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

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Abstract – The Early Toarcian (Early Jurassic, *c.* 183 Ma) was characterized by an Oceanic Anoxic Event (T-OAE), primarily identified by the presence of globally distributed approximately coeval black organic-rich shales. This event corresponded with relatively high marine temperatures, mass extinction, and both positive and negative carbon-isotope excursions. Because most studies of the T-OAE have taken place in northern European and Tethyan palaeogeographic domains, there is considerable controversy as to the regional or global character of this event. Here, we present the first high-resolution integrated chemostratigraphic (carbonate, organic carbon, $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$) 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 CO₂ from the oxidation of organic matter; those suggesting global control suggest introduction of isotopically light carbon into the ocean–atmosphere system from dissociation of gas hydrates or hydrothermal venting of greenhouse gases. Certainly, the recent recognition of the T-OAE in Argentina suggests the impact of this phenomenon was not confined to the northern hemisphere (Al-Suwaidi *et al.* 2010).

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

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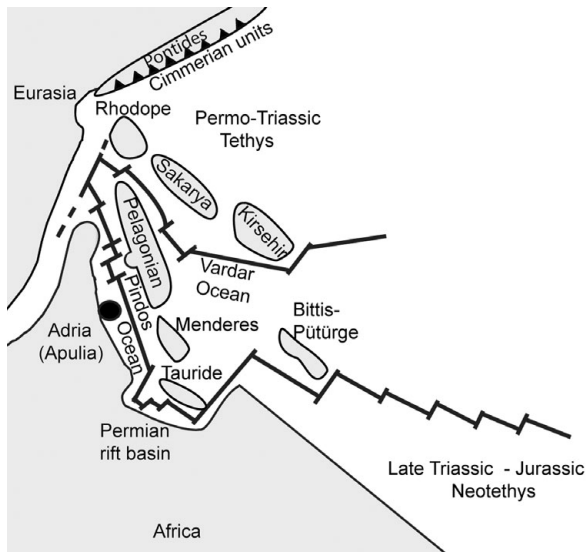


Figure 1. Early Jurassic palaeogeography of the western Tethys Ocean (based on Clift, 1992; Dercourt, Ricou & Vrielynck, 1993; Channell & Kozur, 1997; Degnan & Robertson, 1998; Pe-Piper, 1998). The approximate position of the study area is illustrated by the black circle. The stable segment of Adria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

of the Kastelli Pelites, here unambiguously identified 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

