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Record of Early Toarcian carbon cycle perturbations in a nearshore environment: the Bascharage section (easternmost Paris Basin)

M. Hermoso[1,2], D. Delsate[2], F. Baudin[3,4], L. Le Callonnec[3,4], F. Minoletti[3,4], M. Renard[3,4], and A. Faber[2]

[1]University of Oxford – Department of Earth Sciences, South Parks Road,
Oxford OX1 3AN, UK
[2]Musée National d'Histoire Naturelle – Centre de Recherche Scientifique, 25 Rue Münster,
2160 Luxembourg, Grand-Duchy of Luxembourg
[3]UPMC Université Paris 06 – UMR 7193 ISTeP, 4 Place Jussieu, 75005 Paris, France
[4]CNRS – UMR 7193 ISTeP, 4 Place Jussieu, 75005 Paris, France

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Correspondence to: M. Hermoso (michael.hermoso@earth.ox.ac.uk)

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Abstract

In order to understand the significance of worldwide deposition of black shale facies in the Early Toarcian (∼ 183 Ma), considerable attention has been drawn to this Early Jurassic sub-Stage over the last three decades. The discovery of a pronounced negative carbon isotope excursion (CIE) within the black shales disrupting the generally positive trend in carbon isotopes has stimulated many studies, particularly with a view to establish the local vs. global nature of this major geochemical phenomenon. Here we document the sedimentological and chemostratigraphic evolution of a proximal environment in the Luxembourgian sedimentary area, the so-called Gutland. At Bascharage, Lower Toarcian sediments record the isotopic signature of the Early Toarcian Oceanic Anoxic Event (OAE) by a pronounced positive trend that testifies for widespread anoxia. The expression of the carbon isotope perturbation in this section however, is unusual compared to adjacent NW European sections. A first −7 ‰ negative CIE, whose onset is recorded at the top of the *tenuicostatum* zone, can be assigned to the well-documented and potentially global T-CIE with confidence using the well-constrained ammonite biostratigraphic framework for this section. In this interval, facies contain only a limited amount of carbonate as a result of intense detrital supply in such a proximal and shallow environment. Stratigraphically higher in the section, the *serpentinum* zone records a subsequent CIE (−6 ‰) that is expressed by four negative steps, each being accompanied by positive shifts in the oxygen isotopic composition of carbonate. The preservation state of coccoliths and calcareous dinoflagellates in the second CIE is excellent and comparable to that observed in under- and overlying strata, so this cannot be an artefact of diagenesis. Considering the nature of this record, and the lack of such a pronounced event in the *serpentinum* zone in coeval sections in Europe, we hypothesise that this second CIE was caused by local factors. The geochemical record of carbonate with a relatively light carbon and relatively heavy oxygen isotopic composition is compatible with the so-called Küspert model, by which a CIE can be explained by an influx of ^{12}C-rich and cold waters due to upwelling bottom water masses. With

the ongoing effort of high-resolution studies of the Meso-Cenozoic eras, further CIEs are likely to be found, but it has to be remembered that their (global) significance can only be determined via an integrated sedimentological, mineralogical, micropalaeontological and geochemical approach.

1 Introduction

Despite multiple studies that have attempted characterisation of the evolution in palaeoenvironment coeval with the accumulation of black shales in the Early Toarcian, we still need to gain a mechanistic understanding of the combination of biological and oceanographic processes that drove seawater into an anoxic/euxinic state. The whole Early Jurassic Epoch recorded evidence for oxygen restriction in the European epicontinental seaways, but some interval corresponded to more severe episodes of oxygen depletion, as during the Early Toarcian oceanic anoxic event – commonly referred to as the T-OAE (Jenkyns, 1988). As most of the documented sections hitherto originate from the former European epicontinental seaways, it is essential to detangle the influence of local settings (shallow water depth, short distance from the coast, restricted marine circulation) to infer a global picture of Early Toarcian environmental changes. Hence, there is still a need to document the evolution of seawater physico-chemistry for a wide range of sections in Europe, yet corresponding to contrasting depositional environments.

Even within the European area, which only represented a tiny portion of the global oceanic surface, two realms are recognised on the analysis of sedimentological and geochemical data, each of them being characterised by contrasted records of the T-OAE. The NW European platform corresponded to very shallow marine environments (100 to 200 m water deep; Röhl et al., 2001) with substantial ($> 10\,\%$) accumulation of organic carbon (Baudin et al., 1990). The most studied sedimentary basins representing this environment comprise the Cleveland Basin (Yorkshire), the Paris Basin (France), and the SW German Basin (Küspert et al., 1982; Sælen et al., 2000; Röhl et al., 2001; Bailey et al., 2003; Kemp et al., 2005; Hermoso et al., 2009). By contrast, the Mediterranean realm was more open to the western Tethys and experienced lower degree of anoxia with relatively modest black shale deposition both for their stratigraphic extension and their organic content, typically ranging from 1 to 3 % (Jenkyns and Clayton, 1986; Baudin et al., 1990; Parisi et al., 1996; Hermoso et al., 2009; Sabatino et al., 2009). The isolation of NW European and Mediterranean water masses is further supported by distinct ammonite fauna for the whole duration of the Early Toarcian (Elmi et al., 1994, 1997; Macchioni, 2002). Taxa became subsequently homogenised in the Middle Toarcian owing to the second-order Liassic transgression and the flooding of the NW European realm (Hardenbol et al., 1998). If this was not complicated enough, the expression of the T-OAE, and more broadly speaking, the depositional environments, were yet very different within each of these realms. This feature is explained by active regional tectonic that separated many intracratonic sub-basins by shoals, tectonically corresponding to horsts (Gély and Lorenz, 1996).

