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A global event with a regional character: the Early Toarcian Oceanic Anoxic Event in the Pindos Ocean (northern Peloponnese, Greece)

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Abstract – The Early Toarcian (Early Jurassic, *c*. 183 Ma) was characterized by an Oceanic Anoxic Event (T-OAE), primarily identified by the presence of globally distributed approximately coeval black organic-rich shales. This event corresponded with relatively high marine temperatures, mass extinction, and both positive and negative carbon-isotope excursions. Because most studies of the T-OAE have taken place in northern European and Tethyan palaeogeographic domains, there is considerable controversy as to the regional or global character of this event. Here, we present the first high-resolution integrated chemostratigraphic (carbonate, organic carbon, $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$) and biostratigraphic (calcareous nannofossil) records from the Kastelli Pelites cropping out in the Pindos Zone, western Greece. During the Mesozoic, the Pindos Zone was a deep-sea ocean-margin basin, which formed in mid-Triassic times along the northeast passive margin of Apulia. In two sections through the Kastelli Pelites, the chemostratigraphic and biostratigraphic (nannofossil) signatures of the most organic-rich facies are identified as correlative with the Lower Toarcian, *tenuicostatum/polymorphum–falciferum/serpentinum/levisoni* ammonite zones, indicating that these sediments record the T-OAE. Both sections also display the characteristic negative carbon-isotope excursion in organic matter and carbonate. This occurrence reinforces the global significance of the Early Toarcian Oceanic Anoxic Event.

Keywords: Toarcian Oceanic Anoxic Event, Pindos Zone, carbon isotopes, Greece, Kastelli Pelites.

1. Introduction

The Early Toarcian (*c*. 183 Ma) was associated with global warming (Bailey *et al*. 2003; Jenkyns, 2003), mass extinction (Little & Benton, 1995; Wignall, Newton & Little, 2005) and a globally increased rate of organic carbon burial attributed to an Oceanic Anoxic Event (OAE) (Jenkyns, 1985, 1988, 2010; Karakitsios, 1995; Rigakis & Karakitsios, 1998; Jenkyns, Gröcke & Hesselbo, 2001; Karakitsios *et al*. 2004, 2007). The Toarcian OAE (T-OAE) coincides with an overall positive and interposed negative carbon-isotope excursion that has been recorded in marine organic matter, pelagic and shallow-water marine carbonates, brachiopods and fossil wood (Hesselbo *et al*. 2000, 2007; Schouten *et al*. 2000; Röhl *et al*. 2001; Kemp *et al*. 2005; van Breugel *et al*. 2006; Suan *et al*. 2008, 2010; Woodfine *et al*. 2008; Hermoso *et al*. 2009; Sabatino *et al*. 2009). To date, most research has concentrated on N European and Tethyan palaeogeographic environments, representing shelf seas and drowned carbonate platforms on foundered continental margins (Bernoulli & Jenkyns, 1974, 2009). Thus, an ongoing vigorous debate exists as to whether the recorded patterns of Toarcian carbon burial and carbon-isotope evolution represent only processes occurring within these relatively restricted palaeogeographic marine environments or whether they were truly global in character (e.g. Küspert, 1982; van der Schootbrugge *et al*. 2005; Wignall *et al*. 2006; Hesselbo *et al*. 2007; Svensen *et al*. 2007; Suan *et al*. 2008). Those pointing to local factors suggest overturning of a stratified water column rich in CO_2 from the oxidation of organic matter; those suggesting global control suggest introduction of isotopically light carbon into the ocean–atmosphere system from dissociation of gas hydrates or hydrothermal venting of greenhouse gases. Certainly, the recent recognition of the T-OAE in Argentina suggests the impact of this phenomenon was not confined to the northern hemisphere (Al-Suwaidi *et al*. 2010).

In Greece, only limited geochemical data are available for the T-OAE (Jenkyns, 1988). During the period from the Triassic to the Late Cretaceous, the external Hellenides (western Greece) constituted part of the southern Tethyan margin (Fig. 1), where siliceous and organic carbon-rich sediments were commonly associated facies (Bernoulli & Renz, 1970; Karakitsios, 1995; De Wever & Baudin, 1996). The Ionian and Pindos zones of western Greece (Fig. 2) expose such basinal, thrust-imbricated sediments that document continental (Ionian Zone) and continent–ocean-margin basinal pelagic sequences (Pindos Zone).

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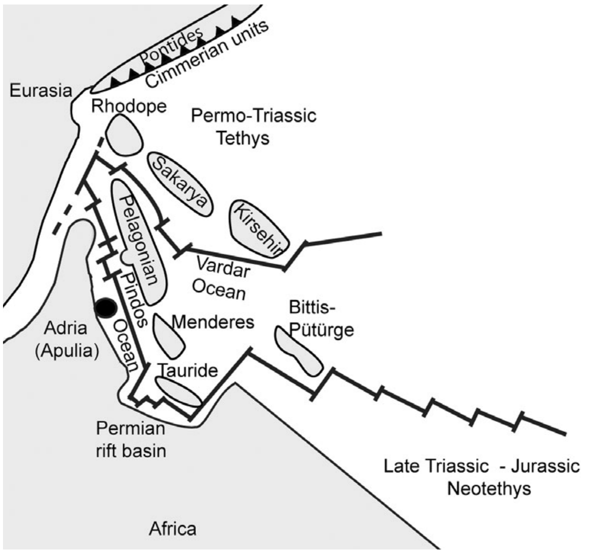

Figure 1. Early Jurassic palaeogeography of the western Tethys Ocean (based on Clift, 1992; Dercourt, Ricou & Vriellynck, 1993; Channell & Kozur, 1997; Degnan & Robertson, 1998; Pe-Piper, 1998). The approximate position of the study area is illustrated by the black circle. The stable segment of Adria is approximately the size of the area now occupied by the Adriatic Sea, parts of eastern Italy, the Southern Alps and Istria.

In this study, we present for the first time a high-resolution isotopic record of the T-OAE in Tethyan ocean-margin sediments, deposited in an area corresponding to the western edge of the Pindos Ocean. Integrated chemostratigraphic and biostratigraphic studies of the Kastelli Pelites, here unambiguously indentified as deposited during the Early Toarcian OAE, strongly reinforce the global character of the T-OAE.

