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

N. KAFOUSIA*†, V. KARAKITSIOS*, H. C. JENKYNS‡ & E. MATTIOLI§

*Department of Geology and Geoenvironment, National University of Athens, Panepistimiopolis, 15784 Athens, Greece
‡Department of Earth Sciences, University of Oxford, South Parks Road, Oxford OX1 3AN, UK
§Université Claude Bernard Lyon I, UMR 5125, CNRS, PaléoEnvironnements et PaléobioSphère, Département des Sciences de la Terre, 2 rue Dubois, 69622 Villeurbanne, France

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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).

†Author for correspondence: nkafousia@geol.uoa.gr

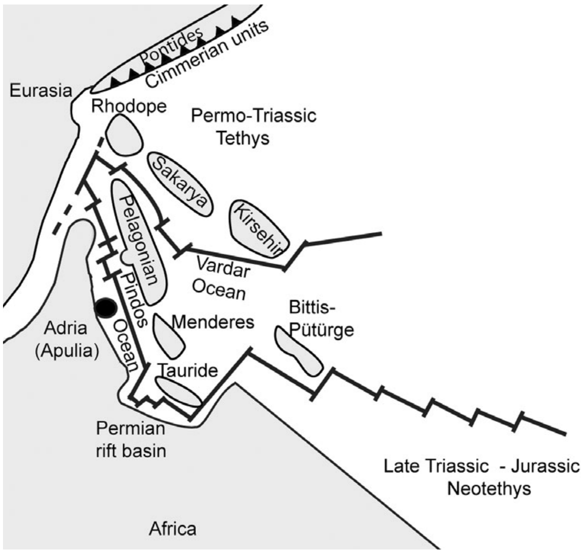

Figure 1. Early Jurassic palaeogeography of the western Tethys Ocean (based on Clift, 1992; Dercourt, Ricou & Vriellynck, 1993; Channell & Kozur, 1997; Degnan & Robertson, 1998; Pe-Piper, 1998). The approximate position of the study area is illustrated by the black circle. The stable segment of Adria 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

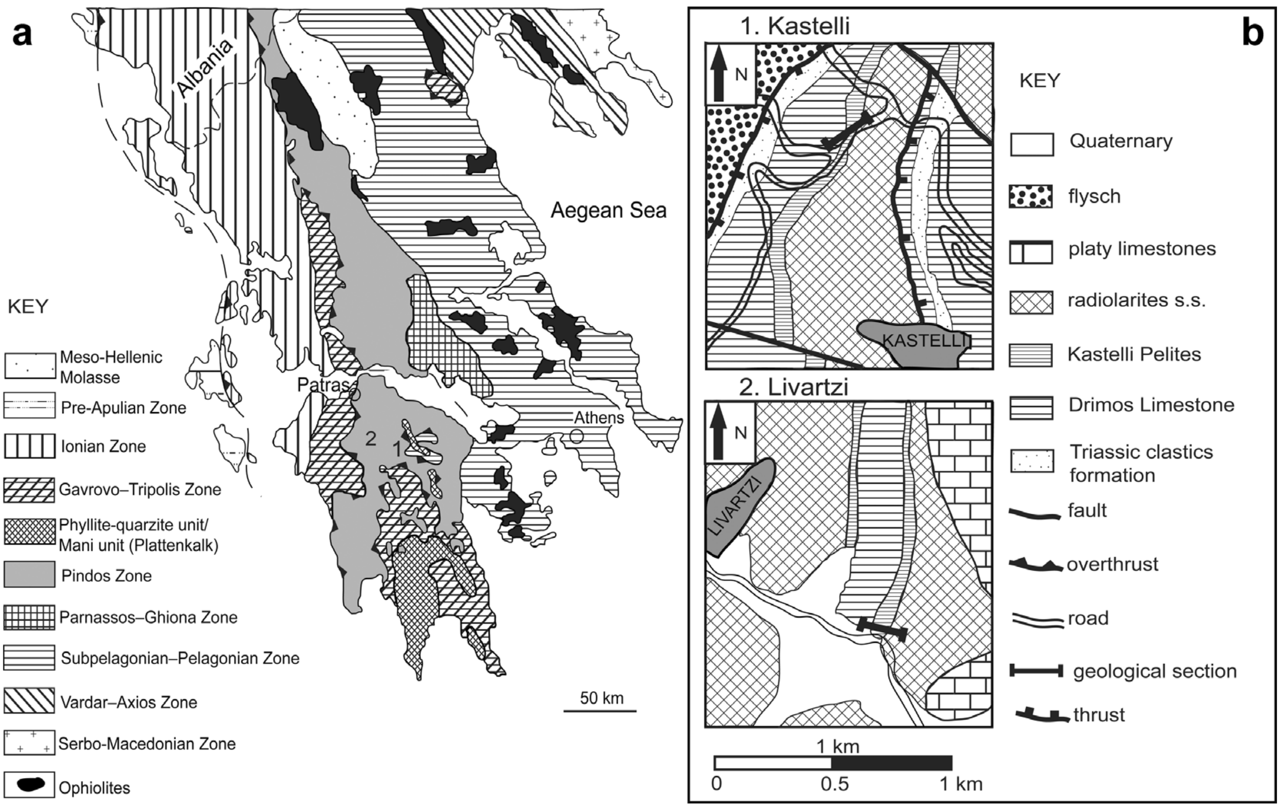

Figure 2. (a) Simplified geological map with the main tectonostratigraphic zones of the Hellenides. (b) Geological map of Kastelli section (above) and Livartzi section (below).

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

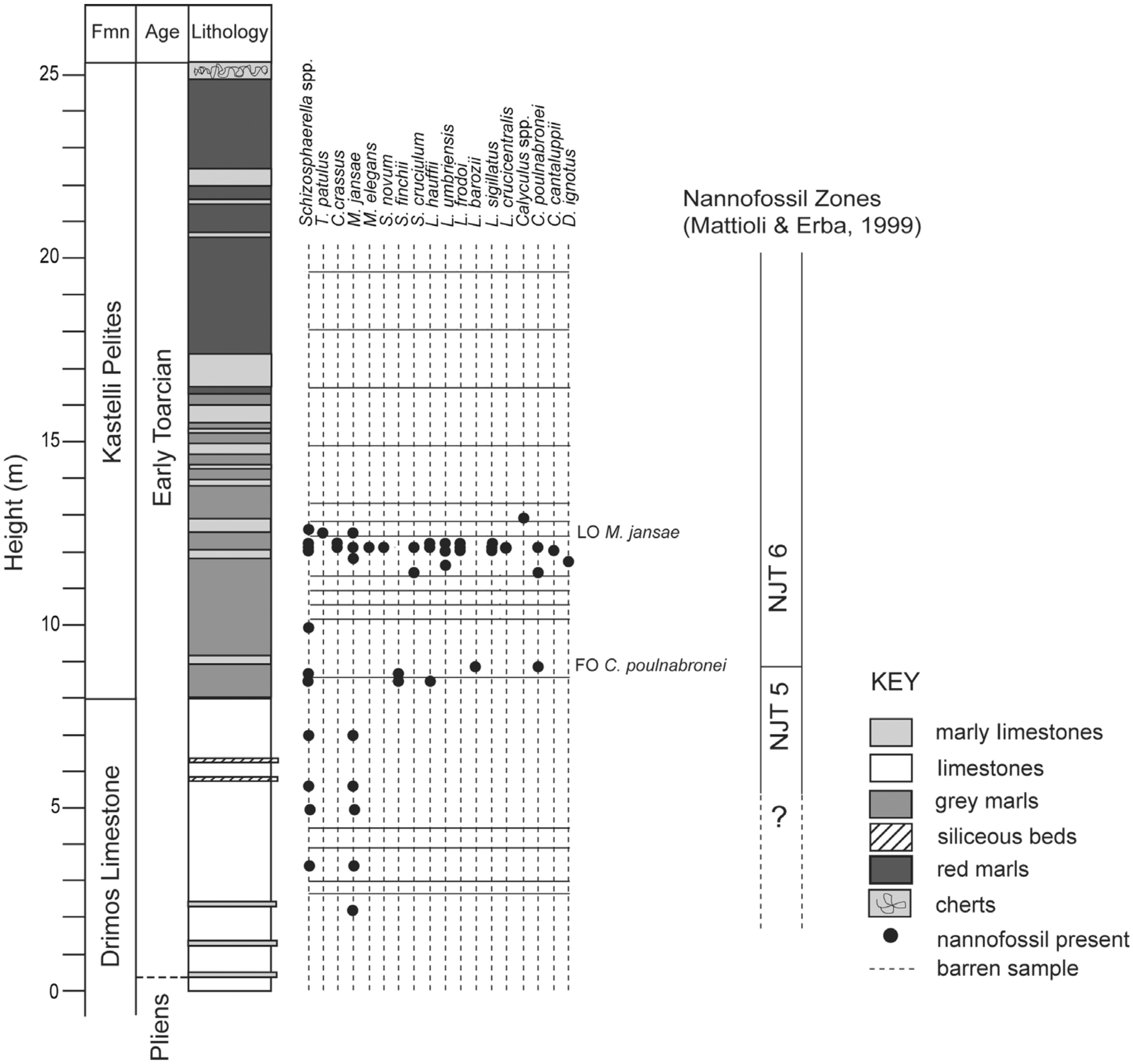

Figure 3. Lithological column and biostratigraphical data from the Kastelli section. Nannofossil zones after Mattioli & Erba (1999).

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

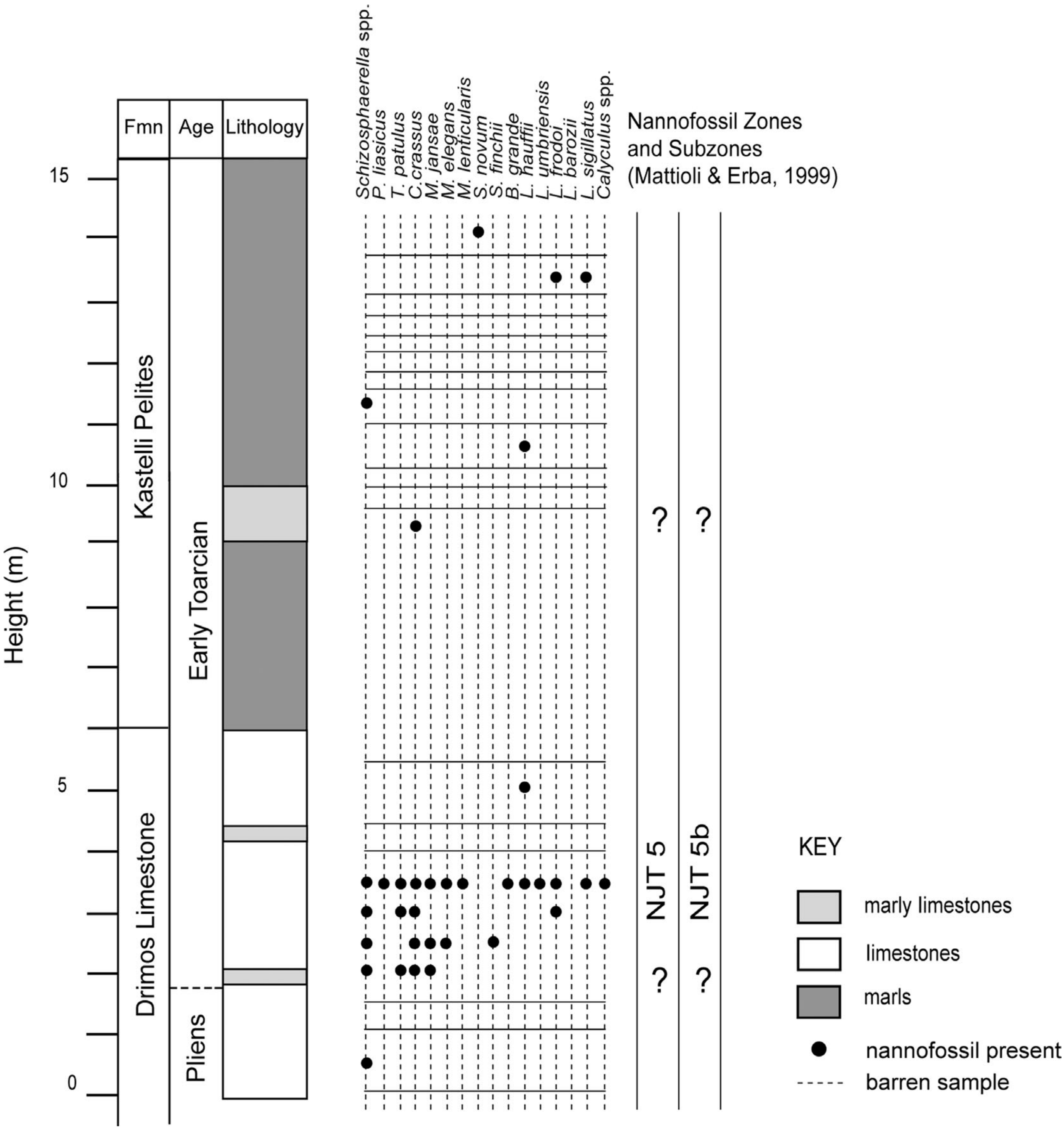

Figure 4. Lithological column and biostratigraphical data from the Livartzi section. Nannofossil zones after Mattioli & Erba (1999).

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

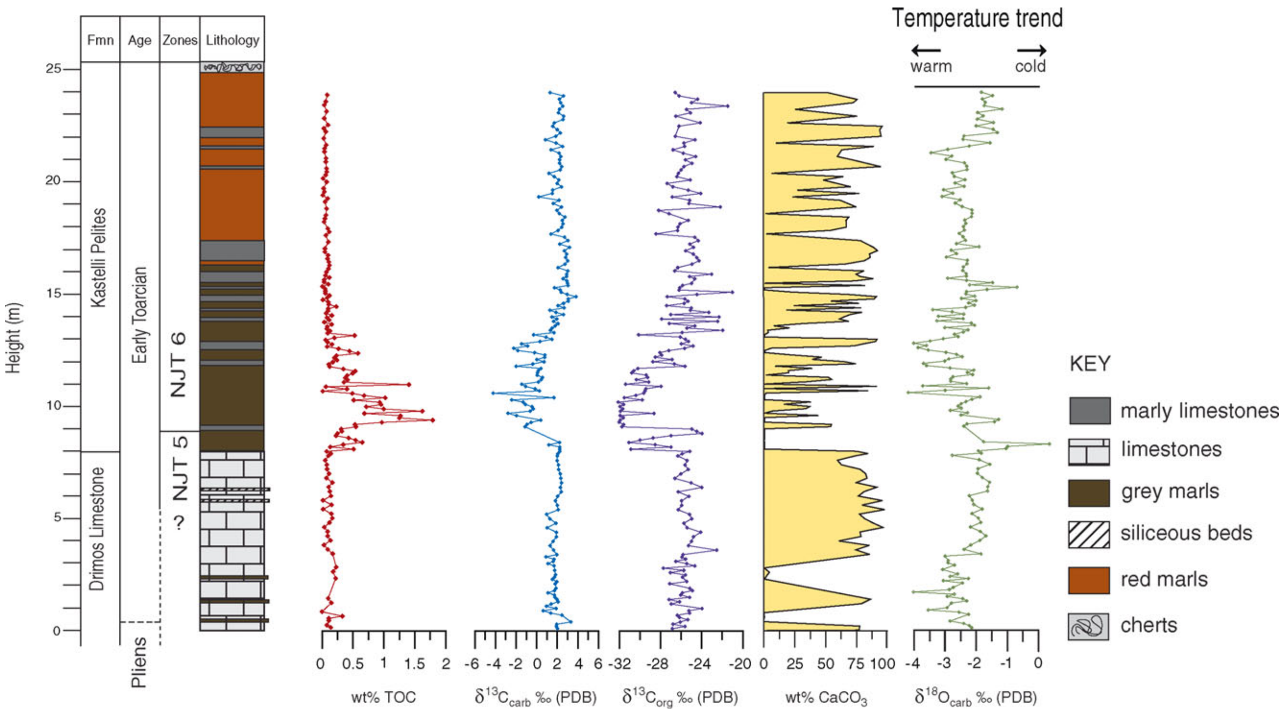

Figure 5. Lithostratigraphical log, bulk TOC, stable-isotope (C, O) and wt % $CaCO_3$ profiles through the Kastelli section. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

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 ‰.

