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Black shale deposition during Toarcian super-greenhouse driven by sea level

M. Hermoso[1], F. Minoletti[2,3], and P. Pellenard[4]

[1]University of Oxford – Department of Earth Sciences, South Parks Road, Oxford OX1 3AN, UK
[2]UPMC Université Paris 06 – UMR7193 ISTeP, 4 Place Jussieu, 75005 Paris, France
[3]CNRS – UMR7193 ISTeP, 4 Place Jussieu, 75005 Paris, France
[4]Université de Bourgogne – UMR CNRS 6282 Biogéosciences, 6 Boulevard Gabriel, 21000 Dijon, France

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

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Abstract

One of the most elusive aspects of the Toarcian Oceanic Anoxic Event (T-OAE) is the paradox between carbon isotopes that indicate intense global primary productivity and organic carbon burial at a global scale, and the delayed expression of anoxia in Europe. During the earliest Toarcian, no black shales were deposited in the European epicontinental seaways, and most organic carbon enrichment of the sediments postdated the T-OAE (defined by the overarching positive trend in the carbon isotopes). In the present studied, we have attempted to establish a sequence stratigraphy framework for Early Toarcian deposits recovered from a core drilled in the Paris Basin using a combination of mineralogical (quartz and clay relative abundance) and geochemical (Si, Zr, Ti and Al) measurements. Combined with the evolution in redox sensitive elements (Fe, V and Mo), the data suggest that expression of anoxia was hampered in European epicontinental seas during most of the T-OAE due to insufficient water depth that prevented stratification of the water column. Only the first stratigraphic occurrence of black shales in Europe corresponds to the "global" event. This interval is characterised by $> 10\,\%$ Total Organic Carbon (TOC) content that contains relatively low concentration of molybdenum compared to subsequent black shale horizons. Additionally, this first black shale occurrence is coeval with the record of the major negative Carbon Isotope Excursion (CIE), likely corresponding to a period of transient greenhouse intensification likely due to massive injection of carbon into the Atmosphere–Ocean system. As a response to enhanced weathering and riverine run-off, increased fresh water supply to the basin may have promoted the development of full anoxic conditions through haline stratification of the water column. In contrast, post T-OAE black shales were restricted to epicontinental seas (higher Mo to TOC ratios) during a period of relative high sea level, and carbon isotopes returning to pre-T-OAE values. Comparing palaeoredox proxies with the inferred sequence stratigraphy for Sancerre suggests that episodes of short-term organic carbon enrichment were primarily driven by third-order sea level changes. These black shales exhibit remarkably well-expressed higher-frequency cyclicities in

the concentration of redox-sensitive elements such as iron or vanadium whose nature has still to be determined through cyclostratigraphic analysis.

1 Introduction

Evidence for widespread oceanic anoxia during the Early Toarcian (183 Ma) relies heavily on sedimentological observation of organic-rich rocks (Jenkyns, 1988). However, as the record of these organic carbon-rich deposits is geographically restricted to the European epicontinental sea, their global significance cannot be ascertained with confidence, although some sections outside Europe reflecting more open oceanic conditions do seem to hint at a coeval organic carbon enrichment (Hori, 1997; Al-Suwaidi et al., 2010; Caruthers et al., 2011; Gröcke et al., 2011; Izumi et al., 2012). Several definitions of black shales have been used by various authors, as pointed out by McArthur et al. (2008). This problem has led to different interpretations pertaining to the stratigraphic relationship between "black shale" occurrence and the carbon isotope curves. In the present study, we define a black shale interval on the basis of sediment lamination rather than a TOC content higher than 5 % (Neuendorf et al., 2005). Indeed, the organic content may be modulated as a result of dilution by clay and carbonate minerals. In the Sancerre core, such laminated intervals, however, systematically exhibit > 2 % TOC and an appreciable amount (∼ 3 %) of pyrite.