2. Geological setting and stratigraphy

The Pindos Zone (Fig. 2) exposes an imbricate thrust belt with allochthonous Mesozoic to Tertiary sedimentary rocks of deep-water facies. The Zone extends into Albania and former Yugoslavia (Dédé *et al*. 1976; Robertson & Karamata, 1994) as well as into Crete (Bonneau, 1984), Rhodes (Aubouin *et al*. 1976) and Turkey (Bernoulli, de Graciansky & Monod, 1974; Argyriadis *et al*. 1980). The sediments of the Pindos Zone originate from an elongate remnant ocean basin that formed in mid-Triassic time along the northeastern passive margin of Apulia between the extensive Gavrovo–Tripolis platform in the present west and the Pelagonian continental block in the east (including also the isolated Parnassos Platform in its western portion). Continental collision in the Aegean area has produced a collage of microcontinental blocks, which were accreted to the active margin of Eurasia in early Tertiary times. Observations on the Greek mainland as well as on the island of Crete confirm that the eastern basal rocks of the Pindos Zone and the southwestern end of the Pelagonian continental terrane were rifted from Gondwana in mid-Triassic times (De Wever, 1976; Bonneau, 1982; Clift, 1992; Degnan & Robertson, 1998; Pe-Piper, 1998). By Early Jurassic

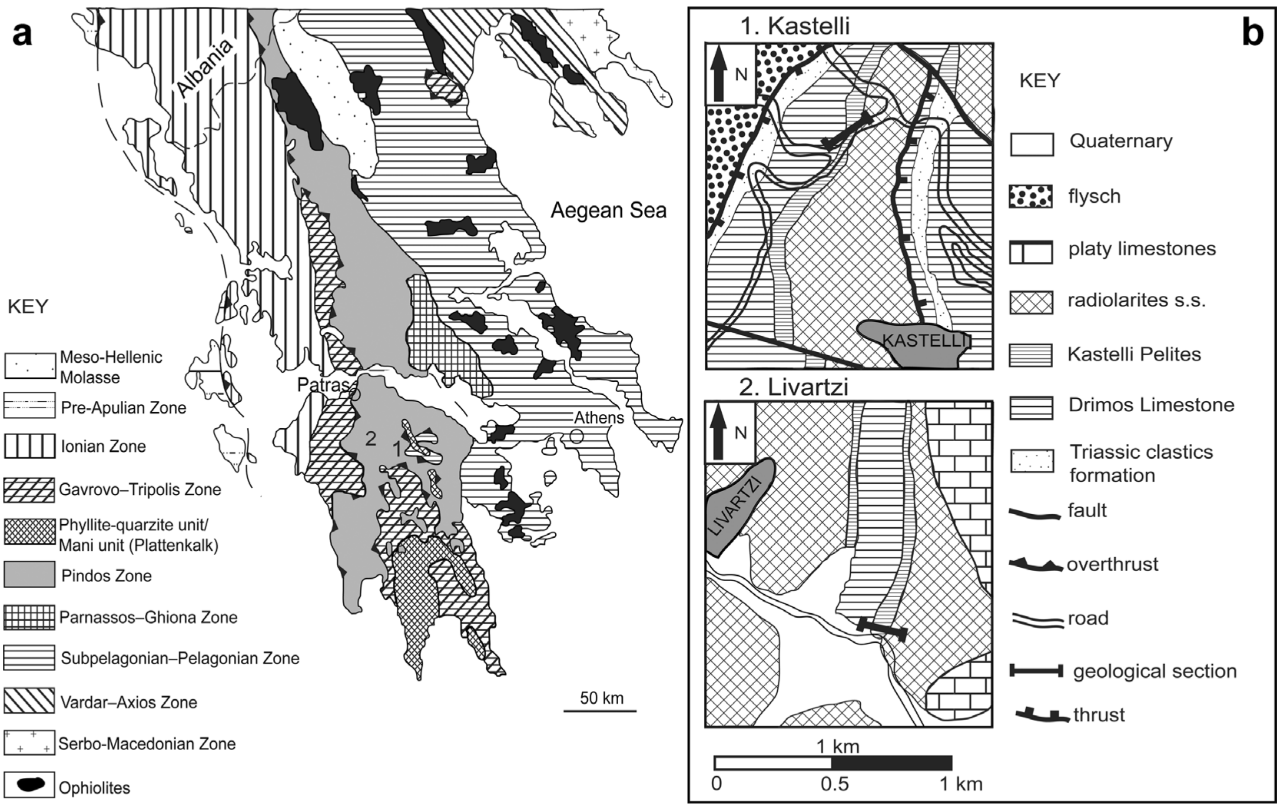

Figure 2. (a) Simplified geological map with the main tectonostratigraphic zones of the Hellenides. (b) Geological map of Kastelli section (above) and Livartzi section (below).

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time at the latest (Fig. 1), actively spreading oceanic basins had opened in both the Pindos and the Vardar Zones on either side of the Pelagonian continental block (De Wever, 1976; Bonneau, 1982; Robertson *et al*. 1991; Clift, 1992; Lefèvre *et al*. 1993; Pe-Piper & Hatzipanagiotou, 1993; Degnan & Robertson, 1998; Pe-Piper, 1998). The evidence indicating the oceanic character of the Pindos Basin is summarized by Degnan & Robertson (1998). The western Pindos Ocean separated Pelagonia from Apulia; the eastern Vardar Ocean separated Pelagonia from the Serbomacedonia and Sarakya microcontinents. Later Mesozoic and Cenozoic convergence resulted in the nappe structure of the Hellenide Orogen and the tectonic dismemberment of the Permian–Triassic rift-related igneous rocks. The amount of orogen-parallel transport during closure of the Pindos and Vardar oceans is uncertain, but most authors argue that it was not large (Robertson *et al*. 1991; Wooler, Smith & White, 1992). The Pindos Zone of western Greece is exceptional since it was deformed into a regular series of thrust sheets during its emplacement, with a minimum of disruption. The present-day westward-vergent fold and thrust sheets have not been affected by major back-thrusting or out-of-sequence thrusting (Degnan & Robertson, 1998).

The sedimentary successions of the Pindos Zone comprise deep-water carbonate, siliciclastic and siliceous rocks, ranging in age from Late Triassic to Eocene (Fleury, 1980; Degnan & Robertson, 1998).

3. Field observations

3.a. Kastelli section

The Kastelli section (37° 54′ N, 22° 02′ E) is located about 200 m westwards of the junction of the Kalavrita–Klitoria and Kalavrita–Aroania roads. In this section, the outcrop is of excellent quality and illustrates, in stratigraphic continuity, the Drimos Limestone Formation, the Kastelli Pelites and the radiolarites *sensu stricto*. The outcrops correspond to the eastern more distal part of the Pindos western margin. From the bottom to top the following lithological units are observed:

(i) The Drimos Limestone Formation, which comprises sediments some 100 m thick. The lower part is 35 m thick and is developed as an alternation of limestones, with filaments (thin-shelled bivalves), and green pelites. This unit, which is chert-bearing, is dated as Norian, at a point about 300 m southwest of this section (J. M. Flament, unpub. Ph.D. thesis, Univ. Lille, 1973). A radiolarian cherty member, about 10 m thick, divides the lower from the upper part, which comprises mainly limestones attaining some 60 m in thickness. A precise age determination in this upper part is not possible with the observed faunas, because they are represented only by some reworked algae and Foraminifera (e.g. *Thaumatoporella* sp. and Textulariida, respectively).

(ii) The Kastelli Pelites, comprising sediments about 35 m thick. The first 8 m consists of a succession of thin-layered (5–10 cm) marly limestones alternating with mainly grey marls (a limestone layer with chert nodules is interbedded in the lower part of the succession). The sequence continues with 3–4 m of red marls, marly clays and clays with some intercalations of marly limestone. Above, there follows some 6 m of mainly marly limestones and marls containing rare black chert layers. In thin-sections of the marly limestones, badly preserved Foraminifera are observed. The succession finishes with 17 m of marly limestones and red marls, cherty in the middle and upper parts. These cherts indicate a passage into the stratigraphically overlying radiolarites *sensu stricto*.

