



Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal

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[1] The timing and causal relationships between the pronounced negative C isotope excursion and paleoenvironmental perturbations associated with the Toarcian oceanic anoxic event (Early Jurassic) remain unclear, particularly because biotic crises and carbonate production decrease appear to have been initiated earlier than the main C isotope anomaly. Here we present a new quantification of Late Pliensbachian–Early Toarcian calcareous nannofossils abundance and size from the Peniche reference section (Portugal) together with O and C isotope records of well-preserved brachiopod shells from the same section. The brachiopod shell $\delta^{13}\text{C}$ curve parallels that of bulk carbonate and records two pronounced negative isotopic excursions, close to the Pliensbachian-Toarcian boundary ($\sim -2\text{‰}$) and during the Toarcian oceanic anoxic event ($\sim -3.5\text{‰}$). Our results indicate that both C isotope negative excursions were characteristic of benthic and shallow-water environments, suggesting that these two carbon cycle perturbations affected all epicontinental reservoirs. Coeval shifts toward lower values of brachiopod oxygen isotope compositions and closely correlated northward migrations of Mediterranean ammonite fauna suggest that both events coincided with major rises in seawater temperatures, probably as a result of increased CO_2 levels and enhanced greenhouse conditions. CO_2 -induced changes in seawater chemistry likely affected the calcification potential of both neritic and pelagic systems, as evidenced by synchronous drops of platform-derived carbonate accumulation and drastic reductions in size ($>3 \mu\text{m}$) of the main pelagic carbonate producer *Schizosphaerella*. We suggest that the Early Toarcian paleoenvironmental crisis occurred in two distinct episodes that were most likely related to two successive phases of intense volcanic degassing in the Karoo-Ferrar province.

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1. Introduction

[2] The Early Toarcian (Early Jurassic, ~ 183 Ma ago) was a time of severe environmental crisis that is characterized by widespread black shale deposits, generally considered as the result of an oceanic anoxic event (OAE) (Toarcian OAE [Jenkyns, 1988]). The OAE coincides with a pronounced negative carbon isotope excursion recorded in marine organic matter, marine carbonate and terrestrial material that has been identified in several localities around the world [Duarte, 1998; Hesselbo *et al.*, 2000; Schouten *et al.*, 2000; Jenkyns *et al.*, 2001; Gröcke *et al.*, 2003; Kemp *et al.*, 2005; Hesselbo *et al.*, 2007]. These records have led to the interpretation that this pronounced negative C isotope excursion was characteristic of all superficial reservoirs, and resulted from massive inputs of isotopically light methane from sedimentary gas hydrates [Hesselbo *et al.*, 2000; Kemp

et al., 2005] or from thermal metamorphism of carbon-rich sediments in the Karoo large igneous province [Svensen *et al.*, 2007; McElwain *et al.*, 2005]. Beside the carbon cycle changes the Early Toarcian was also accompanied by a second-order global mass extinction, marked by particularly high extinction rates of marine faunas at the Pliensbachian-Toarcian (PI-To) transition and during the OAE [Little and Benton, 1995; Harries and Little, 1999; Macchioni and Cecca, 2002; Vörös, 2002; Cecca and Macchioni, 2004]. A generalized carbonate production crisis also took place in the Early Toarcian, characterized by the near disappearance of shallow-water platforms in the Early Toarcian [Dromart *et al.*, 1996; Blomeier and Reijmer, 1999], a significant drop in calcium carbonate contents in basinal successions and by a nannofossil biocalcification crisis during the OAE [Mattioli *et al.*, 2004; Tremolada *et al.*, 2005]. Increased carbon dioxide levels, as a result of flood basalt volcanism or gas hydrate dissociation, have been suggested as a possible trigger for the nanoplankton biocalcification crisis during the OAE [Mattioli *et al.*, 2004; Tremolada *et al.*, 2005]. However, timing between the C isotope anomaly, platform demise, and nannofossil calcification crisis remain unclear, particularly because platform crisis and changes in nanno-

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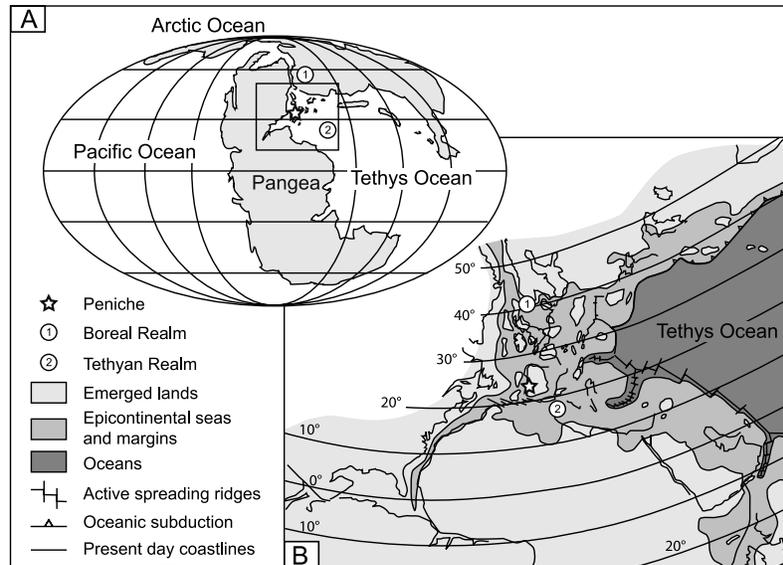


Figure 1. (a) Global paleogeography during the Early Jurassic (modified after C. R. Scotese, www.scotese.com (Paleomap project), 2002). (b) Location of the studied area, located in a paleoseaway between Boreal and Tethyan realms (modified after *Bassoulet et al.* [1993]).

fossil assemblages appear to have been initiated earlier than the OAE [Dromart *et al.*, 1996; Mattioli *et al.*, 2004; Erba, 2004; Tremolada *et al.*, 2005]. Similarly, convincing evidence for a precise temporal relationship connecting paleotemperature changes and carbonate production crises are still lacking, principally because of the absence of reliable paleotemperature proxies during the Early Toarcian. In fact, temperature changes inferred for this period were mainly derived from oxygen isotopes and Mg/Ca ratios of belemnite rostra from hemipelagic settings [e.g., Sælen *et al.*, 1996; McArthur *et al.*, 2000; Bailey *et al.*, 2003; Rosales *et al.*, 2004; van de Schootbrugge *et al.*, 2005a]. Nevertheless, belemnites may have migrated vertically and laterally during their life cycle and coexisting belemnite species may have had a different depth habitat [Wierzbowski, 2002; Voigt *et al.*, 2003; Rosales *et al.*, 2004]. As a result, the paleoceanographic significance of belemnite-derived temperature estimates is still ambiguous. Given the major role played by marine carbonate in the global C cycle, it becomes essential to clarify the timing and possible relationships between paleoenvironmental changes and carbonate production crisis during the Early Toarcian.

[3] In this study we present new quantitative estimates of calcareous nannofossil abundance and size from the well-exposed marl-limestone alternations of Pliensbachian-Toarcian age in the Peniche reference section (Portugal), in order to identify the origin of the sedimentary carbonate and document its evolution throughout this interval. Contrarily to some other sections in Europe that are condensed or incomplete in the lowermost Toarcian [Floquet *et al.*, 2003; Morard *et al.*, 2003; Elmi, 2006], the Peniche section represents relatively continuous sedimentation during the Late Pliensbachian–Early Toarcian interval [Elmi, 2006], and is potentially one of the best candidates for such study. To access potential concomitant temperature and C cycle

changes, we also present carbon and oxygen isotope data obtained from brachiopod shells sampled in the same section. The degree of preservation of brachiopod shells was carefully monitored using scanning electron microscopy (SEM) and cathodoluminescence (CL), in order to detect possible diagenetic overprint of the primary isotopic signals. The brachiopod oxygen isotope data provide the first reliable indications of bottom water temperature changes in a key area on the margin of the Tethys Ocean before and during the Toarcian OAE, and give us the opportunity to explore the possible relationship between pelagic and neritic carbonate production and paleoenvironmental changes during this interval. These data sets are then discussed in the context of the current hypotheses on the nature and origin of global perturbation that occurred in the Late Pliensbachian–Early Toarcian interval.