The intracontinental Paris Basin was formed by sediment accumulation comprised between the main emergent lands inherited from the Hercynian orogenesis: the Central Massif (south), the Armorican Massif (west), the London-Brabant Massif (north), and the Rhenish Basin (east) (Fig. 1a). The basin remained somehow connected eastwards to the SW German Basin, as evidenced by common Boreal ammonite fauna. At the farthest oriental reaches of the Paris Basin, Lower Jurassic sedimentary formations are exposed in the south of Luxembourg and correspond to expanded intervals compared to adjacent sections in NE France (Lucius, 1948; Hanzo and Espitalié, 1993) (Fig. 1b). This region corresponded to proximal environments with substantial detrital influence from the Ardennes at sites of deposition. Abundant body fossils of reptiles, fishes, crustaceans, insects, higher plants confirm the nearshore nature of this region (Delsate et al., 1995, 1999; Henrotay et al., 1998; Nel et al., 2004; Dera et al., 2009).

In the present study, we attempt characterisation of palaeoenvironmental changes through the Pliensbachian–Toarcian transition and the T-OAE as recorded in the Bascharage section exposed in the SW of Luxembourg. In such proximal setting, the

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record is most prone to be affected by local factors such as change in sea level, riverine run-off, coastal circulation, and temperature, and therefore potentially bears maximum modulation of the expression of the global T-OAE. Examining the dynamics of the carbon cycle, in particular with regard to the well-documented prominent negative carbon isotope excursion that is recorded within the T-OAE (Hesselbo et al., 2000) may hence provide valuable information on the impact of local factors on the record of Late Pliensbachian – Early Toarcian climate and the carbon cycle.

2 The Bascharage composite section

2.1 Regional settings

Rocks exposed in the south west of the Grand-Duchy of Luxembourg correspond to Lower Jurassic (Liassic) sedimentary formations (Fig. 1a). Bascharage is a city in the vicinity of the French and Belgian borders (Fig. 1b). The composite section presented in this study is composed by two intervals distant of about 500 m. The first interval (3.6 m-thick) was temporally exposed in the industrial zone “Op Zämer” (Fig. 2). The second interval (7.2 m) is situated along the Prince Henri railway connecting Pétange to Luxembourg City, at the west of the industrial zone “Bommelscheuer”. We can estimate a conservative non-observational hiatus of less than 50 cm between the two sections thanks to topographic data provided by the Luxembourgian railway company. This composite interval spans the Late Pliensbachian and the Early Toarcian sub-Stages. The last metre of the Bommelscheuer outcrop consists of highly altered facies due to the activity of the vegetal cover overlaying the section.

2.2 Sedimentology, lithostratigraphy and biostratigraphy

The “Op Zämer” section exhibits Upper Pliensbachian strata corresponding to the Marnes d’Ottemt Formation (Fig. 2). Facies consist of pale grey clayed sediments with an abundant macrofauna (belemnites, brachiopods, bivalves and ostracods). Another prominent feature of this sedimentary unit dated of the *spinatum* zone is the considerable number of centimetric limonite nodules (from the base up to 80 cm in the section) and subsequently phosphate (apatite) nodules from 80 to 120 cm. The sedimentary unit overlaying the Pliensbachian–Toarcian boundary consists of clayed orange facies in which no ammonite specimens were observed. This level corresponds to the lower part of the Marnes à Semicelatum Formation, biostratigraphically assigned to the *tenuicostatum* zone in SE Belgium (Delsate, 1990; Boulvain et al., 2001). The following unit consists of dark blue/grey calcareous claystone, typical of the Marnes à Semicelatum Formation with many belemnites and large carbonate nodules whose diameters are comprised between 10 and 30 cm. This 80 cm-thick interval is assigned to the *semicelatum* sub-zone of the Early Toarcian. The top of the Op Zämer section exhibits the Lower Toarcian black shales of the Schistes carton Formation (lithostratigraphically equivalent to the Jet Rock Formation in Yorkshire, or to the Posidonienschiefer Formation in SW Germany) that provide compelling evidence for supra-regional anoxia. Black shales consist of very dark and finely laminated sediments, with very scarce macropalaeontological content (restricted to few ammonite specimens and *Bositra* spp. casts). The contact between the Schistes carton lithology and the underlying pale grey marls is sharp and underpinned by many pluricentimetric wood fragments. In adjacent regions in Belgium, a thin sandy bed containing an abundant fish macrofauna has been reported at this transition (Delsate et al., 1999).

The “Bommelscheuer” section spans the Early Toarcian *serpentinum* zone. The exposed black shales correspond to a monotonous lithological unit with, however, a notable level of nodular limestone between 5.3 and 5.5 m in the section (sometimes referred as to the “pains pétrifiés” in regional literature; cf. Hanzo, 1979), and a 30 cm-thick limestone bed at 7.5 m in the composite section. This carbonate level marks the transition between the *elegantulum* and the *falciferum* sub-zones. The total thickness of the Schistes carton Formation in this sedimentary area is in the order of 60 m (Hanzo and Espitalié, 1993). The overlying Marnes à Bifrons Formation of the Middle Toarcian (not exposed at Bascharage) still records evidence of anoxia with sediment lamination (Delsate, 1990; Hanzo and Espitalié, 1993; Boulvain et al., 2001; Dera et al., 2009).

3 Methods

The carbonate content of the sediments were measured at Oxford University using a Strohlein Coulomat 702 apparatus. To remove to organic carbon, crushed samples were roasted overnight at 420 °C and subsequently combusted from 800 to 1200 °C under an oxygen flush. Measured CO_2/CO were quantified by coulometric determination and translated into % weight carbonate by multiplying the carbon content by a factor of 8.3 (the elemental $CaCO_3/C$ ratio). Reproducibility of measurements was usually better than 0.5 %.

