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# Impact of the Middle Jurassic diversification of *Watznaueria* (coccolith-bearing algae) on the carbon cycle and δ$^{13}$C of bulk marine carbonates

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## ABSTRACT

During the Mid Mesozoic Revolution, thought to have started 200 Ma ago (Late Triassic), the production of calcium carbonate in the ocean shifted from platform and epicontinental seas to the open ocean, concurrently with the diversification of coccolithophorids. In this regard, the radiation of the coccolith genus *Watznaueria* during the Middle Jurassic is thought to represent one of the most important steps of this diversification. Nevertheless, the timing of this diversification remains poorly constrained, and its possible impact on global carbon budgets remains unclear. In this study, we present new records of nannofossil fluxes and carbon stable isotope composition from sedimentary deposits of Lower Bajocian age from the Cabo Mondego (Portugal) reference section to further address the possible impact of this diversification on the Middle Jurassic global carbon cycle. Our results show that calcareous nannofossil fluxes increase markedly from the upper part of the Aalenian to the Early Bajocian, coinciding with a 0.75‰ positive shift in carbon isotope compositions of bulk carbonate. Reconstructions of mass accumulation rates indicate that nannofossil fluxes increased by two orders of magnitude (from $10^9$ to $10^{11}$ nannofossils/m$^2$/yr) during the corresponding time interval, mainly related to the rise of *Watznaueria* genus, whose relative abundance jumped from 2% to 20% of the total rock composition. The calculated amount of carbon derived from calcareous nannofossils deposited in the Early Bajocian seas was, however, 10 to 20 times lower than current levels. Mass balance calculations indicate that the increase of nannofossil flux throughout the studied interval was most likely not the main cause of the accompanying isotopic perturbation, suggesting a limited role of the Early Bajocian diversification on the global carbon cycle. Our results show that while the diversification of *Watznaueria* throughout the Bajocian caused a major increase in the flux of pelagic carbonate to the deep ocean, it was most likely quantitatively insufficient to have a large impact on the global biogeochemistry of the oceans.

## 1. Introduction

Pelagic carbonate production is the main output of the carbon cycle from the ocean to the Earth's crust (Sundquist and Visser, 2004) and has a significant impact on climate (e.g., Westbroek et al., 1993; Rost and Riebesell, 2004 and citations within). At present, calcium carbonate ($CaCO_3$) in the open ocean is mainly produced by coccolithophores and planktonic foraminifera. Consequently, the δ$^{13}$C and δ$^{18}$O values of deep-sea carbonates should reflect the composition of the communities of calcareous nannofossils and foraminifers (Bralower, 2002; Stoll and Ziveri, 2004).

The calcareous nannofossils are composed of coccolithophores and other micrometric calcifying *incertae sedis* (e.g., *Schizosphaerella*, *Nannoconus*,…). Coccolithophores, a type of golden-brown algae producing small carbonate platelets called coccoliths, appeared during the Late Triassic, 225 Ma ago (Bown, 2005) and dominated pelagic carbonate production until the rise of planktonic foraminifers at the end of the Early Cretaceous (~— 100 Ma) (Norris, 1991; Hay, 2004). Various studies have pointed out the key role of calcareous nannofossils upon the Jurassic carbon cycle (e.g., Bornemann et al., 2003; Hay, 2004; Erba, 2006; Goddéris et al., 2008; Mattioli et al., 2008, 2009). However, calcareous nannofossils may have been strictly restricted to shelves and shallow marine environments until the Late Jurassic and their abundance was too low to play the key role they are now playing in the modern global carbon cycle (Hay, 2004; Rost and Riebesell, 2004). The shift in carbonate production from shelves to open oceans by pelagic producers, termed the “Mid Mesozoic Revolution” (Ridgwell, 2005), is considered to be a tremendous event in ocean chemistry history, but its precise timing and impact on global carbon budgets remain unclear.

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In this context, the Early Bajocian (Middle Jurassic, ~170 Ma) constitutes a key time interval of the "Mid Mesozoic Revolution" in that it witnessed the diversification of the important coccolith genus *Watznaueria* (Mattioli and Erba, 1999; Erba, 2006; Tiraboschi and Erba, 2010). Indeed, this genus dominated the coccolith community for over 80 Myr, and its initial diversification could have therefore triggered the dominance of coccolithophores over the oceanic carbonate production. Interestingly, the diversification of *Watznaueria* appears to have been time coincident with a major carbon cycle perturbation, as suggested by the marked positive carbon isotope excursion recorded by oceanic carbonates in several European Lower Bajocian marine successions (Corbin, 1994; Bartolini et al., 1996, 1999; Hesselbo et al., 2003; O'Dogherty et al., 2006). Nevertheless, the cause of this excursion remains unclear. It might be linked to an increase in oceanic primary productivity. Furthermore, the change in calcareous nannofossil diversity and abundance are poorly quantified during this interval, hence precluding the reconstruction of potential cause–effect relationships between these events.

In this study, we present new measurements of bulk carbonate carbon isotope composition ($\delta^{13}C_{carb}$) and calcareous nannofossil absolute abundance from the Aalenian–Bajocian reference section at Cabo Mondego, Portugal, in order to address the potential links between diversification of calcareous nannofossil assemblages and carbon cycle dynamics during the Mid Jurassic. Using these records, we quantitatively investigate: (1) the contribution of nannofossil carbonate to the global oceanic carbon cycle, and (2) whether the diversification of *Watznaueria* by changing the bulk carbonate composition may have driven the Early Bajocian positive carbon isotope excursion.

## 2. Geological setting

The Cabo Mondego section is located in the Lusitanian basin, on the western Atlantic coast of Portugal near Figueira da Foz (Fig. 1). The succession is represented by marine deposits of Late Toarcian to Kimmeridgian age (Ruget-Perrot, 1961). Cabo Mondego is the Global Stratotype Section and Point (GSSP) for the Aalenian/Bajocian boundary (Pavia and Enay, 1997) as well as the Auxiliary Stratotype Section and Point (ASSP) for the Bajocian/Bathonian boundary (Fernandez-Lopez et al., 2009). Numerous ammonites, as well as other macro- or micro-paleontological remains such as belemnites, brachiopods, bivalves, ostracods, foraminifers, coccoliths, plant debris, and zoophycos trace fossils have been collected throughout the succession, allowing for the establishment of a precise biostratigraphical framework (Henriques et al., 1994).