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

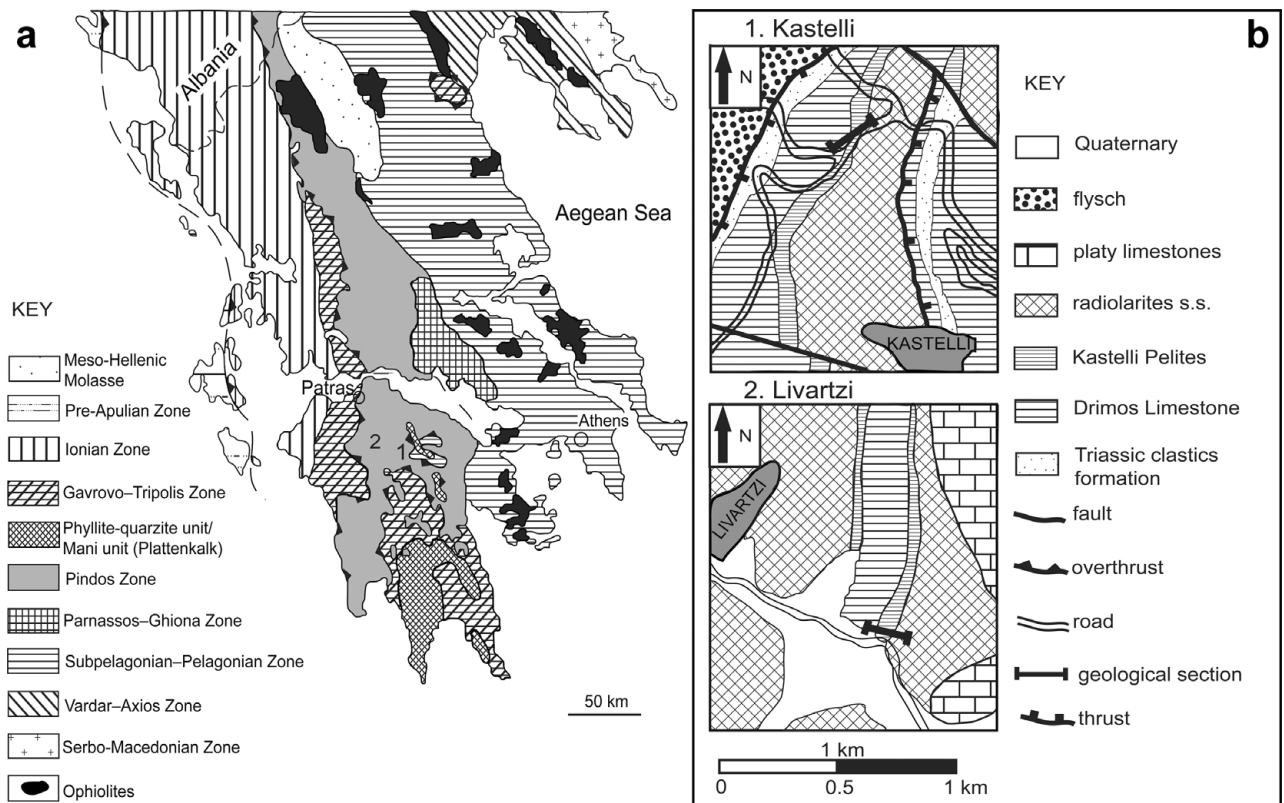


Figure 2. (a) Simplified geological map with the main tectonostratigraphic zones of the Hellenides. (b) Geological map of Kastelli section (above) and Livartzi section (below).

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; Wooller, 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 5 m of marly limestones and red marls, cherty at the top. 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 CaCO₃ 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