A prominent positive trend in carbon isotope ratios (δ^{13}C) testifies for intense and widespread organic carbon burial during the Early Toarcian. Recent geochemical developments also support the idea of global scale anoxia (Pearce et al., 2008; Lu et al., 2010; Gill et al., 2011). Adopting a chemostratigraphic definition of the Early Toarcian OAE, based on the overarching positive trend in δ^{13}C, may be more meaningful than using the stratigraphic extension of black shales deposited in relatively shallow waters. In most documented European sections, black shale intervals are recorded after the termination of the positive carbon isotope shift and thus, their global nature is disputable. This discrepancy, and how various authors have defined "black shales", has led to the concept of Regional OAEs or R-OAE (McArthur et al., 2008).

A companion event of the T-OAE is the pronounced negative carbon isotope excursion (CIE) superimposed upon the $\delta^{13}C$ positive shift (Hesselbo et al., 2000). This sharp isotopic event, probably reflecting injection of isotopically-light carbon into the Ocean–Atmosphere system, is near-synchronous with the base of the black shales in European basins suggesting a causal link (Hesselbo et al., 2000). A causal link between amplification of a greenhouse period and initiation of anoxic/euxinic conditions has been proposed by numerous authors (Hesselbo et al., 2000; Kemp et al., 2005; McElwain et al., 2005; Hermoso et al., 2009a, 2012). Detailed constraints on climatic evolution, sea level change and the degree of water column oxygenation that prevailed before, during and after the T-OAE have yet to be obtained, despite their clear importance for understanding development of an Oceanic Anoxic Event and subsequent Earth system recovery.

The Sancerre borehole drilled in the southern Paris Basin (Fig. 1) has provided decisive arguments on the nature of the negative CIE and its relation with the T-OAE (Hermoso et al., 2009a, b, 2012). This new study on an extended stratigraphic interval of the core aims to constrain the evolution of (i) the relative sea level through the establishment of a sequence stratigraphy framework; and (ii) the degree of water column oxygenation inferred by the concentration of redox-sensitive elements such as Mo, Fe, and V.

2 Methods

The present study presents a detailed mineralogical and geochemical record for the Late Pliensbachian, the whole Early Toarcian and the base of the Middle Toarcian intervals with a view to constraining the depositional settings leading to the expression of the successive black shale intervals. The high-resolution records of carbonate, total organic carbon (TOC) contents, and stable isotopes from previous studies (Hermoso

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et al., 2009a, 2012) have been stratigraphically extended to better constrain the Pliensbachian–Toarcian boundary and to document the *serpentinum–bifrons* Zonal transition.

Determination of concentration of a suite of metals was performed by X-Ray Fluorescence (XRF) using a Thermo Scientific Niton XL3t GOLDD+ apparatus. The resolution step was 10 cm. Standardisation of the raw data expressed in counts per seconds to elemental concentrations was obtained by the "Mining" mode of the instrument, which corresponds to the setting suitable for sediment measurements and expression of the results in ppm of elements. Further correction of the results was achieved by measuring nine certified standards provided by Niton UK Ltd.

Quantification of the calcite/dolomite ratio was performed from finely powdered samples using a Brucker D4 diffractometer with Cu Kα radiation and Ni filter at University of Bourgogne. The relative proportion of the insoluble phases (mostly consisting of quartz, pyrite and clays) was determined from XRD diagrams from decarbonated (10 % HCl) samples. The Quartz/(Quartz + Clay) index was determined by measuring the area of the peak (101) of quartz and those of all well-identified (001) peaks of clay minerals (illite, chlorite, kaolinite).

Total organic (TOC) and inorganic (TIC) carbon contents, and the isotopic composition of carbonate were measured at Oxford following the procedures described in (Hermoso et al., 2012).

3 Results and discussion

3.1 Occurrence of black shale intervals at Sancerre

The total thickness of the Early/Middle Toarcian black shales in the core is approximately 40 m (Lorenz, 1987; Hermoso et al., 2009a). In details, on the basis of sediment lamination, high abundance of organic carbon (> 3 %), and pyrite (> 2 %) content, four discrete black shale intervals can be distinguished in the Sancerre core. They are

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termed Sc1, Sc2, and Sc3 for those occurring in the Schistes carton Fm in the Early Toarcian, and Mb1 in the Marnes à Bifrons Fm in the Middle Toarcian (Fig. 2).