2. Geological Setting and Stratigraphy

[4] The analyzed bulk rock carbonate samples and brachiopod shells were collected from the Peniche section at Ponta do Trovão and Praia do Abalo (GSSP candidate for Pliensbachian-Toarcian boundary) in the Lusitanian Basin (Portugal) (Figure 1). The Peniche section shows a complete and relatively continuous record of hemipelagic sediments deposited during the Early Pliensbachian–Middle Toarcian [Elmi, 2006]. These sediments were deposited in a shallow basin (less than 160–200 m [Bjerrum *et al.*, 2001]), near an emerged crystalline tilted block, located to the west of the modern Atlantic coast [Figure 1] [Mouterde, 1955; Duarte *et al.*, 2004]. During the Toarcian, the area was located in a gateway between Boreal and Tethyan realms at a tropical latitude (20°–30°N) [Bassoulet *et al.*, 1993]. Lithostratigraphy has been described by numerous authors [Mouterde, 1955; Elmi *et al.*, 1996; Duarte *et al.*, 2004; Elmi, 2006]

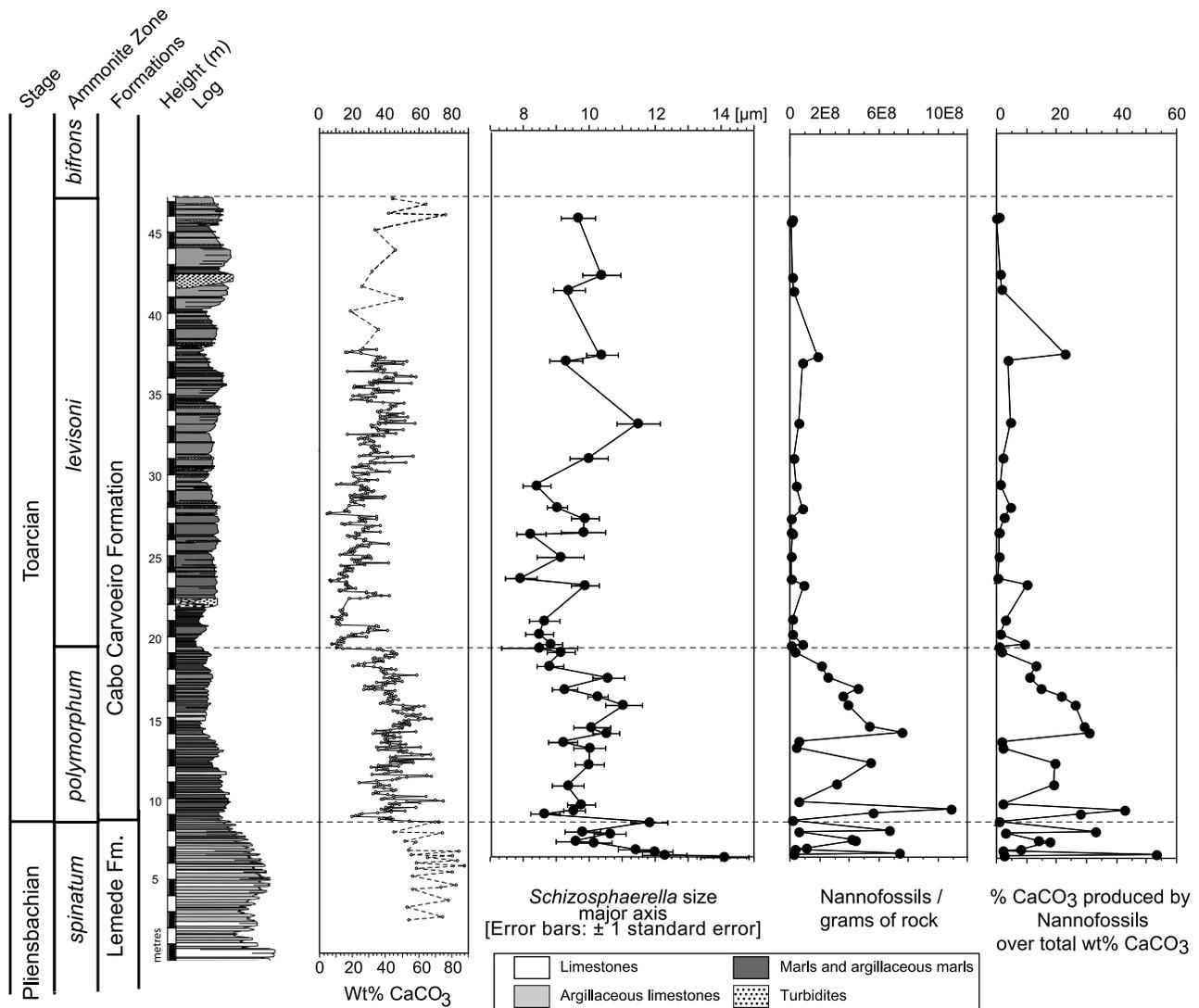


Figure 2. High-resolution carbonate content, size of the nannofossil *Schizosphaerella* (*incertae sedis*), nannofossil absolute abundance, and estimation of the amount of carbonate produced by nannofossils in the Pliensbachian-Toarcian of Peniche (Portugal). See text for explanation.

and ammonite biostratigraphy at the zone level is well established [e.g., Elmi *et al.*, 1996]. The succession is formed by regular marl-limestone alternations ($\text{CaCO}_3 = \sim 60\text{--}90$ wt %; Figure 2) in the Upper Pliensbachian (Lemede Formation), and becomes more argillaceous slightly above the Pliensbachian-Toarcian boundary ($\text{CaCO}_3 = \sim 10\text{--}30$ wt %; Figure 2). In the *polymorphum* zone, both marls and limestones become slightly more calcareous but CaCO_3 contents stay relatively low ($\sim 30\text{--}65$ wt %). Deposits become considerably more argillaceous at the *polymorphum-levisoni* zone boundary ($\text{CaCO}_3 < 10$ wt %). The calcium carbonate concentrations stay low in the first half of the *levisoni* zone ($\sim 10\text{--}30$ wt %), and increase gradually toward the top of the zone ($\sim 40\text{--}70$ wt %). In the uppermost part of the Early Toarcian (*levisoni* zone) the terrigenous input is important, as evidenced by high proportions of quartz, micas and feldspars. The deposits of the *levisoni* ammonite zone are characterized by the

occurrence of numerous silty to sandy turbidite levels. Thus this interval may contain small stratal gaps linked to turbidite deposition.

[5] The total organic carbon content in the section is relatively low (mean $\text{TOC} = 0.5\%$ and maximum $\text{TOC} < 3\%$; Hesselbo *et al.* [2007]) in comparison to that of contemporaneous organic-rich black shales found in the Jet Rock Formation (England) ($\text{TOC} > 8\%$ [Jenkyns *et al.*, 2001]), in the Posidonia shale (Germany) ($\text{TOC} > 15\%$ [Röhl *et al.*, 2001]) or in the “Schistes Cartons” (France) ($\text{TOC} > 15\%$ [van Breugel *et al.*, 2006]). A definition of the interval over which the OAE occurred based solely on high TOC contents appear irrelevant, because enhanced organic matter accumulation extended toward the *bifrons* zone in some sections in northern Europe [Röhl *et al.*, 2001; Jenkyns *et al.*, 2001]. In most sections, however, maximum TOC values and evidences for maximum oxygen depletion are restricted to the interval where a sharp

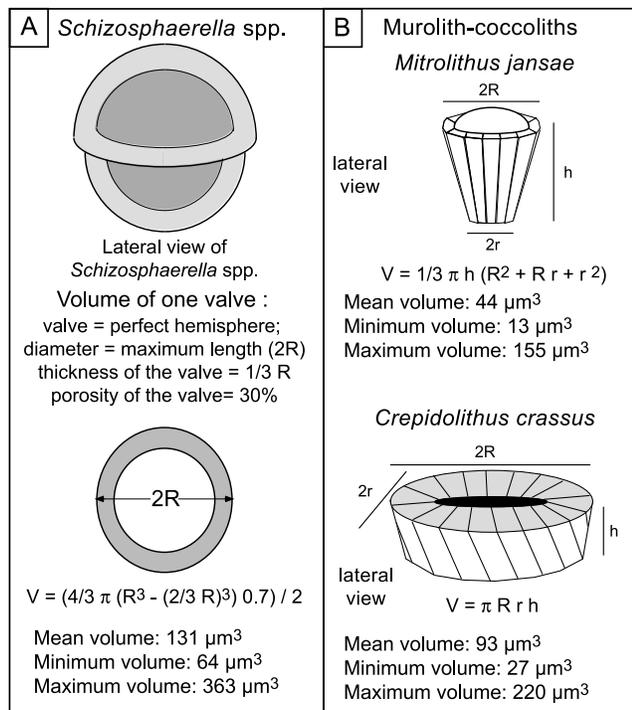


Figure 3. Morphology and characteristic volumes of the three main nannofossil taxa producing pelagic carbonates: (a) nannolith taxon *Schizosphaerella* spp. (see further discussion by *Mattioli and Pittet* [2002]) and (b) coccolith taxa *Mitrolithus jansae* and *Crepidolithus crassus*.

negative carbon isotope excursion is recorded [*Röhl et al.*, 2001; *Jenkyns et al.*, 2001], which may represent a more convenient stratigraphic marker to define the OAE. The frequent occurrence of pyrite and dwarf brachiopods at Peniche suggests that poorly oxygenated conditions were common during the *polymorphum* and basal *levisoni* zones [*Alm eras et al.*, 1995; *Elmi*, 2006]. Maximum oxygen depletion at the seafloor during the studied interval is deduced from the almost complete lack of benthic fauna and the presence of weakly bioturbated marls between 18 m and 30 m (Figure 2). As discussed by *Hesselbo et al.* [2007], both bulk carbonate and fossil wood from the base of the *levisoni* zone record a pronounced negative carbon isotope excursion, that we interpret as corresponding to the negative isotope excursion characteristic of the OAE [*Hesselbo et al.*, 2000; *Jenkyns et al.*, 2001]. In addition, unfavorable conditions in the water column are also indicated by the absence of belemnites in most of the *levisoni* zone [*Hesselbo et al.*, 2007].