Total Organic Carbon (TOC) content and Rock Eval parameters of the organic matter were measured at UMPC Paris using a Rock-Eval II apparatus. The "$\%TOC_{\text{carb-free}}$" reflects the abundance of organic matter in the sediment after removing the carbonate fraction. This figure, which offers a convenient means to track the evolution in the organic carbon in sediments irrespective to more or less dilution by carbonate, is calculated following the formula: $\%TOC_{\text{carb-free}} = (100 \times \%TOC)/(100 - \%CaCO_3)$. Temperature in the pyrolysis programme at which a maximum of hydrocarbon was released is termed T_{max} and provides information on the thermal maturity of the organic matter. The hydrogen index (HI), expressed as mg hydrocarbon per gram of organic carbon, are used to determine the origin of the organic matter, with terrestrial (continental) organic matter being more hydrogen-depleted with respect to oxygen than phytoplanktonic organic matter. The typology of organic matter by Tissot et al. (1971) includes: a Type III with relatively low (< 100 mg of hydrocarbon per gram of TOC) HI characteristic of continental organic matter, and a Type II with higher HI (in the order of 600) that indicate marine phytoplanktonic origin.

Samples were measured for their carbon and oxygen isotopes at Oxford University using a VG Isogas Prism II mass spectrometer with an online VG Isocarb. An approximate mass of 50 mg of sample was finely crushed, and 10 mg was reacted with anhydrous phosphoric acid at 90 °C. Calibration to V-PDB standard is made using the NOCZ internal standard. Reproducibility of the analyses is better than 0.1 ‰ for carbon and oxygen isotopes.

Initial attempts to measure the isotopic composition of the organic matter produced poor quality and unrealistic data that have been discarded. Unfortunately, subsequent δ^{13}C analyses of these samples were not possible.

X-Ray diffraction of samples distributed along the Schistes carton Formation revealed that the carbonate mineralogy is calcium carbonate (Hermoso, 2007). The nature and preservation of calcitic particles in the sediments were examined using both optical and electronic microscopes. Smear slides were observed under a cross-polarised Zeiss microscope fitted with a 63× objective enabling high magnification observation (Minoletti et al., 2009). Some selected samples were investigated with a scanning electron microscope (SEM) to assess the preservation of calcareous nannofossils, which, where present (Schistes carton Formation), was always very good (Fig. 3). Importantly for the interpretation of isotopic signals, no recrystallisation feature or overgrowth on coccoliths were observed throughout the black shale interval.

4 Results

4.1 Carbonate content and total organic carbon

In the Pliensbachian, deposits contained minimum carbonate content with some intervals containing virtually none (Fig. 4). The first lithological unit (0–0.7 m) contains about 15 % of carbonate. The two subsequent units (0.7–1.3 m) are barren of carbonate phase. The grey marls between 1.3 and 2.3 m are relatively rich in calcite up to the nodular level at 1.8 m, and subsequently becomes carbonate-depleted at the top of this unit. With the emplacement of black shales, the carbonate content shows a transient enrichment with content up to 30 %. No carbonate were detected in the black shales comprised between 2.6 and 3.4 m. This observation could be related to weathering of the top of the Op Zämer section although facies did not appear to be macroscopically altered. Above the level that is distinguishable by the presence of small calcareous concretions at 3.5 m, the carbonate fraction of the sediment progressively increases up to the limestone bed at 7.5 m. This increase is considerable by its magnitude with carbonate contents changing from ~ 0 to 60 %. This mineralogical change mostly corresponds to enrichment in calcareous nannofossils in the sediments. It has to be noted that even if the lithological expression of this limestone level is clear with respect to the hosting black shale facies, the increase in carbonate is also elevated in both under- and overlaying sediments. The same remark applies for the interval containing the nodules at about 5.3 m in the section. The top of the section shows a decline in the carbonate content, although the content remains relatively high, about 30 %.

The TOC content is negligible in the upper Pliensbachian and lowermost Toarcian deposits before the onset of black shales (Fig. 4). The organic content in the black shales gradually increases, reaching a maximum of ~ 22 % at 3.5 m in the section. Subsequently, the TOC shows a rapid diminution up to the nodular level at 5.5 m. The organic content of rocks remains at relative high levels of 10 % in the *elegantulum* sub-zone. In the *falciferum* sub-zone, minimum contents of 5 % are observed.

4.2 Carbon and oxygen isotope from bulk carbonate samples

Overall, carbon isotopic ratios measured from bulk carbonate rock are comprised in a substantially wide array (± 10 ‰) (Fig. 4). The δ^{13}C values are strikingly very negative when the carbonate content is low (< 10 %), raising question about the validity of such measurements. During the Pliensbachian, the ratios are stable and about 0 % in sediments with more than 10 % carbonate, corresponding to grey calcareous marls (0 to 0.7 and 1.4 to 2 m). It is otherwise significantly lower, comprised between −4 and −6 ‰ in carbonate-depleted intervals. In the *tenuicostatum* zone, the top of the Marnes à Semicelatum and the base of the black shales characterised by relatively high carbonate content shows δ^{13}C around −7 ‰ and −5 ‰, respectively. Due to the lack of carbonate in the 2.6 to 3.4 m interval, no isotopic ratios were successfully measured. When a carbonate fraction reappears in the sediment at 3.4 m, δ^{13}C are slightly more negative, about −6 ‰ (Fig. 4). This "jump" in δ^{13}C values represents a CIE of ∼ −7 ‰ although the descending limb of this excursion is not well defined. After the non-observational hiatus corresponding to the transition between the Op Zämer to the Bommelscheuer sections, a clear increase in δ^{13}C is observed with ratios reaching ∼ +2 ‰ at 5.4 m. Between 5.4 and 6.8 m (*serpentinum* zone), a stepped negative CIE with a total magnitude of ∼ −6 ‰ is observed, whilst carbonate contents remain relatively high and even show a slight increase throughout this second CIE (disregarding the enriched level containing the calcareous nodules). Above this CIE, the δ^{13}C increase is resumed and maximum isotopic ratios of ∼ +3.5 ‰ are reached at the base of the *falciferum* sub-zone (Figs. 4 and 5). Such high δ^{13}C ratios persist up-section irrespective to the appreciable fluctuations in the carbonate content.

