. Hettangian and Toarcian black shales deposited in the EES show many similarities in organic matter contents, pointing to similar driving mechanisms behind the development of anoxia. The purpose of this review is to summarize the state-of-the-art on evidence for repeated Early Jurassic black shale deposition in the EES, including an assessment of global versus regional driving mechanisms.

GREEN OCEANS AND BLACK SHALES

Hettangian organic matter and photic-zone euxinia

A sedimentary regime characterized by euxinic conditions (anoxic and sulphidic) became established in wide swaths of the EES directly following the end-Triassic mass-extinction event. Such conditions have been inferred from the presence of small pyrite framboids in the basal Blue Lias Formation at Pinhay Bay (Wignall 2001) that formed within the water column. Organic matter preservation was strongly enhanced during the Hettangian. At St Audrie's Bay, total organic carbon (TOC) values are generally above 5 per cent for most of the basal Hettangian Blue Lias Formation (Hesselbo *et al.* 2004). Organic-rich beds in the Lower Hettangian of the Doniford section are dominated by type-I kerogen of bacterial and/or algal origin (Clemence *et al.* 2010). This contrasts with low organic contents and a dominantly terrestrial source for the underlying Rhaetian Lilstock Formation (Bonis *et al.* 2010a; Clemence *et al.* 2010). High TOC values, exceeding 10 per cent, also characterize the uppermost Hettangian and Lower Sinemurian at St Audrie's Bay (Ruhl *et al.* 2010). Amorphous organic matter (AOM), generally thought to represent marine, degraded bacterial and algal organic matter, is abundant throughout the basal Hettangian in St Audrie's Bay (van de Schootbrugge *et al.* 2007), Doniford (van de Schootbrugge, work in progress) and northern Germany (Heunisch *et al.* 2010). High TOC values in Doniford are correlated with high hydrogen index (HI) values (Fig. 2), indicating that organic enrichment was driven by sedimentation of type-I and type-II marine bacterial and/or algal organic matter.

Evidence for photic-zone euxinia during the Hettangian is provided by the presence of diaryl isoprenoid molecules derived from green sulphur bacteria (GSB). GSB require both light and H₂S in the water column for their photosynthetic metabolism. Isorenieratane has been detected in middle Hettangian and middle Sinemurian sediments in a

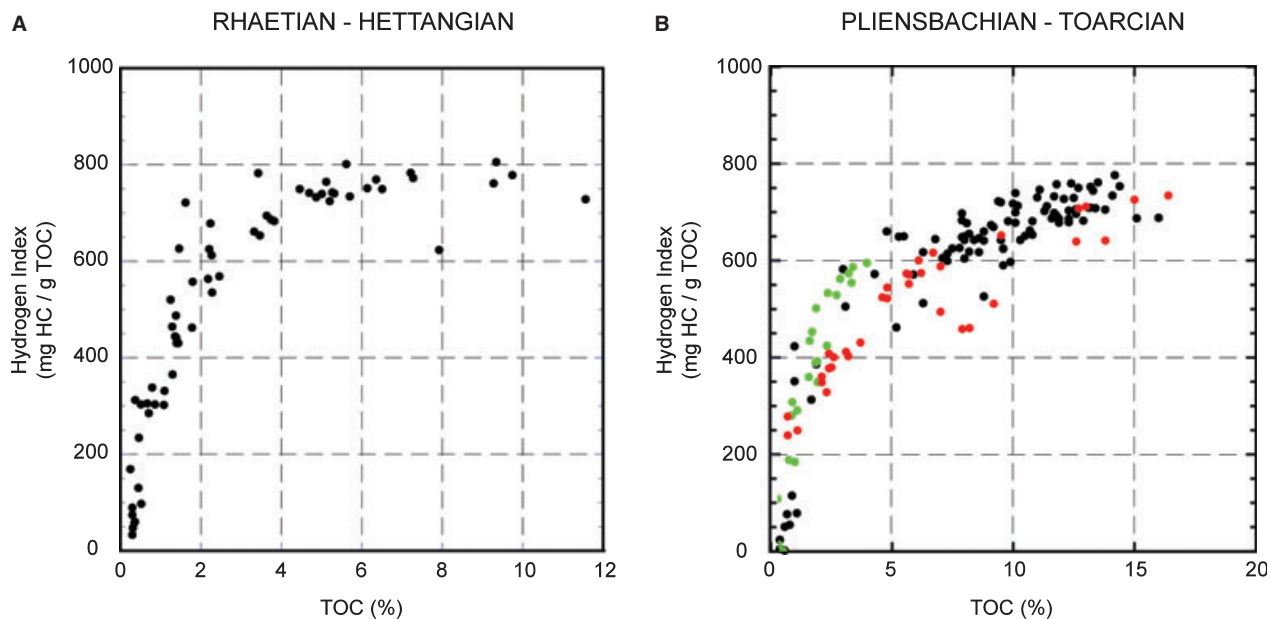


FIG. 2. A, Comparison of Rock-Eval pyrolysis and TOC data for the Rhaetian–Hettangian (data from Clemence *et al.* 2010). B, the Pliensbachian–Toarcian (green dots represent data from Farrimond *et al.* (1994); black dots represent data from Schouten *et al.* (2000); red dots represent data from Saalen *et al.* (2000) showing correlation between high TOC and bacterial or marine algal organic matter with elevated hydrogen index values.

quarry near the village of Frick in the Swiss Jura Mountains (Schwab and Spangenberg 2007). Isorenieratane also occurs in great quantities in shallow marine black shales in the basal Hettangian in cores in northern Germany and Luxemburg (Richoz *et al.* 2012). Surprisingly, amounts of isorenieratane in the Hettangian of the Mariental 1 core drilled in northern Germany (Fig. 3) are higher than those encountered during more illustrious black shale events, such as during the Cenomanian–Turonian OAE-2 (Simons *et al.* 2003) and the anoxia encountered at the Permian–Triassic boundary (Grice *et al.* 2005).

In principle, GSB could have profited from high organic matter flux and sulphate reduction taking place in the sediment with light reaching the shallow sea floor. However, there is ample evidence that changes at the chemocline were mirrored by important changes in photosynthetic algae higher up in the water column and, therefore, that the GSB were also inhabiting the water column rather than the sea floor. Palynological analyses of the St Audrie's Bay section (Hounslow *et al.* 2004; van de Schootbrugge *et al.* 2007; Bonis *et al.* 2010b) document a dominance of acritarchs belonging to the *Michrystidium–Veryhachium* plexus and a strong decrease in dinoflagellate cyst diversity. Abundance of acritarch species in lowermost Jurassic sediments was noted previously by Wall (1965). Palynological analyses of Triassic–Jurassic boundary sections in southern Germany (Fig. 4), northern Germany (Heunisch 1996) and Denmark (Lund

2003) reveal a major change in dominant organic-walled primary producers, from red algal phytoplankton (dinoflagellates) during the Rhaetian to green algae (prasinophytes) and acritarchs in the Hettangian. Diverse assemblages of acritarchs and prasinophytes also occur in the Lower Hettangian at St Audrie's Bay, where prasinophyte phycocysts (vegetative cysts) assigned to *Tasmanites*, *Pleurozonaria* and *Cymatiosphaera* dominate (van de Schootbrugge *et al.* 2007). The red-to-green shift in phytoplankton can be traced further south, to areas located closer to the Tethys Ocean. In Austria, Lower Hettangian phytoplankton assemblages are dominated by prasinophyte remains assigned to *Leiosphaeridia* (Bonis *et al.* 2009). Similar to the UK and southern Germany, the boundary interval in Austria shows an acme in *Cymatiosphaera* (Bonis *et al.* 2010b). The simultaneous onset of photic-zone euxinia and overturn in dominant phytoplankton communities (Fig. 5) suggest that physical–chemical conditions of the entire water column were altered.

Important controls that likely affected both deep photic-zone dwellers, such as GSB, and upper photic-zone primary producers include the availability of bio-limiting nutrients, light conditions, sea surface salinity and sea surface temperature. Combined palynological and inorganic geochemical analyses of the Mingolsheim core (Fig. 4) show that absolute abundance changes from chromophyte (red) to chlorophyte (green) phytoplankton proceeded hand in hand with increases in the abundances of