3. Material and Methods

3.1. Quantification of Nannofossil Abundance and Size

[6] The amount of carbonate produced by nannofossils was calculated using the method described by *Mattioli and Pittet* [2002]. Absolute nannofossil abundance (per gram of rock) was measured according to the technique described by

Geisen et al. [1999]. This absolute quantification was combined with the volume estimation of the most important carbonate producers amongst nannofossils, namely, the *Schizosphaerella* (*incertae sedis*; probably a calcareous dinoflagellate) hemivalves and the largest coccoliths (*Crepidolithus crassus*, *Mitrolithus jansae*). The volume estimates were obtained by measuring the diameter of 30 *Schizosphaerella* hemivalves per sample in light microscope (LM; 1250 X) with an estimated error of $\pm 0.25 \mu\text{m}$ (Figure 2). Volumes of *Schizosphaerella* (average = 131 μm^3) were then measured in each sample according to *Mattioli and Pittet* [2002] (Figure 3).

[7] In different Peniche samples, 85 specimens of *Crepidolithus crassus* and 100 specimens of *Mitrolithus jansae* were measured on images acquired in LM by a CCD camera (Sony XC-77CE mounted on a polarizing microscope ZEISS, Axioscope 40). Measurements were made by means of the software Scion Image (beta version 4.0.2) with an estimated error of $\pm 0.09 \mu\text{m}$. Major and minor axes of coccoliths were measured along with their thickness. On the basis of these measurements, an average volume has been estimated, namely, 93 μm^3 for *C. crassus* and 44 μm^3 for *M. jansae* (Figure 3). As these three taxa are dominant in the assemblages, in terms of size and abundance in the Peniche section (Figures 2 and 3), the estimation roughly approximates the entire pelagic carbonate production [*Mattioli and Pittet*, 2002].

3.2. Sampling and Preservation of Brachiopod Shells

[8] The carbon and oxygen isotope compositions of twenty-six brachiopod shells from the Peniche section were analyzed and their preservation assessed. The measured stable isotope ratio corresponds to a composite of different brachiopod taxa formed by Rhynchonellida (*Nannirhynchia pygmoea*, *Soaresirhynchia bouchardi*; Table S1) and Terebratulida (*Telothyris jauberti*, *Lobothyris arcta*). The sediment matrix was removed mechanically and the shell surface was cleaned with double deionized water in an ultrasonic bath. The primary layer, which is considered to be secreted out from isotopic equilibrium with oceanic water in modern species [*Carpenter and Lohmann*, 1995; *Auclair et al.*, 2003; *Brand et al.*, 2003; *Parkinson et al.*, 2005], was carefully removed with a dental scraper under a binocular microscope. Specialized structures (mainly contained in the posterior part of the shell) and the uppermost part of secondary shell were also avoided as these parts may display isotopic values out of the expected equilibrium with environmental water in modern brachiopod species [*Carpenter and Lohmann*, 1995; *Curry and Fallick*, 2002; *Auclair et al.*, 2003; *Parkinson et al.*, 2005]. Finally, only the innermost part of the fibrous secondary layer of the anterior shell was sampled for isotopic measurements.

[9] Cathodoluminescence analyses were performed on polished longitudinal sections of brachiopod shells at the Universities of Erlangen (Germany) and Paris VI (France). This allowed the identification of the best preserved parts of the shells and the rejection of entirely altered specimens. Unaltered parts of the shell classically appear nonluminescent, whereas incorporation of Mn^{2+} and Fe^{2+} ions, prefer-

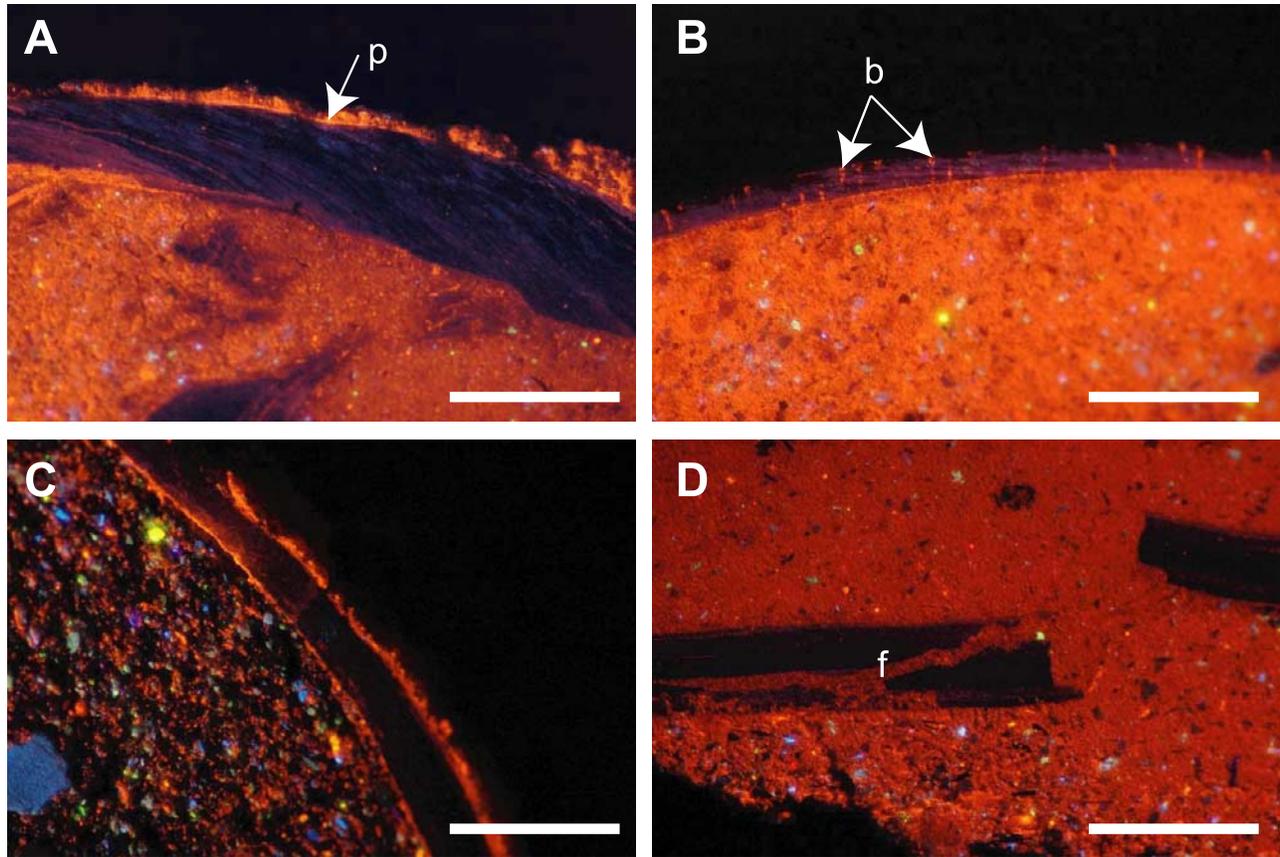


Figure 4. Photographs of the brachiopod samples showing the different degrees of preservation of the shells (longitudinal cross sections). (a) Well-preserved brachiopod shells of *Soaresirhynchia bouchardi* (specimen BB 34). The primary outer layer (labeled p) is luminescent. Except for microfractures located between successive calcite fibers, the fibrous calcite of the secondary layer is nonluminescent. (b) Cross section of *Lobothyris arcta* (specimen BB 17-3). Note the orange luminescence of microborings (labeled b) and the well-preserved structure of the secondary shell. (c) Well-preserved fibrous secondary layer of the undetermined brachiopod specimen BB 56. The bright blue color of the matrix is due to the detrital component of the sediment (quartz and feldspars). This illustrates the increase of detrital input in the upper part of the *levisoni* zone. (d) Cross section of *Telothyris jauberti* (specimen BB 25) showing the crushing of the specimen and the luminescence of the fractured portions of the shell (labeled f). Scale bars are 1 mm.

entially included during diagenetic recrystallization, is an activator of luminescence [Pierson, 1981]. Most of the studied brachiopod shells were nonluminescent, except for the outer primary layer, microborings infillings and microfractured areas (Figure 4). The polished shells were further screened by scanning electron microscopy (SEM), in order to analyze the preservation of the shell microstructures and to ensure the quality of sampling. These analyses revealed the generally good state of preservation of the brachiopod secondary fibrous structures (Figure 5). Most of the brachiopods sampled are unpunctuated and show smooth fibrous surfaces of the secondary layer very similar to recent specimens [e.g., Brand *et al.*, 2003].