By contrast to the carbon isotopes, oxygen isotopic ratios measured in intervals with very low carbonate content show more positive values. The base of the section records δ^{18}O values around an average of −4 ‰. The uppermost Pliensbachian and lowermost Toarcian sediments present an offset of +8 ‰. In the Lower Toarcian interval, including the base of the black shales, the ratios are comprised between −4 and −6 ‰. Such negative δ^{18}O ratios persist throughout the whole black shales at Bascharage. In details, although the variations are not so intense as for δ^{13}C, the evolution in the oxygen isotope ratios mirror those of the carbon isotopes (Figs. 4 and 6). This is especially the case for the significant δ^{13}C increase between 3.4 and 5.4 m, and throughout the second negative CIE in the *serpentinum* zone during which each negative step is seen with a +0.75 to +1 ‰ increase in δ^{18}O (Fig. 6).

4.3 Rock-Eval parameters

Rock Eval assays were only attempted for Toarcian sediments in which TOC content exceeds about 1 % (Figs. 4 and 5). In advance to the black shale facies, i.e. in the Marnes à Semicelatum Formation, there is a clear decrease in T_{max} and increase in hydrogen indexes. Taken together, the Rock-Eval parameters indicate a shift from continental-dominated organic matter towards marine (phytoplanktonic) organic matter. Following the typology of the sedimentary organic matter by Tissot et al. (1971), this change corresponds to a progressive, but marked, transition from Type III to Type II. Stable and persistent Type II composition within black shales is recorded underneath the nodular level of the *elegantulum* sub zone (at ~ 4.8 m). The decrease in T_{max} does not correspond to a change in the thermal evolution of the section, but is related to the change in both the type and preservation of organic matter. Indeed, Type III usually shows higher T_{max} than Type II for the same thermal level (Espitalié et al., 1986) and the oxidation of organic matter remove the labile fraction of the organic matter leading to the selective preservation of a more thermally resistant organic fraction.

Stratigraphically above the nodular level, a decrease in the TOC content is observed, albeit with relatively unchanged HI and T_{max}. An interval between 7.8 and 8.4 m, however, exhibit lower $\text{TOC}_{\text{carb-free}}$ and HI.

5 Discussion

5.1 The Pliensbachian–Toarcian boundary

The base of the section containing more than 10 % of carbonate shows stable isotopic ratios, 0 ‰ (carbon) and −4 ‰ (oxygen). These absolute isotope ratios measured from carbonate at the end of the Pliensbachian are comparable to other data from the Paris Basin (Röhl et al., 2001; Hermoso et al., 2013). This basin-scaled feature may indicate homogenous water masses in the basin, including near-identical temperature status during the end of the Pliensbachian.

Higher in the section, but still in the Pliensbachian, detrital facies and complex mineralogy (phosphate/carbonate) hampers generation of meaningful isotopic records. In nearshore environments, rapid fluctuations in the composition of seawater are related to fresh water supply from the continent (with low δ^{18}O). The delivery of fresh water can overprint the temperature record in $\delta^{18}O_{carb}$. Fluctuations in $\delta^{18}O$ (9 ‰ ranging from very negative to very positive ratios) may indicate unrealistically high change in sea surface temperatures, or even in the isotopic composition of seawater, a reflection of the ice volume and of the local hydrographic regime (between evaporation and precipitation). It has to be acknowledged that no palaeoenvironmental information can be deduced from the Bascharage record to characterise the Pliensbachian–Toarcian transitional climatic change (poor carbonate content with the absence of calcareous nannofossils, presence of phosphate nodules). From a more sedimentological perspective, it can be deduced from the orange clayed, coccolith-barren interval laying on the Stage boundary, a drastic reduction of the water depth. Such a red or orange level immediately after the boundary has been previously reported in France and interpreted as an emersional event (Morard et al., 2003). A prominent sedimentary hiatus is widely observed at the scale of the NE Paris Basin (Boulvain et al., 2001; Van Breugel et al., 2006; Lézin et al., 2013). This stratigraphic feature explains the lack of the record of the CIE across the Stage boundary between the Pliensbachian and the Toarcian, as it was reported from NE England or from the Polish Basin (Littler et al., 2010; Hesselbo and Pienkowski, 2011).

5.2 First CIE and onset of Early Toarcian black shale (*tenuicostatum* zone)

The Marnes à Semicelatum Formation corresponds to sediments that have a typical $\delta^{13}C$ signature of about 0 %. This composition is suddenly dropping, representing a −7 ‰ negative shift in the $\delta^{13}C$ during the *tenuicostatum* zone. This large isotopic offset in this stratigraphic interval is compatible with the well-documented CIE. It is located within the same biostratigraphic interval, and presents a similar magnitude than in other NW European carbonate records (Röhl et al., 2001; Hermoso et al., 2009). Coeval decreased oxygen isotope ratios are registered within this inferred CIE. Low carbonate contents can be explained in near shore environment by substantial high detrital (clay) supply to the site of deposition. During the CIE, reinforcement of the

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detrital supply has been show by mineralogical and geochemical data (Cohen et al., 2004; Brañski, 2012; Hermoso and Pellenard, 2014). This climatic sensitivity of the continental weathering due to increased $p\mathrm{CO}_2$ levels may have been responsible for the dilution of the carbonate phase. Additionally, lower carbonate preservation can be ascribed to an episode of seawater acidification in the Paris Basin (Hermoso et al., 2012).