3.b. Livartzi section

The Livartzi section (37° 55′ N, 21° 55′ E) is located north of the Tripotama–Kalavrita road by the turning towards Livartzi village. The outcrop corresponds to the western (closer to the Tripolis Platform) part of the Pindos margin. Here the Kastelli Pelites are thinner (20 m thick) than those of the Kastelli section itself (35 m thick).

The sampling started in the upper 6 m of the Drimos Limestone Formation, comprising thin layers of marly limestone. Quaternary sediments cover the first 3 m of Kastelli Pelites. After this exposure gap, there follows a 1 m marly limestone bed, and the section continues with the typical Kastelli Pelites Formation, as described for the type locality.

4. Methods

In total, 325 bulk sediment samples were collected from the two sections (191 from Kastelli and 134 from Livartzi). The collected samples were powdered and analysed for weight per cent total organic carbon and the equivalent amount of $CaCO_3$ using a Strohlein Coulomat 702 analyser (details in Jenkyns, 1988), for carbonate carbon and oxygen isotopes using a VG Isogas Prism II mass spectrometer (details in Jenkyns, Gale & Corfield, 1994) and for organic-matter carbon and oxygen isotopes using a Europa Scientific Limited CN biological sample converter connected to a 20–20 stable-isotope gas-ratio mass spectrometer (details in Jenkyns *et al*. 2007). All the above analyses were undertaken in the Department of Earth Sciences and Research Laboratory for Archaeology in the University of Oxford. Results for both sections are given in Tables A1 and A2 in the online Appendix at http://journals.cambridge.org/geo.

A set of 27 samples from Kastelli and 28 from Livartzi was investigated for its content of calcareous nannofossils. Smear-slides were prepared from the powdered rock according to the technique described in Bown & Young (1998), then analysed in an optical polarizing Leitz microscope at × 1250. Nannofossils

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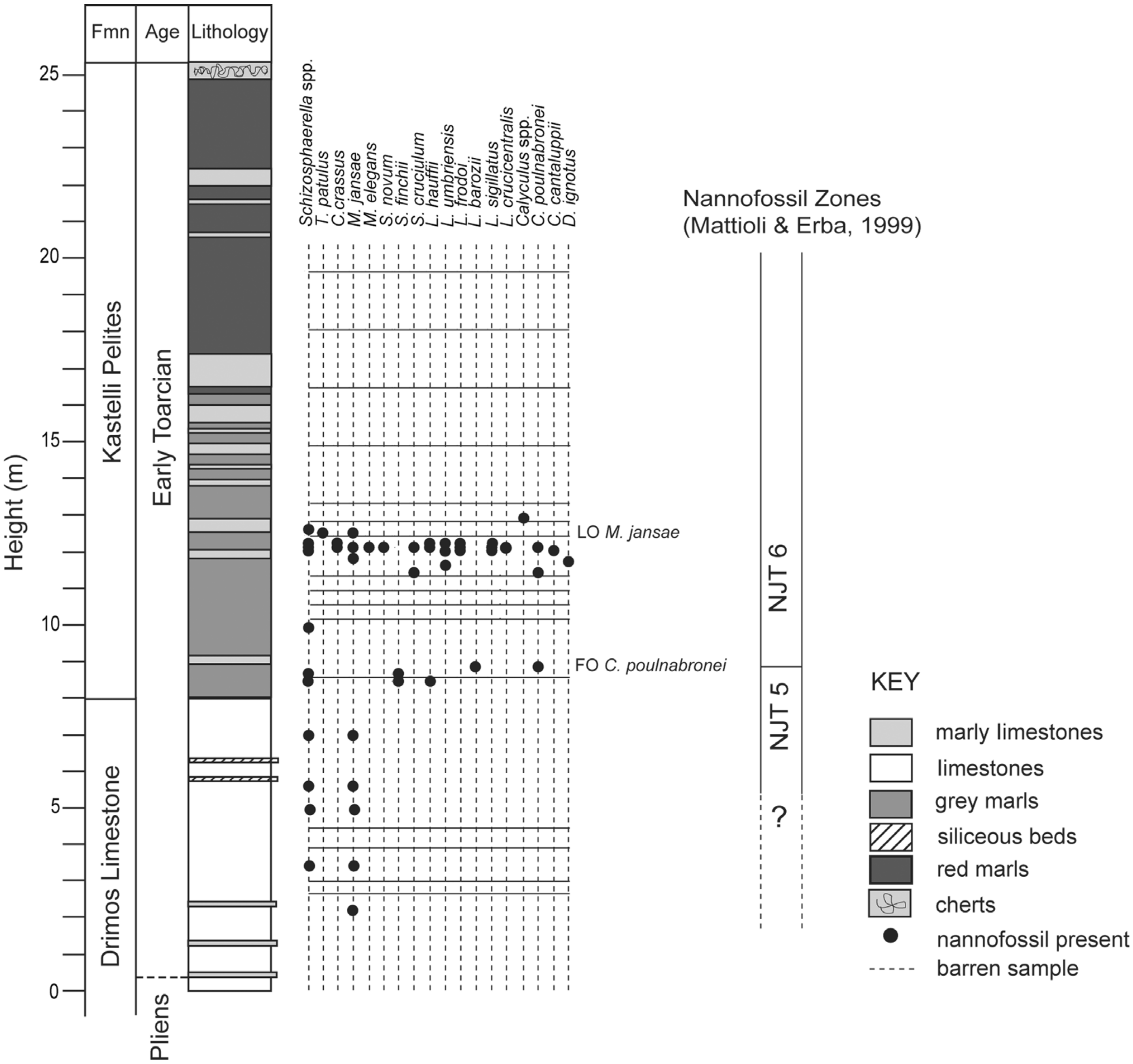

Figure 3. Lithological column and biostratigraphical data from the Kastelli section. Nannofossil zones after Mattioli & Erba (1999).

were counted for each sample in a surface area of the slide varying between 1 and 2 cm^2.

5. Results

5.a. Biostratigraphy

There are very few data concerning the age of the Kastelli Pelites, the lack of ammonites indicating that the sequence was deposited below the aragonite compensation depth. Lyberis, Chotin & Doubinger (1980) attributed the unit to the Late Pliensbachian/Toarcian, comparing the palynological associations with those of the Vicentin Alps. Nevertheless, the only precise data are referred to by Fleury (1980) and De Wever & Origlia-Devos (1982), who suggested an Aalenian age for the top of the Kastelli Pelites unit. Fleury's (1980) data are based on the presence of *Meyendorffina* (*Lucasella*) *cayeuxi* (Lucas) in a limestone layer at the top of Kastelli Pelites in the Karpenission region (central Greece); and De Wever & Origlia-Devos's (1982) data are based on Foraminifera faunas from the Peloponnese. Based on general biostratigraphic and chemostratigraphic considerations, Jenkyns (1988) suggested that the Kastelli Pelites were correlative with other black shales in Greece (in the Ionian Zone) and were formed during the T-OAE.