The interval Sc1, ranging from 348.25 to approximately 344.60 m, represents substantial organic carbon enrichment with TOC reaching 11 %. Because it is closely associated to the negative CIE, this first black shale interval has been extensively studied (Hermoso et al., 2012). This is the only black shale interval that is expressed during the T-OAE, as isotopically defined. It has to be emphasised that prior to Sc1, the first step of the CIE is recorded within a thin interval of organic carbon enrichment (2.5 % TOC), but no sediment lamination is observed. The onset of Sc1 is contemporaneous with the second step of the CIE. The termination of Sc1 is expressed during, and probably caused by a period of bottom water reoxygenation as evidenced by sediment bioturbation and relatively low sulphur (pyrite) content between 344 and 342 m (Fig. 2). The black shale interval Sc2 shows relatively low pyrite content and a notable decrease in the carbonate content. The TOC are lower than recorded within Sc1, $\sim 5\,\%$ in average with maxima at 8 %. The boundary between Sc2 and Sc3, placed at approximately 335 m, is not as clear as that distinguishing Sc1 from Sc2. However, this horizon shows sediment bioturbation. Sc3 represents comparable organic carbon enrichment with respect to Sc2 but the pyrite content is, in average, higher in the former black shale interval (4–5 %). The fourth black shale interval (Mb1) is marked by lower concentration of TOC, carbonate and pyrite, although the sediments remain continuously laminated. The late Early Toarcian (top of *serpentinum* Zone) and Middle Toarcian sediments correspond to very argillaceous deposits.

3.2 Establishing a sequence stratigraphy framework for the Sancerre deposits

Establishing a sequence stratigraphy for the Early Toarcian has proven to be relatively difficult owing to the poor expression of cycles in the lithology (Hesselbo, 2008). Another complication of the present study was that the facies of sedimentary rocks and lithological contrasts between genetic units retrieved in cores is usually less visible than in coeval outcrops on land. The recognition of transgressive–regressive cycles across the Late Pliensbachian to Middle Toarcian interval in this study was determined using a combination of biostratigraphic, sedimentological, mineralogical and geochemical observations and measurements (Fig. 3).

3.2.1 Second-order cycle: the Liassic Transgression

A major, second-order (sensu de Graciansky et al., 1998) sea level rise occurred during the Early Jurassic and is classically attributed to tectonoeustasy (Guillocheau et al., 2000; Hallam, 2001). The stratigraphic position of the base of this cycle T6 is resolved using the biostratigraphic framework and the sedimentology of the Sancerre deposits (Fig. 3). This Maximum Regressive Surface (MRS R5-T6) records an abrupt change in the lithology from sandy limestone (rich in macrofossils) to dark grey calcareous marlstone. In most regions of the NW European realm, this surface has led to the absence of the latest Pliensbachian and earliest Toarcian sediments corresponding to a major sedimentary hiatus at the stage boundary (Morard et al., 2003; Hermoso et al., 2009b). The MFS of T6 occurred around the *serpentinum–bifrons* Zonal transition (= limit between the Early and Middle Toarcian) in the Paris Basin (Gély and Lorenz, 2006; Guillocheau et al., 2000), and can be placed at Sancerre at approximately 322 m, where a maximum in sediment argilosity is observed (Figs. 2, 3).

3.2.2 Third-order eustatic cycles

The relative proportion of coarse vs. fine detrital fractions of the sediment (represented by quartz and clay minerals, respectively) deposited at a given location is driven by accommodation space, and, consequently by the shoreline position (Williams et al., 2001; Coe, 2003). This feature is typically used to recognise eustatic cycles (or parasequences) in sequence stratigraphy (Hardenbol et al., 1998; Williams et al., 2001; Coe, 2003; Hesselbo, 2008). Indeed, changes in the distance between the studied location and the coastline where sediments are supplied may be attributable to sea level change assuming no significant change in the source of detrital supply, nor variation

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of the subsidence rate (Guillocheau et al., 2000). The base of each third-order cycle, called Sequence Boundary (SB) is approximated by the position of the MRS and detected by maxima in the Qz/Qz + Clay curve. The end of the transgression represented by the Maximum Flooding Surface (MFS) corresponds to highest relative proportion of clays (i.e. to low value in Qz/Qz + Clay curve).