Throughout the top of the Marnes à Semicelatum to the Schistes carton Formations, significant increase in coccolith abundance and in hydrogen indices of the organic matter clearly indicates a better preservation of marine-derived organic matter and hence a greater distance of Bascharage from the coast (Fig. 5). The overall evolution in facies and carbonate content is the likely consequence of the third-order transgression during the earliest Toarcian (“Pl 8” cycle sensu Hardenbol et al. (1998). At the onset of black shales, δ^{13}C are still very low (~ -5 ‰) and the measurements can be regarded as primary signals with confidence (coccoliths). The first centimetres of black shales at Bascharage are characterised by relatively high carbonate content, predominantly consisting of coccoliths (Hermoso, 2007) (Fig. 3). The hydrogen indices indicate a mixture between marine (coccolithophore) and terrestrial-derived organic matter, as confirmed by the recovery of many wood fragments. Flooding of epicontinental surfaces led to extraordinary high primary phytoplanktonic productivity (Jenkyns, 2003; Erba, 2004), as also evidenced by a pronounced positive trend in δ^{13}C, and locally by the sedimentation of coccolith calcite (Figs. 4 and 5).

5.3 A second Early Toarcian negative carbon isotope excursion (top of *tenuicostatum* zone)

The broader feature associated with the T-OAE is the positive trend in the carbon isotopes that indicate burial of ^{12}C-rich carbon in form of organic matter. Local factors, such as an insufficient water depth, are not likely to affect the record of this global isotopic trend (Hermoso et al., 2013). This is well illustrated in most of Mediterranean sections in which the δ^{13}C overarching positive trend is recognised without lithological expression of black shales, ruling out a local or diagenetic control on carbon isotope signal in carbonate. Conversely, one process that is prone to substantially alter the pristine isotopic signal is diagenesis.

At Bascharage, the nature and preservational state of the carbonate particles (in majority consisting of calcareous nannofossils in the Schistes carton, Fig. 3) indicate that isotopic measurements reflect a primary signal of the photic zone (Hermoso, 2007; Minoletti et al., 2009). Low T_{max} values indicate that the studied sections did not experience strong thermal diagenesis. The record of a positive trend in δ^{13}C curve provides strong evidence for a primary signal at Bascharage provided samples contain a minimum (~ 10 %) of carbonate. In the following account, we discuss the record and significance of the second CIE in the *serpentinum* zone.

5.3.1 Testing a diagenetic record of the second CIE

There are many geological intervals during which broad correlative trends between δ^{13}C and δ^{18}O were observed, as for the Early Toarcian (Jenkyns and Clayton, 1997; Rosales et al., 2001). The main explanation put forwards to explain this observation is diagenesis (Marshall, 1992). One singularity of the Bascharage section is the observation of concomitant low δ^{13}C/high δ^{18}O, which is a contrasting situation with other intervals thought to have experienced substantial diagenetic alteration of the primary signal (Rosales et al., 2001). An early diagenetic phase that precipitates from bottom (cold) waters would bear more positive δ^{18}O. Concomitantly, because the alkalinity in early diagenetic fluids derives from organic matter decay, δ^{13}C is substantially shifted towards low values (Irwin et al., 1977). However examination of nannofacies in the interval comprising the CIE at Bascharage does not indicate the presence of such diagenetic overprinting (Fig. 3). Carbonate assemblages and their preservational state are similar during the CIE with underlying (disregarding the nodules) and overlying sediments. Both bracketing horizons record global signal, as isotopically evidenced by recognition of the long-term positive trend in δ^{13}C.

5.3.2 A palaeoceanographic explanation?

The oxygen isotope ratios at Bascharage do not exhibit a negative shift concomitant to the negative "CIE 2" (*serpentinum* zone) that would potentially indicate warming or intensification of the riverine supply at Sancerre and elsewhere (Bailey et al., 2003; Hermoso et al., 2013). This response in the δ^{18}O climate-sensitive proxy represents a main difference with the expression of the "CIE 1" (*tenuicostatum* zone). Retaining the primary record of δ^{18}O at Bascharage during the negative CIE, two alternative, not necessarily exclusive, hypotheses may account for higher δ^{18}O and for δ^{18}O/δ^{13}C co-variation during the CIE 2 (Fig. 6). Firstly, each negative step of the descending limb of the carbon isotope excursion may have been coeval with cooling. Such cooling phase may be accompanied by diminished primary (organic) productivity, which in turn, would have led to more negative δ^{13}C in carbonate and organic matter. These two observations are not made at Bascharage. Furthermore, each step of the negative CIE does not correspond to lowered concentrations in TOC or $\text{TOC}_{\text{carb-free}}$. As an alternative, these discrete intervals may have been characterised by reduced input of fresh water into the basin. Both hypotheses are conflicting with our view of palaeoceanographic and palaeoclimatic event during a global event, i.e. reflecting sudden increase of atmospheric $p\text{CO}_2$, regardless of its possible cause(s) as volcanism, methane hydrate release, and/or intrusion of dolerites into organic-rich formations of the Karoo region (Hesselbo et al., 2000; McElwain et al., 2005; Svensen et al., 2007; Suan et al., 2008).

The above-mentioned hypothesis relies on a top-down control of seawater chemistry whereby fluctuations of temperature and isotope composition are predominantly forced by a climatic (atmospheric) control. A bottom-up scenario with upwelling of cold and ^{12}C-rich waters may explain the δ^{18}O/δ^{13}C co-variation that characterises the record of the T-CIE at Bascharage (Fig. 6). This explanation was originally formulated by Küspert (1982), and more recently discussed by Van de Schootbrugge et al. (2005), who claimed that the T-CIE was not a global phenomenon, but only ascribed to a local oceanographic control.