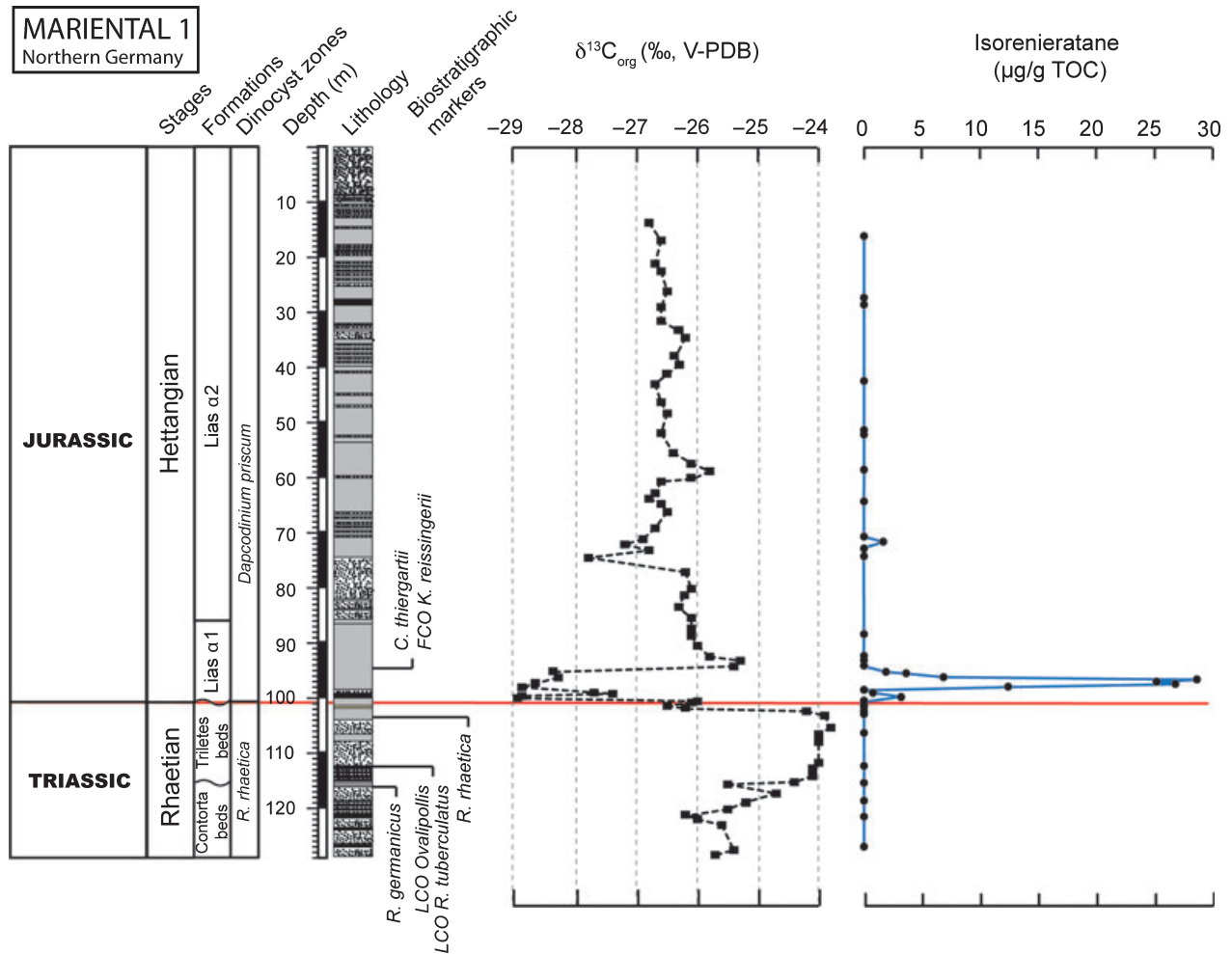


FIG. 3. Organic C-isotope record for the Mariental 1 core and abundance of green sulphur bacterial biomarkers (isorenieratane). Organic C-isotope record for Mariental previously unpublished. Data were measured at the Institute of Geosciences of the Goethe University Frankfurt following standard procedures as outlined in van de Schootbrugge *et al.* (2008). Isorenieratane data are from Richoz *et al.* (2012). Biostratigraphy based on age-dagnostic palynomorphs taken from Heunisch *et al.* (2010).

redox-sensitive trace metals, such as Fe, Cd, U and Mo (Quan *et al.* 2008). These records suggest that anoxic conditions expanded during the Hettangian, reaching a local maximum in the lowermost Sinemurian *Arietites bucklandi* Zone, where U, Cd and Mo show highly elevated abundances (Fig. 4). Members of the green superfamily of algae generally have higher uptake quotas for redox-sensitive trace metals, particularly Fe, compared with members of the red superfamily (Quigg *et al.* 2004). This difference between green and red phytoplankton is thought to be the result of long-term evolutionary dynamics, with prasino-phytes evolving in overall less oxygenated Proterozoic and early Phanerozoic oceans, as opposed to dinoflagellates and coccolithophorids that evolved in well-oxidized Mesozoic oceans (Falkowski *et al.* 2004a, b).

Records of the biolimiting nutrients nitrogen and phosphorus, although incomplete, point towards important

changes across the Triassic–Jurassic boundary. Elevated phosphate (PO_4^{3-}) concentrations occur in association with bone beds and organic-matter-rich sediments of late Rhaetian age in the UK (Suan *et al.* 2011). Rhaetian bone-bed formation can be explained by strong reworking and phosphate-rich waters impinging on shelves during sea-level pulses. The presence of abundant Rhaetian dinoflagellate cysts and epi- and infaunal bivalves (Mander *et al.* 2008) indicates that the water column was mostly oxygenated and that organic matter enrichment was likely driven by high productivity rates. A correlation between phosphate-rich waters and high dinoflagellate abundance can be explained by the observation that dinoflagellates have much higher nutrient uptake quotas for phosphorus when compared with green algae (Litchman *et al.* 2006).

Stratification and photic-zone euxinia may have driven nitrogen depletion in surface waters, favouring organisms

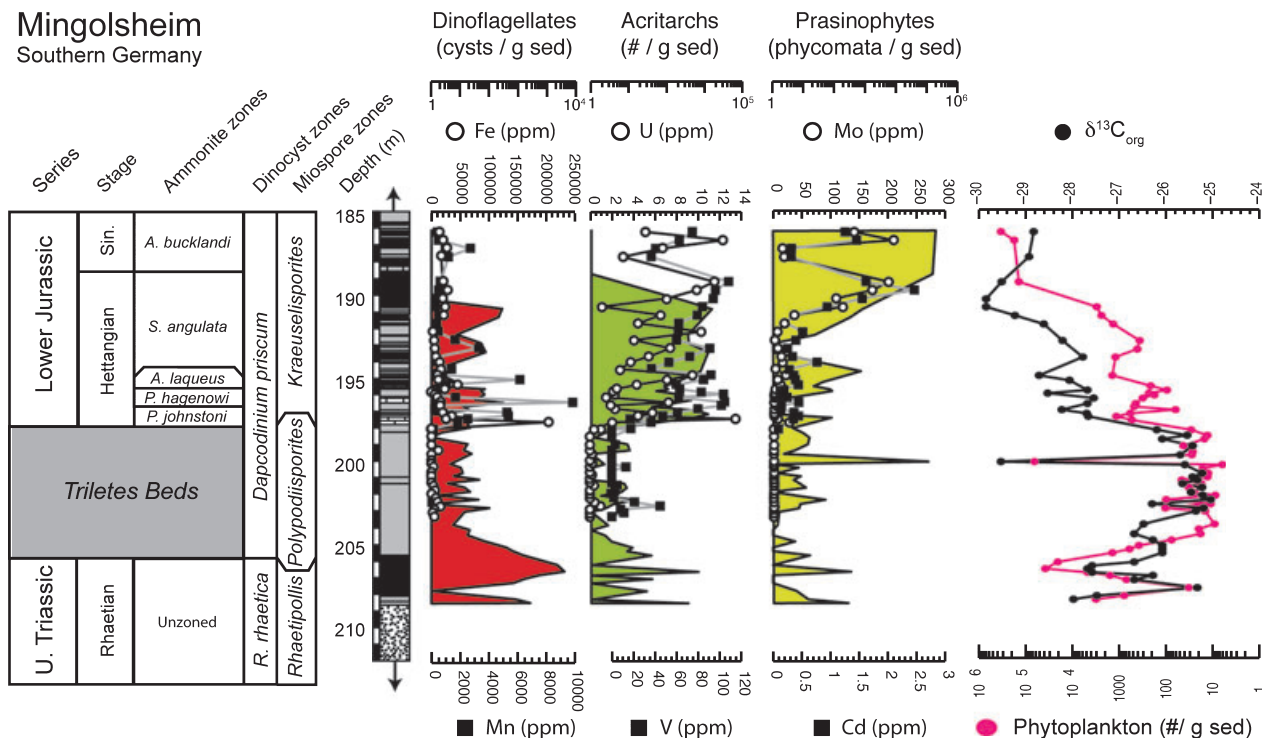


FIG. 4. Palynological and trace element data from the Triassic–Jurassic boundary interval in the Mingolsheim core showing good correlation between increasing amounts of redox-sensitive trace metals and change from red-to-green phytoplankton taxa. Absolute abundances of dinoflagellate cysts, acritarchs and prasinophytes were derived from samples spiked with known amounts of *Lycopodium* spores. Palynological data from Mingolsheim are from van de Schootbrugge *et al.* (2008). Trace element data are from Quan *et al.* (2008). Also shown is the excellent correlation between organic C-isotope record from van de Schootbrugge *et al.* (2008) and total absolute abundance of phytoplankton, suggesting a strong control of organic matter source on Triassic–Jurassic boundary bulk organic C-isotope records for the Mingolsheim core.

with low requirements for nitrate (NO_3^-). Growth experiments by Cochlan and Harrison (1991) have shown that nitrogen-starved specimens of the prasinophyte *Micromonas pusilla* can quickly react to increased levels of ammonium (NH_4^+) in the growth medium. Nitrogen isotope records from northern and southern Germany and the UK, although mainly of local significance, suggest that biological denitrification increased across the Triassic–Jurassic boundary, leading to a decrease in nitrate and an increase in ammonium in the water column (Quan *et al.* 2008; Paris *et al.* 2010; Richoz *et al.* 2012). An increase in ammonium in Hettangian sea water may have favoured prasinophytes, which are also known to have higher uptake quotients for ammonium versus nitrate as compared to dinoflagellates (Litchman *et al.* 2006).

Prasinophyte mass occurrences have repeatedly been connected to lowered surface water salinity for a number of anoxic events (Riegel 1993), such as the Toarcian OAE (discussed below). An overview by Thomsen and Buck (1998) shows that extant prasinophyte species are extremely tolerant towards large variations in sea surface temperature and salinity. The living species *Halosphaera viridis*, generally thought to be a modern analogue for the

fossil genus *Tasmanites*, occurs mainly in the high-latitude Arctic Ocean, but its range extends via the Mediterranean Sea into the Black Sea (see also Ocean Biogeographic Information System; <http://www.iobis.org/>). *Halosphaera viridis* has also been found to occur in coastal waters off South Africa (Sym and Pienaar 1997), suggesting it has a bi-hemispheric distribution today. Unfortunately, there is only sparse information on temperature and salinity changes in the EES across the Rhaetian–Hettangian boundary, which is mainly due to a lack in suitable proxy material. The most promising information is derived from oxygen isotope and Mg/Ca records obtained from the oyster *Liostrea hissingeri* (van de Schootbrugge *et al.* 2007; Korte *et al.* 2009). Combined oxygen isotope and Mg/Ca data suggest that warming of surface waters was accompanied by a substantial freshening across the Triassic–Jurassic boundary.