We undertook detailed biostratigraphical analyses of calcareous nannofossils in an effort to improve and expand the biostratigraphical resolution from previous studies. The nannofossil distribution is summarized in Figures 3 and 4.

5.a.1. Kastelli section

Samples were taken from the limestones at the top of the Drimos Limestone Formation, as well as from the lower to middle part of the Kastelli Pelites for

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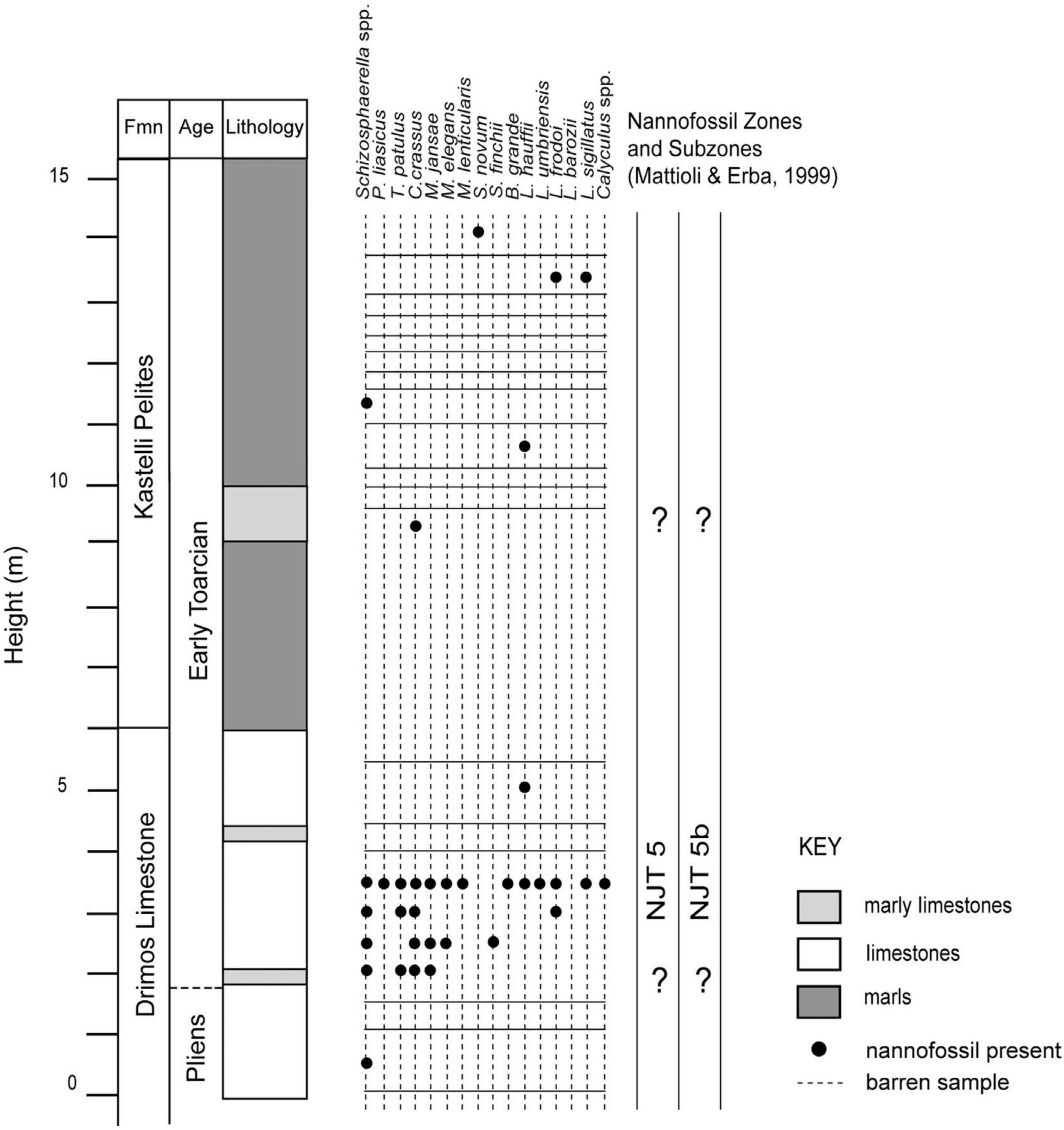

Figure 4. Lithological column and biostratigraphical data from the Livartzi section. Nannofossil zones after Mattioli & Erba (1999).

a thickness of about 20 m. Twelve samples were barren of nannofossils, and the rest contained very few specimens. The assemblage is represented by rare *Schizosphaerella* spp., *Mitrolithus jansae* and *M. elegans*, *Calyculus* spp., *Similiscutum cruciulum*, *S. finchii* and *S. novum*, *Tubirhabdus patulus*, *Crepidolithus crassus*, and various species of the genus *Lotharingius*, including the zonal marker *L. hauffii*. This assemblage allows us to identify the NJT 5 nannofossil Zone (Late Pliensbachian to Early Toarcian). Specimens belonging to the *Carinolithus* genus, namely *C. poulnabronei* and *C. cantaluppii*, were recorded discontinuously starting from sample 34. This occurrence can be used at Kastelli to identify the NJT 6 nannofossil Zone. The last occurrence of *Mitrolithus jansae* was observed in sample 71 (12.5 m). A single specimen of *Discorhabdus ignotus* was encountered in sample 63 (12 m). The first occurrence of this species is fixed at the *tenuicostatum/serpentinum* zonal boundary in central Italy (Mattioli & Erba, 1999), where it is considered to mark the end of the Early Toarcian OAE (Bucefalo Palliani & Mattioli, 1998; Mattioli *et al.* 2004), although in some areas an earlier occurrence of *D. ignotus* is recorded (Mattioli *et al.* 2008; Bodin *et al.* 2010).

5.a.2. Livartzi section

Only 14 samples of the Livartzi section were found to contain calcareous nannofossils. The productive