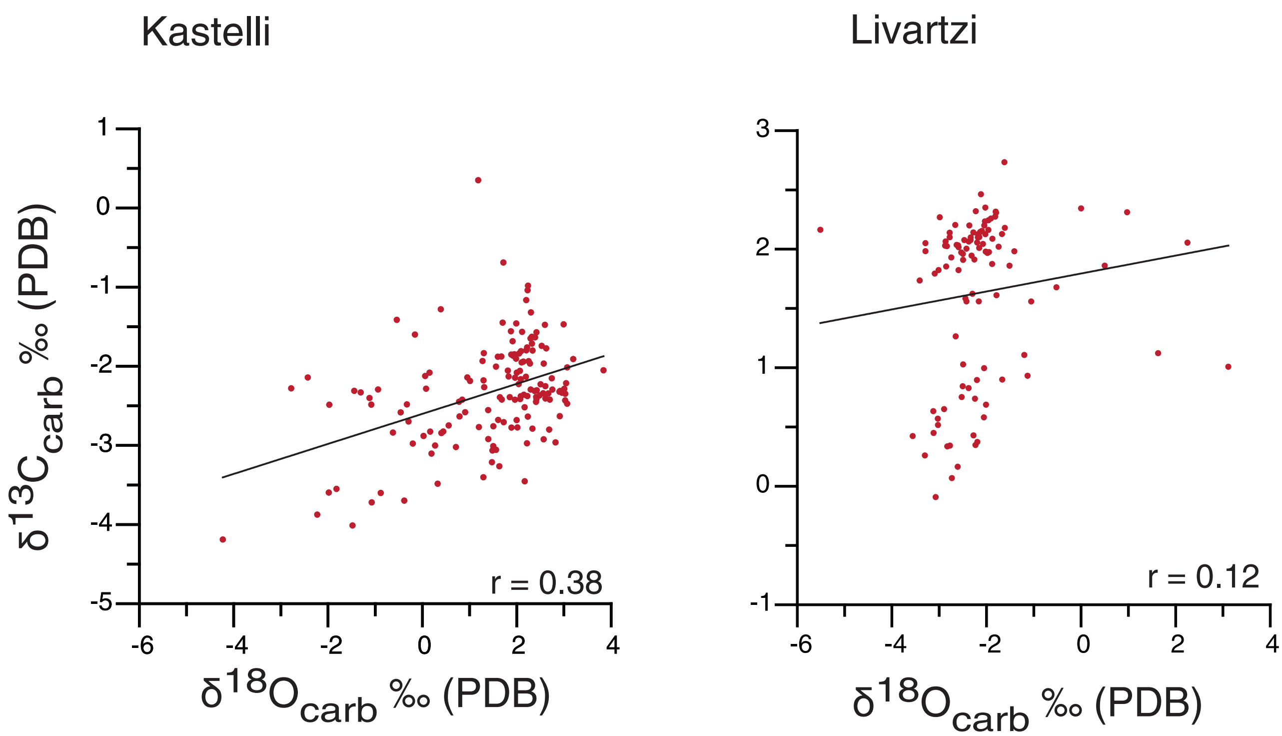

Figure 6. Cross-plot of $\delta^{13}C_{carb}$ and $\delta^{18}O_{carb}$ data from the Kastelli and Livartzi sections. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

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

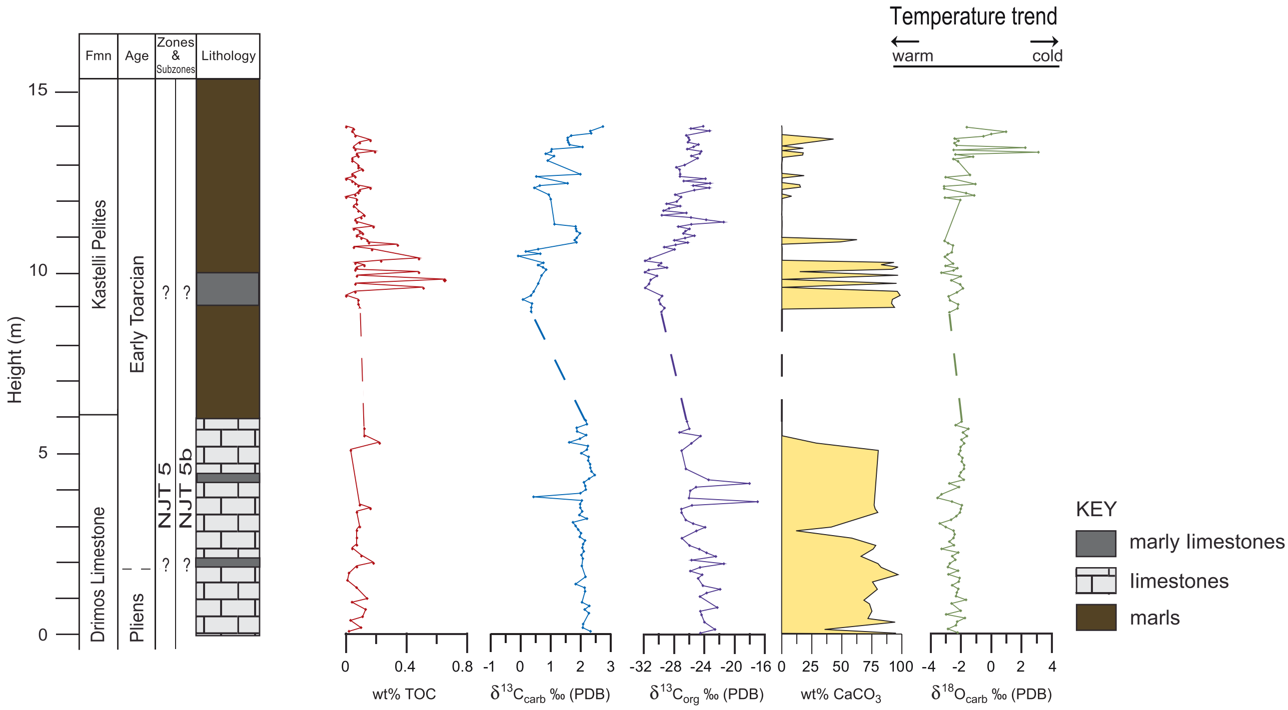

Figure 7. Lithostratigraphical log, bulk TOC, stable-isotope (C, O) and wt % $CaCO_3$ profiles through the Livartzi section. The dashed line represents a sampling gap. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

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.

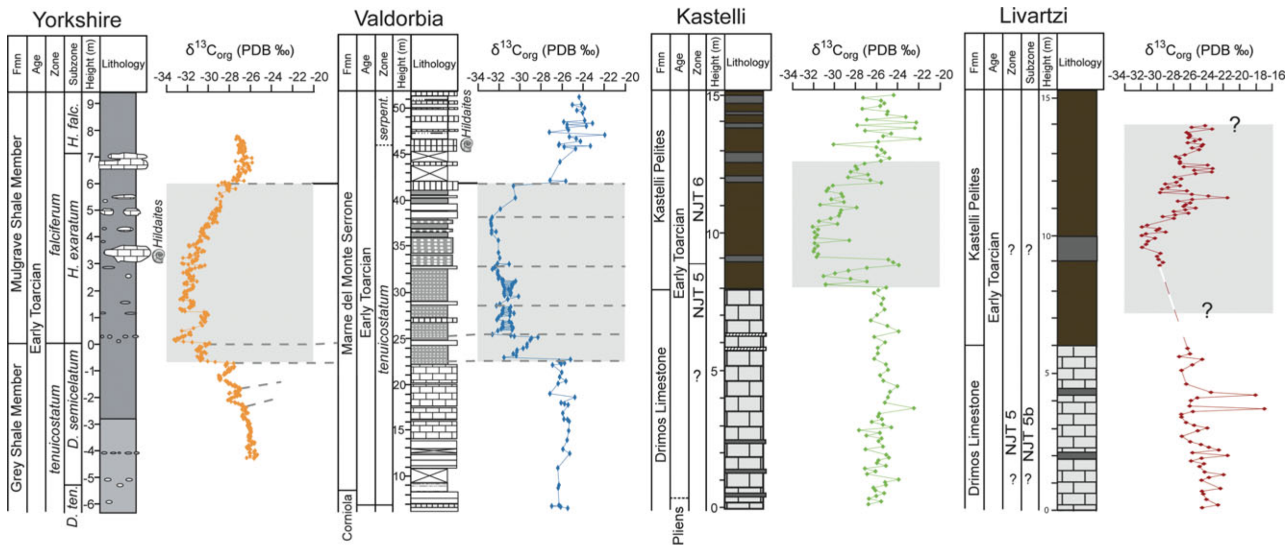

Figure 8. Comparison between the $\delta^{13}C_{org}$ data from Yorkshire, UK (Kemp *et al.* 2005), Valdorbia, Italy (Sabatino *et al.* 2009), and Kastelli and Livartzi, Greece. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

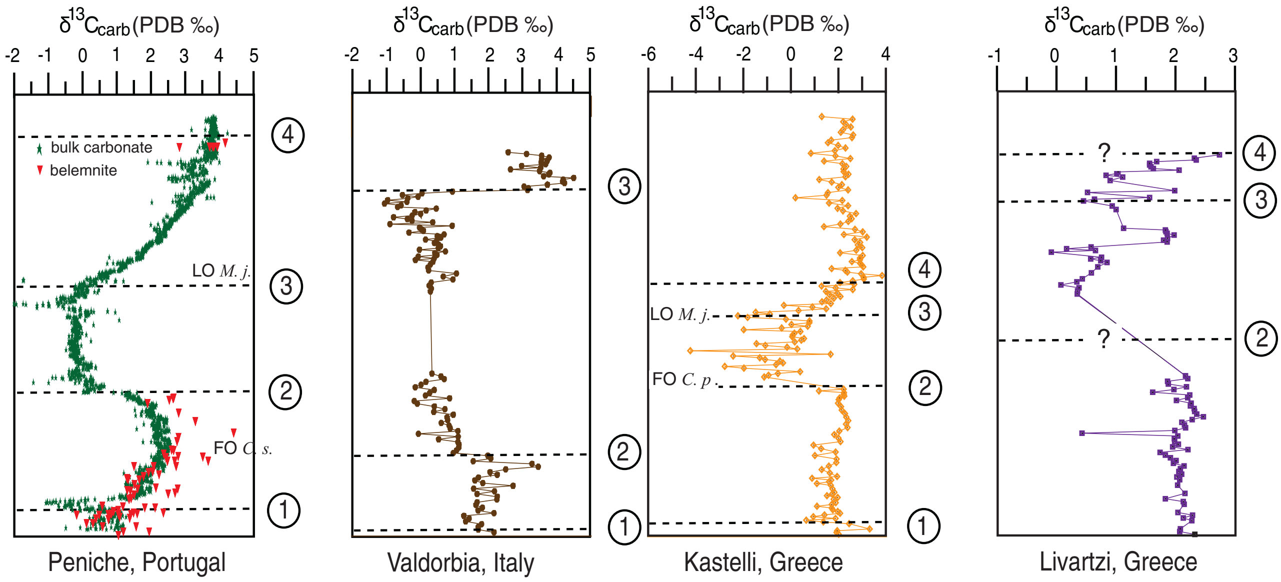

Figure 9. Comparison between the $\delta^{13}C_{carb}$ data from Peniche, Portugal (Hesselbo *et al.* 2007), Valdorbia, Italy (Sabatino *et al.* 2009), and Kastelli and Livartzi, Greece. For a colour version of this figure see online Appendix at http://journals.cambridge.org/geo.

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 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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References

AL-SUWAIDI, A. H., ANGELOZZI, G. N., BAUDIN, F., DAMBORENEA, S. E., HESSELBO, S. P., JENKYNS, H. C., MANCEÑIDO, M. O., & RICCARDI, A. C. 2010. First record of the Early Toarcian Oceanic Anoxic Event from the Southern Hemisphere, Neuquén Basin, Argentina. *Journal of the Geological Society, London* **167**, 633–6.

ARGYRIADIS, I., DE GRACIANSKY, P. C., MARCOUX, J. & RICOU, L. E. 1980. The opening of the Mesozoic Tethys between Eurasia and Arabia-Africa. In *Géologie des chaînes alpines issues de la Téthys* (eds J. Aubouin, J. Debelmas & M. Latreille), pp. 199–214. 26th International Geological Congress, Paris, Colloque C5. *Bureau de Recherches Géologiques et Minières Mémoire*, **115**.

AUBOUIN, J., BONNEAU, M., DAVIDSON, G. J., LEBOULENGER, P., MATESKO, S. & ZAMBETAKIS, A. 1976. Esquisse structurale de l'Arc égéen externe: des Dinarides aux Taurides. *Bulletin de la Societé géologique de France*, 7e série **18**, 327–36.

BAILEY, T. R., ROSENTHAL, Y., MCARTHUR, J. M. & VAN DE SCHOOTBRUGGE, B. 2003. Paleoceanographic changes of the Late Pliensbachian-Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event. *Earth and Planetary Science Letters* **212**, 307–20.

BERNOULLI, D., De GRACIANSKY, P. C. D. & MONOD, O. 1974. The extension of the Lycian Nappes (SW Turkey) into the Southeastern Aegean Islands. *Eclogae Geologicae Helvetiae* **67**, 39–90.

BERNOULLI, D. & JENKYNS, H. C. 1974. Alpine, Mediterranean and central Atlantic Mesozoic facies in relation to the early evolution of the Tethys. In *Modern and Ancient Geosynclinal Sedimentation* (eds R. H. Dott Jr. & R. H. Shaver), pp. 129–60. Society of Economic Paleontologists and Mineralogists, Special Publication 19.

BERNOULLI, D. & JENKYNS, H. C. 2009. Ancient oceans and continental margins of the Alpine-Mediterranean Tethys: deciphering clues from Mesozoic pelagic sediments and ophiolites. *Sedimentology* **56**, 149–90.

BERNOULLI, D. & RENZ, O. 1970. Jurassic carbonate facies and new ammonite faunas from western Greece. *Eclogae Geologicae Helvetiae* **65**, 573–607.

BODIN, S., MATTIOLI, E., FRÖHLICH, S., MARSHALL, J. D., BOUTIB, L., LAHSINI, S. & REDFERN, J. 2010. Toarcian carbon isotope shifts and nutrient changes from the Northern margin of Gondwana (High Atlas, Morocco, Jurassic): palaeoenvironmental implications. *Palaeogeography, Palaeoclimatology, Palaeoecology* **297**, 377–90.

BONNEAU, M. 1982. Evolution géodynamique de l'Arc égéen depuis le Jurassique supérieur jusqu'au Miocène. *Bulletin de la Societé géologique de France*, 7e série **24**, 229–42.

BONNEAU, M. 1984. Correlation of the Hellenide nappes in the south-east Aegean and their tectonic reconstruction. In *The geological Evolution of the Eastern Mediterranean* (eds J. E. Dixon, & A. H. F. Robertson), pp. 517–52. Geological Society of London, Special Publication no. 17.

BOWN, P. R. & YOUNG, J. R. 1998. Chapter 2: techniques. In *Calcareous Nannofossil Biostratigraphy* (ed. P. R. Bown), pp. 16–28. Dordrecht: Kluwer Academic Publishing.

BUCEFALO PALLIANI, R. & MATTIOLI, E. 1998. High resolution integrated microbiostratigraphy of the Lower Jurassic (Late Pliensbachian–Early Toarcian) of Central Italy. *Journal of Micropalaeontology* **17**, 153–72.

BUCEFALO PALLIANI, R., MATTIOLI, E. & RIDING, J. 2002. The response of marine phytoplankton and sedimentary organic matter to the early Toarcian (Lower Jurassic) oceanic anoxic event in northern England. *Marine Micropaleontology* **46**, 223–45.

CHANNELL, J. E. T. & KOZUR, H. W. 1997. How many oceans? Meliata, Vardar, and Pindos oceans in Mesozoic Alpine paleogeography. *Geology* **25**, 183–6.

CLIFT, P. D. 1992. The collision tectonics of the southern Greek Neotethys. *Geologische Rundschau* **81**, 669–79.

DE WEVER, P. 1976. Mise en évidence d'importants affleurements de roches éruptives à la base de la nappe du Pinde-Olonos au sein de la 'Formation à Blocs' (Péloponnése, Gréce). *Annales de la Societé Géologique du Nord* **97**, 123–6.

DE WEVER, P. & BAUDIN, F. 1996. Palaeogeography of radiolarite and organic-rich deposits in Mesozoic Tethys. *Geologische Rundschau* **85**, 310–26.

DE WEVER, P. & ORIGLIA-DEVOS, I. 1982. Datation par les radiolaires des niveaux siliceux du Lias de la Série du Pinde–Olonos (Formation de Drimos, Péloponnèse et Grèce continentale). *Comptes Rendus de l'Académie des Sciences, Paris, Série 2* **294**, 1191–8.