The studied part of the Cabo Mondego section (Fig. 2) extends from the latest Aalenian (Concavum ammonite Zone) to the end of the Early Bajocian (base of the Humphriesianum ammonite Zone). The Early Bajocian is divided into four ammonite zones; Discites, Laeviuscula, Propinquans (equivalent of the Sauzei Zone of other regions), and Humphriesianum. The sedimentary succession consists of alternating marlstone and limestone (Fig. 2) and the carbonate fraction is exclusively micritic or microsparitic calcite (Henriques et al., 1994). The sediments corresponding to the Concavum (~5.5 m thick) and Discites (~7.2 m thick) zones are characterized by irregular nodular beds but fairly regular alternations of ~20 cm argillaceous limestone and marlstone beds. The interval corresponding to the base of the Laeviuscula (~36 m thick) Zone is limestone-dominated. At the base of the Propinquans (~32 m thick) Zone, the argillaceous limestones beds become more regular and thicker in comparison to the base of the section through the Humphriesianum (~7 m) Zone. From the Propinquans Zone, the succession becomes limestone-dominated.

## 3. Material and methods

### 3.1. $CaCO_3$ quantification and bulk carbonate stable isotope measurements

Calcium carbonate ($CaCO_3$) content was measured on forty-one samples. Approximately 300 mg of powdered bulk sediment was dissolved using 1 N HCl and the amount of $CO_2$ released from the sample was measured using a Dietrich-Frühling™ calcimeter. Carbon isotope composition of bulk samples was measured using an auto sampler Multiprep™ coupled to a GV Isoprime® mass spectrometer. For each sample, an aliquot of 350 to 500 μg was reacted with anhydrous oversaturated phosphoric acid at 90 °C for 20 min. Each sample has been duplicated two times. Isotopic compositions are quoted using delta notation in permil relative to VPDB. All sample measurements were duplicated and adjusted to the international reference NIST NBS19. Reproducibility is on average ~0.02‰ (2σ) for $\delta^{13}C_{carb}$ values.

### 3.2. Nannofossil quantification and flux estimation

The forty-one samples selected for nannofossil analysis were from the same intervals as those analyzed for isotopes. Calcareous nannofossil abundance and pelagic carbonate production were calculated following the method developed by Mattioli and Pittet (2002). Samples were prepared following the random settling method for absolute abundance quantification described by Beaufort (1991) and modified by Geisen et al. (1999). Using a Zeiss Axioskop 40 optical microscope with a magnification ×1000, at least 300 specimens per slide were counted. In seventeen slides, however, less than 300 specimens were counted, therefore counting was realized on at least one transverse corresponding to 150 fields of view. Three main nannofossil groups (*Schizosphaerella* spp., an *incertae sedis* frequently attributed to

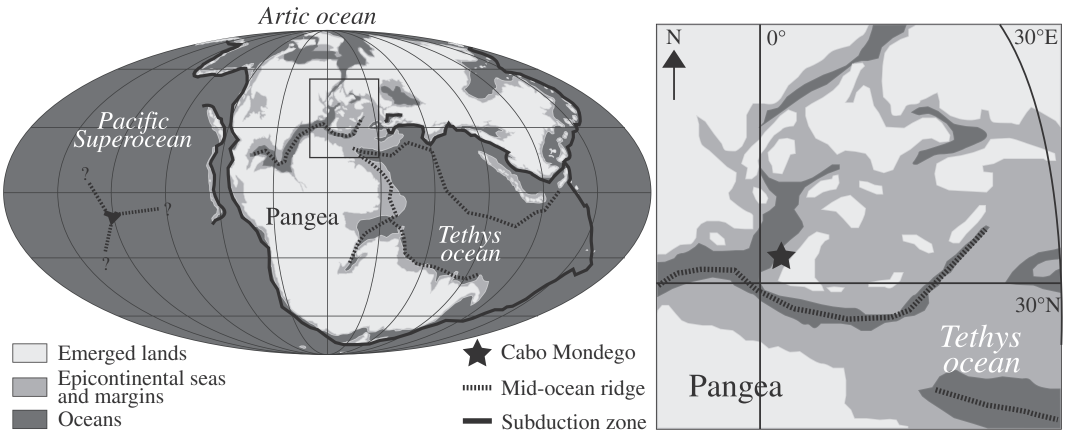

**Fig. 1.** Paleogeographic distribution of oceans and lands during the Middle Jurassic (after Blakey, 2005). On the left, a global view with subduction zones and mid-ocean ridges; and on the right, focus on the western Tethys with the localization of the Cabo Mondego section in the Lusitanian basin.