[10] Carbon and oxygen isotope compositions of brachiopod shells have been determined by using an auto sampler Multiprep coupled to a GV Isoprime[®] mass spectrometer. For each sample, an aliquot of about 300 μg of calcium

carbonate was reacted with anhydrous oversaturated phosphoric acid at 90°C during 20 min. Isotopic compositions are quoted in the delta notation in permil relative to VPDB. All sample measurements were triplicated and adjusted to the international reference NIST NBS19. Reproducibility is 0.1‰ (1σ) for $\delta^{18}\text{O}$ values and 0.05‰ (1σ) for $\delta^{13}\text{C}$ values.

4. Results

4.1. *Schizosphaerella* Size and Carbonate Fraction Produced by Nannofossils

[11] The highest abundance of nannofossils per gram of rock and the largest *Schizosphaerella* valves are recorded in the “couches de passage” (sensu Mouterde [1955]), namely, in the marly semicouplets of the uppermost Pliensbachian alternations (Figure 2). The pelagic carbonate fraction in this interval fluctuates between 18% and 50% of the total carbonate in the marls, and is very low (<5%) in limestones

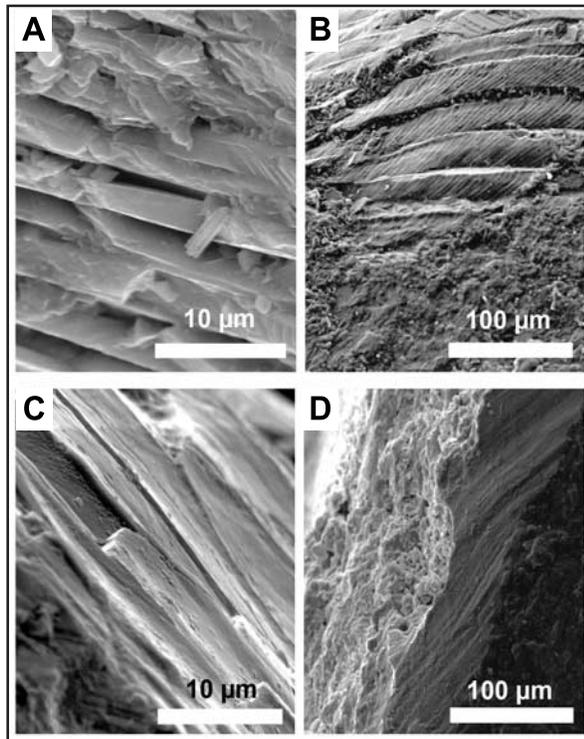


Figure 5. Scanning electron micrographs showing the ultrastructures of Pliensbachian and Toarcian brachiopod shells of *Peniche* analyzed for stable isotope compositions. Well-preserved structure of the secondary layer of (a) *Lobothisyris arcta* (specimen B1), (b) *Soaresirhynchia bouchardi* (specimen B7-2), and (c) *Nannirhynchia pygmoea* (specimen B3 bis). (d) Diagenetically altered structure of the secondary layer of *Nannirhynchia pygmoea*, with poorly individualized calcite fibers.

(Figure 6). The mean *Schizosphaerella* size decreases by about 4 μm passing from the Late Pliensbachian to the Early Toarcian. In the *polymorphum* ammonite zone, *Schizosphaerella* valves become gradually larger (by about 2 μm) and the pelagic fraction is still significantly high but never exceeds 30% of the total carbonate content. The lowest *Schizosphaerella* mean size and nannofossil abundance are recorded during the OAE (corresponding to the most important negative $\delta^{13}\text{C}$ excursion in the lower part of the *levisoni* zone), where the pelagic carbonate fraction generally accounts for less than 5% of the CaCO_3 content (Figure 2). Pelagic carbonate production partly recovers in the second half of the *levisoni* zone (up to 25% of the total carbonate fraction). Nannofossil abundance is, however, lower than in the preanoxic interval. In this interval, *Schizosphaerella* size shows values comparable to those in the preanoxic interval.

[12] This record of nannofossil abundance and size is not considered to be controlled by diagenesis nor by dissolution/corrosion processes in the water column because: 1) nannofossil preservation is variable but generally moderate to good; 2) very delicate and solution-susceptible taxa are recorded all along the studied samples; and 3) the same

trend of a minimum in nannofossil abundance and *Schizosphaerella* size has been recorded during the OAE in other Tethyan settings [Bucefalo Palliani et al., 2002; Mattioli and Pittet, 2002; Mattioli et al., 2004; Tremolada et al., 2005].

4.2. Stable Isotopes

[13] The carbon isotope values of brachiopods are reported in Figure 6 and in Table S1 of the auxiliary material.¹ High-resolution (every 2 cm) carbon isotope data from bulk carbonate obtained from the same section by Hesselbo et al. [2007] are also recorded in Figure 6. The $\delta^{13}\text{C}_{\text{carb}}$ values of carbonate rock are systematically lower than those of brachiopods shells by about -1.5‰ to -2‰ (Figure 6). Although the sampling density of brachiopod shells and carbonate samples reported by Hesselbo et al. [2007] are necessarily different, the $\delta^{13}\text{C}_{\text{brachiopod}}$ and $\delta^{13}\text{C}_{\text{carb}}$ trends are very similar and show a clear parallelism. The $\delta^{13}\text{C}_{\text{brachiopod}}$ curve records the first negative C isotope excursion reported above the PI-To boundary by Hesselbo et al. [2007], with the lowest values less than 1 m above the biostratigraphical boundary. After a distinct positive shift toward higher values of about 3‰ to 4‰ in the *polymorphum* zone, the bulk carbonate and brachiopod values show a marked negative shift to lower values of about 3 ‰ in the lowermost *levisoni* zone (Figure 6). In the second half of the *levisoni* zone, the $\delta^{13}\text{C}_{\text{brachiopod}}$ and $\delta^{13}\text{C}_{\text{carb}}$ values increase again, and reach the maximum in the uppermost *levisoni* zone ($+3.85\text{‰}$ and $+5.72\text{‰}$ respectively).

[14] The highest $\delta^{18}\text{O}_{\text{brachiopod}}$ values are restricted to the uppermost Pliensbachian (*spinatum* zone), with highest values at -0.5‰ . A distinct shift to lower values of about 1‰ is recorded in the lowermost *polymorphum* zone, with minimum values about 20 cm (surface of bed “15E” sensu Mouterde [1955]) above the PI-To boundary. The values increase gradually in the *polymorphum* zone and show a marked decrease again between the *polymorphum* and *levisoni* zones before reaching a minimum of -2.76‰ in the middle of the *levisoni* zone (Figure 6).

5. Discussion

5.1. Evolution of Carbonate Production

[15] During the Toarcian, two main sources are considered to supply the fine-grained micritic carbonate to hemipelagic settings: (1) the para-autochthonous fraction composed of pelagic organisms (calcareous nannofossils, both *Schizosphaerella* and coccolithophorids) [e.g., Noël et al., 1993], and (2) the allochthonous fraction probably imported from adjacent carbonate platforms [e.g., Cobianchi and Picotti, 2001; Mattioli and Pittet, 2002]. The production of this calcite might have been related to carbonate precipitation by paleowhitings in shallow-water environments [Shinn et al., 1989; Robbins et al., 1997]. An additional component of the carbonate is the diagenetic, microbial-mediated carbonate fraction precipitated during early diagenesis of organic matter below the water-sediment interface [Raiswell, 1988; Sass et al., 1991]. In contempo-

¹Auxiliary materials are available in the HTML. doi:10.1029/2007PA001459.