DÉDÉ, S., CILI, P., BUSHI, E. & MAKBUL, Y. 1976. Traits fondamentaux de la tectonique de Cukal. *Permbledhje Studimesh* **20/4**, 15–33.

DEGNAN, P. J. & ROBERTSON, A. H. F. 1998. Mesozoic–early Tertiary passive margin evolution of the Pindos Ocean (NW Peloponnese, Greece). *Sedimentary Geology* **117**, 33–70.

DERCOURT, J., RICOU, L. E. & VRIELLYNCK, B. (eds) 1993. *Atlas Tethys Palaeoenvironmental Maps*. Paris: Gauthier-Villars, 307 pp.

FLEURY, J. J. 1980. Les zones de Gavrovo-Tripolitza et du Pinde-Olonos (Grèce continentale et Péloponèse du nord). Evolution d'une plate-forme et d'un bassin dans leur cadre alpin. *Société Géologique du Nord, Publication* **4**, 1–473.

HERMOSO, M., Le CALLONEC, L., MINOLATTI, F., RENARD, M. & HESSELBO, S. P. 2009. Expression of the Early Toarcian negative carbon-isotope excursion in separated carbonate microfractions (Jurassic, Paris Basin). *Earth and Planetary Science Letters* **277**, 194–203.

HESSELBO, S. P., GRÖCKE, D. R., JENKYNS, H. C., BJERRUM, C. J., FARRIMOND, P., MORGANS BELL, H. S. & GREEN, O. R. 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature* **406**, 392–5.

HESSELBO, S. P., JENKYNS, H. C., DUARTE, L. V. & OLIVEIRA, L. C. V. 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth and Planetary Science Letters* **253**, 455–70.

JENKYNS, H. C. 1985. The Early Toarcian and Cenomanian–Turonian anoxic events in Europe: comparisons and contrasts. *Geologische Rundschau* **74**, 505–18.

JENKYNS, H. C. 1988. The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary, and geochemical evidence. *American Journal of Science* **288**, 101–51.

JENKYNS, H. C. 2003. Evidence for rapid climate change in the Mesozoic–Palaeogene greenhouse world. *Philosophical Transactions of the Royal Society London, Series A* **361**, 1885–916.

JENKYNS, H. C. 2010. The geochemistry of Oceanic Anoxic Events. *Geochemistry, Geophysics, Geosystems* **11**, Q03004, doi:10.1029/2009GC002788, 30 pp.

JENKYNS, H. C. & CLAYTON, C. J. 1986. Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. *Sedimentology* **33**, 87–106.

JENKYNS, H. C. & CLAYTON, C. J. 1997. Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology* **44**, 687–706.

JENKYNS, H. C., GALE, A. S. & CORFIELD, R. M. 1994. Carbon- and oxygen-isotope stratigraphy of the English Chalk and Italian Scaglia and its palaeoclimatic significance. *Geological Magazine* **131**, 1–34.

JENKYNS, H. C., GRÖCKE, D. R. & HESSELBO, S. P. 2001. Nitrogen isotope evidence for water mass denitrification during the Early Toarcian (Jurassic) Oceanic Anoxic Event. *Paleoceanography* **16**, 593–603.

JENKYNS, H. C., JONES, C. E., GRÖCKE, D. R., HESSELBO, S. P. & PARKINSON, D. N. 2002. Chemostratigraphy of the Jurassic System: applications, limitations and implications for palaeoceanography. *Journal of the Geological Society, London* **159**, 351–78.

JENKYNS, H. C., MATTHEWS, A., TSIKOS, H. & EREL, Y. 2007. Nitrate reduction, sulfate reduction, and sedimentary iron isotope evolution during the Cenomanian-Turonian oceanic anoxic event. *Paleoceanography* **22**, PA3208, doi: 10.1029/2006PA001355, pp. 17

JENKYNS, H. C., SARTI, M., MASETTI, D. & HOWARTH, M. K. 1985. Ammonites and stratigraphy of Lower Jurassic black shales and pelagic limestones from the Belluno Trough, Southern Alps, Italy. *Eclogae Geologicae Helvetiae* **78**, 299–311.

KARAKITSIOS, V. 1995. The influence of preexisting structure and halokinesis on organic matter preservations and thrust system evolution in the Ionian Basin, Northwest Greece. *American Association of Petroleum Geologists Bulletin* **79**, 960–80.

KARAKITSIOS, V., TSIKOS, H., VAN BREUGEL, Y., BAKOPOULOS, I. & KOLETTI, L. 2004. Cretaceous Oceanic Anoxic Events in Western Continental Greece. *Bulletin of the Geological Society of Greece* **36**, 846–55.

KARAKITSIOS, V., TSIKOS, H., VAN BRUEGEL, Y., KOLETTI, L., SINNINGHE DAMSTÉ, J. S. & JENKYNS, H. C. 2007. First evidence for the late Cenomanian Oceanic Anoxic Event (OAE2, or 'Bonarelli' event) from the Ionian Zone, western continental Greece. *International Journal of Earth Sciences (Geol. Rundsch.)* **96**, 343–52.

KEMP, D. B., COE, A. L., COHEN, A. S. & SCHWARK, L. 2005. Astronomical pacing of methane release in the Early Jurassic period. *Nature* **437**, 396–9.

KÜSPERT, W. 1982. Environmental changes during oil shale deposition as deduced from stable isotope ratios. In *Cyclic and Event Stratification* (eds G. Einsele & A. Seilacher), pp. 482–501. Berlin: Springer-Verlag.

LEFÈVRE, C., CABANIS, B., FERRIÈRE, J., THIEBAULT, F. & PLATEVOET, R. 1993. Mise en évidence d'une dualité dans le volcanisme triasique hellénique: apport de la géochimie des éléments traces. *Comptes Rendus de l'Académie des Sciences, Paris, Série 2* **316**, 1311–18.

LITTLE, C. T. S. & BENTON, M. J. 1995. Early Jurassic mass extinction: a global long-term event. *Geology* **23**, 495–8.

LITTLER, K., HESSELBO, S. P. & JENKYNS, H. C. 2010. A carbon-isotope perturbation at the Pliensbachian–Toarcian boundary: evidence from the Lias Group, NE England. *Geological Magazine* **147**, 181–92.

LYBERIS, N., CHOTIN, P. & DOUBINGER, J. 1980. Précisions stratigraphiques sur la série du Pinde (Grèce): la durée de sédimentation des 'radiolarites'. *Comptes Rendus de l'Académie des Sciences, Paris, série D* **290**, 1513–16.

MAILLIOT, S., ELMI, S., MATTIOLI, E. & PITTET, B. 2007. Calcareous nannofossil assemblages across Pliensbachian/Toarcian boundary at the Peniche section (Ponta do Trovão, Lusitanian Basin). *Ciências da Terra (Lisbon)* **16**, 1–14.

MAILLIOT, S., MATTIOLI, E., GUEX, J. & PITTET, B. 2006. The Early Toarcian Anoxic Crisis, a synchronous event in the Western Tethys? An approach by Quantitative Biochronology (Unitary Associations), applied on calcareous nannofossils. *Palaeogeography, Palaeoclimatology, Palaeoecology* **240**, 562–86.

MATTIOLI, E. & ERBA, E. 1999. Synthesis of calcareous nannofossil events in Tethyan Lower and Middle Jurassic successions. *Rivista Italiana di Paleontologia e Stratigrafia* **105**, 343–76.

MATTIOLI, E., PITTET, B., BUCEFALO PALLIANI, R., RÖHL, H.-J., SCHMID- RÖHL, A., MORETTINI, E., MORGANS-BELL, H. S. & COHEN, A. S. 2004. Phytoplankton evidence for the timing and correlation of palaeoceanographical changes during the early Toarcian oceanic anoxic event (Early Jurassic). *Journal of the Geological Society, London* **161**, 685–93.

MATTIOLI, E., PITTET, B., SUAN, G. & MAILLOT, S. 2008. Calcareous nannoplankton changes across the early Toarcian oceanic anoxic event in the western Tethys. *Paleoceanography* **23**, PA3208, doi:10.1029/2007PA001435, pp. 17

MCARTHUR, J. M., DONOVAN, D. T., THIRLWALL, M. F., FOUKE, B. W. & MATTEY, D. 2000. Strontium isotope profile of the early Toarcian (Jurassic) oceanic anoxic event, the duration of ammonite biozones, and belemnite palaeotemperatures. *Earth and Planetary Science Letters* **179**, 269–85.

PE-PIPER, G. 1998. The nature of Triassic extension-related magmatism in Greece: evidence from Nd and Pb isotope geochemistry. *Geological Magazine* **135**, 331–48.

PE-PIPER, G. & HATZIPANAGIOTOU, K. 1993. Ophiolitic rocks of the Kerassies-Milia Belt, continental Greece. *Ofioliti* **18**, 157–69.

RIGAKIS, N. & KARAKITSIOS, V. 1998. The source rock horizons of the Ionian Basin (NW Greece). *Marine and Petroleum Geology* **15**, 593–617.

ROBERTSON, A. H. F., CLIFT, P. D., DEGNAN, P. J. & JONES, G. 1991. Palaeogeographic and palaeotectonic evolution of the Eastern Mediterranean Neotethys. *Palaeogeography, Palaeoclimatology, Palaeoecology* **87**, 289–343.

ROBERTSON, A. H. F. & KARAMATA, S. 1994. The role of subduction-accretion processes in the tectonic evolution of the Mesozoic Tethys in Serbia. *Tectonophysics* **234**, 73–94.

RÖHL, H.-J., SCHMID-RÖHL, A., OSCHMANN, W., FRIMMEL, A. & SCHWARK, L. 2001. The Posidonia Shale (Lower Toarcian) of SW-Germany: an oxygen-depleted ecosystem controlled by sea level and palaeoclimate. *Palaeogeography, Palaeoclimatology, Palaeoecology* **165**, 27–52.

ROSALES, I., ROBLES, S. & QUESADA, S. 2004. Elemental and oxygen isotope composition of Early Jurassic belemnites; salinity vs. temperature signals. *Journal of Sedimentary Research* **74**, 342–54.

SABATINO, N., NERI, R., BELLANCA, A., JENKYNS, H. C., BAUDIN, F., PARISI, G. & MASETTI, D. 2009. Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria-Marche Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. *Sedimentology* **56**, 1307–28.

SCHOUTEN, S., Van KAAM-PETERS, H. M. E., RIJPSTRA, W. I. C., SCHOELL, M. & SINNINGHE DAMSTÉ, J. S. 2000. Effects of an oceanic anoxic event on the stable carbon isotopic composition of Early Toarcian carbon. *American Journal of Science* **300**, 1–22.

SUAN, G., MATTIOLI, E., PITTET, B., LÉCUYER, C., SUCHÉRAS-MARX, B., DUARTE, L. V., PHILIPPE, M., REGGIANI, L. & MARTINEAU, F. 2010. Secular environmental precursors to Early Toarcian (Jurassic) extreme climate changes. *Earth and Planetary Science Letters* **290**(3–4), 448–58.

SUAN, G., MATTIOLI, E., PITTET, B., MAILLIOT, S. & LECUYER, C. 2008. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oceanic anoxic event from the Lusitanian Basin, Portugal. *Paleoceanography* **23**, PA1202, doi: 10.1029/2007PA001459, pp. 14

SVENSEN, H., PLANKE, S., CHEVALLIER, L., MALTHE-SØRENSEN, A. CORFU, F. & JAMTVEIT, B. 2007. Hydrothermal venting of greenhouse gases triggering Early Jurassic global warming. *Earth and Planetary Science Letters* **256**, 554–66.

TREMOLADA, F., VAN DE SCHOOTBRUGGE, B. & ERBA, E. 2005. Early Jurassic schizosphaerellid crisis in Cantabria, Spain: implications for calcification rates and phytoplankton evolution across the Toarcian oceanic anoxic event, *Paleoceanography* **20**, PA2011, doi:10.1029/2004PA001120, pp. 11.

VAN BRUEGEL, Y., BAAS, M., SCHOUTEN, S., MATTIOLI, E. & SINNINGHE DAMSTÉ, J. S. 2006. Isorenieratane record in black shales from the Paris Basin, France: constraints on recycling of respired CO_2 as a mechanism for negative carbon isotope shifts during the Toarcian oceanic anoxic event. *Paleoceanography* **21**, PA4220, doi: 10.1029/2006PA001305, pp. 8

VAN DE SCHOOTBRUGGE, B., MCARTHUR, J. M., BAILEY, T. R., ROSENTHAL, Y., WRIGHT, J. D. & MILLER, G. K. 2005. Toarcian oceanic anoxic event: an assessment of global causes using belemnite C isotope records. *Paleoceanography* **20**, PA3008, doi: 10.1029/2004PA001102, pp. 12

WIGNALL, P. B., MCARTHUR, J. M., LITTLE, C. T. S. & HALLAM, A. 2006. Methane release in the Early Jurassic period. *Nature* **441**, E5, doi: 10.1038/nature04905, pp. 1

WIGNALL, P. B., NEWTON, R. J. & LITTLE, C. T. S. 2005. The timing of paleoenvironmental change and cause-and-effect relationships during the Early Jurassic mass extinction in Europe. *American Journal of Science* **305**, 1014–32.

WOODFINE, R. G., JENKYNS, H. C., SARTI, M., BARONCINI, F. & VIOLANTE, C. 2008. The response of two Tethyan carbonate platforms to the early Toarcian (Jurassic) oceanic anoxic event: environmental change and differential subsidence. *Sedimentology* **55**, 1011–28.

WOOLER, D. A., SMITH, A. G. & WHITE, N. 1992. Measuring lithospheric stretching on Tethyan passive margins. *Journal of the Geological Society, London* **149**, 517–32.

A Review of Oceanic Anoxic Events as recorded in the Mesozoic sedimentary record of mainland Greece*

Vasilios Karakitsios[1], Nefeli Kafousia[1] & Harilaos Tsikos[2]

[1]Department of Historical Geology & Paleontology, Faculty of Geology & Geoenvironment, University of Athens, 15784 Panepistimiopolis, Zografou, Athens, Greece
e-mail: vkarak@geol.uoa.gr
[2]Geology Department, Rhodes University, Grahamstown 6140, Republic of South Africa

ABSTRACT: This paper presents an overview of the salient biostratigraphic, isotopic and organic geochemical characteristics of the four most well-established Oceanic Anoxic Events (OAEs) of the Mesozoic era, as recorded in sedimentary sections from the Ionian and Pindos zones of the western Hellenides, Greece. The Toarcian OAE in the Kastelli section of the Pindos Zone is expressed through the characteristic negative carbon isotope excursion in bulk carbonate, near the base of the corresponding organic-rich interval. Carbonate-free, radiolarian-rich black shales of the Lower Aptian *Fourcade* level from the Paliambela section in the Ionian zone, record a negative bulk organic carbon isotope spike at their base, typical of OAE 1a black shales elsewhere. The Early Albian OAE 1b is faithfully recorded in the stratigraphically uppermost black shale layer of the Aptian-Albian "Vigla Shale Member" of the Ionian Zone, with its characteristic molecular organic geochemical and isotopic signatures indicative of partly archaeal derivation for the organic matter. Finally, a thin and highly TOC-enriched black shale layer at the Cenomanian-Turonian boundary within the Vigla limestone succession of the Ionian Zone, is interpreted to represent a condensed stratigraphic equivalent to the *Livello Bonarelli*, the type locality of OAE 2 in Italy, on the basis of isotopic and organic geochemical results. The above records provide new insights into current debates concerning the forcing mechanisms of, and palaeoclimatic responses during OAEs, and constitute an important benchmark for future research on the manifestation and palaeoenvironmental significance of Mesozoic OAEs in mainland Greece.
Key-words: *Oceanic anoxic events, Toarcian, Aptian, Albian, Cenomanian-Turonian, Hellenides*.