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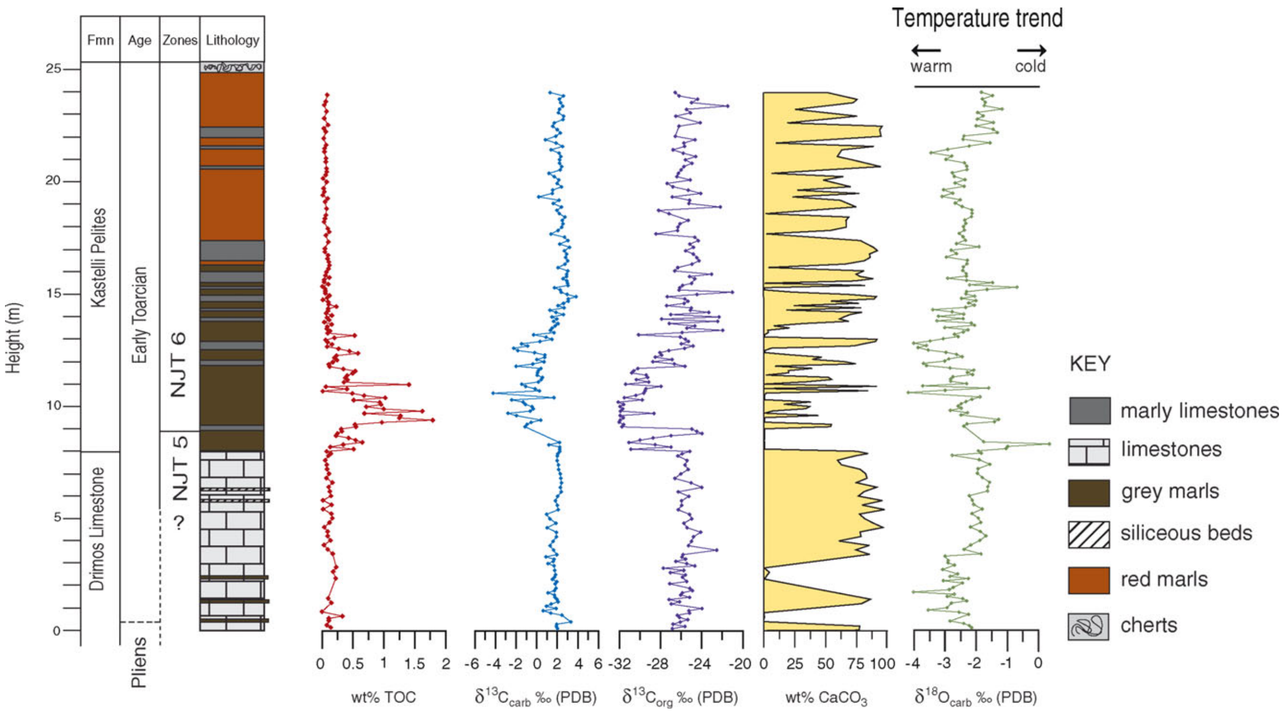

Figure 5. Lithostratigraphical log, bulk TOC, stable-isotope (C, O) and wt % $CaCO_3$ profiles through the Kastelli section. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

samples show assemblages similar to those of the Kastelli section with poorly preserved and rare nannofossils. The interval between samples 11 and 36 (from 1.1 to 3.6 m) represents an exception, because samples are richer, with common *Schizosphaerella* and *M. jansae*. The stratigraphically highest specimen of *M. jansae* is recorded in sample 36 (3.6 m). However, we cannot confidently define this datum level as a last occurrence because the samples studied in the interval above are barren of nannofossils. This assemblage, and the presence in the assemblage of *L. sigillatus*, allows attribution of this interval to the NJT 5b nannofossil Subzone (uppermost Pliensbachian to lowermost Toarcian).

5.b. Chemostratigraphy

5.b.1. Kastelli section

5.b.1.a. Organic carbon and carbonate profiles

Chemostratigraphic data are illustrated in Figure 5. The total organic carbon (TOC) values are very low and stable in the lower part of the section where background values are in the range 0.10–0.20 wt %. After the lowest 7.5 m, the TOC values begin to rise gradually for 1.5 m defining a positive excursion to reach a maximum value of 1.79 wt %. At the top of this interval, values return to background levels.

The carbonate values do not follow any particular trend nor do they respond to the excursion. Up to the level where the TOC excursion begins, the percentage of $CaCO_3$ in the bulk rock fluctuates between 60 and 100 %. When the excursion begins, there is a sudden drop to reach values lower than 10 %; following that, values start to rise again until the top of the studied section, with relative minima being attained every few metres. A similar pattern is seen in other Tethyan pelagic sections recording the T-OAE (e.g. Sabatino *et al.* 2009).

5.b.1.b. Stable-isotope (carbon and oxygen) profiles

The carbon- and oxygen-isotope values in carbonate and the TOC of bulk rock are reported in Figure 5. The bulk carbonate carbon-isotope values record a small positive followed by a negative excursion in the lowest metre of the section. Above this small disturbance, values are very stable within the next 7.5 m of the section, with background values of 2 ‰. Thereafter, $\delta^{13}C_{carb}$ values begin to fall irregularly, reaching a minimum of −5 ‰. The negative excursion extends over the next 5 m before recovery takes place and background values of ∼2 ‰ are restored. What is remarkable is the polarity between the TOC profile and the carbonate carbon-isotope profile, with the two curves appearing as approximate mirror images of one another. The stratigraphical coincidence between the negative carbon-isotope excursion and relative TOC maximum is also observed in Toarcian black shales from northwestern Europe and central Italy (Jenkyns & Clayton, 1997; Jenkyns *et al.* 2002; Mattioli *et al.* 2004).

The organic carbon-isotope profile is slightly different from that of $\delta^{13}C_{carb}$. The first shift is recorded in the interval 8 to 9 m and records a drop from −25.15 ‰ to −31.1 ‰; following this excursion, values return to −24.95 ‰. Above this level, values drop again, to −32.1 ‰, and remain low for approximately 2.5 m. Stratigraphically higher in the section, values become heavier and fluctuate around a background value of −25 ‰.

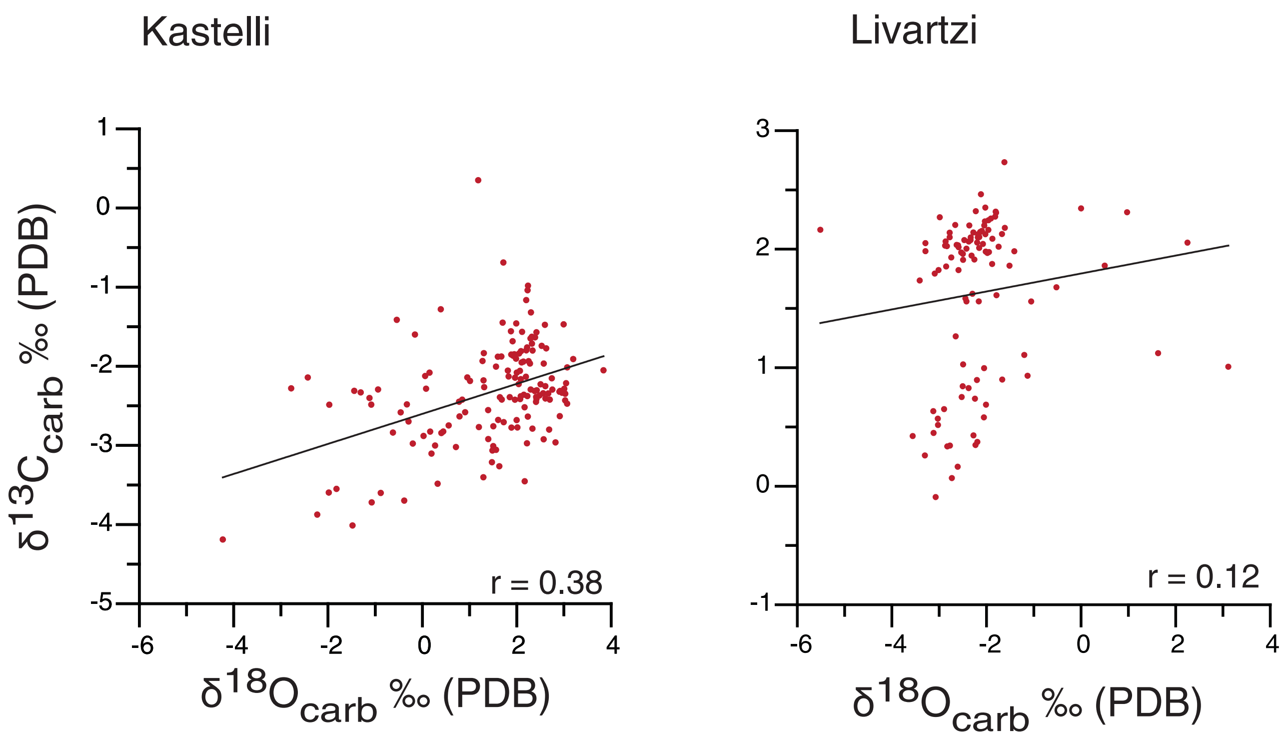

Figure 6. Cross-plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data from the Kastelli and Livartzi sections. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