Toarcian organic matter and photic-zone euxinia

Classic outcrops with expanded Toarcian black shales include those in Yorkshire, for example, at Hawsker Bottoms, or in southern Germany, for example, at Dottern-

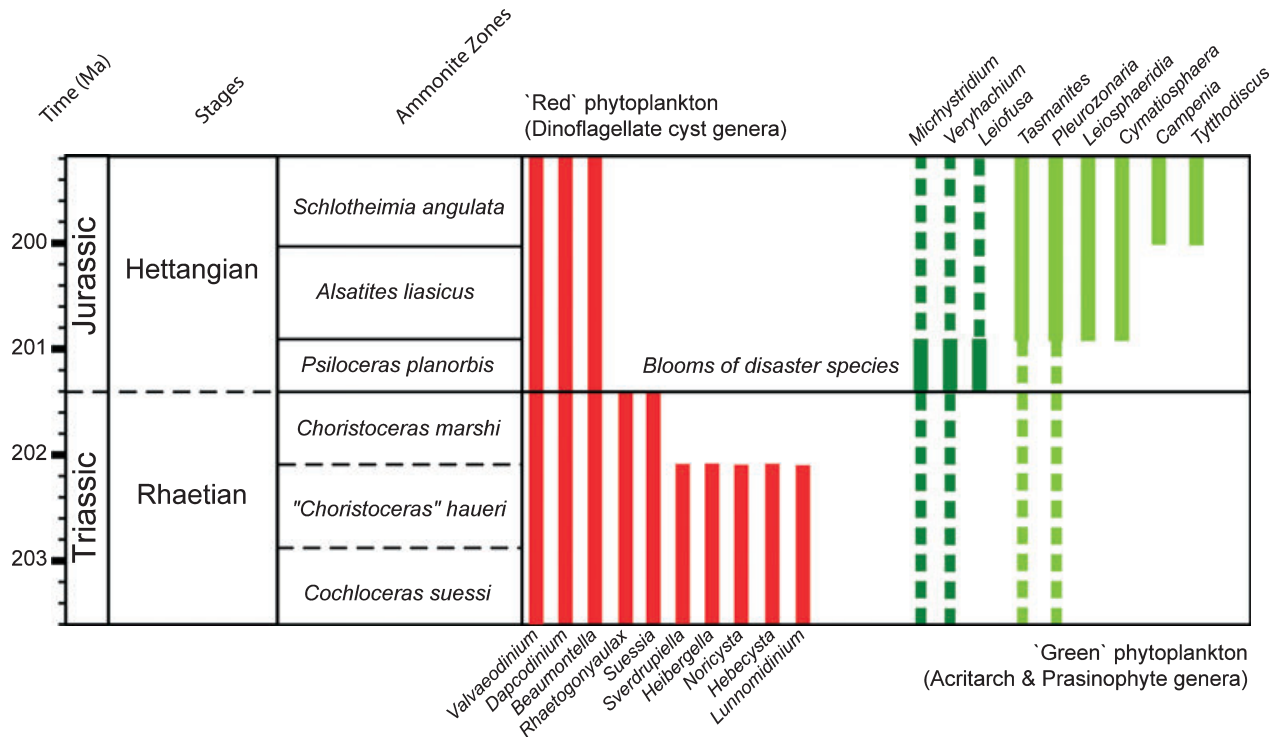


FIG. 5. Range chart of dinoflagellate cyst-producing genera and green algae (prasinophytes) and acritarchs for the Rhaetian–Hettangian transition. The Rhaetian is considered an extinction interval for red algae that are being replaced by ‘disaster taxa’ (acritarchs) and green algae. Data compiled from Bonis *et al.* (2009) and van de Schootbrugge *et al.* (2007).

hausen. Organic enrichment started within the upper part of the *Dactyloceras tenuicostatum* Zone (*semicelatum* Subzone) at both localities and reached maximum values of up to 15 per cent within the *Harpoceras falciferum* Zone (*exaratum* Subzone; Röhl *et al.* 2001). Toarcian strata also exhibit a high prevalence of type-I/II bacterial and algal organic matter associated with high TOC values (Baudin *et al.* 1990). Marine organisms and algae produce lipid- and protein-rich OM, which is hydrogen-rich, and is hence characterized by high HI values (>100 mg HC/g TOC). The dominance of bacteria and algae as the main sources of organic matter in Toarcian black shales is also shown by high pristane, hopane and sterane yields (Farri-mond *et al.* 1989). In contrast, underlying sediments of latest Pliensbachian and earliest Toarcian age are enriched in type-III organic matter of predominantly terrestrial origin (van de Schootbrugge *et al.* 2005a).

Based on elevated concentrations of isorenieratane and its diagenetic cleavage products (aryl isoprenoids) recovered from extremely fresh outcrop material from the Dotternhausen quarry in southern Germany, photic-zone euxinia can be shown to have developed mainly from the *exaratum* Subzone of the *H. falciferum* Zone (Schouten *et al.* 2000; Frimmel *et al.* 2004). Thus far, no isorenieratane has been found in Yorkshire, but diaryl isoprenoids derived from isorenieratene via a process of cyclization

were encountered in sediments from the *exaratum* Subzone at Port Mulgrave (Bowden *et al.* 2006). In addition, the deposition of the ‘sulphur bands’, a series of silty pyritic beds in the *D. tenuicostatum* Zone, signifies episodic shallowing of the chemocline prior to the main phase of euxinia as a result of initial sea-level rise (Wignall 1991). Isorenieratane has also been found in core material retrieved from the Paris Basin (van Breugel *et al.* 2006), where compound-specific C-isotope analyses confirm the ^{13}C -enriched values that result from the peculiar tricarboxylic acid cycle metabolism used by Chlorobiaceae. In samples from the Valdorbis section in Italy Pancost *et al.* (2004) have detected *methyl, isobutyl maleimides*, porphyrin remains that derive from bacteriochlorophylls *c*, *d* and *e*. Brown-coloured strains of the Chlorobiaceae are known to preferentially synthesize *Bchl e* and the light-harvesting carotenoids isorenieratene and β -isorenieratene. Instead, bacteriochlorophylls *c* and *d* are specific for green-coloured strains of the Chlorobiaceae, which also contain carotenoids belonging to the chlorobactene group. Schouten *et al.* (2000) have identified chlorobactene in the Dotternhausen section, suggesting not only the presence of brown-coloured GSB, but also green-coloured GSB (Fig. 6). Green-coloured GSB require more light than brown-coloured GSB and do not tolerate high concentrations of H_2S .

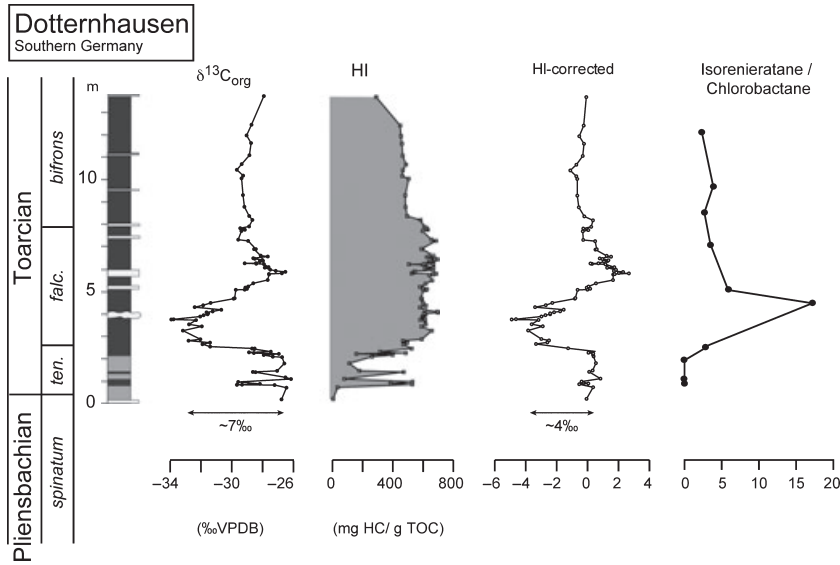


FIG. 6. Geochemical data from the Dotternhausen section. The bulk organic C-isotope data were corrected using the HI and C-isotope data from the *Dactylioceras tenuicostatum* Zone, producing the HI-corrected curve illustrated. Also shown is the ratio of isorenieratane versus chlorobactane, interpreted to mark shallowing of the chemocline and shading from green algae and green-pigmented GSB leading to elevated isorenieratane values. Lithology, biostratigraphy and HI data are from Frimmel *et al.* (2004), $\delta^{13}C_{org}$ data are from Frimmel (2003), and biomarker data are from Schouten *et al.* (2000).

Both Toarcian and Hettangian black shales show important changes both in communities of anoxygenic photosynthetic prokaryotes and in the abundance and diversity of oxygenic photosynthetic unicellular eukaryotes (phytoplankton; Riegel *et al.* 1986; Bucefalo Palliani and Mattioli, 1994; Bucefalo Palliani 1997; Bucefalo Palliani and Riding 1997, 1999; Bucefalo Palliani *et al.* 2002). Preceding the Toarcian OAE, during the uppermost Pliensbachian, phytoplankton assemblages were dominated by red algae (containing chlorophyll *a* and *c*, giving them

a red colour; van de Schootbrugge *et al.* 2005a), predominantly dinoflagellates and coccolithophorids. In the Lower Toarcian *H. falciferum* Zone, these chromophyte algae were abruptly replaced by chlorophytes, which contain predominantly chlorophyll *a* and *b* (giving them a green colour). Dinoflagellates and coccolithophorids temporarily disappeared during deposition of the most anoxic facies in the *exaratum* Subzone (Mattioli and Pittet 2004), and their place was taken by a diverse suite of prasinophytes (Fig. 7). The nearly complete disappearance of the

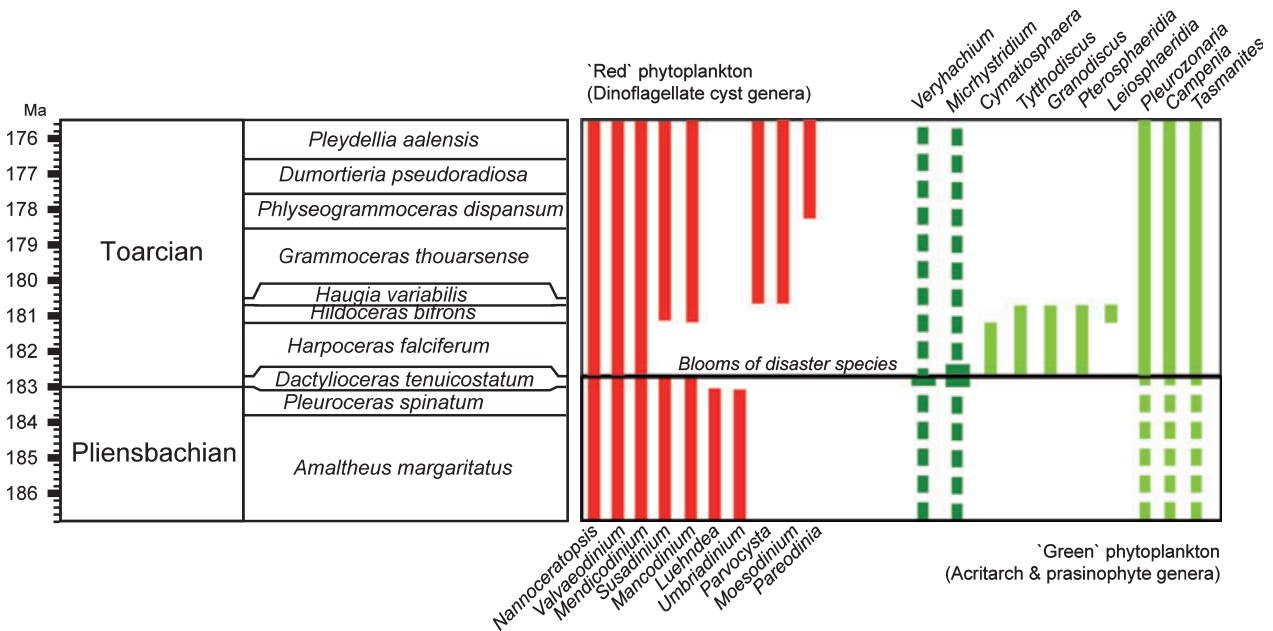


FIG. 7. Range chart for phytoplankton genera across the Pliensbachian–Toarcian transition, showing the replacement of red dinoflagellates by ‘disaster taxa’ (acritarchs) and green algae (prasinophytes). In contrast to the Triassic–Jurassic boundary, the Toarcian OAE does not represent a major mass extinction of dinoflagellates: most species can be considered Lazarus taxa. Further diversification started after the *Halosphaera bifrons* Zone. Based on previous work by Wille (1982) and Bucefalo Palliani and Riding (1999).

presumed deep-dwelling, heavily calcified calcareous dinoflagellate *Schizosphaerella punctulata* and the proliferation of small, opportunistic *r*-selected coccolithophorid taxa is further evidence for a very shallow chemocline during the main phase of anoxia (Tremolada *et al.* 2005).