ΠΕΡΙΛΗΨΗ: Σε αυτήν την εργασία γίνεται μια ανασκόπηση των βιοστρωματογραφικών, ισοτοπικών και οργανικών γεωχημικών χαρακτηριστικών των τεσσάρων, πιο καλά μελετημένων Ωκεάνιων Ανοξικών Γεγονότων (OAEs) του Μεσοζωϊκού, όπως αυτά έχουν καταγραφεί στην Ιόνια Ζώνη και τη Ζώνη της Πίνδου των εξωτερικών Ελληνίδων. Το OAE του Τοαρσίου στην τομή Καστέλλι της Πίνδου, εκφράζεται στα ανθρακικά πετρώματα μέσω της χαρακτηριστικής αρνητικής μεταβολής στις τιμές των ισοτόπων του άνθρακα, κοντά στη βάση του επιπέδου που είναι πλούσιο σε οργανικό υλικό. Οι μαύρες άργιλοι του Κατώτερου Άπτιου, επίπεδο *Fourcade*, από την τομή Παλιάμπελα της Ιονίου οι οποίες δεν έχουν καθόλου ανθρακικό ασβέστιο και είναι πλούσιες σε ακτινόζωα, έχουν καταγράψει μια απότομη αρνητική ισοτοπική μεταβολή στο οργανικό υλικό, η οποία είναι τυπική του OAE 1a ανά τον κόσμο. Το OAE του Κατώτερου Αλβίου, OAE 1b, έχει καταγραφεί στο ανώτερο τμήμα των μαύρων αργίλων του Άπτιου-Άλβιου, στο μέλος των σχιστολίθων Βίγλας της Ιόνιας Ζώνης, με τη χαρακτηριστική του μοριακή οργανική γεωχημική και ισοτοπική υπογραφή που αποδεικνύει την προέλευση του οργανικού υλικού από αρχαία (archaea). Τέλος, ένα λεπτό και πλούσιο σε οργανικό υλικό επίπεδο στο όριο Κενομάνιο-Τουρώνιο στους ασβεστολίθους της Βίγλας της Ιονίου Ζώνης, συσχετίστηκε με το OAE 2, όπως αυτό έχει καταγραφεί στην Ιταλία σαν *Livello Bonarelli* με βάση τα ισοτοπικά και οργανικά γεωχημικά χαρακτηριστικά του. Όλες οι παραπάνω καταγραφές, παρέχουν νέα δεδομένα και συμπεράσματα σχετικά με τους μηχανισμούς που ωθούν στην δημιουργία των OAEs, καθώς και των παλαιοπεριβαλλοντικών αντιδράσεων τους. Επίσης, αποτελούν μια σημαντική βάση για μελλοντική έρευνα που αφορά στη δημιουργία και παλαιοπεριβαλλοντική σημασία των Μεσοζωικών OAE στον Ελλαδικό χώρο.
Λέξεις κλειδιά: *Ωκεάνια Ανοξικά Γεγονότα, Τοάρσιο, Άπτιο, Άλβιο, Κενομάνιο–Τουρώνιο, Ελληνίδες.*

INTRODUCTION

Oceanic anoxic events (OAEs) were first described by SCHLANGER & JENKYNS (1976) as global-scale transient periods of marine anoxia, accompanied by the widespread deposition of organic carbon-rich sediments at the Aptian-Albian and Cenomanian-Turonian boundaries. Subsequent studies on sedimentary sections across the globe have expanded the stratigraphic record of such events, and have resulted in a wealth of palaeobiological and geochemical information that has been used to constrain and elucidate the environmental responses during each OAE. OAEs are widely believed to be associated with major perturbations in the global carbon cycle, the latter faithfully recorded in positive and/or negative carbon-isotope excursions across pelagic and shallow-water marine carbonate successions, associated organic-rich sediments ("black shales") as well as in specific biological components preserved in these sequences such as brachiopods, fossil wood and lipid biomarkers (WEISSERT, 1989; FARRIMOND *et al.*, 1990; HESSELBO *et al.*, 2000; SCHOUTEN *et al.*, 2000; DANELIAN *et al.*, 2004; TSIKOS *et al.*, 2004a; KEMP *et al.*, 2005; KARAKITSIOS, 2007b).

The forcing mechanism behind OAEs is still under debate. Available data suggest abrupt rises in temperature, induced by rapid influx of CO_2 into the ocean-atmosphere system resulting from either dissociation of methane hy-

* Ανασκόπηση των Ωκεάνιων Ανοξικών Γεγονότων που έχουν καταγραφεί στα Μεσοζωϊκά ιζήματα της Ηπειρωτικής Ελλάδας

drates, degassing due to large-scale volcanic activity, and/or widespread devolatilisation of organic-rich sediments (e.g. coal) by intrusive activity or asteroid impacts (Hesselbo *et al.*, 2000; McElwain *et al.*, 2005; Suan *et al.*, 2008; Turgeon & Creaser, 2008; Tejada *et al.*, 2009; Jenkyns, 2010). As a result, no single trigger mechanism can hitherto account for all OAEs identified in the geological record. Current palaeoenvironmental models suggest that global warming was accompanied by an accelerated hydrological cycle, increased continental weathering, enhanced nutrient discharge to the marine and lacustrine environments, intensified upwelling, and resultant increases in primary biological productivity (Erbacher *et al.*, 2001; Jenkyns, 2003, 2010; Kuypers *et al.*, 2004; Parente *et al.*, 2008).

In this paper, we present an overview of the records of four major OAEs as manifested in sedimentary successions preserved in mainland Greece. We specifically present results for the early Toarcian OAE (~ 180 Ma) as well as for the three most well-established OAEs of the Cretaceous, namely the early Aptian (OAE 1a, ~ 120 Ma), early Albian (OAE 1b, ~ 111 Ma) and Cenomanian-Turonian (OAE 2, ~ 93 Ma) OAEs. The biostratigraphic, isotopic and organic geochemical characteristics of these events are presented here on the basis of our studies of four sections from the Pindos and Ionian Zones of the external Hellenides (Fig. 1) that were carried out over the past decade.

REGIONAL GEOLOGICAL BACKGROUND

The western Hellenides constitute part of the Apulian continental block related to the southern passive continental margin of the early Mesozoic to mid-Cenozoic Tethyan Ocean. In the Early Lias, the present part of northwestern Greece was covered by a vast carbonate platform. Prolific carbonate sedimentation resulted in the accumulation of a shallow-water carbonate sequence over a thousand metres in thickness, balanced by strong subsidence events. The general faunal and lithological composition of the formations of the Ionian Zone from the Middle Lias upwards suggest general deepening, even though accumulation of shallow-water carbonates persisted through the entire Jurassic in the Paxos and Gavrovo Zones (Bernoulli & Renz, 1970; Karakitsios, 1992; Karakitsios, 1995; Rigakis & Karakitsios, 1998).

By contrast, pelagic sediments of the Pindos Zone originate from an elongated oceanic basin remnant that formed in mid-Triassic times along the north-east passive margin of Apulia between the extensive Gavrovo-Tripolis platform in the present west, and the Pelagonian continental block in the present east (Clift, 1992; Degnan & Robertson, 1998; Pe-Piper, 1998). Organic carbon contents in the Ionian Zone suggest a higher degree of organic matter accumulation relative to the Pindos Zone; this is in accordance with the more restricted geometry of the Ionian basin *versus* the deeper ocean basin of the Pindos Zone (Baudin & Lachkar, 1990; Karakitsios, 1995; Rigakis & Karakitsios, 1998; Tsikos *et al.*, 2004b; Karakitsios *et al*., 2007; Kafousia *et al.*, 2010).

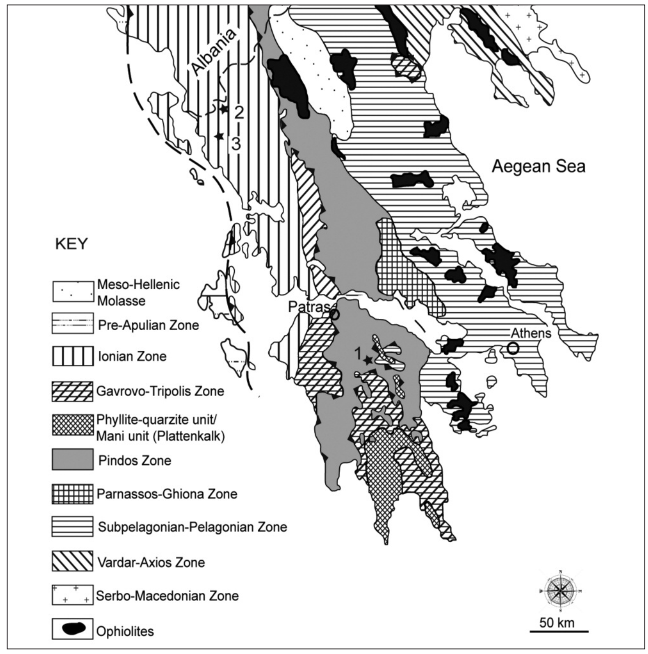

Fig.1. Simplified geological map of Greece and localities of the studied outcrop sections discussed in the paper. 1: Kastelli, 2: Paliambela, 3: Gotzikas.

THE EARLY TOARCIAN OAE

The early Toarcian records a period of global warming (Bailey *et al.*, 2003; Jenkyns, 2003), accompanied by mass extinction events (Wignall *et al.*, 2006) and enhanced organic carbon burial (Jenkyns, 1988; Jenkyns *et al.*, 2001), in response to the earliest known OAE of the Mesozoic. The observed geochemical characteristics of the early Toarcian OAE include increased organic carbon sequestration and a negative and/or positive excursion in carbon isotopes from both carbonate and organic matter. Maximum TOC values of black shales of the lower Toarcian range from ~ 19 wt% to as low as 0.60 wt%; this variation is interpreted in each instance to be the result of variable redox conditions, water depth, degree of water-mass stratification and/or organic productivity (Jenkyns, 1988; Rigakis & Karakitsios, 1998; Jenkyns *et al.*, 2002; Sabatino *et al.*, 2009; Jenkyns, 2010; Kafousia *et al.*, 2010). A negative carbon-isotope excursion is hitherto recorded in most studied sections, whereas a positive one - that otherwise characterizes most other OAEs - is not always present. Carbon isotope values of bulk organic matter during the Toarcian OAE drop below the value of -30‰ from background levels of generally -26 to -27‰, whilst the carbonate-carbon isotope values are commonly more erratic across stratigraphy due to diagenetic overprinting.

Fig. 2 displays the geochemical expression of the Toarcian OAE in the Kastelli section of the Pindos Zone (Kafousia *et al.*, 2010). The contention that the Pindos Zone was a deep ocean during the early Toarcian assists in addressing the relatively low TOC values recorded in this section; nevertheless, a relative increase in TOC across the interpreted OAE

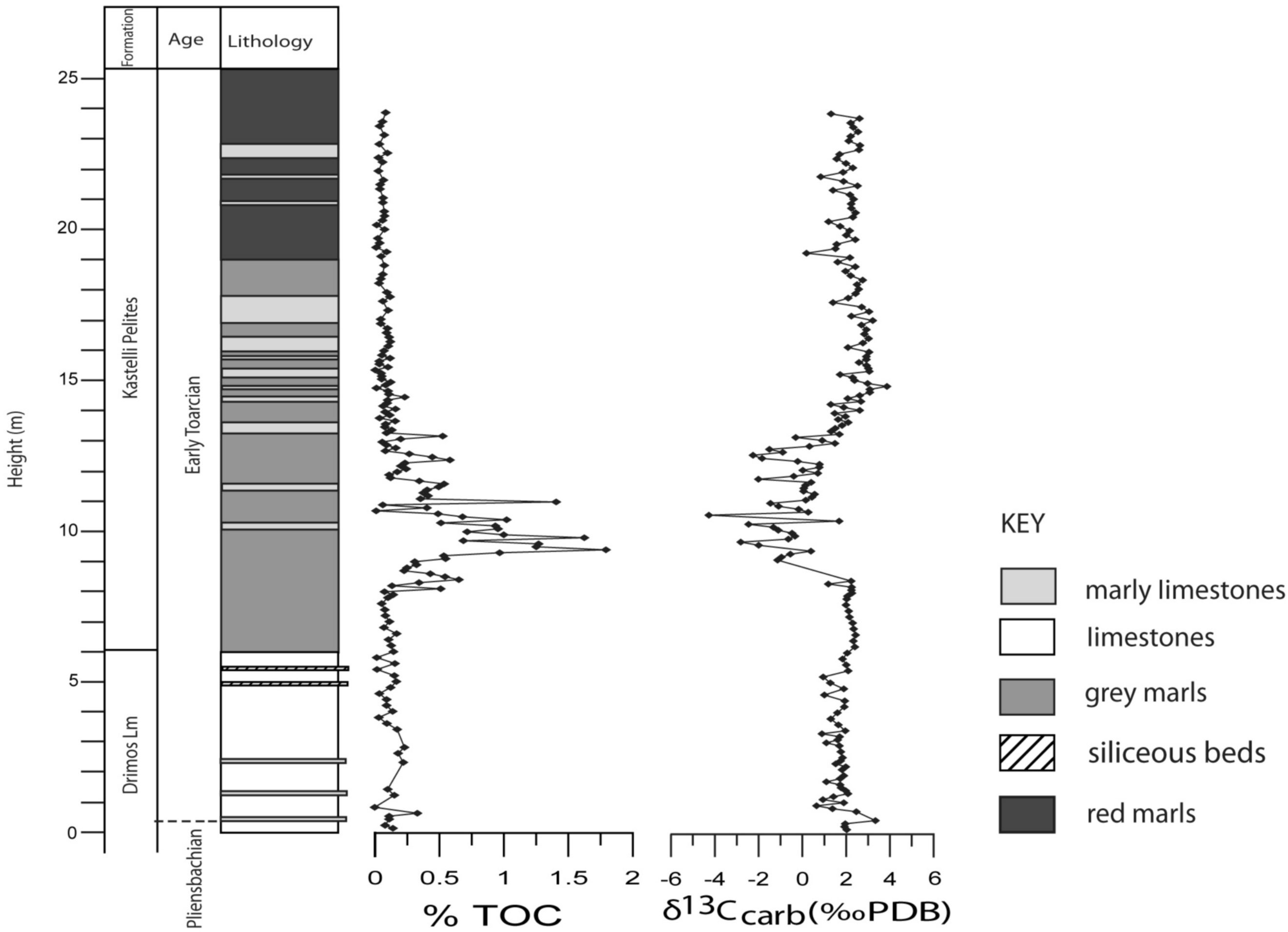

Fig. 2. Lithology, biostratigraphy and chemostratigraphy of the Early Toarcian OAE at the Kastelli section, Pindos Zone (from KAFOUSIA *et al.*, 2010).

interval up to 2 wt% is clearly visible. Across the same interval, a negative excursion of *ca*. 6‰ in bulk carbonate $\delta^{13}C$ values develops that also typifies carbon-isotope data for coeval sections elsewhere; stratigraphically upwards, a low-magnitude positive excursion is also discernible. Work in progress is directed at higher resolution chemostratigraphic records of the Toarcian OAE in both the Pindos and Ionian Zones, the latter known for its substantially higher TOC contents (JENKYNS, 1988; RIGAKIS & KARAKITSIOS, 1998).

THE EARLY APTIAN OAE 1A (*SELLI* EVENT)

The early Aptian OAE 1a (*ca.* 120Ma), is the earliest major OAE in the Cretaceous period. Like the early Toarcian OAE, this event is also characterized by a global distribution of black shales in continental shelf and margin environments (GRÖCKE *et al.*, 1999; JENKYNS, 1999; JENKYNS, 2003; HEIMHOFER *et al.*, 2004). The OAE 1a is accompanied by a dramatic turnover in calcareous nannoplankton ("nannoconid crisis", ERBA, 1994) and high extinction rates of siliceous and calcareous plankton (LECKIE *et al.,* 2002, HEIMHOFER *et al.*, 2004). Palaeotemperature data also suggest an abrupt increase in SST of ~ 8 °C in the run-up to the early Aptian OAE 1a, followed by an interpreted cooling trend (ANDO *et al.*, 2008).

Representative sections of the OAE 1a globally, including the type section in Italy known as the *Livello Selli*, are characterized by a pronounced negative isotopic spike, followed by a positive carbon-isotope excursion in deep- and shallow-marine carbonates, marine organic matter and terrestrial higher plant material (SLITER, 1989; GRÖCKE *et al.*, 1999; JENKYNS, 1999, 2003; HERRLE *et al.*, 2004; VAN BREUGEL *et al.*, 2007). This negative spike is perhaps the most distinctive feature of OAE 1a globally, and coincides with the lowest stratigraphic levels of the organic-rich shales themselves (JENKYNS, 2010). Total organic carbon values of black shales recording OAE 1a in the Alpine-Mediterranean region range between 2-18 wt% (BAUDIN *et al.*, 1998; JENKYNS, 2010); in a core section from Shatsky Rise in the Pacific ocean, TOC values reach 40 wt% (DUMITRESCU & BRASSELL, 2006).