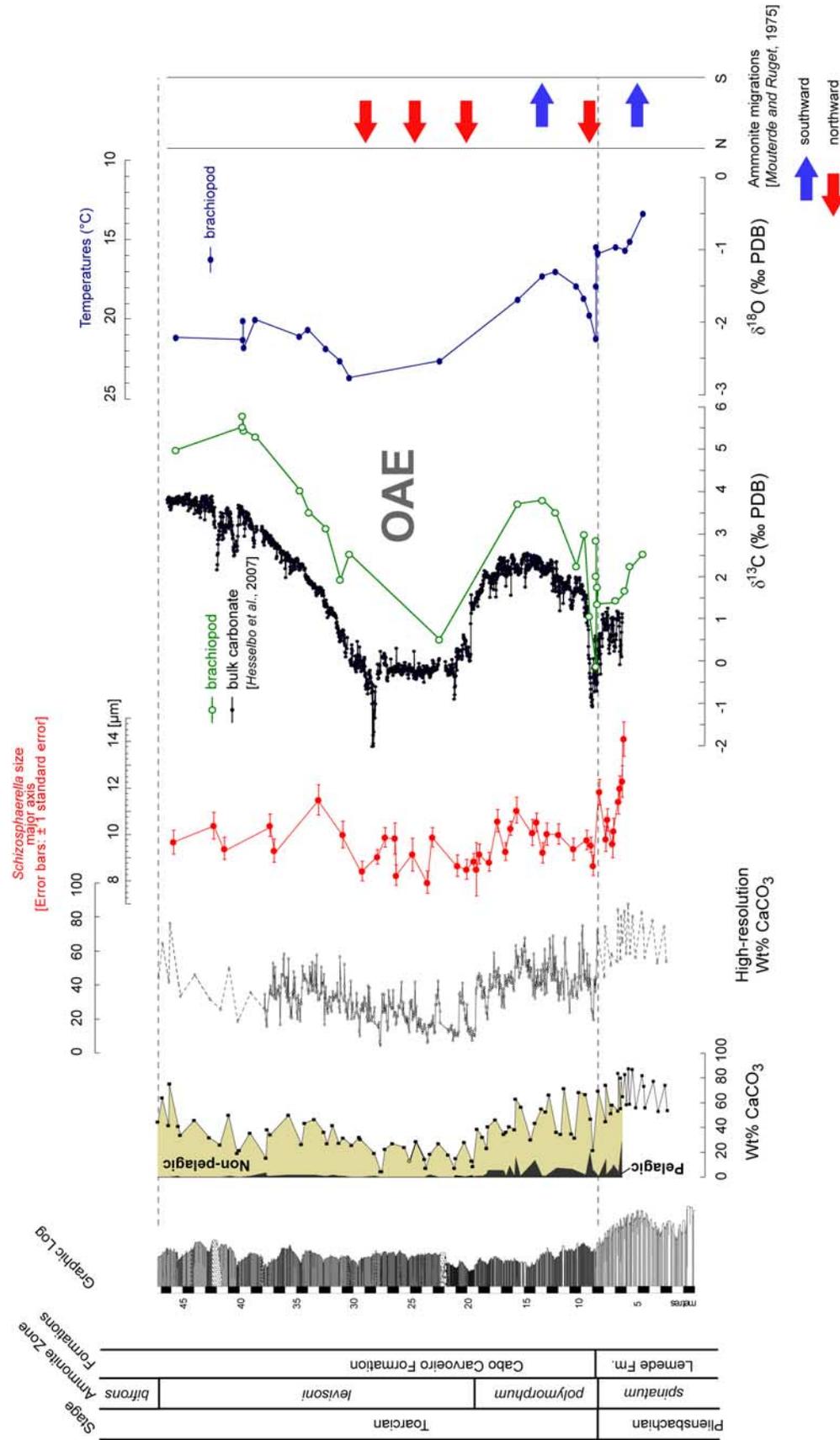


Figure 6. Geochemical (CaCO₃, δ¹⁸O, and δ¹³C) records, size of the nannofossil genus *Schizosphaerella*, and ammonite migrations [Mouterde and Ruget, 1975] in the Pliensbachian-Toarcian of Peniche (Portugal). The high-resolution CaCO₃ record (every 5 cm) is presented for most of the studied interval; the lower-resolution record shows only carbonate content of samples for which a quantification of pelagic nannofossil has been performed. Carbon isotope data from bulk carbonates are from Hesselbo et al. [2007]. Note the synchronicity between minimum δ¹⁸O values, the decrease of nonpelagic carbonate contents, reductions in size of *Schizosphaerella*, and marked δ¹³C negative shifts in the earliest Toarcian (lower part of the *polymorphum* zone) and during the OAE (lower part of the *levisoni* zone). Isotopic temperatures are calculated using the equation of Anderson and Arthur [1983], with a δ¹⁸O_{seawater} of -1‰. Lithology is as in Figure 2.

aneous sections located in NW Europe, the presence of this early diagenetic calcite is clearly evidenced by a nodular and irregular aspect of carbonate-rich levels [Raiswell, 1988; Röhl *et al.*, 2001]. The absence of these features in the Peniche section, in which the thickness of carbonate-rich beds is rather constant and regular throughout the studied interval, indicates that the contribution of the diagenetic carbonate to the total carbonate is probably limited. Because it is formed from organic matter diagenesis, this diagenetic fraction is generally thought to possess a distinct isotopic signature with very negative $\delta^{13}\text{C}$ values (-14‰ to -15‰ ; [Raiswell, 1988]); exceptionally low $\delta^{13}\text{C}_{\text{carb}}$ are restricted to few, discrete horizons of the section [Hesselbo *et al.*, 2007], suggesting that the formation of the organic matter-derived diagenetic calcite is only important at particular levels. Similarly, our quantification suggests that the calcareous nannofossil fraction contributes only to a minor extent to the total carbonate composition in most of the studied interval (<20 wt % in average). Their relative contribution to the whole carbonate is only significant (up to 50 wt %) in some carbonate-poor intervals (*spinatum* and *polymorphum* zones, Figure 2), but is generally low ($<5\%$) in carbonate-rich hemicouplets. The opposite relationship might have been expected if the nannofossil-produced carbonate fraction was the main constituent of the total carbonate. All these observations strongly suggest that the major part of the carbonate mud preserved in the section was most likely produced and exported from adjacent shallow-water carbonate platforms. Previous studies document the existence of adjacent carbonate platforms at the east and to the west of the Peniche area in the Lusitanian Basin during this interval [Wright and Wilson, 1984; Duarte, 1998]. A platform control on basinal carbonate accumulation has been also suggested to explain similar trends of nannofossil carbonate abundance in contemporaneous hemipelagic marl-limestone alternations deposited at equivalent latitudes in the Southern Alps and in central Italy [Cobianchi and Picotti, 2001; Mattioli and Pittet, 2002]. Consequently, the evolution of the carbonate content in the studied interval most likely reflects the intensity of production or export of carbonate mud from adjacent shallow-water platforms. Accordingly, two drastic platform production crises are evidenced in the studied interval, at the very base of the *polymorphum* zone, as deduced by the sharp reduction in CaCO_3 content few centimeters above Pl-To boundary, and at the *polymorphum-levisoni* transition respectively (Figures 2 and 6). These two platform-derived carbonate production crises are also precisely correlated with two marked reductions in size of the most important pelagic carbonate-producer *Schizosphaerella* (Figures 2 and 6). This suggests that two generalized carbonate production crisis occurred in both pelagic and neritic environments at the same time in the Lusitanian Basin during the Early Toarcian. As the same trends in platform-derived accumulation as well as carbonate nannofossil size and abundance have been reported in contemporaneous Tethyan sections [Cobianchi and Picotti, 2001; Mattioli and Pittet, 2002; Mattioli *et al.*, 2004], a local paleoenvironmental control on these signals is here excluded. In addition, the CaCO_3 contents through the Pliensbachian-Toarcian presented here

are very similar to those reported in central Italy and northern Spain [Mattioli and Pittet, 2002; Tremolada *et al.*, 2005] most probably representing a regional or supraregional trend.

5.2. Evolution of Paleotemperatures

[16] Stable isotope compositions of modern brachiopod species have been well studied and most studies have shown that nearly all articulate Terebratulida and Rhynchonellida secrete their secondary fibrous shell in oxygen isotopic equilibrium with ambient seawater [e.g., Carpenter and Lohmann, 1995; Curry and Fallick, 2002; Auclair *et al.*, 2003; Brand *et al.*, 2003; Parkinson *et al.*, 2005]. As a result, extrapolated isotopic temperatures are generally close to measured mean annual seawater temperatures [Carpenter and Lohmann, 1995; Buening and Spero, 1996; Curry and Fallick, 2002; Auclair *et al.*, 2003; Brand *et al.*, 2003; Parkinson *et al.*, 2005]. As articulate brachiopods are assumed to be strictly benthic and generally sessile organisms [see Brand *et al.*, 2003], it is thought that their oxygen isotope composition accurately reflects the temperature or salinity evolution of their habitat. In the framework of this study, the analyzed microsamples were carefully taken from nonspecialized parts of well-preserved secondary layers of shells, considered as secreted in isotopic equilibrium with ambient seawater in modern brachiopods [Carpenter and Lohmann, 1995; Auclair *et al.*, 2003; Parkinson *et al.*, 2005]. The samples were taken on sections spanning more than two or three growth lines on average, and are most probably representative of annual to pluriannual mean paleotemperatures. Consequently, differences between extrapolated paleotemperatures from brachiopod oxygen isotope ratios of different stratigraphical ages are probably biased only to a minor extent by seasonal variability.