The transition from 'red' to 'green' phytoplankton across the Pliensbachian–Toarcian boundary is characterized by a brief proliferation of acritarchs assignable to *Michrhystridium* and *Veryhachium* (Prauss *et al.* 1991). Toarcian black shales in Germany contain a diverse suite of prasinophyte phycmata that bears similarities to assemblages from the Hettangian. The most abundant genera include *Tasmanites*, *Cymatiosphaera*, *Pleurozonaria*, *Campenia*, *Tythyodiscus*, *Granodiscus* and *Pterosphaeridia* (Prauss and Riegel, 1989; Prauss *et al.* 1991; Fig. 7). In addition, Toarcian black shales across the EES, for example in Germany and England, are extremely rich in the problematic, small and spherical, organic-walled microfossil *Halosphaeropsis liassica*. These microfossils have been interpreted to have originated from prasinophytes, possibly as stunted juveniles, or as the remains of pollen of unknown botanical affinity. Authors in favour of a pollen origin name these microfossils *Inaperturopollenites orbiculatus* and refer to the presence of large clusters that can be composed of hundreds of small spherical bodies, resembling other better-known masses of pollen grains (Wille 1982). Whatever the origins of these enigmatic palynomorphs (technically, they should be grouped with the Acritarcha), they occur exclusively associated with Toarcian black shales and have thus far not been reported from Hettangian black shales.

The Toarcian OAE is associated with anomalies in nitrogen isotope records. In one section and two cores from England, and in one section in Italy, positive $\delta^{15}\text{N}$ excursions occur in association with the large negative C-isotope excursion that marks the Toarcian OAE (Jenkyns *et al.* 2001). Of particular interest is the record obtained from the Mochras core, for which also palynological and Rock-Eval data are available (van de Schootbrugge *et al.* 2005a). In the Mochras core, the Lower Toarcian contains abundant *Halosphaeropsis* and other prasinophyte phycmata that occur in sediments with high HI values (van de Schootbrugge *et al.* 2005a). Taken together, the nitrogen isotope and organic matter data suggest that the proliferation of prasinophyte green algae may have been associated with denitrification within the water column (Jenkyns *et al.* 2001).

As for the Hettangian, it is likely that the main mechanism conducive to stratification and green algal proliferation was a lowering of surface water salinity. Similar to what is observed in the Black Sea and some present-day fjords, salinity stratification induced by restriction of circulation is widely seen as a major driving mechanism for the development of photic-zone euxinia during the

Toarcian (Saelen *et al.* 1996, 1998, 2000). McArthur *et al.* (2008) used Mo/TOC ratios to discuss extremely slow overturn of surface waters in the EES analogous to what is observed in present-day anoxic basins such as the Cariaco Basin. Combined Mg/Ca and oxygen isotope data derived from unaltered belemnite calcite provide evidence for a reduction in salinity of 3 PSU and concomitant warming of around 7°C across the Pliensbachian–Toarcian boundary in Germany and the UK (Bailey *et al.* 2003). Freshening of surface waters appears to have decreased southwards, towards the open Tethys, as negative oxygen isotope excursions in belemnite rostra sampled in Spain (Rosales *et al.* 2004) and southern France (Harazim *et al.* 2013) are less pronounced. The north to south salinity gradient within the EES fits with a model proposed by Röhl *et al.* (2001), in which greenhouse warming led to a strengthening of monsoonal circulation triggering increased run-off from Laurasia.

During Hettangian and Toarcian photic-zone euxinia, the proliferation of prasinophyte green algae and GSB was probably directly connected. In present-day stratified euxinic lakes, *light* is the single most important control on the abundance and diversity of phototrophic sulphur bacteria (Takahashi and Ichimura 1970; Parkin and Brock 1980a; Vila and Abella 1994). The amount of light available to phototrophic sulphur bacteria is primarily controlled by the extent of euxinic conditions in the photic zone, that is, the depth of the chemocline. GSB are able to thrive under very low-light levels and can use a wide range of the light spectrum, from blue to green and even far red (700–800 nm). Among GSB, the brown- and green-pigmented strains also have different light preferences. Brown-pigmented Chlorobiaceae, which use isorenieratene as a major carotenoid, occur at greater depths than green-pigmented Chlorobiaceae, which use chlorobactene as a major accessory light-harvesting carotenoid (Vila and Abella 1994). In the Black Sea, brown-pigmented GSB occur at depths of 70–100 m (Koblizek *et al.* 2006) where they have acclimated to extremely low-light intensities of 0.0005 per cent of surface irradiation (Overmann *et al.* 1992).

In addition to light intensity, the quality (colour) of light reaching the chemocline is an important determinant of which phototrophic bacteria dominate. The brown pigmentation in Chlorobiaceae is thought to be an adaptation that serves to capture the light that descends the deepest: short-wavelength light with a blue colour (Vila and Abella 1994). Light in aquatic environments is attenuated with depth, whereby it loses intensity and changes colour. The degree of absorption or scattering of visible light depends mainly on the amount of humic substances and/or the amount of suspended particles in the upper water column (Parkin and Brock 1980b). Suspended particles can be land-derived particulate organic

carbon, phytoplankton that occupy the upper parts of the photic zone or different groups of phototrophic bacteria, causing self-shading. Shading from algae in the upper water column is important in selecting for different groups of phototrophic sulphur bacteria (Vila and Abella 1994). This has been shown for a number of euxinic lakes. In north-eastern Spain, in Lake Vilar, bacteria make up 26 per cent of the total biomass, and the amount of algae is clearly elevated when compared with nearby Lake Ciso, where algae only constitute 12 per cent of the total biomass, but bacteria dominate with 86 per cent (Guerrero *et al.* 1985). Light is also a limiting factor for phototrophic sulphur bacteria in Lake Mendota, Wisconsin (Parkin and Brock, 1980a), where intense cyanobacterial blooms cause rapid extinguishing of light. Even though the water column is largely euxinic and the chemocline occurs at a very shallow depth (6 m), no phototrophic sulphur bacteria are present in Lake Mendota.

Due to their specific absorption in surface waters, different groups of phytoplankton thus influence the colour of light reaching deeper levels of the photic zone and eventually the chemocline. Quantification of biomarker abundance in the Dotternhausen section by Schouten *et al.* (2000; Fig. 6) suggests a seemingly paradoxical relationship between brown- and green-pigmented Chlorobiaceae during the Toarcian OAE. Both isorenieratane and chlorobactane are present within the *H. falciferum* Zone in Dotternhausen, but the ratio of isorenieratane to chlorobactane (i.e. brown- vs. green-pigmented Chlorobiaceae) increases within the *exaratum* Subzone, indicating a deepening of the chemocline rather than a shallowing during the most intense anoxia. However, brown-pigmented GSB use carotenoid pigments in contrast to green-pigmented GSB, which rely primarily on bacteriochlorophyll. Under light stress, brown Chlorobiaceae respond by increasing the amount of carotenoids (i.e. isorenieratane) to increase their light-harvesting capabilities (Montesinos *et al.* 1983; Vila and Abella 1994). Hence, the increase in isorenieratane derived from brown-pigmented GSB in the *exaratum* Subzone could also be taken as a simultaneous increase in H₂S and shading by dense populations of prasinophyte green algae, creating a favourable light climate.

Constraints on light and sulphide availability from biomarker abundances have implications for ultimate controls on Toarcian and Hettangian regional anoxic events. Based on a Os-isotope record of Toarcian black shales, it has been suggested that weathering and erosion increased by 400–800 per cent in the *exaratum* Subzone (Cohen *et al.* 2004). However, such an increase in erosion and associated turbidity is in conflict with the establishment of dense phototrophic sulphur bacterial communities in the water column. In present-day ecosystems, run-off events trigger the death of sulphur bacterial communities in catchments (Banens 1990). An increase in suspension load in the *exaratum*

Subzone is also contradicted by a decrease in overall clay mineral contents (Röhl *et al.* 2001) and low percentage values of vitrinites and fusinites (Riegel *et al.* 1986).

EARLY JURASSIC EUXINIA AND CARBON ISOTOPE RECORDS

Both the Rhaetian–Hettangian and Pliensbachian–Toarcian transitions are marked by a series of negative and positive C-isotope excursions. This observation has led Whiteside and Ward (2011) to designate the Triassic–Jurassic boundary as a time interval of rapid carbon cycle changes following a long period of more stable conditions during the Norian and Rhaetian. The same might be argued for the Pliensbachian–Toarcian transition, which shows at least two negative and two positive excursions followed by a long-term trend towards lower values during the upper Toarcian. Some of these excursions occur both in bulk carbonate and bulk organic matter, suggesting that they reflect large-scale geological and environmental events, such as the release of CO₂ or CH₄ during flood basalt volcanism (Svensen *et al.* 2007) or massive dissociation of seafloor gas hydrates (Hesselbo *et al.* 2000). However, as outlined above, both intervals are also marked by dramatic changes in organic matter composition that likely exerted control on trends and excursions (van de Schootbrugge *et al.* 2005b, 2008).

Understanding similarities and differences in organic matter content and composition is crucial when bulk organic carbon isotope records are used to interpret driving mechanisms behind Hettangian and Toarcian black shale deposition. Variation in $\delta^{13}\text{C}_{\text{org}}$ records may be caused by changes in the isotope composition of atmospheric carbon dioxide and marine dissolved inorganic carbon (DIC), organic matter source or both. Unlike in carbonates, isotopic fractionation in organic matter is strongly dependent on the type of carbon assimilation, potentially driving large offsets from DIC. Mixing the remains of various organisms, from fungi to plants to bacteria, in any bulk sample can lead to extreme isotope shifts that do not reflect the dynamics of the exogenic carbon cycle. In the following, organic C-isotope records for the Triassic–Jurassic boundary and Pliensbachian–Toarcian transition are briefly reviewed. Common interpretations of these records are then discussed against the background of changes in organic matter associated with either event.