Fig. 3 displays comprehensive lithostratigraphic, biostratigraphic and chemostratigraphic data of the "upper siliceous zone" as observed in the Paliambela section of the Ionian Zone (DANELIAN *et al.*, 2004). Here, the OAE 1a has

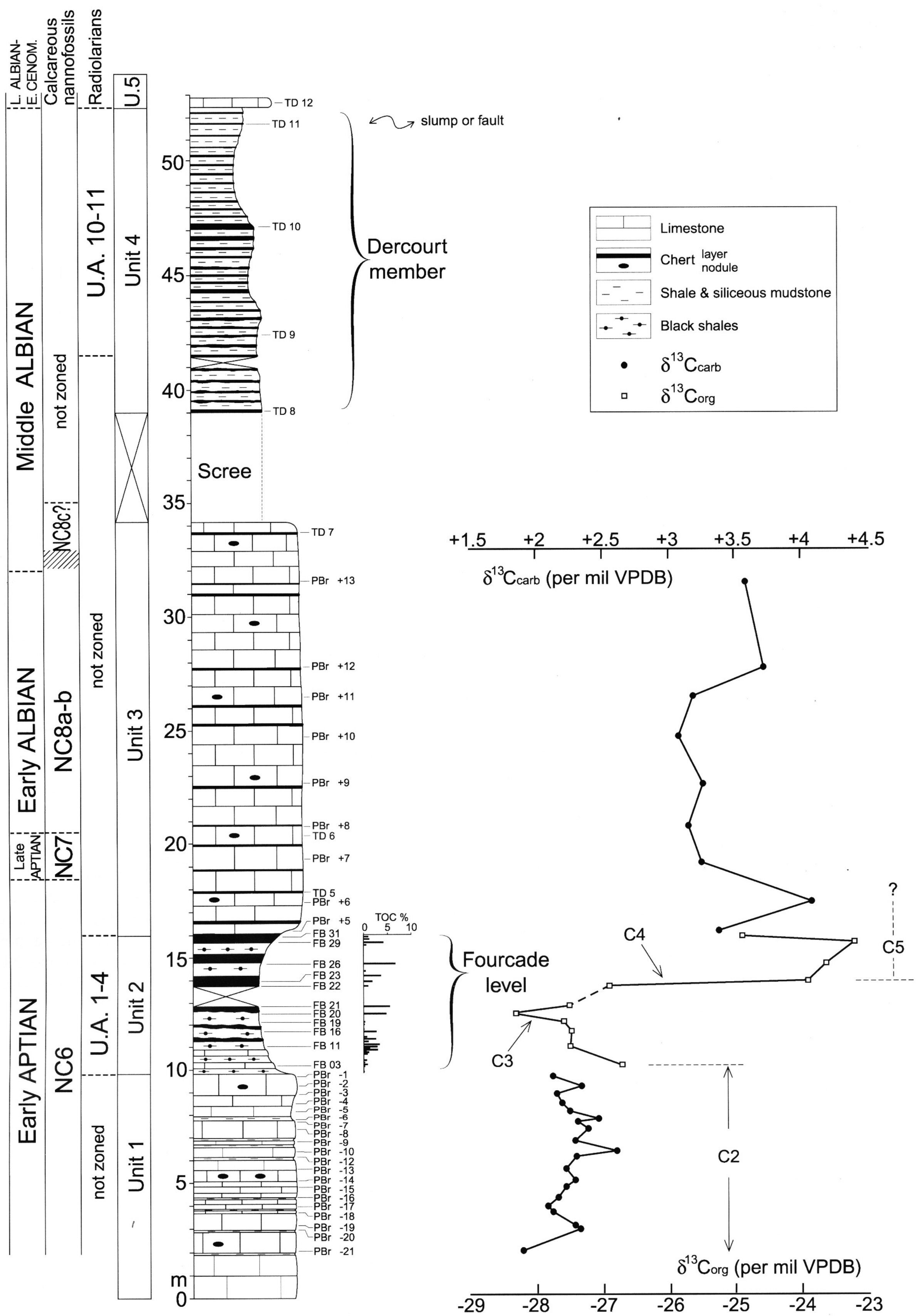

Fig. 3. Lithology, biostratigraphy and carbon isotope stratigraphy of the Early Aptian OAE at Paliambela section, Ionian Zone (modified after DANELIAN *et al.*, 2004).

been termed the *Fourcade level*, though according to Danelian *et al.* (2002) it is essentially a time-equivalent horizon to the *Livello Selli*. This notion is supported by the abundance of preserved marine organic matter and biogenic (radiolarian) silica, absence of nannoconids and presence of abundant nannoliths of remarkably large size. From a chemostratigraphic point of view, the negative $\delta^{13}C$ spike that typifies the lower portion of OAE 1a black shales in Italian sections and elsewhere is faithfully re-produced in bulk organic carbon isotopic values of the Paliambela section, followed stratigraphically upwards by a broadly positive isotopic excursion.

THE EARLY ALBIAN OAE 1B (*PAQUIER* EVENT)

The OAE 1b is characterized by the deposition of laminated, organic-rich shales, first described by Bréhéret (1998) from sites in France, Germany and Austria. Later studies have

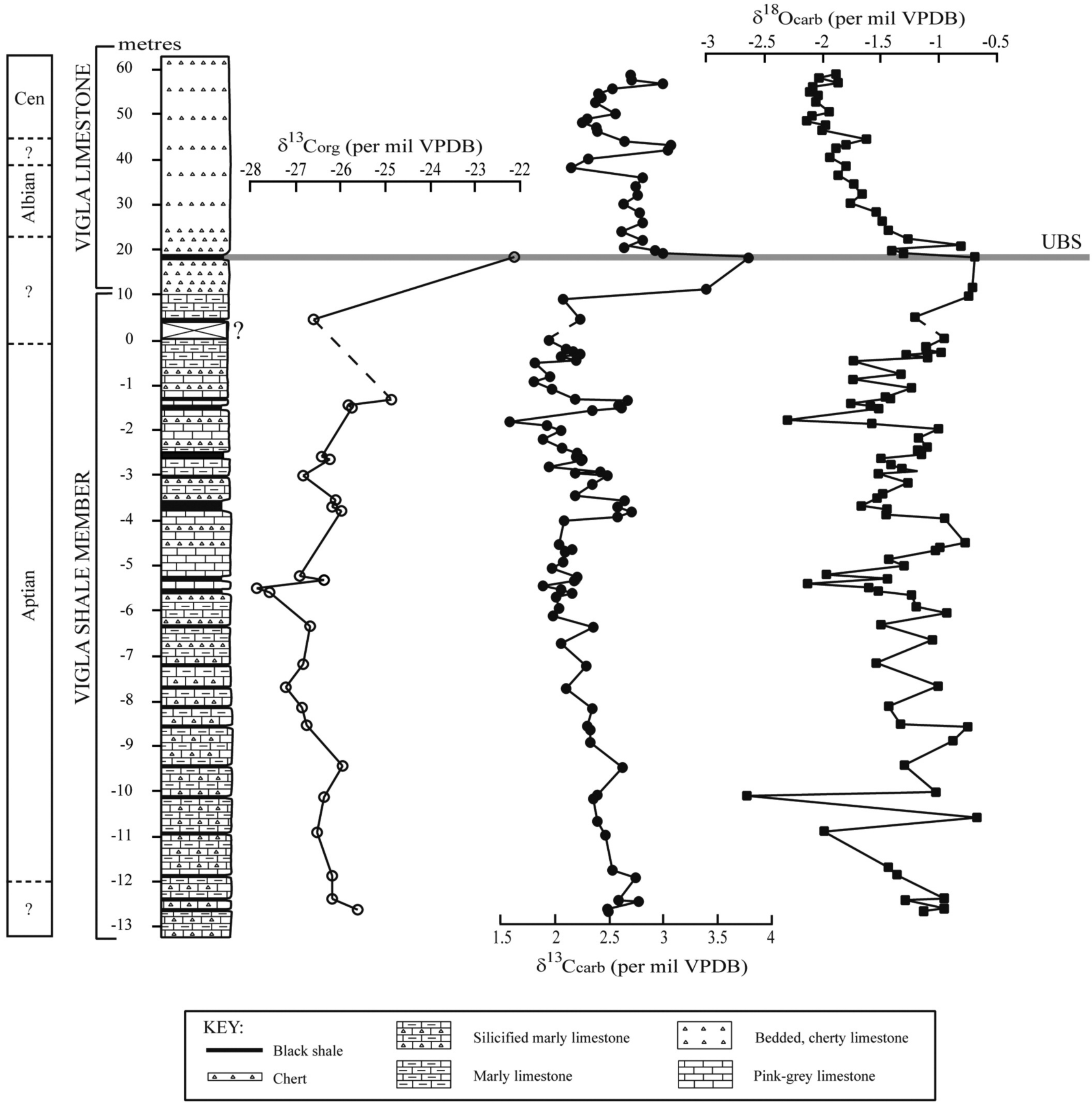

Fig.4. Lithostratigraphy and stable isotope profiles through the Vigla section in the Gotzikas section of the Ionian Zone (modified after Tsikos *et al.*, 2004b). The OAE1b ("Paquier") black shale is highlighted. Note the different scales used for the portions of the section above and below the observation gap.

recorded this event across much of the Tethyan-Atlantic region, including ODP drilling sites (Leckie *et al.*, 2002; Jenkyns, 2003). Stable isotope data from Atlantic sections (Mazagan and Blake Nose) in which evidence for diagenetic alteration is minimal, suggest a rise in sea-surface temperature at the onset of the event, that subsequently prevailed over essentially its entire duration (~ 40-50 ka) (Jenkyns, 2003; Herrle *et al*., 2004; Hofmann *et al*., 2008). The OAE 1b is the shortest of the Cretaceous OAEs (Erbacher *et al.*, 2001), and has received particular attention among other Cretaceous OAEs due to the distinct bio-chemical nature of corresponding black shales. Specifically, organic matter in OAE 1b black shales is known to contain appreciable concentrations of monocyclic isoprenoidal biomarkers, which indicate that archaea were a principal component of the original biomass; this is in marked contrast to OAEs 1a and 2, where organic matter had a predominantly plytoplanktonic source (Kuypers *et al.*, 2002, 2004; Tsikos *et al.*, 2004b; Jenkyns, 2010).

Fig. 4 illustrates the manifestation of the OAE 1b event in Western Greece (Tsikos *et al.*, 2004b). The event is recorded in the uppermost of a series of dm-thick black shale horizons that collectively constitute the organic-rich portion of the Aptian-Albian "Vigla Shale Member". The OAE 1b black shale displays isotopic and organic geochemical characteristics that compare particularly well with time-equivalent sections in the Vocontian Basin, France (*Niveau Paquier*) and the North Atlantic (ODP site 1049C). In particular, the presence of archaeal-derived biomarkers in the Vigla section similarly to both the French and North Atlantic sections, reinforce the suggestion that the OAE 1b represents a biologically distinct event in terms of the expansion of archaea in the Cretaceous marine realm (Tsikos *et al.*, 2004b).

THE CENOMANIAN-TURONIAN OAE 2 (*BONARELLI* EVENT)

The Cenomanian-Turonian OAE 2 is a classic example and probably the best-studied one among OAEs of the Cretaceous. It is characterized by essentially global-scale deposition of organic-rich sediments (Schlanger & Jenkyns, 1976; Jenkyns, 2003; Tsikos *et al.*, 2004a) accompanied by a positive carbon isotope excursion in bulk organic matter of 4-6‰ and in marine carbonates of 2-3‰. The highest magnitude of these excursions has been observed in and around the Atlantic Ocean where large volumes of black shale were deposited (Jenkyns *et al.*, 2007). The duration of the OAE 2 according to the orbital time scale of Sageman *et al.* (2006) is ~ 600 ka for the interval recording the positive carbon isotope excursion and ~ 860 ka if the return of the excursion to background isotopic values is included in the calculations (Jenkyns *et al.*, 2007).

The stratigraphic and isotopic expression of OAE 2 in the Ionian Zone of NW Greece (Karakitsios *et al.*, 2007b) is illustrated in Fig. 5. Characteristic features of OAE 2 in this locality are the substantially thinner and TOC-enriched black

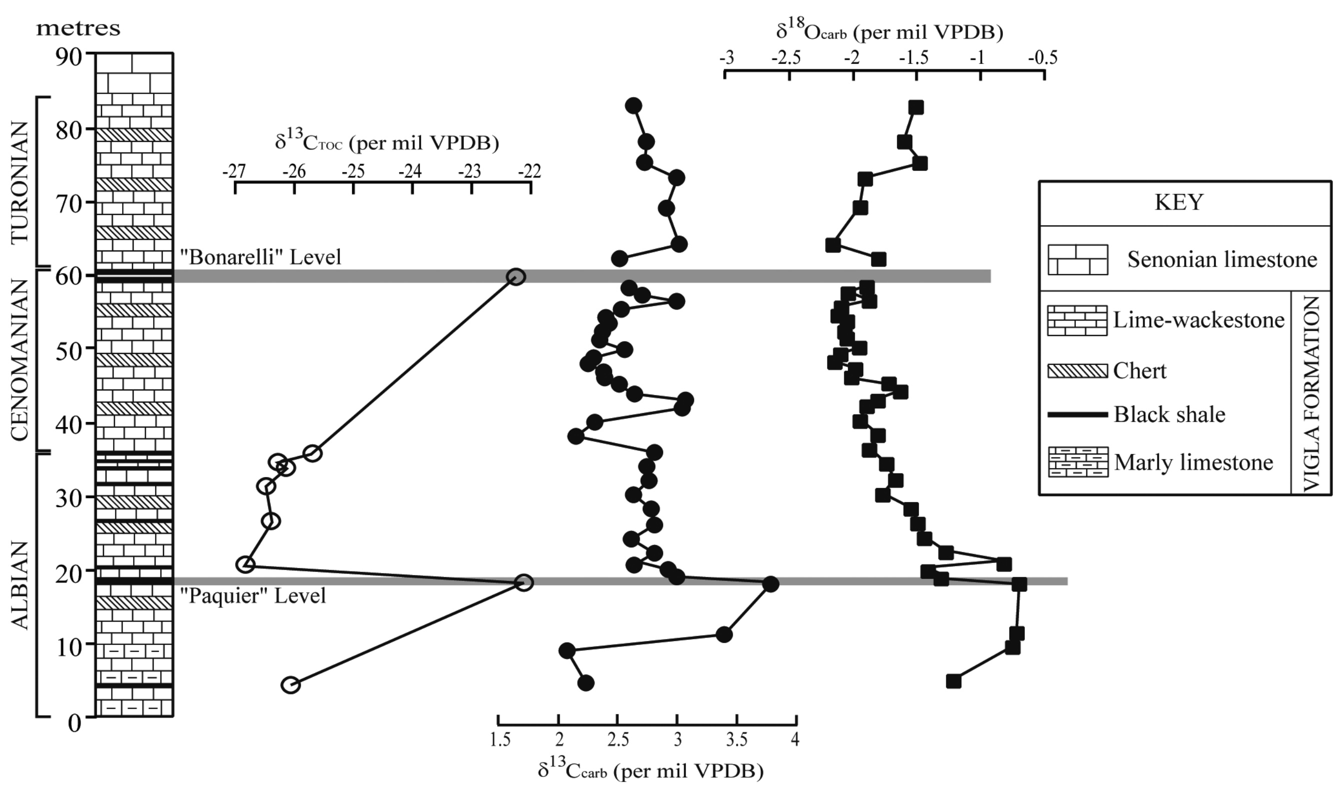

Fig. 5. Bulk stable (C, O) isotope profiles through the upper part of the Vigla Limestone Formation in the Gotzikas section, which includes the Bonarelli-equivalent, OAE 2 black-shale horizon (modified after Karakitsios *et al.*, 2007b).

shale interval in relation to the type locality of the *Livello Bonarelli* in Marche-Umbria, Italy: whereas the *Bonarelli* horizon is approximately one meter thick and has a maximum TOC content of ~ 25 wt% (Tsikos *et al.*, 2004a), the equivalent black shale in the Ionian Zone is approximately 35 cm thick and contains ~ 45 wt% TOC. The latter has therefore been regarded as a substantially condensed equivalent of the *Livello Bonarelli*. Otherwise, in terms of bulk organic carbon isotope signature and molecular organic geochemical composition, both black shales exhibit high $\delta^{13}C$ values of up to 22‰ relative to pre-OAE black shales stratigraphically lower in respective sections, as well as a relative enrichment in 2-methyl hopanoids that are indicative of cyanobacterial derivation (Tsikos *et al.*, 2004a; Karakitsios *et al.*, 2007b; Jenkyns *et al.*, 2007).