[17] In order to estimate paleotemperatures from the $\delta^{18}\text{O}$ values of brachiopod shells, it is necessary to estimate the isotopic composition ($\delta^{18}\text{O}_{\text{seawater}}$) of the Early Jurassic seawater. The modern mean value of surface seawater $\delta^{18}\text{O}_{\text{seawater}}$ is around 0‰ (SMOW). This value can vary strongly with latitude in response to different evaporation/precipitation rates and is unknown for the Early Jurassic. The total melting of present polar icecaps would lower the $\delta^{18}\text{O}_{\text{seawater}}$ value to -1‰ (SMOW) which is generally used for Jurassic paleotemperature calculations, considering that no ice caps were present at that time. The seawater isotopic temperatures were calculated using the thermodependent equation of Anderson and Arthur [1983] for biogenic calcite (Figure 6). As a basis for discussion, a constant seawater $\delta^{18}\text{O}_{\text{water}}$ value of -1‰ is assumed for the whole interval.

[18] The lowest bottom water paleotemperatures are evidenced by our $\delta^{18}\text{O}_{\text{brachiopod}}$ data at the end of the Pliensbachian (Figure 6). Additional evidence of cool seawater temperatures in the area during the Late Pliensbachian comes from the occurrence of subboreal ammonites in the Lusitanian Basin [Mouterde and Ruget, 1975; Mouterde *et al.*, 1979]. The distribution of the wood genus *Xenoxylon* and palynological studies also indicate cooler and wetter terrestrial climate in western Europe and in China in the Late Pliensbachian [Philippe and Thévenard, 1996; Wang *et al.*

al., 2005]. Moreover, presence of glendonites in the latest Pliensbachian at high latitudes [Kaplan, 1978; Nikitenko and Mickey, 2004] also indicates cool climatic conditions in boreal areas during this period. These independent indications of a cool climate in the Late Pliensbachian suggest that low bottom water paleotemperatures evidenced by our data for the *spinatum* zone may have corresponded to a global cold episode. Cool climatic conditions are also compatible with Mg/Ca ratios and $\delta^{18}\text{O}$ values in belemnite rostra, which indicate low seawater temperatures in the time-equivalent series of England, Germany and Spain [Bailey et al., 2003; Rosales et al., 2004; van de Schootbrugge et al., 2005a]. Interestingly, our oxygen isotope values of brachiopod shells are comparable or even slightly lower than those previously reported for belemnites from the western Tethys [Bailey et al., 2003; Rosales et al., 2004; van de Schootbrugge et al., 2005a]. If these oxygen isotope compositions are only interpreted in terms of paleotemperatures, brachiopod-derived temperatures are higher than those inferred from belemnites. Belemnite data from the same section seem to confirm this trend [De Oliveira et al., 2006]. These similarities in the brachiopod and belemnite O isotope compositions, also reported for other geological periods [Wierzbowski, 2002; Voigt et al., 2003] may suggest that belemnites preferred near-bottom or intermediate waters. This would imply that belemnite rostra, contrarily to what is generally presumed, may not constitute a true monitor of sea surface isotopic compositions.

[19] About 20 cm above the PI-To transition, the abrupt shift toward lower values of the $\delta^{18}\text{O}_{\text{brachiopod}}$ suggests a significant increase of bottom water temperatures (~ 4 to 5°C ; Figure 6). This inferred warming precisely corresponds to the short invasion of Mediterranean ammonite taxa *Dactyloceras* (*Eodactylites*) in the Lusitanian Basin at the very beginning of the *polymorphum* zone (*mirabile* Subzone) [Mouterde and Ruget, 1975; Mouterde et al., 1979] and also correlates with an important disruption of Boreal-Tethyan provinciality of ammonite fauna [Macchioni and Cecca, 2002]. This important event of bottom water warming is followed by a gradual cooling of about 4°C in the middle of the *polymorphum* zone (Figure 6). This cooling also correlates to the presence of subboreal ammonite fauna in the Lusitanian Basin [Mouterde et al., 1979]. Similarly to the PI-To transition, the marked shift to lower $\delta^{18}\text{O}_{\text{brachiopod}}$ values recorded higher in the section (lower part of the *levisoni* zone; Figure 6) is associated to the northward spread of brachiopod and ammonite fauna from the Mediterranean area into the Lusitanian Basin [Mouterde and Ruget, 1975]. Important seawater warming across this interval is also suggested by $\delta^{18}\text{O}$ and Mg/Ca ratios of belemnite rostra from England, Spain and Germany [Bailey et al., 2003; Rosales et al., 2004; van de Schootbrugge et al., 2005a].

[20] Northward migrations of Tethyan ammonite fauna and evidence of increase of seawater temperatures in the western Tethys strongly suggest that the two successive $\delta^{18}\text{O}_{\text{brachiopod}}$ shifts recorded near the PI-To boundary and during the OAE most probably reflect regional or even global trends of temperature rise. Furthermore, the second decrease of O isotope values in the *levisoni* zone at Peniche correlates with high CO_2 levels inferred from stomatal data

in Denmark, consistent with an increase in temperatures on a global scale [McElwain et al., 2005; Hesselbo et al., 2007].

[21] If changes in $\delta^{18}\text{O}_{\text{brachiopod}}$ are only interpreted in terms of paleotemperature, bottom water paleotemperatures increased from about 14°C in the Late Pliensbachian to about 20°C in the earliest Early Toarcian (basal *polymorphum* zone, *mirabile* Subzone) and from about 17°C in the middle *polymorphum* zone to about 24°C in the middle part of the *levisoni* zone. As this magnitude of inferred temperature changes over the studied interval is enormous (about 10°C) it is possible that additional paleoceanographic or paleoclimatic factors have influenced the value of our measured $\delta^{18}\text{O}_{\text{brachiopod}}$ ratios. As the $\delta^{18}\text{O}$ of seawater is also controlled by local or regional variations in the hydrological budget, expressed in salinity changes, our oxygen isotope record may also reflect fluctuations of seawater salinity. Indeed, peak abundance of *Tasmanites* [Bucefalo Palliani et al., 2002] and belemnite geochemistry ($\delta^{18}\text{O}$, Mg/Ca) [Bailey et al., 2003; Rosales et al., 2004; van de Schootbrugge et al., 2005a] suggest an important freshwater input and reduced salinity in surface seawaters during the OAE. Reduced bottom water salinity, in response to higher continental runoff [Cohen et al., 2004] might have lowered the oxygen isotope values in this interval. However, bottom seawaters are generally less affected by salinity changes than surface seawaters in today's oceans [e.g., Lear et al., 2000], and modern brachiopods generally have preference for normal salinity (≥ 30 per mil) seawaters [Brand et al., 2003]. Consequently, the $\delta^{18}\text{O}$ values of brachiopods were most probably influenced to a minor extent by these possible salinity changes. The Late Pliensbachian and most of the *tenuicostatum* zone (\sim *polymorphum* equivalent) were possibly characterized by low CO_2 levels and icehouse conditions [Guex et al., 2001; Morard et al., 2003; van de Schootbrugge et al., 2005a; McElwain et al., 2005], as indicated by the association of a sea level lowstand, glendonite occurrence at high latitudes [Kaplan, 1978; Nikitenko and Mickey, 2004] and evidence of low tropical seawater temperatures (as shown by our data and previous studies [Bailey et al., 2003; Rosales et al., 2004; van de Schootbrugge et al., 2005a]). Ice storage ($\delta^{18}\text{O} = \sim -40$ to -30‰) at high latitudes in the latest Pliensbachian (*spinatum* zone) and possibly during a part of the Early Toarcian (middle part of the *polymorphum* zone) might have raised the global $\delta^{18}\text{O}_{\text{seawater}}$. As a result, paleotemperatures during these intervals might have been slightly higher by a few degrees Celsius than those calculated by our first approximation with a $\delta^{18}\text{O}_{\text{seawater}}$ of -1‰ . Alternatively, climate-induced changes in marine circulation might have amplified the warming trend. Indeed, the numerical paleoceanographic modeling of the Laurusian Seaway suggest that significant changes in the thermohaline circulation may have induced important paleotemperature modifications at the Peniche paleolatitude [Bjerrum et al., 2001]. One or a combination of these mechanisms can be used to explain the large magnitude of our $\delta^{18}\text{O}_{\text{brachiopod}}$ shifts. Because the presence of continental ice at high latitudes during at least part of the studied interval has great implications for sea level changes and marine circulation, paleotemperature

reconstructions outside western Tethys during the Late Pliensbachian–Early Toarcian are needed to unambiguously resolve this issue.