It has to be noted that a ~ −1.5 ‰ CIE subsequent to the "main" CIE has recently been reported in the Sancerre borehole, between 328 and 324 m deep in the core (Hermoso and Pellenard, 2014). In the recent paper by Lézin et al. (2013), it appears also very likely that what they have interpreted as the "global" CIE was the CIE 2 in the *serpentinum* zone. This possible basin-scaled correlation may indicate a regional event that affected the whole Paris Basin, albeit with a stronger magnitude in nearshore environments such as that of Bascharage.

Further investigation on this $\delta^{18}O/\delta^{13}C$ co-variation has to be undertaken. Notably, generating a nitrogen isotope profile through this interval would enable testing an upwelling explanation for this geochemical feature.

6 Conclusions

Upper Pliensbachian and lowermost Toarcian sediments at Bascharage have largely revealed to be unsuitable to apply carbonate-based isotopic proxies. Hence, palaeoenvironmental characterisation of this interval remains relatively unconstrained for this section. This feature may confirm the previously established near-emersional event around the stage boundary.

Deposition of black shales in the Early Toarcian interval overlies a transitional facies consisting of grey marls with abundant marine fauna indicating re-establishment of full marine conditions. The "worldwide" CIE (CIE 1) comprised in the *tenuicostatum* zone is recognised at Bascharage with its full amplitude compared to adjacent sections (~ −7 ‰) although carbonate particles are not composed of well-preserved coccoliths raising questions on the reliability of these measurements. The record of the CIE 1 predates the emplacement of full anoxia and consecutive black shale deposition, as it is the case elsewhere in the south of the Paris Basin. With continuing sea level rise, reinvasion of coccoliths enabled sedimentation of carbonate and phytoplanktonic organic matter. Substantial high primary productivity led to anoxia, as observed at the scale of the whole NW European realm, and perhaps, more widely regarding the positive trend in carbon isotope as they are driven by a global phenomenon. Surprisingly, in the *serpentinum* zone a second prominent and stepped carbon isotope excursion (CIE 2) is registered, with a magnitude of −6 %. Higher δ^{18}O during each of the carbon isotope negative steps provide evidence for a local control. We interpret this response in the "local" carbon cycle and in decreased temperatures of surface water mass by advection of bottom water masses. Future work, as generation of $\delta^{13}C_{org}$, $\delta^{15}N_{org}$ or TEX$_{86}$-based temperature estimates may help constraining palaeoenvironmental changes in such nearshore realm, together with a palaeoecological characterisation of nannofossil assemblages.

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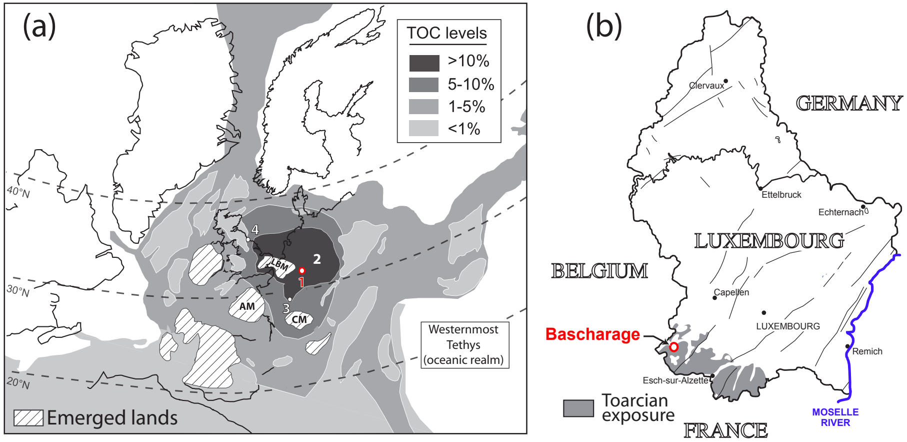

Fig. 1. (a) Palaeogeographic reconstruction of the Early Jurassic epicontinental seaway, and geographic distribution of organic-rich rocks. Greyscale shades reflect average contents of total organic carbon (TOC); key is inset upper right. Emergent lands delineating the Paris basin are hatched. CM: Central Massif; AM: Armorican Massif LBM: London-Brabant Massif (also comprising the Rhenish Massif in its oriental portion). The map indicates the location of the Bascharage (1), Dotternhausen (2) and the Sancerre borehole (3). Source: Bassoulet et al. (1993); Baudin et al. (1990); Van de Schootbrugge et al. (2005); Hermoso et al. (2009). **(b)** Location of the Bascharage section in NW Luxembourg. The grey area represents exposures of Toarcian deposits. Map from Service Géologique (1998).