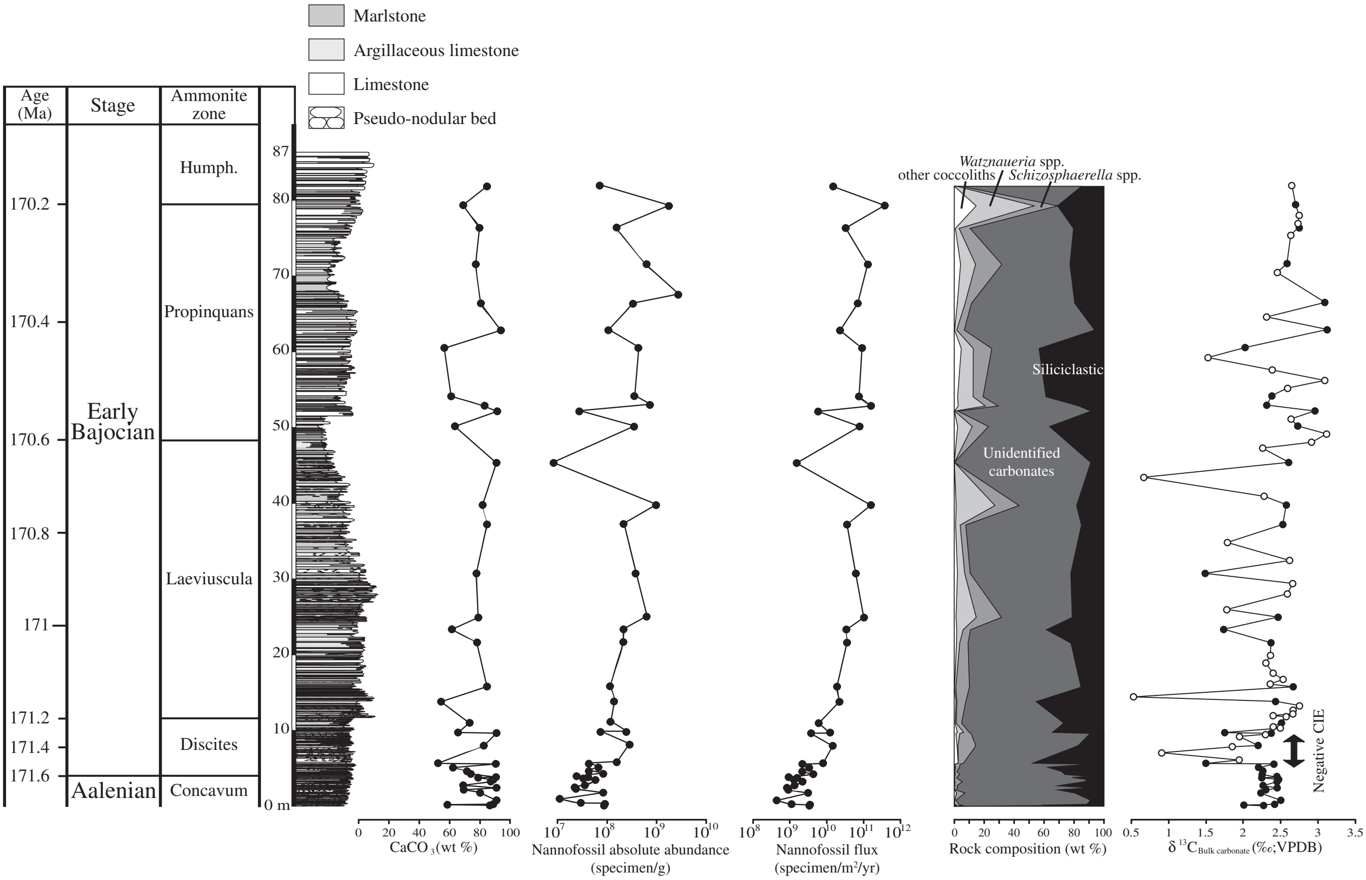

**Fig. 2.** Data from the Cabo Mondego section from the latest Aalenian to the end of the Early Bajocian. This figure shows the amount of $CaCO_3$ (wt %), nannofossil flux (nanno/m²/yr), rock composition (wt %) separated in five component classes (*Watznaueria* spp., other coccoliths, *Schizosphaerella* spp., unidentified carbonates and siliciclastics, mostly clays) and the $\delta^{13}C_{carb}$. In the $\delta^{13}C_{carb}$ curve, only full black circles correspond to samples studied for nannofossil fluxes.

calcareous dinoflagellates (Bown, 1987), *Watznaueria* spp. and other coccoliths) were distinguished in order to separate the two main Jurassic pelagic producers, namely *Schizosphaerella* spp. and *Watznaueria* spp. The fluxes were calculated using the sedimentation rate based on the duration of each ammonite zone according the chronostratigraphy in Gradstein et al. (2004). Due to the lack of data for both the sedimentation rate and dating of the Early Bajocian, we assumed that the sedimentation rate was constant throughout a given ammonite zone.

### 3.3. Carbon fluxes estimation at Cabo Mondego

In order to estimate the mass of inorganic carbon produced by nannofossils and preserved within the sediment, mass measurements of the three groups already defined (*Schizosphaerella* spp., *Watznaueria* spp. and other coccoliths) were performed following the methodology of Mattioli and Pittet (2002). Coccoliths are round to elliptical in shape and, the axis of maximum length is referred as the major axis, and its orthogonal as the minor axis. The lengths of both major and minor axes of coccoliths were measured, and for some species the lengths of major and minor axes of the central area were also measured. About two thousand five hundred measurements were performed on thirty-one nannofossil species. A carbon flux was calculated as follows:

$$C_{\mathrm{flux}} = (12/100) \times \mathrm{Flux}_{\mathrm{CaCO3}}. \qquad (1)$$

$$\text{With } \mathrm{Flux}_{\mathrm{CaCO3}} = \sum_{i=1}^{n} (\text{species}_i \text{ mass} \times \text{species}_i \text{ absolute abundance} \times \text{sedimentation rate} \times 2.7).$$

$\mathrm{Flux}_{\mathrm{CaCO3}}$ in g/m²/yr is the flux of carbonate produced by calcareous nannofossils and preserved in the sediment, species mass is in grams and species absolute abundance corresponds to the nannofossil/gram of rock. Sedimentation rates are in m/Ma, and 2.7 is the calcite density in g/cm$^3$.

### 3.4. Carbon fluxes from nannofossils extrapolated at the world-scale

This model aims to quantify the mass of nannofossil calcite transferred to the oceanic sediments, which is the pelagic carbonate production minus the carbonate loss during dissolution in the water column. In fact, the carbonate dissolved in the water column remains in the oceanic reservoir, and only the carbon of the carbonate sediments ($C_{\mathrm{flux}}$) belongs to the lithospheric reservoir.

In order to estimate the possible contribution of nannofossil pelagic carbonate to the carbon cycle, we assume as a working hypothesis that biogenic carbonate sediments recovered from the Cabo Mondego reference section (GSSP) for the Aalenian/Bajocian boundary reflect global trends in oceanic sedimentation during the studied time interval. This section has been selected because (1) it is the international reference for the Aalenian–Bajocian interval; (2) no site in oceanic drilling project has reported continuous Bajocian calcareous deposits; and (3) the Lusitanian Basin was an open sea connected to the Tethys and proto-Atlantic oceans.