Oxygen-isotope values are generally in the range of −2 ‰ (Fig. 5), which is a typical value for $\delta^{18}O$ in Tethyan Pliensbachian/Toarcian boundary carbonates, boreal belemnites and brachiopods (Jenkyns & Clayton, 1986; McArthur *et al.* 2000; Jenkyns *et al.* 2002; Rosales, Robles & Quesada, 2004; Suan *et al.* 2008). At the 8.5 m level of the section, there is a positive spike of about 2 ‰, above which there is a shift towards lighter values. The lighter values correspond stratigraphically to the negative excursion of the carbon isotopes. $\delta^{18}O$ values remain low and do not return to −2 ‰ until the 21.5 m level of the section. To what extent these carbonates record primary palaeotemperature signals and to what extent they have been modified by diagenesis is not known, but some primary signature is assumed, given the correlation with palaeotemperature trends established elsewhere in Europe (Bailey *et al.* 2003; Jenkyns, 2003). The cross-plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ values (Fig. 6) gives a Pearson's correlation coefficient value *r* of 0.38, which implies moderate correlation between oxygen- and carbon-isotopic values. If it is assumed that an increase in temperature (lowering $\delta^{18}O$ values) would follow from an introduction of isotopically light carbon in the ocean–atmosphere system (as CH_4 or CO_2), some correlation between $\delta^{18}O$ and $\delta^{13}C$ would be expected (e.g. Jenkyns, 2003).

5.b.2. *Livartzi section*

5.b.2.a. Organic carbon and carbonate profiles

The TOC values and the percentage of $CaCO_3$ in bulk rock are reported in Figure 7. In this section, the TOC values are even lower than those at Kastelli, ranging from undetectable to 0.6 wt %. Nevertheless, an interval of relatively high values is located between the 9.6 and 11.2 m levels. Above and below that interval, TOC values are close to zero. The $CaCO_3$ content of the section is in general relatively high (> 70 %), except for levels higher than that of the TOC maximum, where $CaCO_3$ values drop to less than 10 %.

5.b.2.b. Stable-isotope (carbon and oxygen) profiles

The carbonate carbon-isotope and the organic carbon-isotope stratigraphy of the Livartzi section are shown in Figure 7. This section has two distinct negative excursions. The $\delta^{13}C_{carb}$ in the Drimos Limestone Formation is very stable and constant at ∼2 ‰. Above the 3 m sampling gap, values drop until they reach a minimum of −0.09 ‰, then remain low for ∼1.5 m. Thereafter follows the second negative excursion that extends over a greater thickness of section (∼2 m) but only drops to 0.45 ‰. Towards the top of the section, $\delta^{13}C_{carb}$ values become higher.

The organic carbon-isotope profile approximately tracks the carbonate carbon-isotope profile, although there are differences. The $\delta^{13}C_{org}$ signal in the limestones of the lower part of the section shows scattered data points, probably because only isotopically variable refractory carbon is present, given the very low TOC values. Stratigraphically higher, just after the gap, the isotopic values are low, reaching the minimum value of −31.85 ‰. The values remain low for ∼1.5 m. Higher in the section there is an increase of 8.5 ‰, above which values begin to fall again through the rest of

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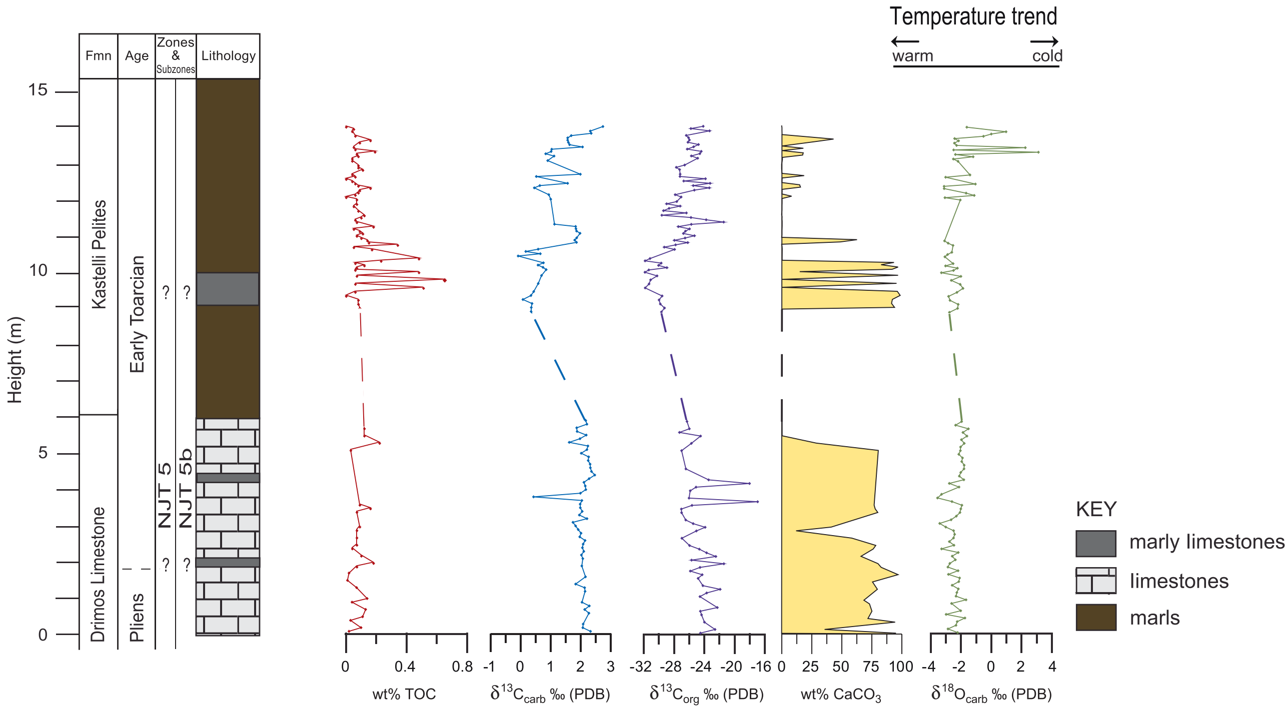

Figure 7. Lithostratigraphical log, bulk TOC, stable-isotope (C, O) and wt % $CaCO_3$ profiles through the Livartzi section. The dashed line represents a sampling gap. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

the section. In the upper part of the section the $\delta^{13}C_{org}$ values fluctuate around −25 ‰.