[22] In Peniche, the highest calculated bottom water temperatures occur within the interval of probably most pronounced dysoxic/anoxic conditions in the basal part of the *levisoni* zone (pyrite abundance and lack of benthic taxa). The end of dysoxic/anoxic conditions, marked by the reappearance of benthic taxa after the C isotope excursion, is characterized by a cooling of bottom waters of about 3°C (Figure 6). Similarly, benthic fossils are scarce or even absent in a 30 cm thick interval of argillaceous, finely laminated mudstones situated just above the first Lower Toarcian carbonate-rich bed (*polymorphum* zone). Thus it seems most likely that a more or less direct relationship existed between the seafloor oxygenation and bottom water temperatures. As warm waters generally contain less dissolved oxygen than cold waters, a possible explanation is that the reduced production or propagation of cold waters could have caused a decreased ventilation of the seafloor. The production of these well-oxygenated, cool bottom water masses may have been reduced in response to high-latitude climate warming. This oxygen depletion at the seafloor during the OAE could then have been reinforced by density stratification, as a consequence of higher freshwater input due to an increase of humidity and weathering rates [Sælen et al., 1996; Röhl et al., 2001; Bailey et al., 2003; Cohen et al., 2004; van de Schootbrugge et al., 2005b].

5.3. Two Similar Episodes of Environmental Perturbation in the Early Toarcian?

[23] Our results indicate two phases of important paleoenvironmental changes in the Early Toarcian, both of which are characterized by a major drop of platform-derived carbonate accumulation, reduction in size of the pelagic carbonate producer *Schizosphaerella*, and major rise in bottom seawater temperatures as evidenced by brachiopod $\delta^{18}\text{O}$ values. These two stratigraphically limited intervals also correlate with periods of high extinction rates of benthic marine faunas [Alm eras et al., 1995; Little and Benton, 1995; V oros, 2002] and correspond to two distinct events of mass extinction in ammonoids [Macchioni and Cecca, 2002; Cecca and Macchioni, 2004] in the whole western Tethys. This suggests that the Early Toarcian paleoenvironmental crisis occurred during two episodes of maximum stress: the first crisis is recorded in the earliest Early Toarcian while the most severe changes are recorded during the OAE (Figure 7). Importantly, each event corresponds precisely to a pronounced negative excursion recorded in bulk and brachiopod carbonate (Figure 6). The origin of the negative C isotope excursion recorded in diverse settings during the OAE has been a subject of much debate [e.g., K uspert, 1982; Gr ocke et al., 2003; Hesselbo et al., 2000; van de Schootbrugge et al., 2005b; Kemp et al., 2005; McElwain et al., 2005; Wignall et al., 2005; Hesselbo et al., 2007], but recently published data suggest that it was most likely related to global rather than regional changes [Hesselbo et al., 2000; Cohen et al., 2004; McElwain et al., 2005; Kemp et al., 2005; van Breugel et

al., 2006; Hesselbo et al., 2007]. We interpret the first isotopic shift close to the PI-To transition as also reflecting a global signature, as suggested by $\delta^{13}\text{C}$ values of both brachiopod and platform-derived carbonate that indicate that the entire water column was affected by these C cycle changes (Figure 6). The widespread nature of the first C isotope event in the marine reservoir is suggested by a contemporaneous excursion of about -1.5‰ close to the PI-To boundary recorded in belemnite and bulk carbonate in England [McArthur et al., 2000; Jenkyns et al., 2001; van de Schootbrugge et al., 2005a]. C isotope compositions of fossil wood from the Peniche section [Hesselbo et al., 2007] strongly suggest that both excursions were also characteristic of the atmospheric reservoir, and thus reflect a global signal.

[24] Massive injections of isotopically light carbon to atmosphere/hydrosphere reservoirs, regardless of their source, appear to be the only convincing mechanisms able to explain these negative C isotope excursions [e.g., van Breugel et al., 2006; Hesselbo et al., 2007]. From current knowledge, significant injections of carbon to the atmospheric reservoir in the geological past should have induced dramatic rises of atmospheric CO_2 levels. This assumption is consistent with the rise of marine temperatures inferred from our brachiopod O isotopes (Figure 6), and in accordance with the 2 to $3\times$ increase of CO_2 levels at the start of the second negative $\delta^{13}\text{C}$ excursion also corresponding to the T-OAE [McElwain et al., 2005]. Furthermore, comparisons between isotopic compositions of marine organic and inorganic carbon also suggest an important $p\text{CO}_2$ increase during the second carbon isotope perturbation [van de Schootbrugge et al., 2005a]. Consequently, it seems that the two carbonate production crises evidenced by our results were somehow related to two distinct episodes of high $p\text{CO}_2$. Such increases of atmospheric $p\text{CO}_2$ have been shown to slow down calcification of modern corals and of two species of coccolithophorids via changes of ocean chemistry [Gattuso et al., 1998; Riebesell et al., 2000]. Similarly, it is projected that the abiotic carbonate production of today's carbonate platforms is likely to decline considerably as a response to rising $p\text{CO}_2$ caused by anthropogenic burning of fossil fuels [Morse et al., 2006]. Accordingly, the two carbonate production crises that affected both platform-derived and nannofossil carbonate in the Early Toarcian may have been directly related to CO_2 -induced changes in seawater chemistry. The dramatic reduction in size of *Schizosphaerella* recorded at Peniche across the two successive C isotope negative excursions (and also recorded during the OAE in Italy [Mattioli et al., 2004]) and undercalcified coccolith specimens reported during the OAE [Mattioli et al., 2004] might support this hypothesis. High rates of continental runoff, increase of nutrient input, and reduced salinity, that are the known features of the OAE as well as the predicted consequences of high CO_2 levels and elevated temperatures [e.g., Bailey et al., 2003; Cohen et al., 2004; Tremolada et al., 2005] may have also induced dramatic changes in trophic conditions on both neritic carbonate platforms and pelagic realm (Figure 7). Such changes in trophic levels are well documented in platform and pelagic settings in several

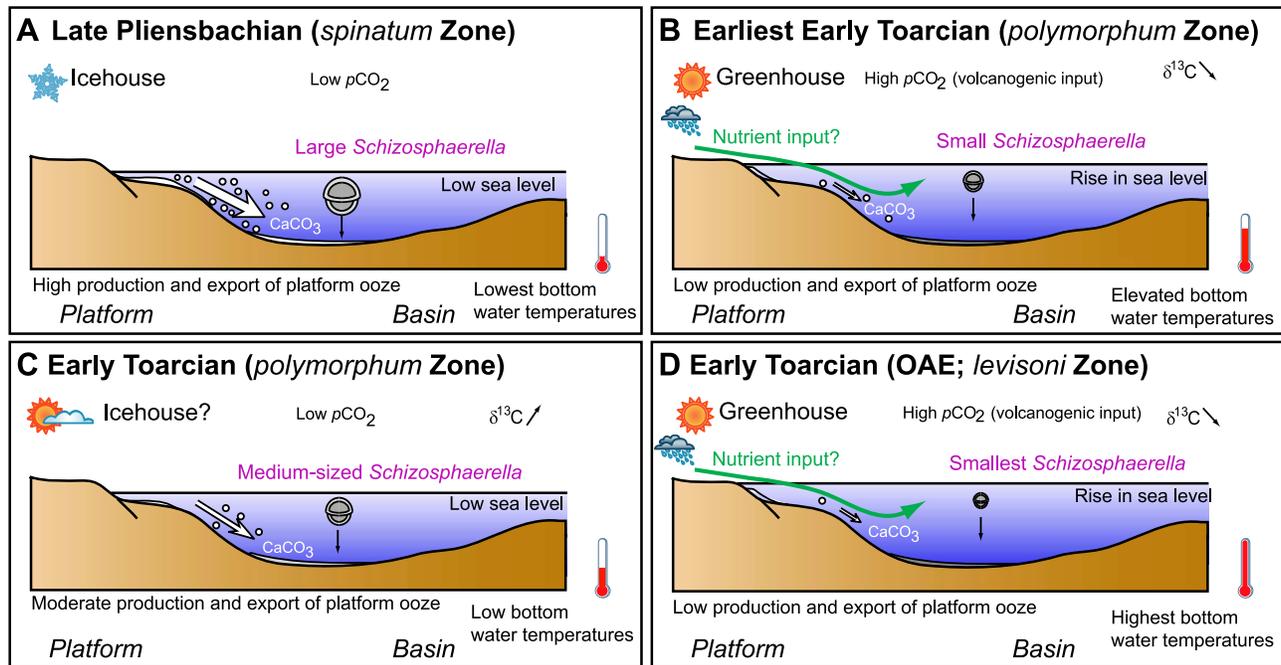


Figure 7. Schematic paleoceanographic model for the (a) Late Pliensbachian, (b) lowermost Early Toarcian (basal *polymorphum* zone), (c) Early Toarcian (middle *polymorphum* zone), (d) lower part of the *levisoni* zone. The late Pliensbachian and the middle *polymorphum* zone were likely characterized by low CO_2 levels and possibly by icehouse conditions. During the earliest Toarcian and during the OAE, increased atmospheric CO_2 (possibly as a consequence of thermogenic methane production in the Karoo-Ferrar large igneous province) likely triggered dramatic changes in ocean chemistry and trophic conditions that affected the calcification potential of both pelagic producers (*Schizosphaerella*) and neritic shallow-water carbonate platforms.