Rhaetian–Hettangian organic carbon isotopes

The Triassic–Jurassic boundary interval is associated with large variations in the carbon isotope record. The main extinction interval, below the biostratigraphic boundary,

is associated with one or several (up to 3) negative isotope excursions (CIEs) in $\delta^{13}\text{C}_{\text{org}}$ records from localities around the globe (Hesselbo *et al.* 2002; Lindström *et al.* 2012). The negative shift also occurs in records of *n*-alkanes (Ruhl *et al.* 2011) and taxonomically identified leaf material (Bacon *et al.* 2011). A similar CIE has been observed in some marine carbonate sediments (Galli *et al.* 2005). Above the extinction horizon, there is evidence for a large and protracted positive excursion in $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{13}\text{C}_{\text{carb}}$ (Williford *et al.* 2007; van de Schootbrugge *et al.* 2008), although such a positive excursion is not evident in all records. For example, in the St Audrie's Bay record, the emphasis has been put on a major negative CIE in organic matter ('main' excursion of Hesselbo *et al.*, 2002) that dominates all of the Hettangian stage.

The negative excursions in $\delta^{13}\text{C}_{\text{org}}$ below the biostratigraphic Triassic–Jurassic boundary have generally been interpreted to reflect variations in the $\delta^{13}\text{C}$ composition of marine DIC and atmospheric CO_2 , driven by the release of ^{13}C -depleted carbon from methane hydrates (Palfy *et al.* 2001) or sedimentary organic carbon volatilized during CAMP volcanism (Beerling and Berner 2002; Hesselbo *et al.* 2002; Ruhl and Kürschner 2011). Because the magnitude of the $\delta^{13}\text{C}$ excursion depends both on the amount and isotope composition of carbon released, the carbon isotope record alone is insufficient to distinguish between these possibilities. The lack of a deep-sea carbonate record, or likely even deep-sea carbonate sediments, prohibits using the behaviour of the carbonate compensation depth to obtain additional constraints on the magnitude of carbon release, as has been used in studies of more recent events such as the Palaeocene–Eocene Thermal Maximum (PETM; Zachos *et al.* 2005). Under either of these scenarios, however, the large magnitude of the carbon isotope shifts requires thousands of gigatons (Gt; 1 Gt = 10^{15} g) of carbon release.

Despite the limitations of the Triassic–Jurassic rock record, two observations suggest that the negative excursions in $\delta^{13}\text{C}_{\text{org}}$ are not simple reflections of variations in the isotope composition of marine DIC and atmospheric CO_2 . First, variation in $\delta^{13}\text{C}_{\text{org}}$ records exhibits statistically significant correlation with the taxonomic composition of associated palynomorphs. At Mingolsheim, where $\delta^{13}\text{C}_{\text{org}}$ data and palynological counts were performed on the same samples, palynological compositional variation accounts for 74 per cent of the variation in $\delta^{13}\text{C}_{\text{org}}$ (van de Schootbrugge *et al.* 2008). A comparison of absolute abundance counts of phytoplankton and $\delta^{13}\text{C}_{\text{org}}$ values shows a remarkable correlation within the Mingolsheim core (Fig. 4). Although the palynological assemblage only represents a part of the organic matter present in any sample, normally larger plant remains are not counted, this almost perfect correlation between marine organic matter and variations in $\delta^{13}\text{C}_{\text{org}}$ for the Rhaetian through

Hettangian is problematic for interpretations of organic carbon isotope records as purely driven by changes in the exogenic carbon cycle.

In the Mariental 1 core, where samples were not matched and so $\delta^{13}\text{C}_{\text{org}}$ data had to be interpolated to the positions of the palynological samples, and the organic matter has a proportionally greater terrestrial component, palynological variation still explained 27 per cent of the variation in $\delta^{13}\text{C}_{\text{org}}$. Moreover, the nature of the correlation between the $\delta^{13}\text{C}_{\text{org}}$ record and the palynological assemblages is comparable between northern and southern Germany. More positive values of $\delta^{13}\text{C}_{\text{org}}$ were associated with high abundances of fern spores, whereas more negative values were associated with conifer pollen. The predicted end-member isotope compositions for spores and pollen, the only highly abundant components of the assemblages, are similar between the two sites. This correlation could result either from a direct control of organic matter source on the $\delta^{13}\text{C}_{\text{org}}$ record or be due to a common cause, such as environmental change, that both altered the $\delta^{13}\text{C}$ of CO_2 and the composition of plant communities. At present, it is difficult to distinguish between these possibilities.

The close correspondence of outlying negative $\delta^{13}\text{C}_{\text{org}}$ values at Mingolsheim (Fig. 4) and unusual palynological assemblages suggests a direct compositional control on $\delta^{13}\text{C}_{\text{org}}$, but the observation of a negative shift in *n*-alkanes and taxonomically identified leaves is more easily interpreted to reflect a true shift in the $\delta^{13}\text{C}$ of the exogenic carbon reservoir. However, the interpretation of an 8‰ negative CIE in *n*-alkanes to reflect the release of 12 000 GT of carbon via the destabilization of subseafloor gas hydrates (Ruhl *et al.* 2011) may be questioned. First of all, plants may increase their fractionation due to changes in $p\text{CO}_2$ or humidity, or both. Moreover, changes in plant communities, such as occurred at the Triassic–Jurassic boundary, may also have imprinted the carbon isotope record. Similar observations were made for the PETM, where biomarkers from gymnosperms and angiosperms show different signatures (Schouten *et al.* 2007). Green algae, the predecessors of land plants, also contain *n*-alkanes, which may be significantly depleted in ^{13}C (Grice *et al.* 1997). What is problematic is that the level in Austria that contains the 8‰ negative CIE is enriched with *Botryococcus braunii* and prasinophyte green algae (Bonis *et al.* 2009). Because some strains of *Botryococcus braunii* have been suggested to be potential producers of high-molecular-weight odd-numbered *n*-alkanes, the above correspondence leaves open the possibility that this excursion is also related to changes in organic matter composition rather than to changes in the isotopic composition of atmospheric CO_2 . More specific organic molecules are needed from the boundary interval to convincingly show an atmospheric signal.

Toarcian organic carbon isotopes

The Pliensbachian–Toarcian transition is characterized by two negative and two positive excursions. A first negative CIE occurs close to Pliensbachian–Toarcian boundary in Portugal and the UK and is best expressed in bulk organic matter (Hesselbo *et al.* 2007; Suan *et al.* 2008; Littler *et al.* 2010; Fig. 8). This first negative CIE is followed by a positive shift (Fig. 8) in the *D. tenuicostatum* Zone that has been recognized with bulk organic carbon, bulk carbonate, wood, belemnites and brachiopods (Hesselbo *et al.* 2007; Suan *et al.* 2008; Littler *et al.* 2010; Korte and Hesselbo, 2011). However, the most prominent CIE of the Pliensbachian–Toarcian interval is the negative excursion (Fig. 8) at the transition from the *D. tenuicostatum* to *H. falciferum* Zones. This negative CIE is well known from northern and southern European successions (Küspert 1982; Hesselbo *et al.* 2000; Röhl *et al.* 2001; Kafousia *et al.* 2011). More recently, it has also been identified in Argentina (Al-Suwaidi *et al.* 2010), Canada (Caruthers *et al.* 2011), Japan (Gröcke *et al.* 2011; Izumi *et al.* 2012) and northern Siberia (Suan *et al.* 2011). It

remains unclear whether all these excursions truly correlate with the negative CIE that is so characteristic of the Toarcian in Europe, because some of the sections outside of the EES lack reliable biostratigraphic constraints, or the biostratigraphic frameworks are difficult to correlate with those in Europe (Gröcke *et al.* 2011).

The main CIE within the *exaratum* Subzone has been interpreted to reflect either global perturbations of the carbon cycle (Hesselbo *et al.* 2000) or local signals of water mass chemistry (Küspert 1982) related to changes in organic matter sources, recycling of respired CO₂ and early diagenetic processes in the sediment. The former explanation is supported by C-isotope records obtained from wood particles (Hesselbo and Pienkowski 2011), suggesting that the perturbation affected not only marine carbon reservoirs, but also atmospheric CO₂. The latter scenario is supported by the repeated observation that some reservoirs, such as biogenic calcites, do not record the isotope excursions, at least not the negative ones (van de Schootbrugge *et al.* 2005b; Gomez *et al.* 2008). It appears possible, if not likely, that the excursions were driven by both global and local changes. Separating these