Oxygen-isotope values fluctuate in this section also around −2 ‰ (Fig. 7). There is a small negative spike of about 1 ‰ at the level of the first carbon-isotope negative excursion. Higher in the section, around the level of the second carbon-isotope negative excursion, the $\delta^{18}O$ values become heavier, reaching values up to ~4 ‰. The latter values are relatively high in comparison with other Tethyan Toarcian values. Moreover, as shown in Figure 6, the Pearson's correlation coefficient value of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ from this section is 0.12, which corresponds to a low degree of correlation between the isotopic values. Given the considerable difference between this and the Kastelli section, it is apparent that the $\delta^{18}O$ values have been modified by diagenesis and do not record a primary isotopic record.

6. Discussion

6.a. New biostratigraphic data based on calcareous nannofossils

In spite of the paucity of calcareous nannofossil assemblages recorded in the two studied sections, some significant biostratigraphic results are presented in this work that allow direct dating of the carbon-isotope curves from Kastelli and Livartzi in addition to correlation with biostratigraphically well-dated $\delta^{13}C$ records from elsewhere. Although the standard chronostratigraphy of the Jurassic is based upon ammonite biostratigraphy, an increasing number of works present effective correlation of the Early Toarcian negative isotope excursion (CIE) across the western Tethys based upon the ranges of calcareous nannofossils (Bucefalo Palliani, Mattioli & Riding, 2002; Mattioli *et al*. 2004, 2008; Tremolada, van de Schootbrugge & Erba, 2005; Mailliot *et al*. 2006, 2007; Bodin *et al*. 2010). In fact, the recognition of the NJT 6 nannofossil Zone in the Kastelli section allows unambiguous referral of the main negative CIE recorded in the Pindos Zone to the Early Toarcian and allows correlation with comparable phenomena associated with the Early Toarcian OAE in other NW European areas (Tremolada, van de Schootbrugge & Erba, 2005; Mattioli *et al*. 2008) as well as a section in N Africa (Bodin *et al*. 2010).

A preceding negative excursion of 2 ‰ below the main carbon-isotope excursion has been recorded in Peniche (Portugal) and constitutes a chemostratigraphic marker for the Pliensbachian/Toarcian boundary (Hesselbo *et al*. 2007). In the Kastelli section, the carbonate carbon-isotope profile starts with a positive excursion of ~1 ‰, and follows with a negative excursion of the same range. This negative excursion is not clearly dated by calcareous nannofossils in the Kastelli section, but it lies just below an interval assigned to the NJT 5 Zone, spanning the Late Pliensbachian–Early Toarcian interval. This negative excursion resembles those also observed at the stage boundary in Yorkshire (NE England), Valdorbia, (Marche–Umbria, Italy) and the High Atlas of Morocco, as recorded by Sabatino *et al*. (2009), Littler, Hesselbo & Jenkyns (2010) and Bodin *et al*. (2010). Given the occurrence of this feature in the Pindos Zone, this isotopic feature, as proposed by Hesselbo *et al*. (2007) as at least a regional marker, is likely be of global significance.

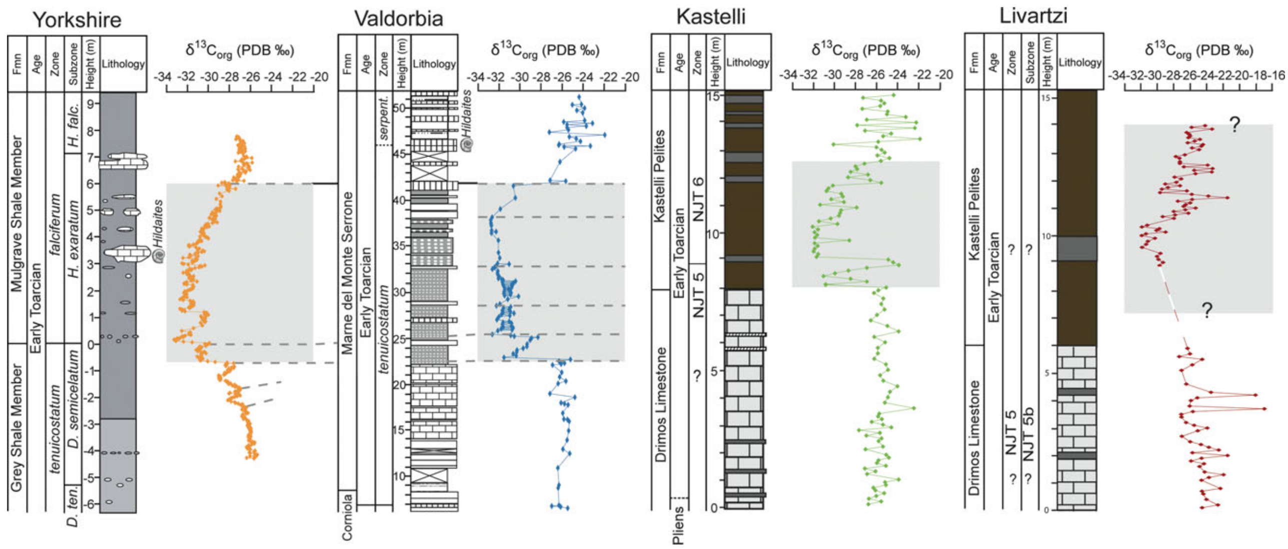

Figure 8. Comparison between the $\delta^{13}C_{org}$ data from Yorkshire, UK (Kemp *et al.* 2005), Valdorbia, Italy (Sabatino *et al.* 2009), and Kastelli and Livartzi, Greece. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