The total carbon flux is expressed as follows:

$$C_{\mathrm{total}} = C_{\mathrm{flux}} \times S. \qquad (2)$$

$C_{\mathrm{total}}$ in g C/yr is the total amount of carbon produced from calcareous nannofossils and preserved in the sediment, and S in m² is the surface of ocean floor covered by pelagic nannofossil carbonate sediments. Because S is unknown for the Aalenian–Early Bajocian, we tested three hypothetical S values. The first hypothesis takes into account a Middle Jurassic production of nannofossils restricted to the shallow seas of the continental shelf (Hay, 2004), which were located in between 60°N and 60°S. We selected this latitude range because sections from Siberia and Alaska located north of 60°N, and Canada and Scotland located slightly below 60°N during the Middle Jurassic do not contain limestone or marlstone deposits (Imlay, 1976; Morton, 1992; Hall et al., 2004; Basov et al., 2009). Following this hypothesis, S would correspond to ~6% of the Earth's surface during this period (measured from Blakey, 2005). In the second hypothesis, nannofossil carbonate production was considered for both shallow seas and open-ocean. We have used the present-day estimates of S in this second hypothesis. Namely, we assume that the sedimentation was three times lower in the open-ocean than in the shelves, as it was demonstrated for modern oceans (Baumann et al., 2004). Global S value corresponds to the present-day percentage of the seafloor shallower than the present-day Carbonate Compensation Depth (CCD). S reached 11% of the Earth's surface, shared between the shallow seas (6%) and the open oceans (5%). Depth of the CCD (Feely et al., 2004) was calculated using the GLODAP (Key et al., 2004) and CARINA (The CARINA group) databases coupled to ODV4 software (Schlitzer, 2010). No estimation of Middle Jurassic S has been done because of the lack of oceanic paleobathymetry map and reliable estimation of the CCD depth. The third hypothesis takes into account fluxes equivalent to those calculated at Cabo Mondego and applied to the global ocean. Thus, S corresponds to 70% of the surface of the Earth (measured from Blakey, 2005).

### 3.5. Calculation of the $\delta^{13}$C value of each nannofossil group

Mass carbonate production of each nannofossil groups (see Sections 3.2. and 3.3.) was performed to estimate their contribution to the total carbonate content. The remaining unidentified carbonate, assumed to be carbonate fraction likely produced in shallow carbonate platforms then exported to the open-ocean (Mattioli and Pittet, 2002; Pittet and Mattioli, 2002), is attributed to a fourth group called unidentified carbonates. The mass of this group corresponds to the total carbonate mass minus the nannofossil mass calculations. From these mass balance calculations and from the bulk carbonate $\delta^{13}$C values, we quantify the $\delta^{13}$C of each group. We assume $\delta^{13}$C of each group and seawater did not change through time as we want to explore the possibility that the observed bulk $\delta^{13}$C variations only rely on the change in composition of bulk carbonate components. The bulk carbonate $\delta^{13}$C can be calculated using the following mass balance equation:

$$\delta^{13}\mathrm{C}_{\mathrm{carb}} = \sum_{i=1}^{n} M_i \times \delta^{13}\mathrm{C}_i. \qquad (3)$$

M is the mass of component $i$ and can also be expressed as the relative contribution of component $i$ to the total amount of carbonate. $\delta^{13}\mathrm{C}_i$ is the carbon isotope signature of the component $i$.

Assuming that $\delta^{13}\mathrm{C}_i$ of each bulk carbonate components remained constant during the interval studied, Eq. (3) gives rise to a linear system of $N=41$ equations (as many as the analyzed samples) with four unknown values of $\delta^{13}\mathrm{C}_i$, namely the three nannofossil groups and unidentified carbonates. This system of linear equations is therefore overdetermined and thus can be solved. This system of equations can be expressed in a matrix form:

$$D = M \times d. \qquad (4)$$

D is an $N\times1$ dimensional vector that corresponds to all the measured $\delta^{13}\mathrm{C}_{\mathrm{carb}}$ values. M is an $N\times4$ matrix that represents the mass of each component $i$. d is a $4\times N$ matrix that represents the $\delta^{13}$C of each component $i$. Eq. (4) can be solved for d:

$$d = \left(M^T \times M\right)^{-1} \times M^T \times D. \qquad (5)$$

$M^T$ is the transposed matrix of M. The resolution of this equation therefore provides least squares estimates (Sokal and Rohlf, 1995) of the $\delta^{13}$C of each component $i$ of the carbonate fraction.

Two scenarios are taken into account. In the first one, the complete dataset was used as input. Diagenetic alteration tends to decrease the bulk $\delta^{13}$C (Allan and Matthews, 1982; Derry, 2010). In the second scenario, we have excluded from the entire dataset the lowest bulk $\delta^{13}$C samples and we have randomly selected from this new dataset 24 samples. By using the mass balance equation, the $\delta^{13}\mathrm{C}_{\mathrm{carb}}$ values are calculated and compared to the measured $\delta^{13}\mathrm{C}_{\mathrm{carb}}$ values (Fig. 4).

## 4. Results

### 4.1. Calcium carbonate content and carbon isotope $\delta^{13}\mathrm{C}_{\mathrm{carb}}$

The percentage of $CaCO_3$ measured in the different samples varies between 52% and 94% (Fig. 2) with a mean value around 80%. No stratigraphic trend is visible.