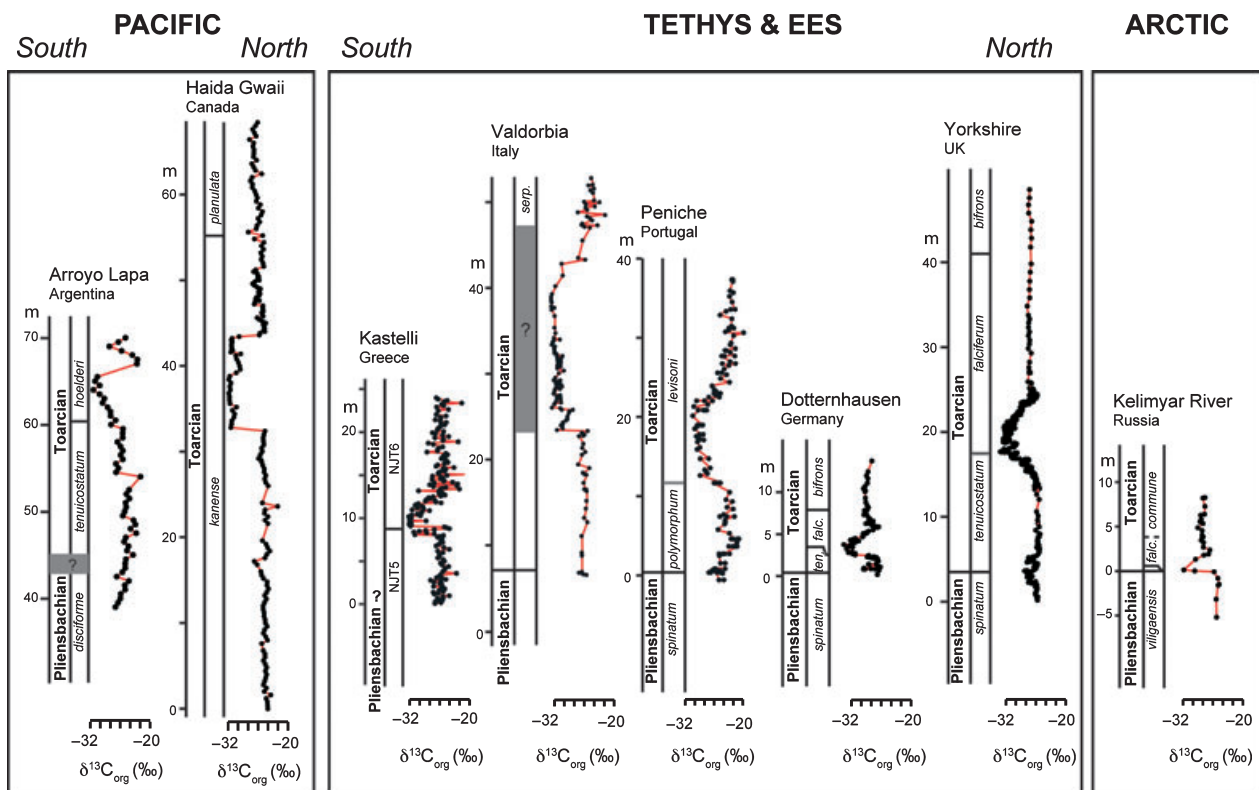


FIG. 8. Overview of Pliensbachian–Toarcian bulk organic C-isotope records. Data from Canada after Caruthers *et al.* (2011); from Argentina after Al-Suwaidi *et al.* (2010); data from Greece after Kafousia *et al.* (2011); from Portugal after Hesselbo *et al.* (2007); from Italy after Sabatino *et al.* (2009); from Germany after Frimmel (2003); from England after Kemp *et al.* (2005) and Littler *et al.* (2010); from Russia after Suan *et al.* (2011). The biostratigraphy of the sections is as given in the above sources, except for Valdorbina, where the ammonite biostratigraphy is from Bilotta *et al.* (2010). The shaded zones correspond to intervals with no age-dagnostic ammonites. Abbreviations: *falc.*, *falciferum*; *serp.*, *serpentinus*; *ten.*, *tenuicostatum*.

signals will be pivotal if C-isotope records are to be used for reconstructing carbon cycle perturbations and their driving mechanisms (Beerling and Brentnall 2007).

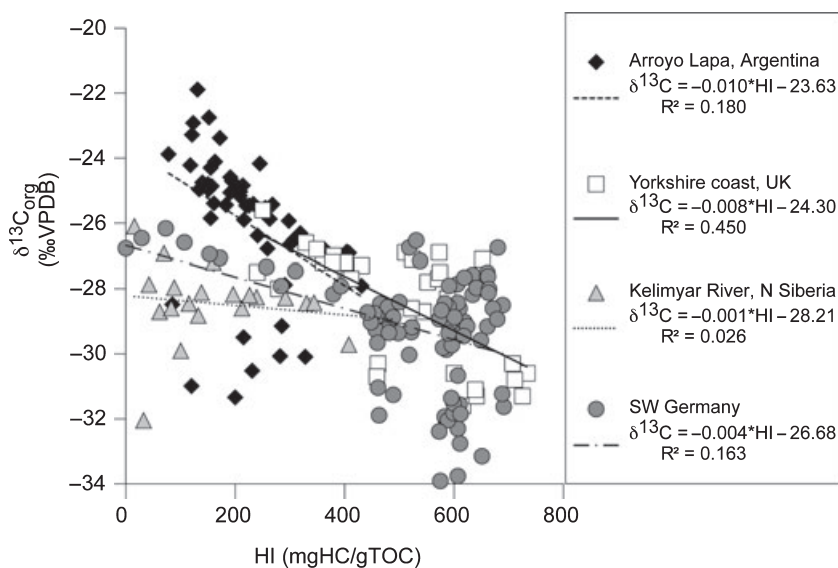
Even within a geographically restricted area, such as the EES, both the magnitude and shape of the PI–To carbon isotope profiles are highly variable and differ substantially among various materials analysed. For instance, the magnitude of the *H. falciferum* negative CIE varies from *c.* 2–6‰ in carbonate material (brachiopods and bulk carbonate) to *c.* 6–8‰ in organic material (wood and bulk organic carbon). As discussed above, combined palynological and organic geochemical analyses indicate that the onset of the T-OAE was associated with major changes in the main type of organic matter: marine organic matter dominates TOC-rich intervals in the Lower Toarcian in Germany and Italy, while terrestrial organic matter dominates the underlying less organic-rich sediments. The influence of these major changes in the main type of preserved organic matter on the $\delta^{13}\text{C}_{\text{org}}$ records has generally been poorly integrated when interpreting organic C-isotope trends across the T-OAE. Comparison between sediments dominated by marine organic matter and fossil wood particles collected from the same horizons (Hesselbo *et al.* 2000; Al-Suwaidi *et al.* 2010) indicates that the marine organic matter is ^{13}C -depleted relative to terrestrial organic matter (Hesselbo *et al.* 2000).

The influence of organic matter on $\delta^{13}\text{C}_{\text{org}}$ can be tested by comparing $\delta^{13}\text{C}_{\text{org}}$ values with coeval HI values (Saalen *et al.* 2000). The $\delta^{13}\text{C}_{\text{org}}$ and HI values from the UK, Germany, Argentina and Siberia reveal a negative correlation, suggesting that part of the $\delta^{13}\text{C}_{\text{org}}$ profiles might reflect changes in organic matter sourcing (Fig. 9). This relationship is well illustrated in the Dotternhausen section, where two black shale levels of the *D. tenuicosta-*

tum Zone (the ‘Tafelfleins’ and ‘Seegrasschiefer’ beds (Röhl *et al.* 2001; Frimmel, 2003; Frimmel *et al.* 2004) show high HI values exactly coinciding with abrupt negative CIEs that are absent from the carbonate C-isotope record. However, the slope of the correlation between HI and $\delta^{13}\text{C}_{\text{org}}$ values differs significantly from site to site, suggesting that the isotopic contrast between terrestrial and marine organic matter or the nature of the producers might have varied geographically during the Toarcian.

Despite a general correlation, the scatter plots display some distinct outliers (Fig. 9), suggesting that the $\delta^{13}\text{C}_{\text{org}}$ profiles cannot be entirely explained by changes in organic matter sourcing or alternatively that such changes are not recorded by HI values. These residual changes were calculated for the Dotternhausen section by subtracting the $\delta^{13}\text{C}$ values reconstructed from the cross-plots from the $\delta^{13}\text{C}_{\text{org}}$ data (Fig. 6). This correction of the $\delta^{13}\text{C}_{\text{org}}$ profile reveals a more subdued *c.* 4‰ negative CIE in the lower *H. falciferum* Zone, followed by a more pronounced positive CIE in the middle part of this zone (Fig. 6). Interestingly, the overall shape and reduced magnitude of the obtained residual changes in $\delta^{13}\text{C}_{\text{org}}$ for both sections are strikingly similar to that of the bulk carbonate isotope ($\delta^{13}\text{C}_{\text{carb}}$) record from organic-poor sections in Portugal, Italy and Greece. The ‘corrected’ $\delta^{13}\text{C}_{\text{org}}$ profile is also notable for the absence of a long-term trend towards lower $\delta^{13}\text{C}_{\text{org}}$ values, suggesting that this trend simply reflects increased preservation of isotopically lighter marine organic matter. This interpretation is further supported by the absence of such a long-term negative trend in records from Italy, where lower $\delta^{13}\text{C}_{\text{org}}$ values are absent in the essentially organic lean carbonates in the upper part of the *H. falciferum* Zone (Sabatino *et al.* 2009). The profound influence of changing organic matter sources on bulk $\delta^{13}\text{C}_{\text{org}}$ records for the Toarcian

FIG. 9. Cross-plots of bulk organic C-isotope values and hydrogen index values for two sections in the European Epicontinental Seaway (Yorkshire, Dotternhausen), Siberia and Argentina. All records show decreasing C-isotope values with increasing HI values, although the correlation is not as strong for all records. The data from Yorkshire after Saalen *et al.* (2000); Dotternhausen data after Frimmel *et al.* (2004) and Frimmel (2003); data from Argentina after Al-Suwaidi *et al.* (2010); data from Siberia are after Suan *et al.* (2011).



suggests that these cannot simply be used on a one-to-one basis for reconstructing global carbon cycle perturbations without careful consideration of the organic matter sources.

BLACK SHALES AND MASS EXTINCTION

Both the Rhaetian–Hettangian and Pliensbachian–Toarcian transitions are associated with mass-extinction events that affected both marine benthic and planktic organisms. Both extinctions were not abrupt events (Harries and Little 1999), but affected different groups of organisms at different times (Tanner *et al.* 2004). The ubiquitous deep-water Triassic bivalve *Monotis* went extinct at the Norian–Rhaetian boundary, and this appears to have heralded major changes in shallower settings (Wignall *et al.* 2007). Although in some areas in Austria reef organisms survived until the end of the Triassic (e.g. the famous Adnet reefs close to Salzburg), the Rhaetian reefs of the Dachstein Platform disappeared during the Rhaetian. On land, floral changes commenced during the latest Rhaetian (van de Schootbrugge *et al.* 2009), but it remains unclear how floral changes connect to the extinction of primitive dinosaurs that appears to have started earlier (Benton 1986). Even less is known about the timing of changes in vertebrate communities related to the Pliensbachian–Toarcian transition (Benton 1995; Allain and Aquesbi 2008), and there is little comprehensive information on vegetation changes on landmasses surrounding the EES. This is partly due to the scarcity of terrestrial palynomorphs relative to amorphous and marine organic matter in Toarcian black shales in Europe. In less organic-rich sediments in Greenland, a remarkable increase in the pollen *Cerebropollenites macroverrucosus* is observed at the Pliensbachian–Toarcian boundary (Koppelhus and Dam 2003). Interestingly, the incoming of *Cerebropollenites thiergartii*, an ancestral or sister species, is now widely used as a biostratigraphic marker for the Triassic–Jurassic boundary (Kürschner *et al.* 2007). Unfortunately, the botanical affinity of both species is unclear, but unravelling its ecological requirements could prove pivotal for our understanding of environmental change on land during Early Jurassic anoxia in the oceans.

The spread of anoxia was undoubtedly a major factor in the extinction of bivalves and other benthic organisms during the Early Toarcian. However, similar to what is observed for the Triassic–Jurassic boundary, it is increasingly clear that the extinction of benthic organisms, including bivalves and corals, across the Pliensbachian–Toarcian boundary commenced prior to the onset of widespread anoxia with high extinction rates already occurring in the *A. margaritatus* and *P. spinatum* Zones

(Little and Benton 1995). Reefs along the northern margin of Gondwana became drowned during the latest Pliensbachian (Blomeier and Reijmer 1999), and the absence of black shales in Morocco suggests other mechanisms than anoxia were responsible. As discussed, organic-walled phytoplankton also showed stepwise reductions in diversity for both time intervals, followed by the proliferation of disaster taxa. Ammonites show a similar response to both crises: they suffered an extinction prior to the onset of anoxic conditions, but appear to have recovered rapidly in so-called evolutionary bursts (Harries and Little 1999; Dera *et al.* 2010). It thus appears that the development of anoxic conditions in the shallow EES appears not to have been the ultimate cause of these extinctions, but was itself a result of ongoing changes in the geosphere.