contemporaneous sections [Blomeier and Reijmer, 1999; Cobianchi and Picotti, 2001; Mattioli and Pittet, 2004; Tremolada et al., 2005]. These factors, driving to stressing conditions in oceanic surface waters, might have amplified the initial effects of the CO_2 rise on the calcification potential of carbonate systems during both events.

[25] Our data provide evidence that two similar episodes of rising seawater temperatures, carbonate production crisis, and isotopically light carbon input to all superficial reservoirs occurred in the Early Toarcian. High-precision radiometric dating indicates that the emplacement of the Karoo-Ferrar province, one of the largest igneous provinces of the Phanerozoic Eon, was contemporaneous with these events [Pálffy and Smith, 2000]. Two successive, time-spaced events of isotopically light carbon release are not only conformable with the episodic nature of flood basalt volcanism [Lin and van Keken, 2005] but are also compatible with evidences of brief and volumetrically important events of magmatism in the Karoo province [Jourdan et al., 2007], suggesting that these major paleoenvironmental perturbations were directly or indirectly linked to paroxysmal phases of intense subaerial volcanism. A large source of “light” carbon may have been provided indirectly by the thermal metamorphism of organic-rich sediments in the Karoo-Ferrar province [McElwain et al., 2005; Svensen et al., 2007]. Such production of thermogenic methane in the

Karoo province is well supported by geological evidence and radiometric U-Pb dating from the western Karoo Basin in South Africa. The total amount of C released in the atmosphere by this mechanism may have exceeded 7000 Gt [Svensen et al., 2007].

[26] Elevated levels of greenhouse gases and input of “light” carbon during the OAE may have been reinforced by several pulses of astronomically driven gas hydrate dissociation, as suggested by the orbital pacing of large shifts to lower $\delta^{13}\text{C}$ values identified in Yorkshire by Kemp et al. [2005]. These abrupt shifts of the C isotope record identified in Yorkshire were possibly paced by the astronomical precession, and thus may have occurred in less than a few kiloannum [Kemp et al., 2005]. These pulses of “light” carbon release are possibly recorded by the abrupt C isotope negative shifts from bulk carbonates at ~ 19.5 m, ~ 21 m and ~ 28 m at Peniche (Figure 6), which are reminiscent to those shown by the organic carbon isotope data in Yorkshire at -0.8 m, 0 m and 2.8 m [Kemp et al., 2005]. These events should have been accompanied by rapid increases of atmospheric CO_2 levels and may have induced rapid events of “ocean acidification” [Kemp et al., 2005; Beerling and Brentnall, 2007], which are possibly reflected by the sharp and cyclical drops in the total carbonate content at ~ 19.5 m, ~ 21 m, and ~ 28 m (Figures 2 and 6). It should be noted, however, that several abrupt decreases of the

CaCO₃ content at Peniche are not accompanied by any apparent shift to lower values of the C isotope record (e.g., at 18.2 m, 23 m, or 34.8 m; Figure 6). This suggests that these possible pulses of gas hydrate dissociation may have occurred in conjunction with other astronomically forced mechanisms that might have controlled the carbonate production on a short timescale, which may include atmospheric carbon dioxide levels, continental runoff, temperature, nutrient supply or fluctuations of the sea level [Hinnov and Park, 1999].

[27] Our $\delta^{13}\text{C}$ record from brachiopod shells, although having a low resolution in the first half of the *levisoni* zone (because of the scarcity of brachiopod shell in this interval), reveal an excursion of about -3.5‰ that is similar in magnitude to the record of bulk carbonate from Peniche [Hesselbo et al., 2007] and Dogna (north Italy [Jenkyns et al., 2001]). However, the magnitude of the excursion in the carbon isotope data from organic matter and fossil wood appear about twice time larger (-7 to -8‰) [Schouten et al., 2000; Hesselbo et al., 2000; Jenkyns et al., 2001; Kemp et al., 2005; Hesselbo et al., 2007]. Similarly, the abrupt shifts toward lower $\delta^{13}\text{C}$ values of the high-resolution data from organic carbon in Yorkshire [Kemp et al., 2005] appear about twice time larger than those present in the bulk carbonates of Peniche [Hesselbo et al., 2007]. Given the good preservation state of the brachiopod shells, this may suggest that a magnitude of about -3.5‰ may be more realistic value than that of about -7 to -8‰ inferred from fossil wood isotopic compositions and from marine organic matter [Schouten et al., 2000; Hesselbo et al., 2000; Jenkyns et al., 2001; Hesselbo et al., 2007]. Then, it is possible that differences between the isotopic composition of the inorganic (marine carbonate) and organic carbon (marine organic matter and fossil wood) resulted from higher fractionation effects in response to elevated $p\text{CO}_2$ [Kump and Arthur, 1999; van de Schootbrugge et al., 2005a] or from changes in the hydrological cycle [Hesselbo et al., 2007].

[28] The Early Toarcian may have lasted no more than 2 Ma [Gradstein et al., 2004], suggesting that the two carbon isotope excursions and associated environmental changes took place in a relatively brief interval and possibly occurred at very fast rates. Coeval episodes of strongly reduced carbonate production, possibly in conjunction with pronounced sea level changes, may have profoundly influenced the depositional dynamics in epicontinental shelves prior to and during the OAE. The probable consequences of these perturbations are the pronounced facies changes, condensation levels or even hiatuses [Blomeier and Reijmer, 1999; Guex et al., 2001; Morard et al., 2003; Elmi, 2006; McArthur and Wignall, 2007] that often characterize Lower Toarcian sections. A better understanding and integration of these biases on the stratigraphic record would help to

establish a more robust timescale for the Early Toarcian. Indeed, the carbon isotope excursion associated with the OAE is estimated to have lasted less than about 200 ka [Kemp et al., 2005] to about 1000 ka [McArthur et al., 2000]. Since each of these estimates imply very different rates of environmental change, and hence different sources of carbon release, a better calibration of the Early Toarcian timescale become crucial to determine the origin of one the most severe environmental crisis of the last 200 Ma.

6. Conclusions

[29] A quantification of nannofossil size and abundance performed in Late Pliensbachian–Early Toarcian marl-limestone alternations of the Peniche reference section (Portugal) reveal that the largest part of the bulk carbonate was not produced by calcareous nannofossils but most likely imported from adjacent shallow-water carbonate platforms. Brachiopod shells and bulk carbonates from the same section record synchronously two major $\delta^{13}\text{C}$ negative excursions, just above the Pliensbachian-Toarcian boundary ($\sim -2\text{‰}$) and during the OAE ($\sim -3.5\text{‰}$) respectively, indicating that these two pronounced C isotope excursions were most likely driven by regional or even global mechanisms rather than local, basin-restricted factors. Coeval shifts to lower values of the brachiopod oxygen isotope compositions and closely correlated northward migrations of Mediterranean ammonite fauna suggest that both C isotope negative excursions coincided with major rises in seawater temperatures. Our results indicate that these two excursions occurred synchronously with significant carbonate production crises on both neritic and pelagic realms, as suggested by concomitant decreases of platform-derived carbonate mud and dramatic reductions in size of the main pelagic carbonate-producer *Schizosphaerella*. These data are best explained by two distinct phases of massive release of isotopically light CO₂ and enhanced greenhouse conditions, which in turn affected the calcification potential and trophic levels of both pelagic and neritic systems. We propose that the Early Toarcian paleoenvironmental perturbation occurred in two episodes of similar paleoceanographic and biotic changes, which most likely resulted from two successive phases of intense sub-aerial volcanogenic degassing.

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