The $\delta^{13}\mathrm{C}_{\mathrm{carb}}$ varies between 1.49‰ and 3.12‰ (Fig. 2). From the lowest part of the section up to the beginning of the Discites Zone (~5.6 m), the $\delta^{13}\mathrm{C}_{\mathrm{carb}}$ fluctuates between 2.25‰ and 2.5‰, reflecting the lithological shift from marlstones to argillaceous limestones. The values increase from about 2.5‰ to 3‰ toward the top of the section. Eight samples have low $\delta^{13}\mathrm{C}_{\mathrm{carb}}$ values (between 1.5‰ and 2.2‰) which may reflect the overprint of diagenesis in some parts of the section (Fig. 3A). Diagenesis often lowers the $\delta^{13}$C values of carbonates due to either organic matter mineralization or fluid–rock interactions (Allan and Matthews, 1982; Derry, 2010). A $\delta^{13}$C–$\delta^{18}$O plot (Fig. 3B) shows no significant correlation ($r=0.177$ with $p=0.27$), which confirms that diagenesis has not affected all the samples.

### 4.2. Nannofossil absolute abundances and fluxes

There is an overall increase in nannofossil abundance and flux concomitant with an increase of $\delta^{13}$C values upsection. The quantification of the absolute abundance of nannofossils varies between $9.4\times10^6$ nanno/g and $1.8\times10^9$ nanno/g over the interval studied (Fig. 2). In the Aalenian and the Discites Zone of the Early Bajocian, the absolute abundances vary between $2\times10^7$ nanno/g and $7\times10^7$ nanno/g, and they increase upsection. The short-term variations are linked to the calcium carbonate content with higher values in marlstones. Increasing absolute abundance continues until the middle of Laeviuscula Zone reaching values around $5\times10^8$ nanno/g. In the rest of the Early Bajocian, absolute abundances are higher than those of the Aalenian/Discites Zone and fluctuate between $2\times10^8$ nanno/g and $7\times10^8$ nanno/g. However, these fluctuations do not seem to be completely linked to the calcium carbonate content.

The reconstructed nannofossil fluxes vary between $4.3\times10^8$ nannofossil/m²/year and $3.7\times10^{11}$ nanno/m²/yr over the interval studied (Fig. 2). At the end of the Aalenian, fluxes are around $10^9$ nanno/m²/yr, and increase markedly within the Discites and Laeviuscula zones of the Bajocian up to values around $10^{11}$ nanno/m²/yr. Nannofossil fluxes remained rather constant around $10^{11}$ from the middle of the Laeviuscula Zone until the end of the Early Bajocian, but two samples (CM47 and CM53) show low fluxes similar to those recorded in Aalenian samples. Absolute abundances and fluxes are similar, thus the sedimentation rate variations do not explain the increase in nannofossil abundances.

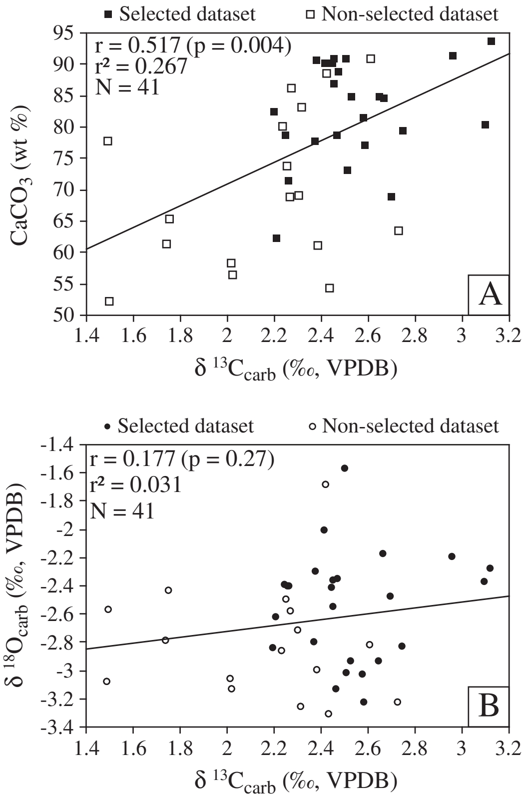

**Fig. 3.** A. Regression plot between $CaCO_3$ (wt %) and $\delta^{13}C_{carb}$ with r = 0.517 (p = 0.004). B. Regression plot between $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$. No significant correlation is observed (r = 0.177 with p = 0.27). Full markers correspond to the selected dataset and open markers to the rest of the dataset.

### 4.3. Contribution of nannofossils to the total carbonate content

We calculated the contribution of nannofossils to the rock composition (see Material and methods section). The pelagic carbonate production is divided into three groups representing the main contributors, namely *Watznaueria* spp., *Schizosphaerella* spp. and other coccoliths. The rest of the sediment is assumed to be composed of unidentified carbonate sediment (carbonate fraction likely produced in shallow carbonate platforms, then exported to the open-ocean; Mattioli and Pittet, 2002; Pittet and Mattioli, 2002) and siliciclastics, mainly clays. Over the entire section, the main contributor to the rock composition is the unidentified carbonate fraction, with the exception of CM70, which is mainly composed of pelagic carbonate. Unidentified carbonate and siliciclastics account for at least 40% and 10% of the total rock composition, respectively. At the end of the Aalenian, the nannofossil contribution to the bulk rock is minor and mainly controlled by the abundance of *Schizosphaerella* spp. (Fig. 2). During the Early Bajocian, the nannofossil contribution is not negligible. In the Discites Zone, the contribution of *Schizosphaerella* spp. increases slightly and remains broadly constant up to the end of this Zone. In the middle of the Laeviuscula Zone, the contribution of *Watznaueria* spp. to the rock composition increases sharply and becomes as important as the contribution of *Schizosphaerella* spp. Other coccoliths are minor contributors throughout the whole section, except for a few samples (Fig. 2).

### 4.4. Estimations of nannofossil contribution to the global Mid-Jurassic carbon cycle

The results of the three hypotheses relative to the estimation of the surface S are presented in Table 1. Hypotheses 1 and 2 provide similar estimations of carbon fluxes for the Aalenian (~$2.3\times10^{12}$ g C/yr) and the Early Bajocian (~$13\times10^{12}$ g C/yr). Hypothesis 3 generates fluxes ten times higher than in the case of the two previous hypotheses; indeed Aalenian and Early Bajocian fluxes equal ~$23\times10^{12}$ g C/yr and ~$130\times10^{12}$ g C/yr, respectively. It is noteworthy that calculations made for the Early Bajocian in the framework of the third hypothesis give results similar to present-day estimates.