CONCLUSIONS

The last few years have seen an unprecedented burst in published research on the geological manifestation of Mesozoic OAEs in mainland Greece. In all instances and in line with modern research on OAEs, a fully integrated approach was employed, utilizing detailed biostratigraphy, isotope chemostratigraphy and organic geochemical studies at bulk and molecular level. We have demonstrated in this review how important such integrated studies are in allowing us to appreciate the particularities and complications of the geological records of such short-term palaeoenvironmental events. We also recognize that there is still a lot of untouched potential in Greece for future research on this topic, that will most certainly lead to further refinement of our findings and a better understanding of these remarkable events in Earth history. This is becoming increasingly pertinent in the current day and age, where understanding the mechanisms of past abrupt climate change can provide unrivalled clues as to how our present climate is changing and will continue to evolve. It is our hope that the work that we have comprehensively presented in this overview has paved the ground for more research on OAEs on Greek soil, and we will look forward to new such results and ideas from researchers in Greece and beyond.

ACKNOWLEDGEMENTS

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REFERENCES

ANDO, A., KAIHO, K., KAWAHATA, H. & T. KAKEGAWA (2008). Timing and magnitude of early Aptian extreme warming: Unraveling primary $\delta^{18}O$ variation in indurated pelagic carbonates at Deep Sea Drilling Project Site 463, central Pacific Ocean. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 260(3-4), 463-476.

BAILEY, T.R., ROSENTHAL, Y., McARTHUR, J.M. & B. VAN DER SCHOOTBRUGGE (2003). Paleoceanographic changes of the Late Pliensbachian-Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event. *Earth and Planetary Science Letters*, 212, 307-320.

BAUDIN, F., FIET, N., COCCIONI, R. & S. GALEOTTI (1998). Organic matter characterisation of the Selli Level (Umbria-Marche Basin, central Italy). *Cretaceous Research*, 19(6), 701-714.

BAUDIN, F. & G. LACHKAR (1990). Geochemical And Palynological Studies Of Late Lias In Ionian Zone (Greece) - Example Of An Anoxic Sedimentation Preserved In A Distensive Paleomargin. *Bulletin De La Societe Geologique De France*, 6(1), 123-132.

BERNOULLI, D. & O. RENZ (1970). Jurassic carbonate facies and new ammonite faunas from Western Greece. *Eclogae Geologicae Helvetiae*, 63/2, 573-607.

BRÉHÉRET, J.G. (1985). Indices d'un événement anoxique étendu à la Téthys alpine, à l' Albien inférieur (évément Paquier). *Comptes Rendus De L Academie Des Sciences Paris*, 300(Série II), 355-358.

BRUMSACK, H.-J. (2006). The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232(2-4), 344-361.

CLIFT, P. D. (1992). The collision tectonics of the southern Greek Neotethys. *Geologische Rundschau* 81(3), 669-679.

DANELIAN, T., BAUDIN, F., GARDIN, S., BELTRAN, C. & E. MASURE (2002). Early Aptian productivity increase as recorded in the Fourcade level of the Ionian zone of Greece. *Comptes Rendus De L Academie Des Sciences, Géoscience*, 334, 1087-1093.

DANELIAN, T., TSIKOS, H., GARDIN, S., BAUDIN, F., BELLIER, J.P. & L. EMMANUEL (2004). Global and regional palaeoceanographic changes as recorded in the mid-Cretaceous (Aptian-Albian) sequence of the Ionian zone (NW Greece). *Journal of the Geological Society*, 161(4), 703-709.

DEGNAN, P.J. & A.H.F. ROBERTSON (1998). Mesozoic-early Tertiary passive margin evolution of the Pindos ocean (NW Peloponnese, Greece). *Sedimentary Geology*, 117(1-2), 33-70.

DUMITRESCU, M. & S.C. BRASSELL (2006). Compositional and isotopic characteristics of organic matter for the early Aptian Oceanic Anoxic Event at Shatsky Rise, ODP Leg 198. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 235(1-3), 168-191.

ERBA, E. (1994). Nannofossils and Superplumes: The Early Aptian "Nannoconid Crisis". *Paleoceanography*, 9(3), 483-501.

ERBACHER, J., HUBER, B.T., NORRIS, R.D. & M. MARKEY (2001). Increased thermohaline stratification as possible cause for an oceanic anoxic event in the Cretaceous period. *Nature*, 409, 325-327.

FARRIMOND, P., EGLINTON, G., BRASSELL, S.C. & H.C. JENKYNS (1990). The Cenomanian/Turonian anoxic event in Europe: an organic geochemical study. *Marine and Petroleum Geology*, 7(1), 75.

FORSTER, A., SCHOUTEN, S., MORIYA, K., WILSON, P.A. & J.S. SINNINGHE DAMSTÉ (2007). Tropical warming and intermittent cooling during the Cenomanian/Turonian oceanic anoxic event 2: Sea surface temperature records from the equatorial Atlantic. *Paleoceanography*, 22(1), PA1219. doi: 1029/2006PA001349

GRÖCKE, D., HESSELBO, S.P. & H.C. JENKYNS (1999). Carbon-isotope composition of Lower Cretaceous fossil wood: Ocean-atmosphere chemistry and relation to sea-level change. *Geology*, 27, 155-158.

HEIMHOFER, U., HOCHULI, P.A., HERRLE, J.O., ANDERSEN, N. & H. WEISSERT (2004). Absence of major vegetation and palaeoatmospheric pCO2 changes associated with oceanic anoxic event 1a (Early Aptian, SE France). *Earth and Planetary Science Letters*, 223(3-4), 303-318.

HERRLE, J.O., KOLLER, P., FRIEDRICH, O., ERLENKEUSER, H. & C. HEMLEBEN (2004). High-resolution carbon isotope records of the Aptian to Lower Albian from SE France and the Mazagan Plateau (DSDP Site 545): a stratigraphic tool for paleoceanographic and paleobiologic reconstruction. *Earth and Planetary Science Letters*, 218(1-2), 149-161.

HESSELBO, S.P., GRÖCKE, D.R., JENKYNS, H.C., BJERRUM, C.J., FARRIMOND, P., MORGANS BELL, H.S. & O.R. GREEB (2000). Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature*, 406, 392-395.

HOFMANN, P., STUSSER, I., WAGNER, T., SCHOUTEN, S. & J.S. SINNINGHE DAMSTÉ (2008). Climate-ocean coupling off North-West Africa during the Lower Albian: The Oceanic Anoxic Event 1b. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 262(3), 157-165.

JENKYNS, H.C. (1988). The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary, and geochemical evidence. *American Journal of Science*, 288, 101-151.

JENKYNS, H.C. (1999). Mesozoic anoxic events and palaeoclimate. *Zbl. Geol. Palaeont.*, Teil I, 943-949.

JENKYNS, H.C. (2003). Evidence for rapid climate change in the Mesozoic-Palaeogene greenhouse world. *Philosophical Transactions - Royal Society. Mathematical, Physical and Engineering Sciences*, 361, 1885-1916.

JENKYNS, H.C. (2010). Geochemistry of oceanic anoxic events. *Geochemistry Geophysics Geosystems*, 11(3), doi:10.1029/2009GC002788.

JENKYNS, H.C. & C.J. CLAYTON (1986). Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. *Sedimentology*, 33(1), 87-106.

JENKYNS, H.C., GRÖCKE, D.R. & S.P. HESSELBO (2001). Nitrogen isotope evidence for water mass denitrification during the Early Toarcian (Jurassic) Oceanic Anoxic Event. *Paleoceanography*, 16, 593-603.

JENKYNS, H.C., JONES, C.E., GRÖCKE, D.R., HESSELBO, S.P. & D.N. PARKINSON (2002). Chemostratigraphy of the Jurassic system; applications, limitations and implications for palaeoceanography. *Journal of the Geological Society of London*, 159(4), 351-378.

JENKYNS, H.C., MATTHEWS, A., TSIKOS, H. & Y. EREL (2007). Nitrate resuction, sulfate reduction, and sedimentary iron isotope evolution during the Cenomanian-Turonian oceanic anoxic event. *Paleoceanography*, 22, PA3208.

KAFOUSIA, N., KARAKITSIOS, V., & H.C. JENKYNS (2010). Preliminary data from the first record of the Toarcian Oceanic Anoxic Event in the sediments of the Pindos Zone (Greece). *Bulletin of the Geological society of Greece*, 43, No 2, 627-633

KARAKITSIOS, V. (1992). Ouverture et inversion tectonique du bassin Ionien (Epire, Grèce). *Annales Géologiques des Pays Helléniques*, 35(series 1), 185-318.

KARAKITSIOS, V. (1995). The influence of preexisting structure and halokinesis on organic matter preservations and thrust system evolution in the Ionian basin, Northwest Greece. *American Association of Petroleum Geologists Bulletin*, 79(7), 960-980.

KARAKITSIOS, V., TSIKOS, H., AGIADI-KATSIAOUNI, K., DERMITZOGLOU, S. & E. CHATZICHARALAMBOUS (2007a). The use of carbon and oxygen stable isotopes in the study of global palaeoceanographic changes: examples from the Cretaceous sedimentary rocks of Western Greece. *Bulletin Geol. Soc. Greece*, 39a, 41-56.

KARAKITSIOS, V., TSIKOS, H., VAN BRUEGEL, Y., KOLETTI, L., SINNINGHE DAMSTÉ, S.J., & H.C. JENKYNS, (2007b). First evidence for the Cenomanian-Turonian oceanic anoxic event (OAE2, "Bonarelli" event) from the Ionian Zone, western continental Greece. *International Journal of Earth Sciences (Geol. Rundsch.)*, 96, 343-352.

KEMP, D.B., COE, A.L., COHEN, A.S. & L. SCHWARK (2005). Astronomical pacing of methane release in the Early Jurassic period. *Nature*, 437(7057), 396-399.

KUYPERS, M.M.M., BLOKKER, P., HOPMANS, E.C., KINKEL, H., PANCOST, R.D., SCHOUTEN, S. & J.S. SINNINGHE DAMSTÉ (2002). Archaeal remains dominate marine organic matter from the early Albian oceanic anoxic event 1b. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 185(1-2), 211-234.

KUYPERS, M.M.M., VAN BREUGEL, Y., SCHOUTEN, S., ERBA, E. & J.S. SINNINGHE DAMSTÉ (2004). N_2-fixing cyanobacteria supplied nutrient N for Cretaceous oceanic anoxic events. *Geology*, 32(10), 853-856.

LECKIE, R.M., BRALOWER, T.J. & R. CASHMAN (2002). Oceanic anoxic events and plankton evolution: Biotic response to tectonic forcing during the mid-Cretaceous. *Paleoceanography*, 17(3), 1041.

McELWAIN, J.C, WADE-MURPHY, J. & S.P. HESSELBO (2005). Changes in carbon dioxide during an oceanic anoxic event linked to intrusion into Gondwana coals. *Nature*, 435(26), 479-482.

PARENTE, M., FRIJIA, G., DI LUCIA, M., JENKYNS, H.C., WOODFINE, G.R. & F. BARONCINI (2008). Stepwise extinction of larger foraminifers at the Cenomanian-Turonian boundary: A shallow-water perspective on nutrient fluctuations during Oceanic Anoxic Event 2 (Bonarelli Event). *Geology*, 36(9), 715-718.

PE-PIPER, G. (1998). The nature of Triassic extension-related magmatism in Greece: evidence from Nd and Pb isotope geochemistry. *Geological Magazine*, 135(3), 331-348.

RIGAKIS, N. & V. KARAKITSIOS (1998). The source rock horizons of the Ionian Basin (NW Greece). *Marine and Petroleum Geology*, 15(7), 593-617.

ROSALES, I., ROBLES, S. & S. QUESADA (2004). Elemental and oxygen isotope composition of Early Jurassic belemnites; salinity vs. temperature signals. *Journal of Sedimentary Research*, 74(3), 342-354.

SABATINO, N., NERI, R., BELLANCA, A., JENKYNS, H.C., BAUDIN, F., PARISI, G. & D. MASETTI (2009). Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria-Marche Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. *Sedimentology*, 56(5), 1307-1328.

SCHLANGER, S.O. & H.C. JENKYNS (1976). Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw*, 55(3-4), 179-184.

SCHOUTEN, S., VAN KAAM-PETERS, H.M.E., RIJPSTRA, W.I.C., SCHOELL, M. & J.S. SINNINGHE DAMSTÉ (2000). Effects of an oceanic anoxic event on the stable carbon isotopic composition of Early Toarcian carbon. *American Journal of Science*, 300, 1-22.

SLITER, W.V. (1989). Aptian anoxia in the Pacific Basin. *Geology*, 17, 909-912.

SUAN, G., MATTIOLI, E., PITTET, B., MAILLIOT, S. & C. LECUYER (2008). Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oveanic anoxic event from the Lusitanian Basin, Portugal. *Paleoceanography*, 23, PA1202.

TEJADA, M.L.G., SUZUKI, K., KURODA, J., COCCIONI, R., MAHONEY, J.J., OHKOUCHI, N., SAKAMOTO, T. & Y. TATSUMI (2009). Ontong Java Plateau eruption as a trigger for the early Aptian oceanic anoxic event. *Geology*, 37(9), 855-858.

TSIKOS, H., JENKYNS, H.C., WALSWORTH-BELL, B., PETRIZZO, M.R., FORSTER, A., KOLONIC, S., ERBA, E., PREMOLI SILVA, I., BAAS, M., WAGNER, T. & J.S. SINNINGHE

DAMSTÉ (2004a). Carbon-isotope stratigraphy recorded by the Cenomanian-Turonian Oceanic Anoxic Event: correlation and implications based on three key localities. *Journal of the Geological Society of London*, 161(4), 711-719.

TSIKOS, H., KARAKITSIOS, V., VAN BRUEGEL, Y., WALSWORTH-BELL, B., BOMBARDIERE, L., ROSE PETRIZZO, M., SINNINGHE DAMSTÉ, S.J., SCHOUTEN, S., ERBA, E., PREMOLI-SILVA I., FARRIMOND P., TYSON, R.V. & H.C. JENKYNS (2004b). Organic-carbon deposition in the Cretaceous of the Ionian Basin, NW Greece: the Paquier Event (OAE 1b) revisited. *Geological Magazine*, 141(1), 401-416.

TURGEON, S. & R.A. CREASER (2008). Cretaceous oceanic anoxic event 2 triggered by a massive magmatic episode. *Nature*, 454, doi:10.1038/nature07076.

VAN BREUGEL Y., SCHOUTEN S., TSIKOS H., ERBA E., PRICE G.D. & J.S. SINNINGHE DAMSTÉ (2007). Synchronous negative carbon isotope shifts in marine and terrestrial biomarkers at the onset of the Aptian oceanic anoxic event-1a: Evidence for the release of methane into the atmosphere. *Paleoceanography*, 22, PA1210, doi:10.1029/2006PA001341

WEISSERT, H. (1989). C-Isotope stratigraphy, a monitor of paleoenvironmental change: A case study from the early cretaceous. *Surveys in Geophysics*, 10(1), 1-61.

WIGNALL, P.B., HALLAM, A., NEWTON, R.J., SHA, J.G., REEVES, E., MATTIOLI, E. & S. CROWLEY (2006). An eastern Tethyan (Tibetan) record of the Early Jurassic (Toarcian) mass extinction event. *Geobiology*, 4(3), 179-190.

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PRELIMINARY DATA FROM THE FIRST RECORD OF THE EARLY TOARCIAN OCEANIC ANOXIC EVENT IN THE SEDIMENTS OF THE PINDOS ZONE (GREECE)

Abstract

The Early Toarcian Oceanic Anoxic Event (ca 183 Ma) coincides with high palaeotemperatures, regional anoxia to euxinia, marine transgression, mass extinction and high rates of organic-carbon burial in a global context. Most of the detailed studies of this event have investigated deposits formed in the epicontinental seas of northern Europe, although coeval organic-rich shales are known locally in the Tethyan region. However, the global or regional character of this event is still under debate.

In this study we present, for the first time, a high-resolution geochemical record of the Early Toarcian Oceanic Anoxic event in pelagic sediments (Kastelli Pelites) formed in a long-lived Mesozoic deep-sea basin, corresponding to the western passive margin of the Pindos Ocean of western Greece.

Our data record both the positive excursion in total organic carbon (TOC) and the characteristic negative excursion in $\delta^{13}C_{carb}$. The $\delta^{13}C_{carb}$ values are very stable in the bottom of the section (~2‰), whereas higher in the section the values drop down to ~ -5‰. Following this negative excursion, the carbonate carbon-isotope ratios return to background values. The TOC excursion is modest, rising from a background of 0.05% to ~ 2% and then returning to a background of 0.04%.