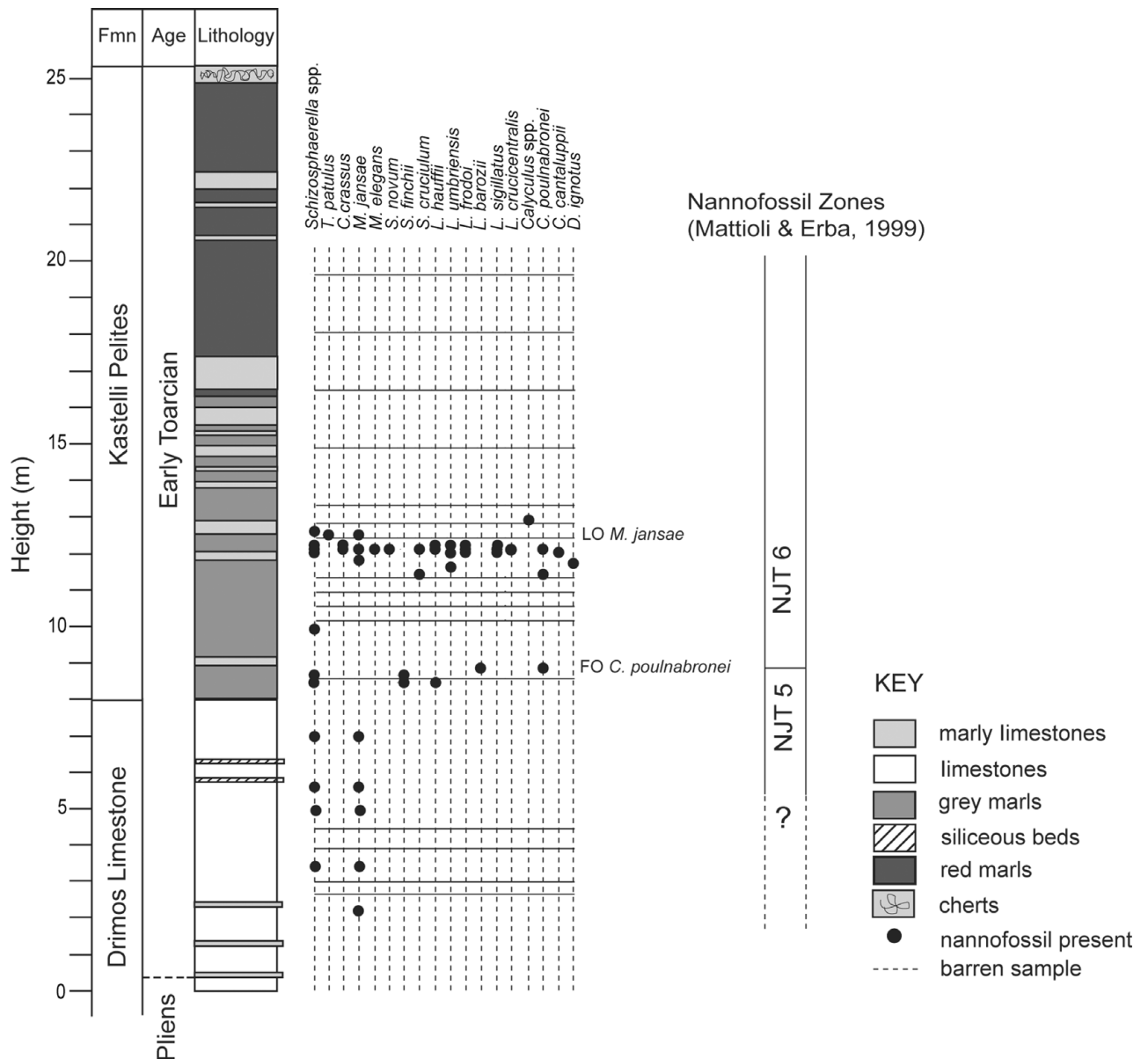


Figure 3. Lithological column and biostratigraphical data from the Kastelli section. Nannofossil zones after Mattioli & Erba (1999).

222 were counted for each sample in a surface area of the
 223 slide varying between 1 and 2 cm².

224 **5. Results**

225 **5.a. Biostratigraphy**

226 There are very few data concerning the age of the
 227 Kastelli Pelites, the lack of ammonites indicating that
 228 the sequence was deposited below the aragonite compen-
 229 sation depth. Lyberis, Chotin & Doubinger (1980)
 230 attributed the unit to the Late Pliensbachian/Toarcian,
 231 comparing the palynological associations with those
 232 of the Vicentin Alps. Nevertheless, the only precise
 233 data are referred to by Fleury (1980) and de Wever
 234 & Origlia-Devos (1982), who suggest an Aalenian
 235 age for the top of the Kastelli Pelites unit. Fleury's
 236 (1980) data are based on the presence of *Meyendorffina*
 237 (*Lucasella*) *cayeuxi* (Lucas) in a limestone layer at

the top of Kastelli Pelites in the Karpenission region 238
 (central Greece); and de Wever & Origlia-Devos's 239
 (1982) data are based on Foraminifera faunas from 240
 the Peloponnese. Based on general biostratigraphic 241
 and chemostratigraphic considerations, Jenkyns (1988) 242
 suggested that the Kastelli Pelites were correlative with 243
 other black shales in Greece (in the Ionian Zone) and 244
 were formed during the T-OAE. 245

We undertook detailed biostratigraphical analyses of 246
 calcareous nannofossils in an effort to improve and 247
 expand the biostratigraphical resolution from previous 248
 studies. The nannofossil distribution is summarized in 249
 Figures 3 and 4. 250

251 *5.a.1. Kastelli section*

Samples were taken from the limestones at the top 252
 of the Drimos Limestone Formation, as well as from 253
 the lower to middle part of the Kastelli Pelites for 254