**Table 1**
Worldwide sedimentary rates of inorganic carbon derived from pelagic carbonates. Flux value in g C/yr corresponds to the geometric mean. Errors were calculated based on the standard error around the mean. Four published estimated global carbon fluxes transferred to the modern seafloor are also given for comparison.

| References | Value (g C/yr) | Lower error | Higher error | Time interval |
|---|---|---|---|---|
| Hypothesis S1 | $2\times10^{12}$ | $1.5\times10^{12}$ | $3.7\times10^{12}$ | Aalenian |
| Hypothesis S1 | $1.1\times10^{13}$ | $7.5\times10^{12}$ | $2.1\times10^{13}$ | Early Bajocian |
| Hypothesis S2 | $2.6\times10^{12}$ | $1.9\times10^{12}$ | $4.7\times10^{12}$ | Aalenian |
| Hypothesis S2 | $1.4\times10^{13}$ | $1.2\times10^{13}$ | $2.6\times10^{13}$ | Early Bajocian |
| Hypothesis S3 | $2.3\times10^{13}$ | $1.7\times10^{13}$ | $4.2\times10^{13}$ | Aalenian |
| Hypothesis S3 | $1.3\times10^{14}$ | $8.5\times10^{13}$ | $2.3\times10^{14}$ | Early Bajocian |
| Mackenzie and Morse (1992) | $1.4\times10^{14}$ | – | – | Middle Jurassic |
| Milliman (1993) | $3.6\times10^{14}$ | – | – | Present |
| Westbroek et al. (1993) | $1.7\times10^{14}$ | – | – | Present |
| Sundquist and Visser (2004) | $2\times10^{14}$ | – | – | Present |
| Emerson and Hedges (2008) | $1.7\times10^{14}$ | – | – | Present |

### 4.5. Modeled $\delta^{13}C$

In the first mass balance calculation (Fig. 4) taking into account all the carbon isotope data, twenty-four of the forty-one studied bulk rocks have modeled $\delta^{13}C_{carb}$ values that fit well with measured $\delta^{13}C_{carb}$ (considering that the difference between both values is lower than 0.2‰). In the second simulation (Fig. 4), modeled $\delta^{13}C_{carb}$ values are systematically shifted by ~0.2‰ toward higher $\delta^{13}C_{carb}$ values compared to the first experiment, a similar trend being nevertheless preserved. This isotopic shift could be due to the bias induced by the sample selection that would tend to overestimate the modeled $\delta^{13}C_{carb}$.

The unidentified carbonate is the main component of the carbonate fraction, representing from 50 to almost 100% of the carbonate. Our results show that only half of the modeled $\delta^{13}C_{carb}$ values are in good agreement with the measured ones. The model fails to reproduce the $\delta^{13}C_{carb}$ values of eighteen out of the forty-one samples in the 0.2‰ range of accepted difference. Belonging to these outliers are the low $\delta^{13}C_{carb}$ values that may have been affected by diagenesis. The model also fails to reproduce the highly variable $\delta^{13}C_{carb}$ values of the samples located toward the top of the section. The failure of the model to reproduce some values is probably linked to changes in $\delta^{13}C_{carb}$ composition of possible producers of the unidentified carbonate, which remains the main component of bulk carbonate or diagenetic transformation of the original $\delta^{13}C_{carb}$.

Based on modeled $\delta^{13}C_{carb}$, $\delta^{13}C$ for each of the four carbonate contributors have been calculated. For the whole dataset, $\delta^{13}C_{\textit{Watznaueria}} = 4.3‰$, $\delta^{13}C_{\text{other coccoliths}} = -2.8‰$, $\delta^{13}C_{\textit{Schizosphaerella}} = 2.3‰$ and $\delta^{13}C_{\text{Unidentified Carb}} = 2.4‰$. For the set of samples excluding suspected diagenetic outliers, $\delta^{13}C_{\textit{Watznaueria}} = 3.3‰$, $\delta^{13}C_{\text{other coccoliths}} = 2‰$, $\delta^{13}C_{\textit{Schizosphaerella}} = 1.9‰$ and $\delta^{13}C_{\text{Unidentified Carb}} = 2.6‰$.

## 5. Discussion

### 5.1. Diagenetic overprint on Cabo Mondego deposits

The diagenetic overprint must be taken into account in order to correctly identify carbon isotope variations from changes in the carbon cycle rather than in the burial history of the rock. The diagenetic perturbation by rock–water interactions is very efficient on $\delta^{18}O$ due to the oxygen isotopic composition of the water itself. Rainwater is