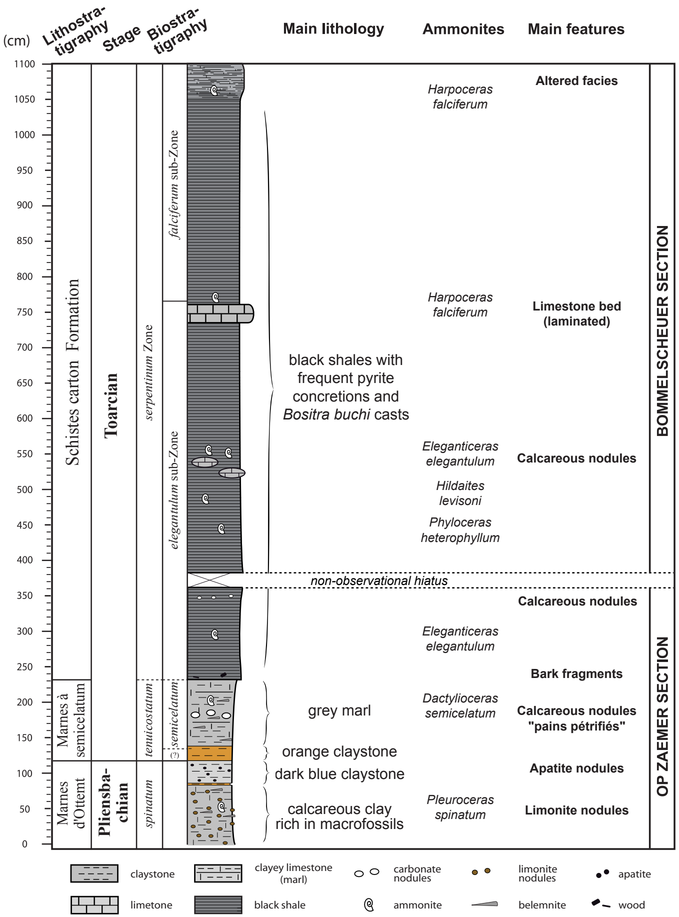

Fig. 2. Lithostratigraphy, biostratigraphy and main lithological description of the composite section of Bascharage spanning the Late Pliensbachian to Early Toarcian intervals of the Op Zämer and Bommelscheuer outcrops.

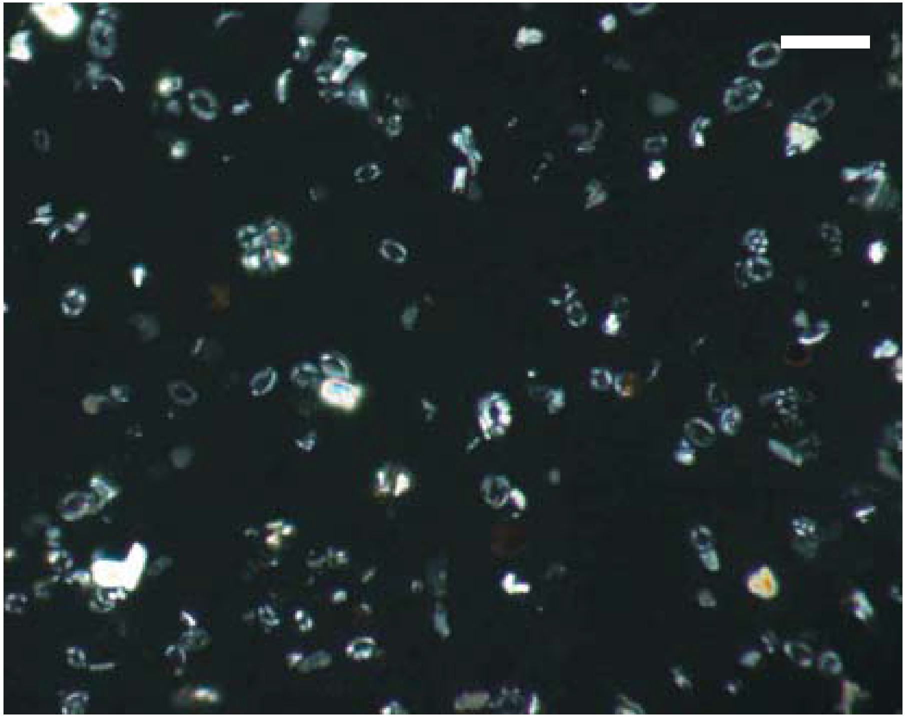

Fig. 3. Cross-polarised microphotograph of lower Toarcian black shales exposed at Bascharage – sample from the Schistes carton Formation at 6 m in the section. This image illustrates the good preservational state of coccoliths and the reduced abundance of diagenetic particles (scale bar: 10 µm). Microseparated assemblage taken from Minoletti et al. (2009).

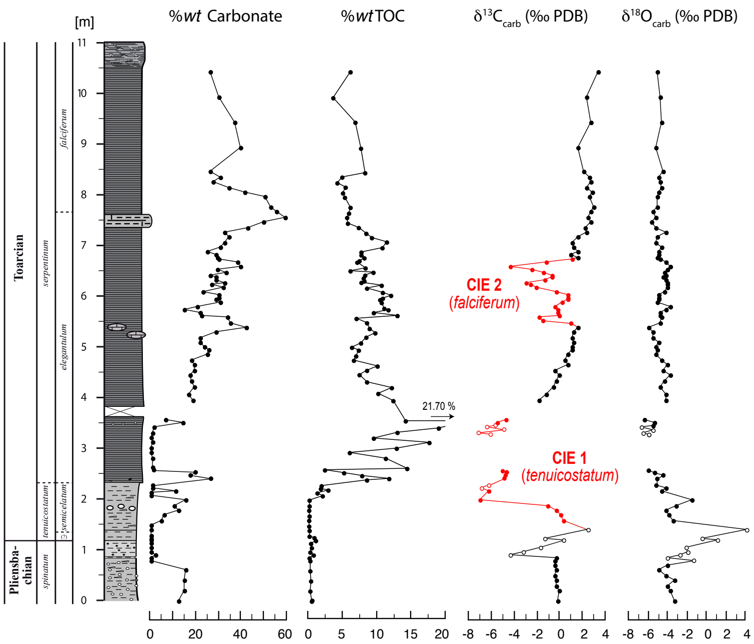

Fig. 4. Evolution in carbonate (%$CaCO_3$) and total organic carbon (%TOC) content, and stable isotopes (carbon and oxygen) from carbonate for the Bascharage section. Open circles indicate samples with very low (typically < 10 %) carbonate content, challenging the validity or meaning of stable isotopes data in such clayed facies. During the Early Toarcian, the oceanic anoxic event is expressed by the overarching positive trend in carbon isotope ratios, accompanied by an increase in the carbonate (coccolith) content in Bascharage. Red portions of the curves represent the CIEs: a first one with a magnitude of −6 ‰ in the *tenuicostatum* zone, which can be stratigraphically assigned to the widely documented T-CIE. A subsequent −6 ‰ and stepped CIE (CIE 2) in the *serpentinum* zone is expressed in well-preserved coccolith-bearing sediments. Coeval oxygen isotope shows heavier signatures during each of the fourth step of the second CIE (see Fig. 6 for a close-up).