As suggested by Bailey *et al.* (2003), the Toarcian OAE was ‘rooted’ in events that occurred prior to the onset of widespread anoxia. Compilation of oxygen isotope data from belemnites and fish teeth by Dera *et al.* (2009b) brings to light an important cooling phase during the Late Pliensbachian. This cooling trend was reversed during the latest Pliensbachian by a warming trend, and temperatures continued to increase across the Pliensbachian–Toarcian boundary reaching a zenith within the *H. falciferum* Zone. Combined Mg/Ca and oxygen isotope records indicate that warming across the *D. tenuicostatum*–*H. falciferum* Zone boundary was accompanied by salinity decrease in surface waters (Bailey *et al.* 2003). Based on a study of brachiopod records, Garcia Joral *et al.* (2011) concluded that temperature rather than anoxia was the driving force behind diversity loss. The onset of warming during the latest Pliensbachian is also evident in high-resolution records from the Grands Causses Basin (France; Harazim *et al.* 2013) and clearly predates the proposed release of methane within the Lower Toarcian *exaratum* Subzone.

Temperature changes during the latest Pliensbachian go hand in hand with major changes in sea level from generally lower sea levels during the Pliensbachian cooling phase towards overall rising sea levels associated with Toarcian warming and anoxia. A major hiatus and/or significant condensation at the Pliensbachian–Toarcian transition is evident across the EES, for example in the Grands Causses Basin in southern France, where the uppermost part of the *P. spinatum* and lowermost part of the *D. tenuicostatum* Zone are missing (Guex *et al.* 2001; Morard *et al.* 2003; Morard 2004). In the Provence sub-Basin, carbonate platforms drowned during a successive series of sea-level rises, which started prior to the Toarcian oceanic anoxic event and the negative CIE (Leonide *et al.* 2011).

Invoking glacio-eustatic sea-level changes for the Mesozoic has long been taboo (Price 1999), but there is increasingly more than just circumstantial evidence to

propose the build-up of ice during the Late Pliensbachian. New isotopic work on belemnites and bivalves from the UK by Korte and Hesselbo (2011) strongly points in this direction. Evidence in the form of ice-rafted dropstones in Siberia described by Suan *et al.* (2011) that co-occur together with glendonites in sediments underlying a spectacular erosional unconformity is possibly only the tip of the proverbial iceberg. In such a scenario, first proposed by Prauss and Riegel (1989), the Toarcian OAE would be the result of rapid flooding of previously well-oxygenated basins with low-salinity surface waters, triggering intense stratification (McArthur *et al.* 2008).

Sea-level changes modulated by climate change and tectonics also played an important role during the Rhaetian–Hettangian transition. The base of the Jurassic marks a first-order sea-level rise that is particularly pronounced in the EES, but is also evident in the Panthalassa Ocean, for example, in Nevada (Hallam 1997; Hallam and Wignall 1997, 2000). Along the margins of the Tethys Ocean, such as in the Calcareous Alps (Austria), platform sediments spanning the Triassic–Jurassic boundary show a major erosional unconformity. For example, the interior part of the Steinplatte Platform has karst-filling sediments that are time-equivalent to boundary sediments in Germany (Piller 1981). These platform sediments preserve a record of short-lived, but significant sea-level fall at the time of the end-Triassic extinction, followed by long-term transgression. Sedimentary gaps are omnipresent along the northern margin of Gondwana, for example, in Oman, Iran and India (Watts 1990; Bhargava and Bassi 1998; Immenhauser *et al.* 1998), but in the New York Canyon section (Nevada), sea-level fall did not lead to emersion (Guex *et al.* 2004), but substantial shallowing has been inferred by Hallam and Wignall (2000). Sea-level changes along the northern and southern Tethyan margins were certainly also overprinted by major tectonic movements. McRoberts *et al.* (1997) have explained an estimated 30-m sea-level fall at the Triassic–Jurassic boundary to have resulted from large-scale tectonic activities related to the opening of the Central Atlantic Ocean.

CONTROLS ON BLACK SHALE DEPOSITION

Methane

Methane release to the atmosphere from the destabilization of gas hydrates has been invoked by a number of authors to explain both the end-Triassic extinction event and the Toarcian OAE (Hesselbo *et al.* 2000; Palfy *et al.* 2001; Beerling and Berner, 2002; Hesselbo *et al.* 2007; Ruhl *et al.* 2011). Destabilization of methane clathrates requires a trigger, such as ongoing global warming

induced by other mechanisms (Beerling and Berner 2002; Beerling and Brentnall 2007). There is yet no conclusive evidence to show that methane release was the cause of anoxia developing or of the mass-extinction events at the Rhaetian–Hettangian and Pliensbachian–Toarcian boundaries. Based on a new detailed C-isotope record from a series of cores drilled in the Danish Basin (Lindström *et al.* 2012), the negative excursion that has been linked to methane release by Ruhl *et al.* (2011) postdates the extinction of plant species that would have been most sensitive to the carbon release event. Similarly, the first marine extinction pulse at the Pliensbachian–Toarcian boundary predates the postulated release of methane by several 100 000 years (Wignall *et al.* 2005; Caswell *et al.* 2009). Also the onset of anoxia within the *D. tenuicostatum* Zone appears to predate the main negative CIE that occurs within the *H. falciferum* Zone (Wignall *et al.* 2005).

Today, methane seepage occurs along continental margins worldwide (Campbell 2006), and in accordance with uniformitarian principles, it was likely also a common process on ancient shelves. At present, there are only three known Early Jurassic cold seep sites, and only two have a biostratigraphic age that places them within close range from the Toarcian OAE. Sinemurian mud mounds described from Kilve in Somerset unlikely played a role in the exogenic carbon cycle as they are of exceedingly small scale (Allison *et al.* 2008; Price *et al.* 2008). Exotic carbonate bodies rich in bivalves and serpulids, and with anomalously light carbon isotope signatures, have been described from the Pliensbachian–Toarcian transition in the Neuquen Basin (Argentina). Surprisingly, these occurrences have received very little attention as they were first described by Gomez-Perez (2003) and their exact age and significance for the debate on the Toarcian OAE remains poorly understood. Evidence for possible widespread methane release during the Late Pliensbachian in southern France was recently presented by van de Schootbrugge *et al.* (2010) based on a reinterpretation of tubular carbonate concretions known as *Tisosa siphonalis* that occur in the *gibbosus* Subzone of the *A. margaritatus* Zone. The tubular concretions bear geochemical and morphological signatures of subsurface hydrocarbon conduits and occur in astonishing numbers across the Grands Causses Basin. However, carbon isotope and sedimentological evidence (van de Schootbrugge, ongoing research) suggest that the palaeo-seafloor corresponding to the time of carbonate concretion formation was located at the top of the *A. margaritatus* Zone, well before the onset of anoxia during the Early Toarcian.

The uppermost Pliensbachian appears to have been a time of increased authigenic carbonate deposition in the EES. Carbonate concretions are common in successions dominated by marls, such as in northern Germany, where

several levels within the Late Pliensbachian *P. spinatum* Zone also contain glendonites (Teichert and Luppold 2009). These previously undescribed glendonites occur partly as small bipyramidal dispersed calcite crystals or within sideritic concretions. Although normally seen as indicators for cold climates, carbon isotope analyses of Pliensbachian glendonites show extremely negative values up to -40‰ , which can only be an expression of the involvement of methane during the complex formation pathway of these pseudomorphs of ikaite (Teichert and Luppold 2009). As discussed by van de Schootbrugge *et al.* (2010), an important prerequisite for concretion growth is a slowdown in sedimentation rates and stabilization of the sulphate–methane transition zone within the sedimentary pile. Such a slowdown in sedimentation rates would have been aided by major sea-level fall and climatic changes at the end of the Pliensbachian.

Volcanism

The only viable mechanism that can explain the sequence of events for the Triassic–Jurassic and Pliensbachian–Toarcian boundaries and their aftermaths is the emplacement of LIPs. The Triassic–Jurassic boundary is temporally overlapping with the emplacement of the Central Atlantic Magmatic Province that heralded the break-up of the supercontinent Pangaea. Although much smaller in size than the CAMP, the Karoo–Ferrar LIP straddles the Pliensbachian–Toarcian boundary and must be considered as one of the major events of the later part of the Early Jurassic.

As alkaline igneous rocks are common in rift basins, it was only fairly recently that the intrusives and extrusives associated with the rifting of the Atlantic were recognized as being a product of a single, geologically brief, large-scale igneous event (Marzoli *et al.* 1999). Compilation of radiometric dates indicate that over a period of approximately 8 myr, peaking at around 200 Ma, large amounts of tholeiitic basalt were extruded (Hames *et al.* 2000; Marzoli *et al.* 2004; Nomade *et al.* 2006; Verati *et al.* 2007). The scale of the volcanics is enormous: the preserved thickness of basalts in Morocco is hundreds of metres, and sills in northern Brazil are on average 500 m thick and cover 1 million square kilometres in the subsurface (Marzoli *et al.* 1999). Where the basalts have been eroded, the remaining plumbing bears testimony to the magnitude of the event: dyke swarms in Amazonia are 200 m wide and 300 km long. A single dike in the Iberian Peninsula has been traced for more than 500 km. Despite their size, the basalt flows were emplaced rapidly. Cyclostratigraphy in the Newark Basin suggests that the main eruptive phase occurred in <600 kyrs (Olsen *et al.* 1996). Radiometric data from Morocco indicate that the amount

of polar wander measured between flows is on the same magnitude as the secular variation observed in the last few hundred years (Knight *et al.* 2004). Temporal overlap with the end-Triassic mass extinction is mainly based on radiometric dates from ashes in marine sections (Palfy and Smith 2000; Schaltegger *et al.* 2008; Schoene *et al.* 2010). Additionally, the established magneto-stratigraphic framework allows for the synchronicity of events (Muttoni *et al.* 2010), as does the palynology (Cirilli *et al.* 2009).