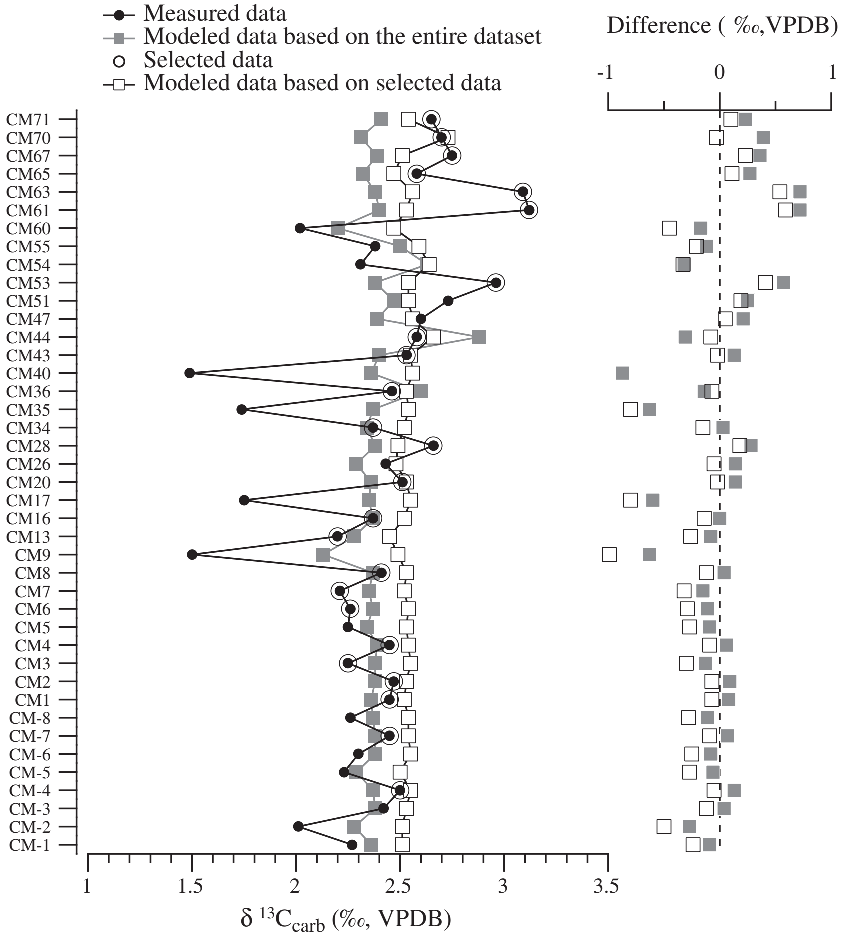

**Fig. 4.** Comparison of measured (full black circles) and modeled (full gray and empty squares) bulk δ$^{13}$C values. The first simulation (full gray squares) has been made with all the dataset and the second simulation (empty squares) with a set of 17 selected data (empty points) in order to avoid a possible diagenetic effect. Modeled δ$^{13}C_{carb}$ values from the first simulation are systematically shifted by ~0.2‰ toward higher δ$^{13}C_{carb}$ values compared. The difference between measured and modeled δ$^{13}$C value is shown in the right panel.

depleted in $^{18}$O in comparison to oceanic water. When circulating through the argillaceous limestones, water dissolves $CaCO_3$ and concentrates $CO_3^{2-}$ ions. Similarly, δ$^{13}$C can be potentially affected by water with a high concentration of $CO_3^{2-}$ ions. It is generally accepted that limestones are less affected by geochemical diagenesis than argillaceous limestones. Based on the correlation between δ$^{18}$O and δ$^{13}$C, the diagenetic overprint seems to be reduced (Fig. 3B) (Allan and Matthews, 1982) indicating that few samples have been altered according to our results. As a result, the most negative δ$^{13}$C values have been extracted from calculations in the model.

Nannofossils are generally more abundant in argillaceous limestones and marlstones than in limestones (Mattioli and Pittet, 2002; Pittet and Mattioli, 2002), although preservation is better in marlstones. Overgrowth of nannofossils is often observed in limestones (Roth and Thierstein, 1972). Hence, between nannofossil recrystallization (mostly observed in limestones) and isotopic diagenesis (mostly observed in marlstones), the diagenetic process seems to be different and probably not synchronous in the rock. Nevertheless, at Cabo Mondego the nannofossil preservation is generally moderate with few overgrowth; the central area structures are often broken but not lost. Moreover, large (e.g., *Crepidolithus crassus*) and very small (e.g., *Biscutum dubium*) coccoliths are preserved as well as rare specimens (e.g., *Triscutum tiziense*), allowing us to be confident in both our estimations of flux and in the preservation of the original nannofossil assemblage. The diagenetic effect by recrystallization has been carefully taken into account for the nannofossil measurements by avoiding affected coccoliths. Even if few samples with diagenetic overprint have been identified from the isotopic geochemistry and nannofossil counts, it seems to be limited to few samples.

### *5.2. δ$^{13}$C events during the Aalenian–Early Bajocian*

The Aalenian/Bajocian boundary is marked by a negative δ$^{13}$C excursion (Fig. 2). This negative excursion is recorded in various sequences of bulk carbonates in Italy, France and Spain (Corbin, 1994; Bartolini et al., 1996, 1999; O'Dogherty et al., 2006) as well as in fossil wood from England (Hesselbo et al., 2003) and in belemnites from Scotland (Jenkyns et al., 2002). Bartolini and Larson (2001) argued that this isotopic event may have been linked to an increase in volcanic activity, a conclusion based on the record of this negative excursion in various paleogeographic settings, along with perturbations of both marine and terrestrial carbon reservoirs. Volcanic activity injects carbon with low $^{13}C/^{12}C$ ratio into the atmosphere relative to the seawater carbon reservoir. This increase in volcanic activity would be linked to contemporaneous major tectonic changes such as the opening of the Atlantic Ocean (Labails et al., 2010 and references within) and changes in the Pacific plate motions associated with subduction zones (Bartolini and Larson, 2001). At Cabo Mondego, the negative excursion is recorded but remains stratigraphically short.

A positive excursion is documented (Fig. 2) in carbonate deposits from Italy, France, and Spain (Corbin, 1994; Bartolini et al., 1996, 1999; O'Dogherty et al., 2006) subsequent to the negative excursion, even though it is poorly documented in terrestrial material (Hesselbo et al., 2003) and hence subject to discussion. Local changes in the DIC

(Dissolved Inorganic Carbon), pool driven by changes in primary production are unlikely to account for that positive excursion since it has been identified in several basins. On a more global scale, an increase in the ocean's primary production would have affected the global DIC and eventually been recorded in the atmospheric reservoir. So far, there is a lack of carbon isotope data from the terrestrial realm. Nevertheless, several studies have proposed that this positive carbon isotope excursion may be linked to an increase in primary production (Bartolini et al., 1999; O'Dogherty et al., 2006; Brigaud et al., 2009). The diversification of *Watznaueria* (Tiraboschi and Erba, 2010) and radiolarians (Bartolini et al., 1996) could account for this increase in marine productivity. However, such a positive excursion would require a preferential sink of $^{12}$C in the ocean such as a long-term sedimentary burial of organic matter. We test an alternative explanation for this positive $\delta^{13}$C excursion since such organic matter-rich deposits have not yet been identified in the Early Bajocian.