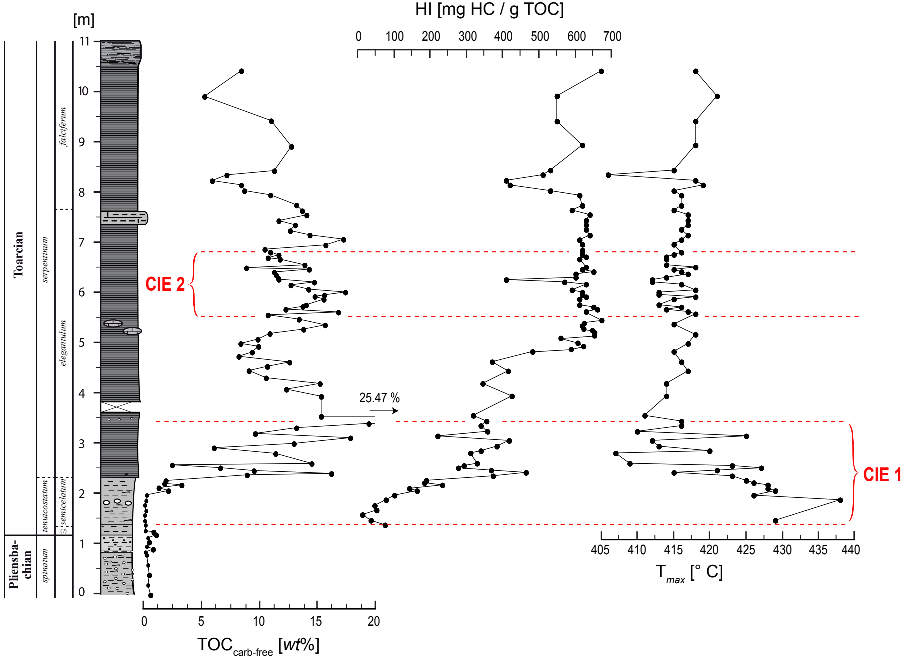

Fig. 5. Evolution of the carbonate-free total organic carbon (TOC$_{\text{carb-free}}$) and Rock-Eval parameters of the organic matter such as $T_{\max}$ and HI (hydrogen indices) for the Bascharage section. Emplacement of black shales (Schistes carton) is registered with substantial increase in the hydrogen indices, indicating a change from terrestrial to marine-derived organic matter, which in turns potentially indicates sea level rise. The same interval records a significant increase of coccolith sedimentation coccoliths (Fig. 3). The stratigraphic position of the two CIEs is bracketed between the red dashed lines.

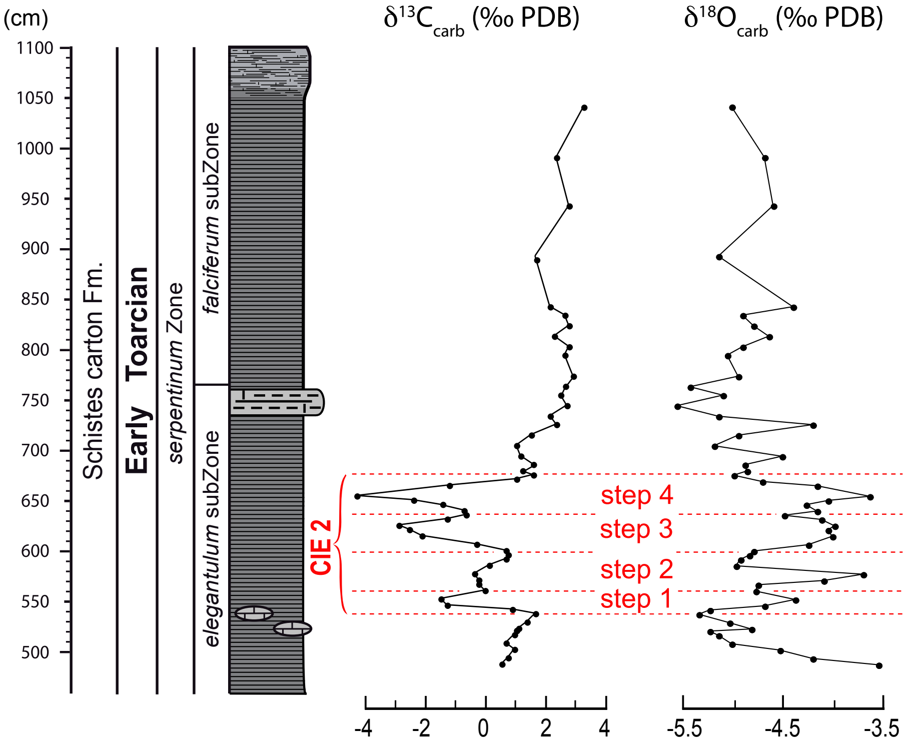

Fig. 6. Close-up of the CIE 2 in the *serpentinum* zone showing the anti-correlation of carbon and oxygen ratios in coccolith-bearing carbonate.