The presumed mechanism through which the volcanism caused an environmental perturbation that precipitated the biotic crisis is via volatile release, especially of CO_2 and SO_2 . With an estimated original volume of $2 \times 10^6 \text{ km}^3$ and *c.* 0.1 per cent volatiles, McHone (2003) calculated a total emission of 5.19×10^{12} tons of carbon, 2.31×10^{12} tons of sulphur, 1.11×10^{12} tons of fluorine and 1.58×10^{12} tons of chlorine. However, this is almost certainly on the lower side as the estimate does not include the volatiles released by interactions with sediments, which remain underconstrained. Anecdotal observations of coal bodies and metamorphosed sediments abutting intrusions in the eastern United States (van Houten 1971; Robbins *et al.* 1988) suggest a possibly much higher total. Data from geochemistry of CAMP basalts in the southern Iberian Peninsula indicate the assimilation of up to 10 per cent of pure CaCO_3 end-member in discrete lithologic zones (Martins *et al.* 2008), which represents a 100-fold increase over unadulterated basalts. On the sedimentary side, palaeosol evidence supports pulses of CO_2 release around the boundary (Schaller *et al.* 2011), and stomatal indices indicate a general increase in pCO_2 in the Hettangian (McElwain *et al.* 1999). The effect of massive volatile release could have been transient ocean acidification (Beerling and Berner 2002; Hautmann *et al.* 2008) and other environmental perturbations, such as global warming, that precipitated the development of anoxia during the Hettangian.

Radiometric dating indicates that there was also a temporal overlap between the onset of the Toarcian OAE and the emplacement of one of the largest igneous provinces of the Phanerozoic, the Karoo–Ferrar province. Voluminous successions of sills, dikes and lava flows of this province now cover large areas and form the Karoo Group in southern Africa and the Ferrar Group in Antarctica. Although the total duration of igneous activity may have exceeded 6 myr (Jourdan *et al.* 2005), compilation of $^{40}\text{Ar}/^{39}\text{Ar}$ ages indicate a peak of LIP activity at around 182 Ma, which broadly coincides with the estimated age of the Toarcian mass extinction and environmental changes (Palfy and Smith 2000; Jourdan *et al.* 2008). In addition, palaeomagnetic data indicate that thick (up to 500 m) lava flows of the Karoo Group were emplaced extremely rapid (possibly in less than a few kyrs Moulin *et al.* 2011) and may hence have released large

amounts of volcanic gases to the atmosphere. Importantly, a significant part of the LIP was emplaced intrusively, hence forming a large and complex network of sills and dikes that intruded older sedimentary rocks (Svensen *et al.* 2007). It has been proposed that these intrusions produced, through contact metamorphism, large amounts of volatiles (CO₂ and CH₄) that would have largely exceeded volumes produced by magma degassing alone and could hence have dramatically impacted carbon atmospheric dioxide levels and climate (Svensen *et al.* 2007). Evidence for massive release of these volatiles comes from the occurrence of large fields of eruptive ‘breccia pipes’ within the Karoo Basin as well as marked changes in TOC contents and vitrinite reflectance in the sedimentary units immediately surrounding some sills (Svensen *et al.* 2007). On the other hand, the thermal metamorphism of coals as an effective mechanism for producing greenhouse gases was questioned by Gröcke *et al.* (2008), based on geochemical and petrographic data showing that the intrusion of some Karoo dikes into coal deposits produced only small amounts of CH₄.

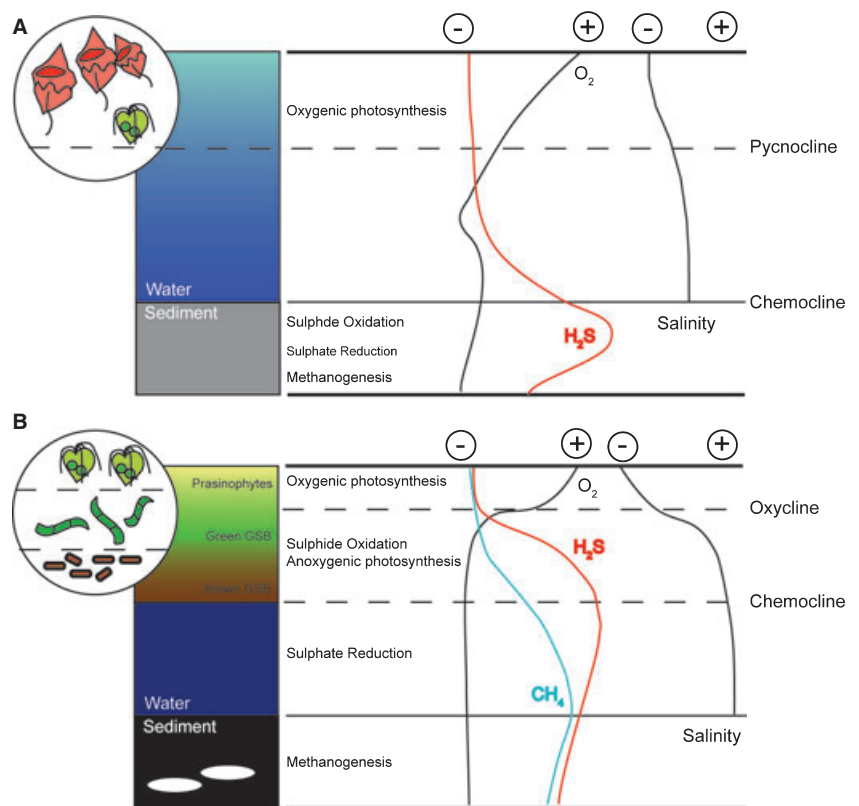
CONCLUSIONS

Widespread deposition of black shales in the EES occurred in the aftermath of the Triassic–Jurassic and Pliensbachian–Toarcian mass-extinction events. In both

cases, black shale deposition was associated with photic-zone euxinia, as shown by the presence of fossilized remains of GSB (Chlorobiaceae). Phototrophic GSB were likely important primary producers during these time intervals, which is reflected in the abundance of AOM with a type-I and type-II signatures and high HI values. More importantly, the proliferation of GSB was accompanied by major changes in phytoplankton communities, suggesting wholesale changes in physico-chemical conditions in the water column. The Triassic–Jurassic boundary represented a real bottleneck for chromophyte (red) algae. Cyst-producing dinoflagellates virtually disappeared from the EES for many million years after the Triassic–Jurassic boundary and were replaced by archaic taxa belonging to chlorophyte (green) algal lineages, including acritarchs and prasinophytes. This scenario was repeated during the deposition of Toarcian black shales.

Based on characteristic assemblages of primary (phytoplankton) and secondary (phototrophic bacteria) producers, physical–chemical conditions of the water column in the EES prior to and during euxinia can be reconstructed schematically (Fig. 10). During periods of well-oxygenated water mass conditions, cyst-forming dinoflagellates were at an ecological advantage. During periods of restriction and salinity-enhanced stratification, prasinophyte green algae profited from ammonium availability. The controlling factors on sulphur bacteria, light and sulphide concentration, demanded a shallow chemocline, leading to an

FIG. 10. Conceptual model for water column conditions. A, Conditions prior to development of anoxic conditions during the Rhaetian and Pliensbachian. B, Conditions during development of photic-zone euxinia for both the Hettangian and Toarcian.



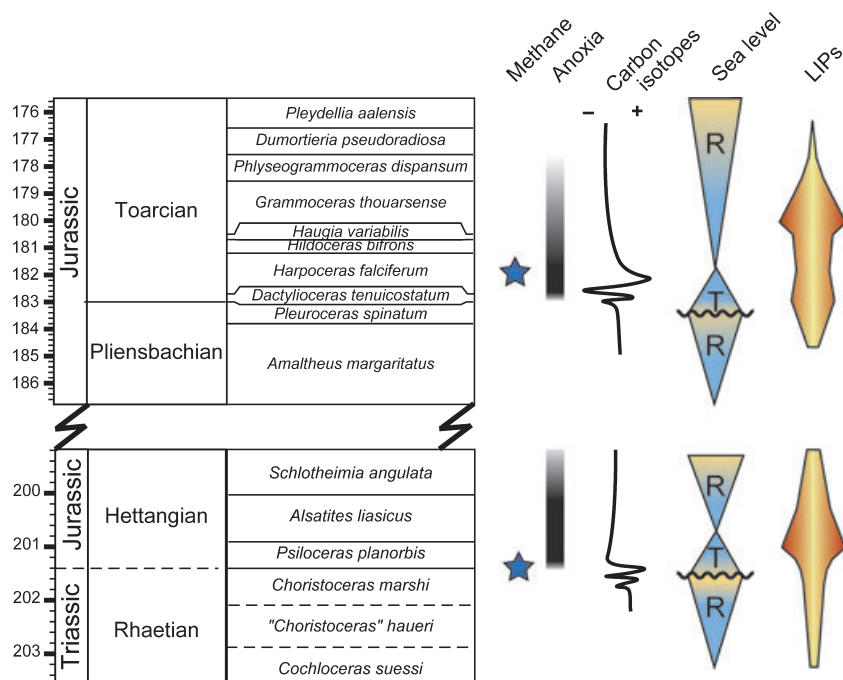


FIG. 11. Summary diagram for the Rhaetian–Hettangian and Pliensbachian–Toarcian showing relationships between anoxia, negative C-isotope excursions, sea-level change, hypothesized methane release from gas hydrates and timing of emplacement of large igneous provinces.

upwards shift in redox boundaries from the sediment into the water column. As a result, Hettangian and Toarcian water masses in the EES were probably by default rich in methane, but this methane was likely incorporated in diagenetic carbonates, leading to anomalies in C-isotope records that should not be confounded to indicate global changes in exogenic carbon reservoirs.

Both the Rhaetian–Hettangian and Pliensbachian–Toarcian transitions are associated with a series of positive and negative carbon isotope excursions that are best expressed in organic matter. Because of important changes in organic matter associated with either event shown by palynological and organic geochemical studies, $\delta^{13}\text{C}_{\text{org}}$ records should be interpreted with caution. For the Triassic–Jurassic boundary, organic C-isotope records appear to reflect the relative strength of marine organic matter deposition, whereby more marine organic matter imparted a lighter C-isotope signature to the bulk signal. These changes in organic matter sources were likely contemporaneous over large distances, and some of the excursions might appear also fortuitously simultaneous.

Many of the palaeo-environmental changes associated with Rhaetian–Hettangian and Pliensbachian–Toarcian boundaries can be explained by a similar scenario, in which the emplacement of a LIP takes centre stage (Fig. 11). This raises important questions about the driving mechanisms behind black shale events during the Sinemurian and Pliensbachian, for which there is no direct link with flood basalt activity. The temporal mismatch between methane release from gas hydrates and the onset of euxinia and mass extinction suggests that at best meth-

ane release was a consequence and not a driving mechanism. There is increasing evidence that the release of volatiles to the atmosphere from widespread flood basalt volcanism, especially through interaction with surrounding crustal rocks, was among the prime causes for the end-Triassic and Pliensbachian–Toarcian mass extinction and ensuing marine anoxic events.

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