### 5.3. Impact of the Watznaueria diversification on the Mid-Jurassic carbon cycle

Abundances of coccoliths and *Schizosphaerella* spp. were almost constant during the Early Bajocian while the diversification of *Watznaueria* accounted for the increase in the carbonate pelagic production during the Early Bajocian (Fig. 2). Three scenarios were tested for calculating the carbon flux derived from the pelagic carbonate produced by these three main nannofossil contributors (Table 1). The two first hypotheses are considered as plausible scenarios while the third one is an extreme scenario, considered to be unrealistic. Indeed, it seems unlikely that during Middle Jurassic high primary productivity would be present in the entire oceanic realm. However, this non-realistic third scenario is the only one able to generate a sizable effect on the Early Bajocian carbon cycle and to produce a carbon flux similar to that observed in the present-day pelagic realm. The first and second hypotheses gave similar outputs with emphasis on the low rate of production and exportation of pelagic carbonate to the deep ocean when compared to modern oceans. The computed carbon flux is ten times lower than the inorganic carbon flux estimated for the Middle Jurassic by Mackenzie and Morse (1992). Even if the pelagic carbonate production remained relatively low in comparison to the total carbonate production, both scenarios predict that the total carbon flux resulting from the pelagic carbonate production increased five times between the Aalenian and the Early Bajocian. Consequently, we propose that the *Watznaueria* diversification largely increased the pelagic carbonate production and the participation of pelagic carbonate producers in the oceanic carbon cycle.

Erba (2006) suggested that the diversification of *Watznaueria* during the Middle Jurassic had a noticeable impact on carbonate sedimentation while Hay (2004) proposed that the impact of nannofossils was limited until the Late Jurassic. Even though pelagic carbonate production increased throughout the Middle Jurassic in relation to the diversification of *Watznaueria*, our data and calculations show that the nannofossil production rate remained too low, precluding any sizable impact on the carbon cycle and changes in both the DIC concentration and carbon isotope composition. Hence, the Early Bajocian positive excursion was most likely not caused by an increase of the inorganic carbon flux resulting from pelagic carbonate producers.

### 5.4. Impact of Watznaueria on the $\delta^{13}C_{carb}$

The diversification of *Watznaueria* apparently did not have any sizable impact on the global carbon cycle during the Early Bajocian. Based on this result, we conclude that this diversification did not change the $\delta^{13}$C value of the dissolved inorganic carbon (DIC) of the seawater. However the increase of the pelagic carbonate production is concomitant with the changing carbon isotope composition of bulk carbonate rocks (Fig. 2). As Bralower (2002; p. 9) suggested about the PETM: “Thus it is theoretically possible that the 2.5‰ shift in bulk $\delta^{13}$C values in the PETM at Site 690 that correlates with the major nannoplankton assemblage turnover event results from the turnover itself.” Our data show that the appearance of the genus *Watznaueria* represents a major turnover in the nannoplankton community and thereby highly increased the amount of pelagic carbonate. In modern species, the $\delta^{13}$C of coccoliths is depending on the calcite growth rate (Ziveri et al., 2003). Assuming that *Watznaueria* had a similar production rate as *Emiliania huxleyi* (Erba, 2006), calculated $\delta^{13}$C values for the *Watznaueria* spp. contributors based on selected dataset are close to cultured *E. huxleyi* (Ziveri et al., 2003). Nevertheless, our model failed to calculate $\delta^{13}$C for other coccoliths close to measured values in living coccoliths (Ziveri et al., 2003) and *Schizosphaerella* spp. close to measured values in calcareous dinoflagellates (Zonneveld et al., 2007). We assume that the contribution of unidentified carbonate material is very important in the studied sediments and that micrite compositions are not homogenous during the Early Bajocian. Unfortunately, change in composition of this large fraction itself through the section cannot be quantified. However, given its large dominance in terms of mass, is very likely to have the most significant influence on the measured $\delta^{13}C_{carb}$ values. Moreover, we note that the selected dataset is mainly based on limestone samples that limit the natural range of difference between limestone and marlstone $\delta^{13}C_{carb}$, hence precluding identification of possible influence of more important nannofossil contribution to the bulk carbonate. Nevertheless, our results demonstrate that the contribution of the calcareous nannofossil is not high enough to account for the Early Bajocian positive excursion by the rise of the pelagic carbonate and the increase of the genus *Watznaueria* primary production alone.

Based on our results, neither the increase in nannofossil flux nor change in the nannofossil community can explain the Early Bajocian $\delta^{13}$C positive excursion. No oceanic sink of $^{12}$C has yet been identified. We thus suggest that such large organic matter storage may have been concentrated in marginal seas and terrestrial realms as it has been proposed for a relatively similar geochemical event during the Late Valanginian (Weissert Event; Westermann et al., 2010).

## 6. Conclusion

The goal of this study was to identify the contribution of pelagic carbonate production to both carbon cycle and carbon isotope composition of Middle Jurassic bulk carbonate rocks. Based on our analyses and calculations, we conclude that:

(1) Pelagic carbonate fluxes increased from $10^9$ to $10^{11}$ nannofossils/m²/yr during the Early Bajocian in relation to diversification of the genus *Watznaueria*,
(2) The flux of inorganic carbon produced by pelagic carbonate producers for the Mid Jurassic was 10 to 20 times lower than present day values,
(3) The contributions of the genus *Watznaueria* to the carbonate realm cannot explain the Early Bajocian $\delta^{13}C_{carb}$ positive excursion.

Hence, the shift in carbonate production from platforms to the open ocean, called the Mid Mesozoic Revolution (Ridgwell, 2005), did not take place during the Early Bajocian. Even if this event started since the rise of the calcareous nannoplankton during the Late Triassic, the key change postdated the Early Bajocian and might have taken place during the Late Jurassic (Hay, 2004). However, after the diversification of the genus *Watznaueria* was an important step in pelagic carbonate development, as illustrated by the increase by a factor of five of the inorganic carbon flux to the deep ocean from the Aalenian to the Early Bajocian. The rise of *Watznaueria* did not explain the Early Bajocian $\delta^{13}C_{carb}$ positive excursion. The cause of this major carbon cycle perturbation thus remains unclear.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.gloplacha.2012.02.007.

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