The lowest part of the studied interval in the Pliensbachian corresponds to the end of the regression of cycle Pl6 and terminates at 360 m where a prominent peak in the proportion of quartz is recorded (Fig. 3). This level corresponds to the MRS Pl7. The uppermost Pliensbachian sediments record cycle the Pl7, with a probable position of the MFS at 357 m. The end of this third-order regression is contemporaneous with that of the R5 (second-order) cycle, both leading to the sedimentary unconformity that characterises the Pliensbachian–Toarcian boundary.

In the Toarcian, the subsequent transgression (second- and third orders) is seen with decreasing Qz/Qz + Clay ratios up to the MFS Pl8. This relative high sea level and maximum distance to the coast correspond to a minimum of coarse sedimentation at 350.50 m. It is worth noting that this level stratigraphically corresponds to the base of the dolostone. The termination of this first intra-Toarcian eustatic cycle is followed by relatively coarse detrital sedimentation interval between 342 and 341 m. In the *serpentinum* Zone, this MRS probably led to another notable sedimentary unconformity as evidenced by a stepwise change in all the detrital elements normalised to aluminium (Fig. 3). The transgression of the subsequent cycle, Toa1, terminates at the level of the MFS associated with a bioturbated interval (336–335 m). Substantial enrichment in fine detrital material followed during the transgressive portion of Toa2. The coincidence of the second and third order cycle in the depositional setting is here illustrated by the considerable amount of clay across Toa2 as a consequence of maximum distance of Sancerre to the coastline. Lower TOC contents (∼ 3 %) and carbonate contents (∼ 20 %) in Mb1 can be explained by enhanced riverine run-off with accompanying lower δ^{18}O, and dilution of pelagic sedimentation by clay minerals (Fig. 3).

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3.3 Sea level and degree of oxygen depletion across the Early and Middle Toarcian

3.3.1 Vanadium and iron

The earliest Toarcian sediments record sea level rise that terminates at the base of the dolostone (350.50 m). At the end of this transgression, enhanced precipitation of dolomite may have been favoured by deepwater starvation and reduced sedimentation rate, a characteristic of MFSs (Coe, 2003). The two peaks in the Fe/Al curve expressed within the dolostone and Sc1 are attributable to high dolomite content as this phase bears an appreciable amount of Fe (Hermoso et al., 2009b).

As the scavenging of vanadium is promoted with seawater anoxia, the concentration of V and the V/Al ratio are commonly used to retrace the strength of oxygen depletion in the water column (Tribovillard et al., 2006). The V/Al ratios are relatively stable in the lower part of the studied interval. A pronounced augmentation is seen in the V/Al curve during Sc1. Within Sc1, maximum V/Al ratios were reached when maximum pCO_2 is registered on the basis of isotopic evidence ($\Delta^{13}C = \delta^{13}C_{org} - \delta^{13}C_{carb}$) at 346.80 m (see Hermoso et al., 2012). This coincidence is suggestive of a link between pCO_2 and oxygen demand in the water column through intense primary productivity. A sharp subsequent decrease in V/Al subsequently although pCO_2 remained continuously high (McElwain et al., 2005; Hermoso et al., 2012). Indeed, at the Sc1–Sc2 transition, the V/Al ratio returned to background and minimum values observed in the earliest Toarcian sediments. Hence, the end of Sc1 and reoxygenation of bottom waters are best explained by the sea level fall (regression of Pl8) re-establishing an insufficiently water column to allow stratification as it was the case before this black shale interval.