Because both relative enrichment in TOC and the negative carbon-isotope excursion that characterize the Toarcian OAE are recorded in some of the deepest marine sediments of the Tethyan region, the global significance of the event is reinforced.

Key words: *Toarcian, Oceanic Anoxic Event, Pindos Zone.*

1. Introduction

The early Toarcian (ca 183 Ma) coincides with high palaeotemperatures (Bailey et al. 2003), regional anoxia to euxinia, marine transgression, mass extinction (Little and Benton 1995) and high rates of organic-carbon burial, attributed to a so-called Oceanic Anoxic Event (Schlanger and Jenkyns 1976; Jenkyns 1988; Karakitsios 1995; Rigakis and Karakitsios 1998; Jenkyns et al. 2001). The geochemical characteristics of the early Toarcian OAE (or T-OAE) are a relative maximum in total organic carbon (TOC) and a broad, locally subdued positive carbon-isotope excursion punctuated by an abrupt negative excursion, recorded in marine organic matter, marine pelagic and shallow-water carbonate and terrestrial organic material (Jenkyns and Clayton, 1986, 1997; Hesselbo et al. 2000; Jenkyns et al. 2001; Jenkyns, 2003, 2010; Kemp et al. 2005; Hesselbo et al. 2007; Woodfine et al., 2008). Most of the detailed studies of this event have investigated deposits formed in the epicontinental seas of northern Europe (e.g. Hesselbo et al. 2000; Kemp et al. 2005), although coeval organic-rich shales are known locally in the Tethyan region (Jenkyns et al., 1985; Jenkyns and Clayton, 1986; Jenkyns, 1988; Sabatino et al. 2009). However, the global or regional character of this event is still under debate (van der Schootbrugge et al. 2005; Hesselbo et al. 2007; Suan et al. 2008).

In this study we present, for the first time, a high-resolution geochemical record of the Early Toarcian Oceanic Anoxic event in pelagic sediments formed in a long-lived Mesozoic deep-sea basin, corresponding to the western passive margin of the Pindos Ocean of western Greece. We undertook Total Organic Carbon (TOC) and stable carbon-isotopic analyses in the Kastelli section from the Pindos Zone (North Peloponnesus).

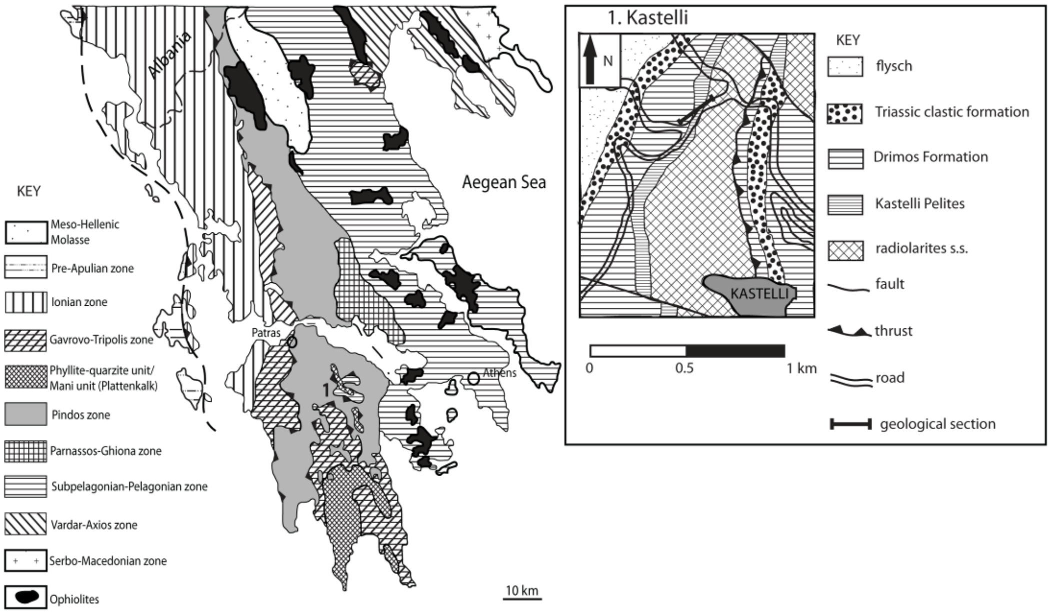

Fig. 1 (left): Simplified geological map showing the main tectono-stratigraphic zones of the Hellenides; (right): Geological map illustrating the general position of the Kastelli section.

2. Geological setting

The study area is located to the Pindos Zone (Western Greece) which belongs to the external Hellenides (Fig. 1). The sediments of the Pindos Zone originate from an elongate remnant ocean basin that formed in mid-Triassic times along the north-east passive margin of Apulia between the extensive Gavrovo–Tripolis platform in the present west and the Pelagonian continental block in the east (Degnan and Robertson 1998). The Pindos Zone of Western Greece is exceptional because 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. 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 and Robertson (1998) describe the series as follows: the oldest sediments (Carnian) comprise disrupted siliciclastic turbidites (with plant remains), largely derived from a metamorphic source to the west and deposited on young oceanic basement. From the Norian to the end-Maastrichtian, variable thicknesses of hemipelagic–pelagic carbonates, marls and proximal carbonate debris flows accumulated in westerly areas, while mainly pelagic carbonate and more distal calciturbidites were deposited further east. This pattern was interrupted by an extended period of siliceous, radiolarian-dominated sedimentation (radiolarites) during the Aalenian to Tithonian stages of the Jurassic. From the Maastrichtian onwards, progressive closure of the Pindos oceanic basin is recorded by a gradual change in sediment composition (late Maastrichtian "couches de passage") from dominantly carbonate deposition to siliciclastic sediment (flysch) derived from the north and east. During the Eocene, complete closure of the Pindos Ocean resulted in the detachment of its deep-sea sedimentary cover from its oceanic basement as an accretionary prism and emplacement westwards onto the adjacent carbonate platform, ending up as a series of thin-skinned thrust sheets.

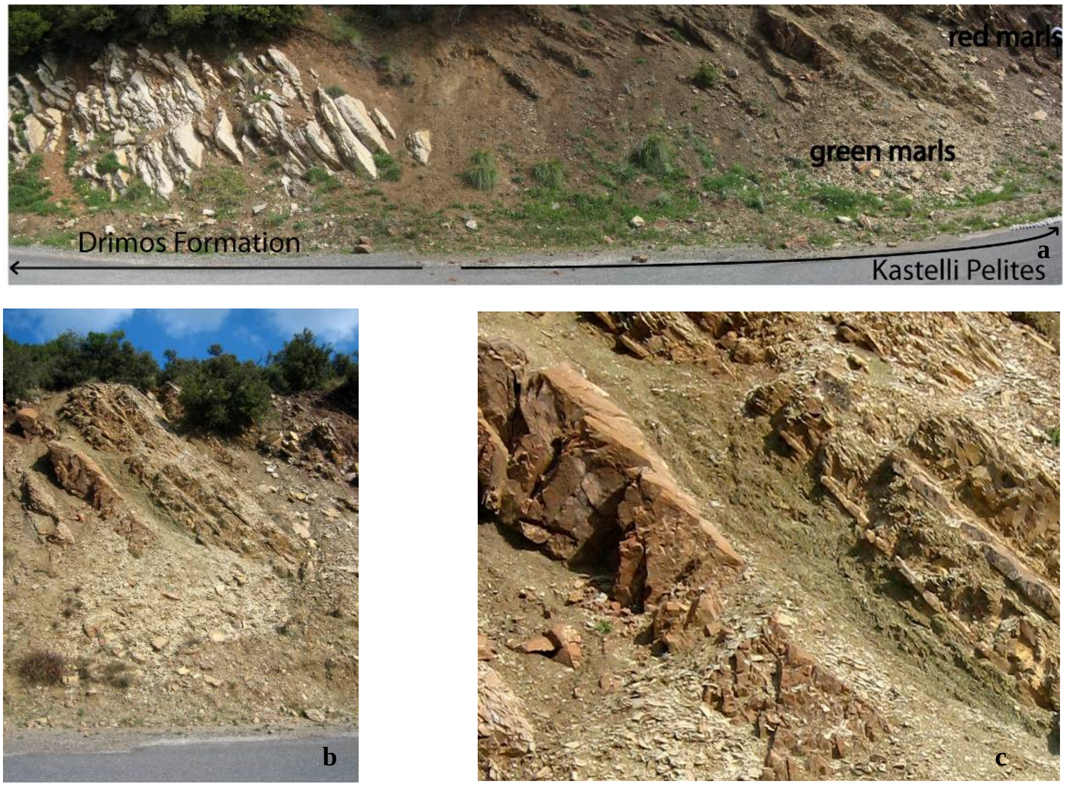

Fig. 2 (a): view of the whole section (b): green marls at the base of the Kastelli Pelites formation (c): detail of the green marls

In the Kastelli section (Fig. 1 and 2), from bottom to top, the following are observed:

- Drimos Formation, which in the upper part comprises mainly limestones attaining some 60 m in thickness. The observed faunas in this upper part, containing only some reworked algae and Foraminifera (e.g. *Thaumatoporella sp*. and Textulariida respectively), do not allow determination of a precise age.

- Kastelli Pelites, comprising sediments of about 35 m thick. The first 5 m consists of a succession of thin-layered (5-10 cm) marly limestones alternating with marls, followed by a succession of 10 m of mainly green organic carbon-rich clays, marly limestones and rare chert intercalations. The section continues with about 10 m of red marls and some intercalations of marly limestones, followed by 5 m of red-green marly limestones and marls. In thin-sections of the marly limestones, badly preserved Foraminifera are observed. The succession ends with 5 m of marly limestones and red marls, cherty at top. These cherts indicate a passage into the stratigraphically overlying radiolarites *s.s*.

There are very few data concerning the age of Kastelli Pelites. Lyberis et al. (1980) attributed the formation to the Upper Pliensbachian–Toarcian, comparing the palynological associations observed in the Greek mainland with those of the Vicentinian Alps, Italy. Nevertheless, the only precise data are referred to by Fleury (1980) and de Wever and Origlia-Devos (1982), who suggested an Aalenian age for the top of the Kastelli Pelites. 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 and Origlia-Devos's (1982) data are based on foraminiferal faunas from the Peloponessus. Based on general biostratigraphic and diagnostic chemostratigraphic signatures described in an earlier (Jenkyns 1988) and the present work, we suggest that the Kastelli Pelites are correlative with other biostratigraphically well-dated Lower Toarcian black shales in Greece (e.g. Ionian Zone) and were formed during the Oceanic Anoxic Event. This interpretation would place most or all of the Kastelli Pelites in the *tenuicostatum* and the overlying *falciferum/levisoni/serpentinum* and possibly *bifrons* Zones (c.f. Jenkyns et al., 2002; Hesselbo et al., 2007).

3. Methods

A set of 191 bulk sediments was collected from the Kastelli section. The collected samples were powdered and analysed for weight percent total organic carbon using a Strohlein Coulomat 702 analyser (details in Jenkyns, 1988) and for carbonate carbon isotopes using a VG Isogas Prism II mass spectrometer (details in Jenkyns et al., 1994). All the above analyses were undertaken in the Department of Earth Sciences in the University of Oxford.

4. Conclusions–Results

In the Kastelli section, the TOC percentage is very low (Figure 3). The background values of TOC fluctuate around 0.10–0.20 wt% and cover most parts of the section. After the lowest 7.5 m, TOC values begin to rise gradually for 1.5 m, until the maximum value of 1.79 wt% is attained. After this positive excursion, values return to background values until the end of the studied section.

In the same figure the carbon-isotope values in carbonate are reported. The bulk carbonate carbon-isotope values record a small positive followed by a negative excursion in the lowest metre of the section: $\delta^{13}C_{carb}$ values climb up to 3.32‰ and drop down to 0.64‰. A similar excursion, but with a larger range of values, has been reported in Peniche, Portugal and Yorkshire, northeast England (Hesselbo et al. 2007; Littler et al. 2010) at the Pliensbachian–Toarcian boundary, and this age assignment is adopted for the Kastelli section. Above the stage boundary, values are stable around 2‰. The background values continue up to the next 7.50 m of the section, where $\delta^{13}C_{carb}$ begins to fall irregularly, reaching a minimum of -5‰. The negative excursion persists over the next 5 m. Following that, values begin to recover and indicate a broad positive excursion up to 3.83‰, as seen in many other European sections whose biostratigraphy is well constrained (Jenkyns and Clayton, 1986, 1997; Jenkyns, 2003; Sabatino et al., 2009).

Comparing the TOC and carbon-isotope curves, the polarity between them is noteworthy. Such a stratigraphical coincidence between the negative carbon-isotope excursion and TOC maximum has also been observed in Lower Toarcian black shales in northern Europe (Jenkyns and Clayton 1997; Jenkyns et al. 2002). The TOC values are, however, very low compared with other coeval Toarcian sections from northern Europe, where values reach up to 15%. This difference probably relates to relatively elevated organic productivity, enhanced watermass stratification, more frequent and prolonged euxinic conditions and lesser water depths in the more boreal epicontinental seaway (Jenkyns et al. 2002; Sabatino et al. 2009; Jenkyns, 2010).

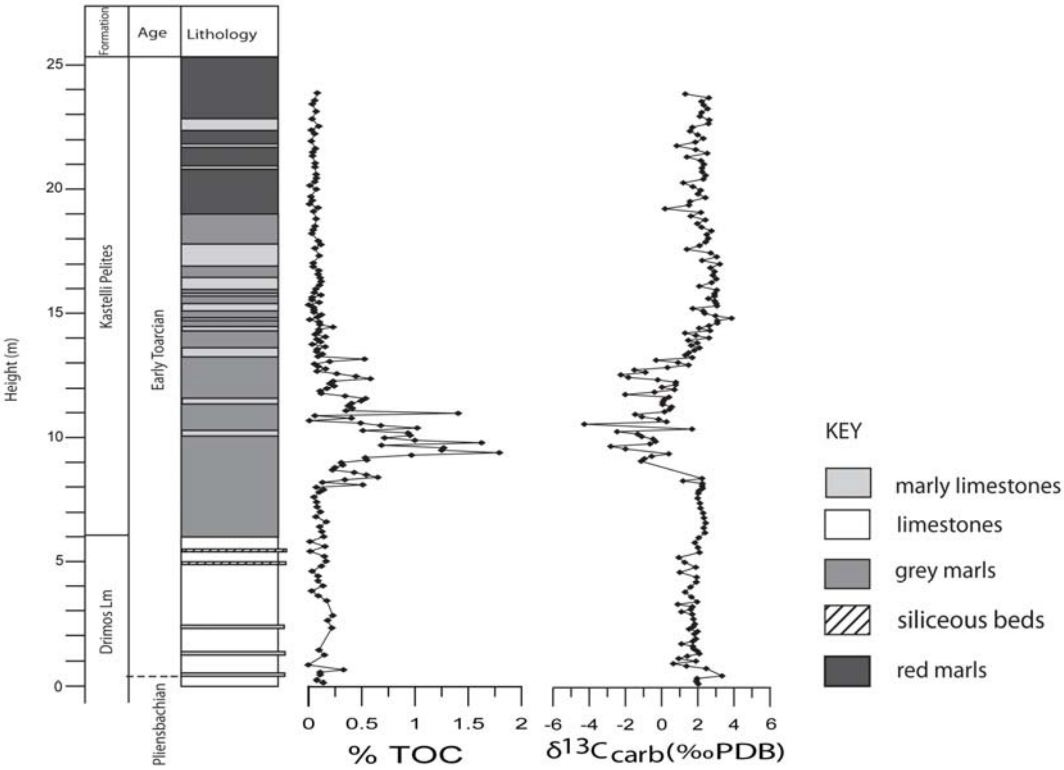

Fig. 3 Lithological column, bulk TOC and stable carbon carbonate-isotope profile for the Kastelli section.

Even though this research is preliminary, the record of the Toarcian OAE from these deep-marine sediments reinforces the global character of this event. Further studies of this section and comparison with coeval horizons of the Ionian Zone (lower Posidonia beds) are in progress. Integration of these results will shed further light on the causes and effects of the early Toarcian Oceanic Anoxic Event.

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6. References

Bailey, T. R., Rosenthal, Y., McArthur, J. M. and van der Schootbrugge, B., 2003. Paleoceanographic changes of the Late Pliensbachian–Early Toarcian interval: a possible link to the genesis of an Oceanic Anoxic Event. *Earth and Planetary Science Letters* 212, 307-320.