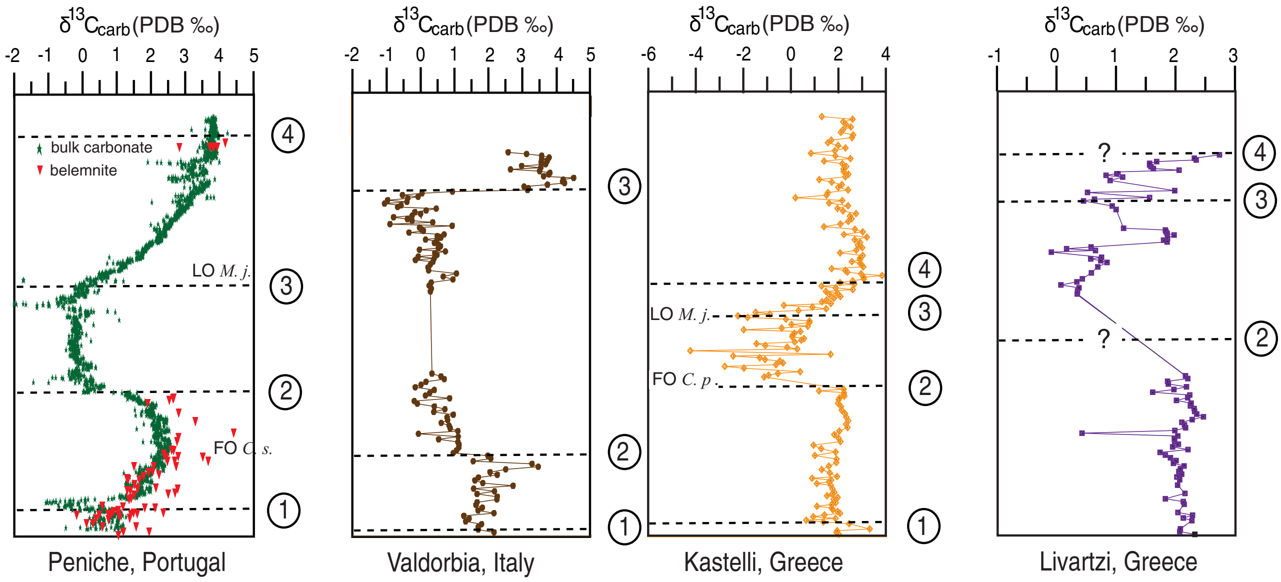

Figure 9. Comparison between the $\delta^{13}C_{carb}$ data from Peniche, Portugal (Hesselbo *et al.* 2007), Valdorbia, Italy (Sabatino *et al.* 2009), and Kastelli and Livartzi, Greece. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

6.b. The preservation of the organic matter

In both stratigraphic sections, the TOC content is very low, especially in Livartzi, where it does not exceed 1 %. TOC values in the Toarcian black shales of northern Europe are much higher, rising to ∼15 %, probably because of relatively elevated organic productivity, a high degree of water mass stratification, local euxinic conditions and lesser water depth (Jenkyns *et al.* 2002; Sabatino *et al.* 2009; Jenkyns, 2010). The palaeodepth of the Pindos Ocean was probably greater than that of typical Tethyan continental margins, as preserved in the Alps and the Apennines, and certainly greater than the epicontinental seas of northern Europe. With greater palaeodepths, organic matter would have had a greater transit distance and transit time to the sea floor, thus increasing the chance of oxidation before burial.

6.c. European correlation of the carbon-isotope record and implications for the regional character of the OAE

Suggested chemostratigraphic correlations between the Greek sections in the Pindos Zone and other extensively studied sections in Europe are illustrated in Figures 8 and 9. In Figure 8, the correlation is based mostly on the $\delta^{13}C_{org}$ data from Yorkshire, Valdorbia, Kastelli and Livartzi, whereas in Figure 9, correlation is based mostly on the $\delta^{13}C_{carb}$ data from Peniche, Valdorbia, Kastelli and Livartzi, using the four 'key' levels described by Hesselbo *et al.* (2007).

In Figure 8, the grey band and the dashed lines in the Yorkshire and Valdorbia profiles are based on $\delta^{13}C_{org}$ data and their spectral analyses, whereas the comparison between these two sections and the Greek sections is based only on the shape of the

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carbon-isotope excursion. In all four compared sections, the negative carbon-isotope excursion has a similar range of values, but each profile differs in detail. The Greek sections have a relatively small negative excursion in $\delta^{13}C_{org}$ of ~ -5 ‰, after which values return to background values (~ -25 ‰). The grey band in the Greek sections marks the extent of the negative carbon-isotope excursion, which covers most, but not all, of the OAE interval, as defined in Yorkshire (Jenkyns, 2010). A suggested correlation between the Kastelli, Valdorbia and Peniche sections (Fig. 9) includes the Pliensbachian/Toarcian excursion (Level 1). Level 1 is not recognizable in the Livartzi section.

In both the Kastelli and Livartzi sections, the positive shift that is marked in Peniche directly above Level 1 is subdued. Level 2 is marked in all sections by the beginning of the negative carbon-isotope excursion. In Peniche, Level 2 is located at the *polymorphum–levisoni* zonal boundary and occurs above the first occurrence (FO) of the nannofossil *Carinolithus superbus* and *Carinolithus poulnabronei* (Mailliot *et al*. 2007). The nannofossil zone of *C. superbus* (referred to as NJT 6) has been suggested to coincide with the OAE (Mattioli *et al*. 2004). In the Kastelli section, the FO of *C. poulnabronei*, whose first occurrence is stratigraphically very close to that of *C. superbus* (Mattioli & Erba, 1999; Mailliot *et al*. 2007), is located in Level 2, although the lack of carbonate in adjacent parts of the section introduces some stratigraphic uncertainty. Neither the beginning of the negative carbon-isotope excursion nor the NJT 6 Zone is apparent in the Livartzi section; we therefore can only place Level 2 approximately at this location.

Level 3 in Peniche and Valdorbia is where $\delta^{13}C_{carb}$ values reach a minimum and thereafter begin to increase. In Peniche, this level corresponds also to the TOC maximum (Hesselbo *et al*. 2007) whereas, in the other three sections, TOC values have already reached background values at this level. In Peniche, the last occurrence (LO) of *Mitrolithus jansae* is marked slightly above Level 3 (Mattioli *et al*. 2008), whereas in Kastelli, it corresponds to Level 3. The top of the section in Peniche is marked as Level 4 and it correlates with the end of the negative excursion and this can also be identified in the Kastelli section, although it is less clear-cut in the Livartzi section.

Although there is some minor diachroneity in nannofossil first and last occurrence datum levels with respect to the $\delta^{13}C$ record, a striking correlation is documented in this study between the different isotope levels occurring across the negative carbon-isotope excursion in the Kastelli Pelites and other, more fossiliferous ammonite-bearing sections, underscoring the widespread nature of the event (Jenkyns *et al*. 1985, 2002; Jenkyns & Clayton, 1986, 1997; Mattioli *et al*. 2008; Sabatino *et al*. 2009).

7. Conclusions

Integrated chemostratigraphy and biostratigraphy confirm for the first time the age of the Kastelli Pelites of the Pindos Zone in Greece. They were formed during the Early Toarcian OAE and belong to the NJT 6 nannofossil Zone, correlative with the *tenuicostatum–falciferum* zones of northern Europe or its equivalents in southern Europe (*tenuicostatum/polymorphum–falciferum/serpentinum/levisoni* zones). The record of the T-OAE from these deep-marine sediments, which were part of the Tethyan Ocean, strongly supports the postulated global character of the T-OAE. The stratigraphic distribution of nannofossils and the shape of the negative carbon-isotope excursion differ from some different European sections, suggesting a degree of regional environmental control and/or diagenetic effects. The carbon-isotope profile from Kastelli resembles that of Valdorbia, Marche–Umbria, Italy (Sabatino *et al*. 2009), whereas that from Livartzi resembles that of Yorkshire, NE England (Kemp *et al*. 2005). The small negative excursion in carbon isotopes recently recorded at the Pliensbachian/Toarcian boundary in Peniche, Portugal, in Valdorbia, Italy, the High Atlas of Morocco and in Yorkshire, England, is also identified in the type section of the Kastelli Pelites.

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