The transition between Sc1 and Sc2 corresponds to the top of an upward-shallowing sequence. This regressive surface at 342 m is accompanied by a prominent hiatus in the sedimentary record as illustrated by peaks in all detrital elements (Fig. 3). This surface is also recognised in the well-studied Yorkshire succession where an important sedimentary hiatus has been suggested at the equivalent stratigraphic level (Jenkyns et al., 2002). It has to be noted that the Early Toarcian positive trend in $\delta^{13}C$ terminates at this level, pinpointing the unconformity. Above this level, a long-term decrease in carbon isotope values is recorded up to the *bifrons* Zone. This stratigraphic level may hence denote the end of the widespread deposition of organic-rich facies.

Above the sedimentary unconformity at 342 m, a subsequent progressive increase in the Fe/Al (that cannot be explained by a mineralogical control) and V/Al ratios are noted, and both the curves show remarkable stacked cyclicities, which are particularly well expressed across Sc2 and Sc3 (Fig. 4). The reoxygenation event between Sc2 and Sc3 is confirmed by minimum Fe/Al and V/Al ratios at ~ 335 m, and was likely driven by the episode of sea level fall, subsequent to the MFS of cycle Toa1 (Figs. 3, 4). These cycles become less visible in the Marnes à Bifrons Fm deposited during the Middle Toarcian. This attenuation of the signal is the likely result of enhanced dilution of metal concentration by clay minerals. As the present study does not address the nature of these cycles, further cyclostratigraphic work are required to identify their control. However, these high-frequency cyclicities may correspond to the expression of eccentricity that is a common feature in the sedimentary record of Jurassic sequences (Kemp et al., 2005, 2011; Boulila et al., 2011). The transition between Sc3 and Mb1 is the only one to express transgression. The sediments remained continuously laminated. The absence of reoxygenation across the MRS Toa2 can be explained by the maximum bathymetry owing to the maximum flooding of the epicontinental surfaces (proximity of the MFS of the second-order cycle T6).

3.3.2 Molybdenum and TOC

The Mo content normalised to the %TOC can be used to diagnose widespread (low Mo/TOC) vs. regionally restricted (high Mo/TOC) black shale deposition (Algeo and Lyons, 2006; Algeo and Maynard, 2008; Pearce et al., 2008). Mo/TOC is at a minimum in Sc1. The black shale interval Sc2 records intermediate ratios, and in Sc3 the Mo/TOC values reach a maximum, about 3-times those measured in Sc1. This stratigraphic evolution would indicate that the first black shale interval associated with the negative CIE corresponded to a widespread, probably global, episode of carbon deposition whereas the subsequent intervals were of less and less global significance. A similar evolution in the extension of anoxia during the Toarcian has also been found in the composite section of Yorkshire (Pearce et al., 2008) and in the NE of the Paris Basin (Lézin et al., 2013) providing compelling evidence for a progressive reduction in the lateral repartitioning of black shale deposition at the scale of NW European seas. As an alternative explanation, increased Mo concentrations may reflect increasing strength in the connection between the basin and the open ocean leading to enhanced seawater Mo delivery and deposition at Sancerre. In both cases, sea level rise is the primary parameter driving Mo enrichment during the Early/Middle Toarcian.

3.4 Implications for the T-OAE and conclusions

During the earliest Toarcian in NW Europe, the water depth was modest allowing permanent mixing by winds and storms (Röhl et al., 2001). Such a physical oceanographic setting prevented the full expression of seawater anoxia in epicontinental seas. At this stage, expression of the T-OAE was probably restricted to the deep and open ocean, where intense primary productivity, increase of the oxygen demand, and substantial export of organic carbon to the seafloor led to the deposition of black shale facies. Associated with the first step of the CIE (and restricted to it), the TOC content transiently reaches $\sim 3\,\%$ in bioturbated sediments (still without black shale expression). This δ^{13}C/TOC relationship, also observed for the second step of the CIE, suggests a link between emission of isotopically light carbon and enhanced organic carbon burial. Subsequently, the second step of the CIE may have represented a tipping point driving seawater from dysoxia toward proper anoxia. Expression of anoxia was allowed by a sufficiently deep water column consecutive to the Pl8 transgression (Fig. 3). With the cumulative inputs of carbon into the Atmosphere–Ocean system, substantial reinforcement of anoxic conditions may explain why strongest oxygen depletion and maximum TOC contents occurred within the first black shale interval compared to