De Wever, P. and Origlia-Devos, I., 1982. Datation par les Radiolaires des niveaux siliceux du Lias de la Série du Pinde–Olonos (Formation de Drimos, Péloponnèse et Grèce continentale). *C. R. Acad. Sci. Paris, sér. II* 294, 1191-1198.

Degnan, P. J. and Robertson, A. H. F., 1998. Mesozoic–early Tertiary passive margin evolution of the Pindos ocean (NW Peloponnese, Greece). *Sedimentary Geology* 117, 33-70.

Fleury, J. J., 1980. Les zones de Gavrovo-Tripolitza et du Pinde-Olonos (Grèce continentale et Péloponèse du nord). Evolution d'une plate-forme et d'un bassin dans leur cadre alpin. *Publication Societé Géol. Nord* 4, 1-473.

Hesselbo, S. P., Gröcke, D. R., Jenkyns, H. C., Bjerrum, C. J., Farrimond, P., Morgans Bell, H. S. and Green, O. R., 2000. Massive dissociation of gas hydrate during a Jurassic oceanic anoxic event. *Nature* 406, 392-395.

Hesselbo, S. P., Jenkyns, H. C., Duarte, L. V. and Oliveira, L. C. V., 2007. Carbon-isotope record of the Early Jurassic (Toarcian) Oceanic Anoxic Event from fossil wood and marine carbonate (Lusitanian Basin, Portugal). *Earth and Planetary Science Letters* 253(3-4), 455.

Jenkyns, H. C., 1988. The early Toarcian (Jurassic) anoxic event: stratigraphic, sedimentary, and geochemical evidence. *American Journal of Science* 288, 101-151.

Jenkyns, H. C., 2003. Evidence for rapid climate change in the Mesozoic-Palaeogene greenhouse world. *Phil Trans. R. Soc., Series A* 361, 1885-1916.

Jenkyns, H. C. 2010. The geochemistry of Oceanic Anoxic Events. *Geochem. Geophys. Geosyst*., doi:10.1029/2009GC002788, in press.

Jenkyns, H. C. and Clayton, C. J., 1986. Black shales and carbon isotopes in pelagic sediments from the Tethyan Lower Jurassic. *Sedimentology* 33, 87-106.

Jenkyns, H. C. and Clayton, C. J., 1997. Lower Jurassic epicontinental carbonates and mudstones from England and Wales: chemostratigraphic signals and the early Toarcian anoxic event. *Sedimentology* 44, 687-706.

Jenkyns, H.C., Sarti, M., Masetti, D. and Howarth, M.K. 1985. Ammonites and stratigraphy of Lower Jurassic black shales and pelagic limestones from the Belluno Trough, Southern Alps, Italy. *Eclogae Geologicae Helvetiae*, 78, 299-301.

Jenkyns, H. C., Gale, A. S. and Corfield, R. M., 1994. Carbon- and oxygen-isotope stratigraphy of the English Chalk and Italian Scaglia and its palaeoclimatic significance. *Geological Magazine* 131, 1-34.

Jenkyns, H. C., Gröcke, D. R. and Hesselbo, S. P., 2001. Nitrogen isotope evidence for water mass denitrification during the Early Toarcian (Jurassic) Oceanic Anoxic Event. *Paleoceanography* 16, 593-603.

Jenkyns, H. C., Jones, C. E., Gröcke, D. R., Hesselbo, S. P. and Parkinson, D. N., 2002. Chemostratigraphy of the Jurassic System; applications, limitations and implications for palaeoceanography. *Journal of the Geological Society of London* 159, 351-378.

Karakitsios, V., 1995. The influence of preexisting structure and halokinesis on organic matter preservation and thrust system evolution in the Ionian Basin, Northwest Greece. *American Association of Petroleum Geologists Bulletin* 79, 960-980.

Kemp, D. B., Coe, A. L., Cohen, A. S. and Schwark, L., 2005. Astronomical pacing of methane release in the Early Jurassic period. *Nature* 437, 396-399.

Little, C. T. S. and Benton, M. J., 1995. Early Jurassic mass extinction: A global long-term event. *Geology* 23, 495-498.

Littler, K., Hesselbo, P. S. and H.C., J., 2010. A carbon-isotope perturbation at the Pliensbachian-Toarcian boundary: evidence from the Lias Group, NE England. *Geological Magazine,* doi: 10.1017/S0016756809990458, in press.

Lyberis, N., Chotin, P. and Doubinger, J., 1980. Précisions stratigraphiques sur la série du Pinde (Grèce): la durée de sédimentation des "radiolarites". *Comptes Rendus de l' Académie des Sciences, Paris, série D,* 290, 1513-1516.

Rigakis, N. and Karakitsios, V., 1998. The source rock horizons of the Ionian Basin (NW Greece). *Marine and Petroleum Geology* 15, 593-617.

Sabatino, N., Neri, R., Bellanca, A., Jenkyns, H. C., Baudin, F., Parisi, G. and Masetti, D., 2009. Carbon-isotope records of the Early Jurassic (Toarcian) oceanic anoxic event from the Valdorbia (Umbria–Marche Apennines) and Monte Mangart (Julian Alps) sections: palaeoceanographic and stratigraphic implications. *Sedimentology* 56, 1307-1328.

Schlanger, S. O. and Jenkyns, H. C., 1976. Cretaceous oceanic anoxic events: causes and consequences. *Geologie en Mijnbouw* 55, 179-184.

Suan, G., Mattioli, E., Pittet, B., Mailliot, S. and Lecuyer, C., 2008. Evidence for major environmental perturbation prior to and during the Toarcian (Early Jurassic) oveanic anoxic event from the Lusitanian Basin, Portugal. *Paleoceanography* 23, PA1202, doi: 10.1029/2007PA001459.

van der Schootbrugge, B., McArthur, J. M., Bailey, T. R., Rosenthal, Y., Wright, J. D. and Miller, G. K., 2005. Toarcian oceanic anoxic event: An assessment of global causes using belemnite C isotope records. *Paleoceanography* 20, PA3008, doi: 10.1029/2004PA001102.

Woodfine, R.G., Jenkyns, H.C., Sarti, M., Baroncini, F. and Violante, C. 2008. The response of two Tethyan carbonate platforms to the early Toarcian (Jurassic) oceanic anoxic event: environmental change and differential subsidence. *Sedimentology*, 55, 1011-1028.

Symposium: Climate and Ocean Dynamics of the Cretaceous Greenhouse World

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Carbon-cycle perturbation during the Toarcian OAE (T-OAE) recorded in Pindos Zone, Greece

N. Kafousia[1*], V. Karakitsios[1], H.C. Jenkyns[2] & E. Mattioli[3]

[1] Department of Geology and Geoenvironment, National University of Athens, Panepistimiopolis 15784, Athens, Greece, ([*]correspondence: nkafousia@geol.uoa.gr), (vkarak@geol.uoa.gr)

[2]Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, United Kingdom, (hughj@earth.ox.ac.uk)

[3]Université Claude Bernard Lyon I, UMR 5125, CNRS, PaléoEnvironnements et PaléobioSphère, Département des Sciences de la Terre, 2 rue Dubois, 69622 Villeurbanne, France (emanuela.mattioli@univ-lyon1.fr)

Abstract

The carbon cycle of the Early Toarcian has been affected by a severe perturbation that is recorded by a negative and/or positive excursion in its isotopic signal accompanied by increased burial of marine organic carbon during an Oceanic Anoxic Event (T-OAE). This isotopic excursion has been recorded in pelagic and shallow-water carbonates and marine and terrestrial organic matter. There are several proposed explanations for the causes of this perturbation, divided into two main categories: one suggesting local oceanographic control, the other suggesting factors influencing the entire ocean–atmosphere system. The first explains the T-OAE by overturning of a stratified water column rich in CO_2 from the oxidation of organic matter, while the latter suggests introduction of isotopically light carbon into the atmosphere and hydrosphere from either dissociation of gas hydrates or hydrothermal/volcanic venting of greenhouse gases.

In this paper, we present the first organic-carbon isotope and biostratigraphic profiles in bulk rock from two different Lower Toarcian sections from the Pindos Zone of western Greece. These pelagic sediments, which record the geochemical signature of the Oceanic Anoxic Event (T-OAE), originate from an elongate remnant ocean basin (Pindos Ocean) that formed in mid-Triassic times along the northeast passive margin of Apulia between the extensive Gavrovo–Tripolis carbonate platform in the west and the Pelagonian continental block in the east.

In both sections through a unit known as the Kastelli Pelites, new nannofossil data indicate an early Toarcian age. The negative carbon-isotope excursion that characterizes the OAE is present and is divided in two smaller segments. In the first section (Kastelli), the $\delta^{13}C_{org}$ values drop down to –31.1‰ in the first segment and drop again, to -32.1‰, in the second. Above and below the negative excursion values fluctuate around background values of ~ -25‰.

In the second examined section, Livartzi, $\delta^{13}C_{org}$ values in the limestones of the lower part of the section shows scattered data points, but in general values are in the same range as in the Kastelli section. In this section, the first part of the negative excursion reaches a minimum value of -31.85‰ while, in the second minimum, values fall to ~-30‰.

The study of two different sections of the same Zone provides strong proof for the age of the Kastelli Pelites and also the presence of the T-OAE in the Pindos Zone. Therefore, since these sediments comprise some of the deepest marine sediments of the Tethyan region, the global significance of this event is reinforced.

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submission@cbga2010.org

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Preliminary results of the palynological investigation of the Toarcian deposits of Ionian Zone (Western Greece)

Kouli K.[1], Kafousia N.[1] and Karakitsios V.[1]
[1]*Department of Historical Geology and Palaeontology, Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens, 15784 Zografou, Greece akouli@geol.uoa.gr, nkafousia@geol.uoa.gr, vkarak@geol.uoa.gr.*

Abstract
In this study we present preliminary palynological data from Lower Toarcian deposits of the Ionian Zone (Western Greece). The Ionian Zone belongs to the external Hellenides and during the Mesozoic constituted part of the southern Tethyan margin. The initially shallow carbonate platform of the Ionian Basin began to break up in the early Pliensbachian. The first deepening of the basin has been recorded in Siniais Limestones that are followed by Posidonia Beds (Karakitsios 1992). The occurrence of macroremains of the conifer *Brachyphyllum nepos* (Karakitsios and Velitzelos 1994), together with geochemical and palynological studies (Baudin and Lachkar 1990) of Toarcian deposits of the Ionian Zone, suggested the presence of a tropical biome in the broader area.
The 20-m outcrop examined (Toka section) begins in the upper part of the Siniais Limestones and continues into the lower part of the overlying Posidonia Beds. In the studied deposits previous research (Kafousia et al. 2008) has documented the local expression of the global Toarcian Oceanic Anoxic Event. The Early Toarcian Oceanic Anoxic Event has been associated with exceptionally high rates of organic-carbon burial, marine anoxia to euxinia, sea transgression, high palaeotemperatures and mass extinction and is generally considered as a significant climatic driven event.
Palynological investigation of the deposits aims to contribute further to our knowledge about the Toarcian palaeoenvironmental conditions, while the resulting dataset is an additional contribution to the Jurassic biostratigraphy of the Ionian Zone. Most studied samples yielded a considerable amount of palynological residue, including moderate diverse and fairly well preserved palynomorph assemblages of pollen, spores and dinoflagellate cysts. Additionally in palynospectra from organic rich horizons a significant quantity of amorphous organic matter has been recorded.

References
Baudin F. and Lachkar G., 1990. Géochimie organique et palynologie du Lias supérieur en zone Ionienne (Grèce): example d'une sédimentation anoxique conservée dans une paléomarge en distension. Bull. Soc. Géol. France 8 VI/I: 123-132.
Kafousia N., Karakitsios V. and Jenkyns H.C., 2008. High- and low-resolution isotopic data record the Toarcian Oceanic Anoxic Event in the Ionian Zone, Western Greece" SDGG, Heft 58, Abstract volume -26th IAS Regional Meeting/ SEPM-CES SEDIMENT 2008
Karakitsios V., 1992. Ouverture et inversion tectonique du bassin ionien (Epire, Grèce). Ann. Geol. Pays Hell. 35: 185-318
Karakitsios V. and Velitzelos E., 1994. Discovery of the conifer *Brachyphyllum nepos* SAPORTA in the Lower Posidonia beds (Toarcian) of the Ionian zone (Epirus, NW-Greece). Bull. Geol. Soc. Greece XXX/2: 207-215.

"Death in soil" or what can we learn from groundwater for the genesis of soil organic matter

M. Kaestner[1]*, A. Miltner[1], P. Bombach[1] and B. Schmidt-Brücken[2]

[1]Department of Environmental Biotechnology (formerly Bioremediation), UFZ-Centre for Environmental Research, 04318 Leipzig, Germany
[2]Institute of materials science, TU Dresden, 01069 Dresden, Germany

Soil microorganisms do not only catalyze the transformation of plant residues to soil organic matter, but also serve as considerable carbon source for the formation of refractory soil organic matter by providing cell fragments as structural interfacial surfaces in soil systems.

After incubation of ^{13}C-labeled Gram negative bacteria in soil for 224 days, we could show that 44% of the bulk carbon remained in soil [1] whereas only 10% were found in living biomass fatty acids (PLFA) [2]and ~15 % in amino acids [3] of the living microbial food web [4]. This shows that 30 – 35 % of the remaining bulk C from Gram negative microbial biomass was stabilized in non-living soil organic matter (SOM). Surprisingly, 95% of the added labeled biomass proteins remained in soil which clearly indicates the stabilization of proteins in cell aggregations being more resistant to biodegradation than free proteins and amino acids. Scanning electron micrographs of the soil showed very rarely intact cells but highly abundant patchy organic cover material of 20 to 50 nm^2 size on the mineral surfaces.

A possible mechanism for this stabilization and the observed material could be found by analyses of microbial communities and biofilms developing on Biosep© beads within *in situ* microcosms exposed to contaminated aquifers. Scanning electron micrographs of the developing biofilms on the beads showed the formation of such patchy material found in the soil by fragmentation of empty bacterial cell envelopes (cell walls) and all stages of decay. The fragmentation of these cell walls provided a mechanistic explanation for the observed stabilisation, the genesis of SOM derived from dead bacterial cells, and the enzyme activity always found associated to SOM.

[1] Kindler *et al*. (2006) *Soil Biol. Biochem.* **38**, 2860-2870. [2] Kindler *et al*. (2009) *Org. Geochem.* **40**, 29-37. [3] Kindler *et al*. (2009) *Org. Geochem.* in revision. [4] Lueders *et al*. (2006) *Appl. Environ. Microbiol.* **72**, 5342-5348.

Indications for the global character of the Early Toarcian Oceanic Anoxic Event: Evidence from the Pindos Zone, western Greece

N. Kafousia[1]*, V. Karakitsios[1] and H.C. Jenkyns[2]

[1]Department of Geology and Geoenvironment, National University of Athens, Panepistimiopolis 15784, Athens, Greece (*correspondence: nkafousia@geol.uoa.gr) (vkarak@geol.uoa.gr)
[2]Department of Earth Sciences, University of Oxford, Parks Road, Oxford OX1 3PR, United Kingdom (hughj@earth.ox.ac.uk)

In this paper, we present the first carbonate-carbon isotope profiles in bulk rock from two different Lower Toarcian sections from the Pindos Zone of western Greece. These pelagic sediments, which record the geochemical signature of the Oceanic Anoxic Event (OAE), originate from an elongate remnant ocean basin that started to form in mid-Triassic times along the northeast passive margin of Apulia between the extensive Gavrovo–Tripolis carbonate platform in the west and the Pelagonian continental block in the east.

In both sections, the negative carbon-isotope excursion that characterizes the OAE is present. In the first section (Kastelli), the $\delta^{13}C_{carb}$ values are very stable within the lowest 8 m, with background values of ~2‰. At the top of this interval, values begin to fall, reaching a minimun of ~-5‰. The negative excursion extends over ~7 m, at the summit of which $\delta^{13}C_{carb}$ values return to background levels.

The second examined section is Livartzi. Here, $\delta^{13}C_{carb}$ values have the same background levels as in the Kastelli section; this value is retained for the first 6 m. The negative excursion that follows is divided in two smaller segments. The first (stratigraphically lower) excursion drops to ~ -0.5‰; the second to ~0‰. After this irregular excursion, values increase again, reaching ~ 3‰.

Examination of the two different sections provides definitive proof for the impact of the Toarcian Oceanic Anoxic Event in the Pindos Zone. This occurrence reinforces the intepretation of this event as global in character, because some of the deepest marine sediments of the Tethyan region accumulated in the Pindos Zone.