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the subsequent black shales. The first black shale interval is the only one that recorded enhanced input of fresh water, as expressed in the oxygen isotopes at Sancerre (although a part of this shift may be attributable to warming), and in the osmium profile from the coeval stratigraphic interval in Yorkshire (Cohen et al., 2004). Taken together, this would indicate that the triggering of full anoxia at the base of Sc1 was allowed by the depth of the water column, but triggered by emplacement of a haline stratification regime. The termination of the expression of "global" black shale in NW Europeans seas can be explained by a conjunction of factors as the drawdown of excess carbon by the continental weathering and carbon export to the seafloor, and by reoxygenation of the water column in a context of a relative sea level fall.

Subsequent, post-OAE, black shales in the *serpentinum* Zone were deposited under a thicker water column, as it was likely the case in coeval European Toarcian sections. The onset of black shales occurred during a transgressive trend with re-increased $\delta^{18}O$ values. Importantly, it clearly appears that variations in the redox conditions of the water column during these Regional-OAEs (sensu McArthur et al., 2008) were primarily driven by third-order sea level changes. A higher frequency modulation of oxygen availability in the water column was probably exerted by orbital (climatic) forcing. Further work is required to fully understand these short-term fluctuations in the redox state of the water column.

Supplementary material related to this article is available online at: http://www.clim-past-discuss.net/9/4365/2013/cpd-9-4365-2013-supplement.pdf.

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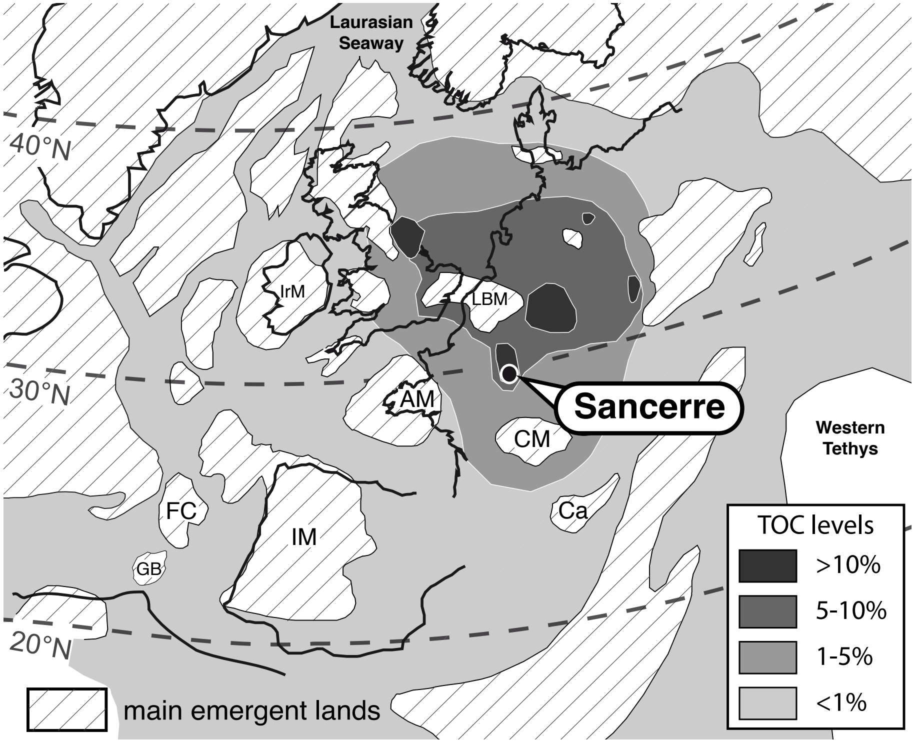

Fig. 1. Palaeogeographic map of the Early Jurassic archipelago, and the geographic distribution of organic-rich rocks. Greyscale shades indicate the content range of Total Organic Carbon (TOC); key is embedded bottom right. Emergent land delineating the basins are hatched: IrM for Irish Massive; LBM for London-Brabant Massif; AM for Armorican Massif; CM for Central Massif; Ca for Calabria; IM for Iberian Meseta; FC for Cap Flemish; and GB for Galicia Bank. The map indicates the location of the Sancerre borehole. Figure taken from Hermoso et al. (2009b).

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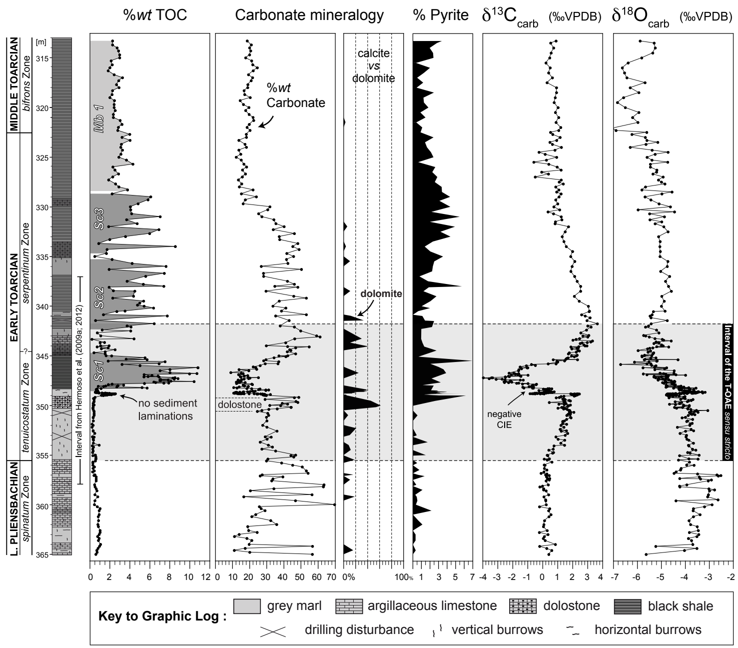

Fig. 2. Organic carbon enrichments for the Late Pliensbachian–Middle Toarcian interval of Sancerre core (southern Paris Basin). From left to right: Total Organic Carbon (TOC), carbonate content and calcite to dolomite ratio, pyrite content, and bulk carbon ($\delta^{13}C_{carb}$) and oxygen ($\delta^{18}O_{carb}$) isotope ratios. Isotopic data in the interval from 358 to 337 m are predominantly from previous studies on this core material (Hermoso et al., 2009a, 2012). Based on the abundance of TOC, pyrite and presence of lamination of the sediments, four successive black shale intervals are recognised (Sc1, Sc2, Sc3 and Mb1). Only the first black shale interval (Sc1) is recorded within the T-OAE. The onset of the first black shale is stratigraphically associated with the second step of the negative CIE and is accompanied by a pronounced decrease in the $\delta^{18}O$. Subsequent (post T-OAE) black shales are not synchronous with isotopic events. The biostratigraphic framework is from Lorenz (1987).

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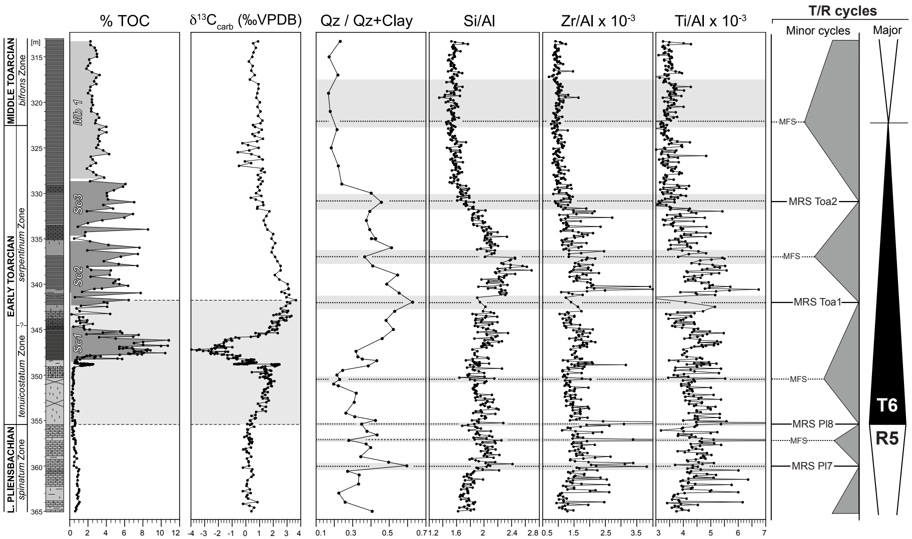

Fig. 3. Evolution in the Qz/Qz + Clay ratio, concentration of detrital elements (Si, Zr, Ti, Al), and attempt of a sequence stratigraphy framework throughout the successive black shale intervals. Representation of eustatic cycles and the name of these cycles on the right of the figure are inspired from de Graciansky et al. (1998). Major and minor cycles correspond to second- and third-order cycles, respectively (sensu de Graciansky et al., 1998). MFS is for Maximum Flooding Surface; MRS for Maximum Regressive Surface (~ Sequence Boundary). Horizontal dashed lines drawn within the grey boxes indicate a more precise position of key eustatic surfaces using geochemical elements.

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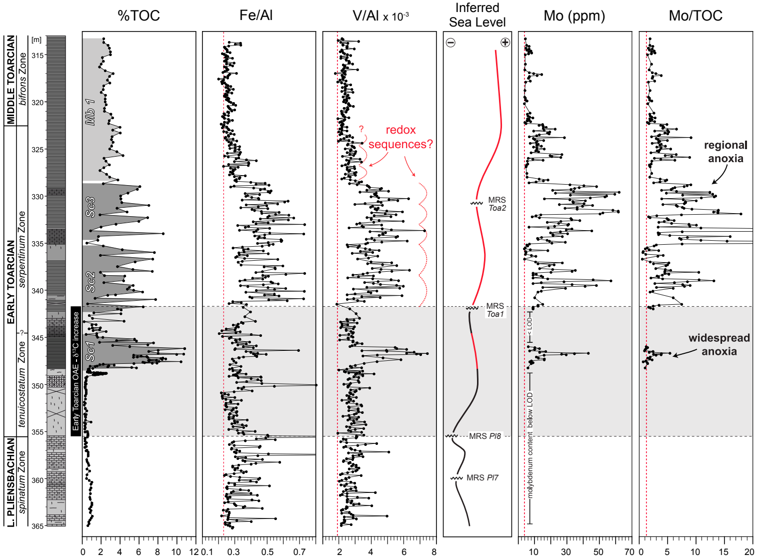

Fig. 4. Evolution in the concentration of redox-sensitive elements (Fe, V, Mo) and inferred relative sea level curve throughout the successive black shale intervals. Baseline levels of each marker are reported with vertical red dashed lines indicating the limit of detection (LOD) of Mo measurements. A peak in V/Al is coincident with the expression of Sc1 after steady and low values during the earliest Toarcian. During this first black shale interval, the Fe/Al ratio seems to be driven by the dolomite content (Fig. 2). Subsequently, both Fe/Al and V/Al curves show relative high levels, similar fluctuations throughout Sc2–Sc3–Mb1 black shales, and allow recognition of tentative redox parasequences during the deposition of Sc2 and Sc3. The curve in the middle panel depicts the evolution of the relative sea level inferred from the sequence stratigraphy (Fig. 3). Red portions in the sea level curve on the right denote periods of relatively high water depth allowing water column stratification and full expression of anoxia. The Mo/TOC curve indicates widespread anoxic conditions during deposition of Sc1 (during the T-OAE). On the basis on the molybdenum content, it can be inferred that the subsequent (post T-OAE) black shale had more regional significance.

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