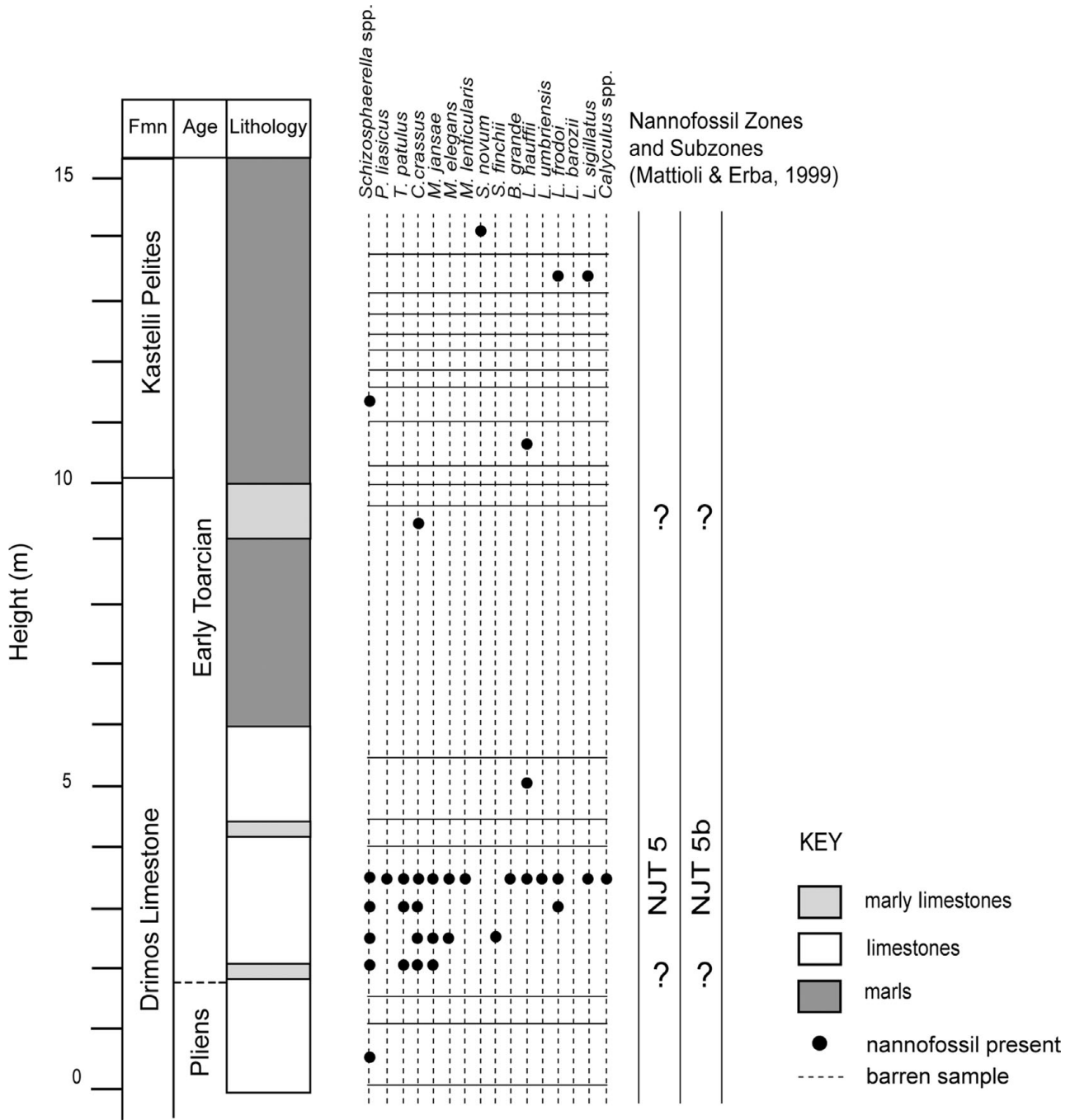


Figure 4. Lithological column and biostratigraphical data from the Livartzi section. Nannofossil zones after Mattioli & Erba (1999).

255 a thickness of about 20 m. Twelve samples were
 256 barren of nannofossils, and the rest contained very
 257 few specimens. The assemblage is represented by rare
 258 *Schizosphaerella* spp., *Mitrolithus jansae* and *M. elegans*,
 259 *Calyculus* spp., *Similiscutum cruciulum*, *S. finchii*
 260 and *S. novum*, *Tubirhabdus patulus*, *Crepidolithus*
 261 *crassus*, and various species of the genus *Lotharingius*,
 262 including the zonal marker *L. hauffii*. This assemblage
 263 allows us to identify the NJT 5 nannofossil Zone (Late
 264 Pliensbachian to Early Toarcian). Specimens belonging
 265 to the *Carinolithus* genus, namely *C. poulabronei*
 266 and *C. cantaluppii*, were recorded discontinuously
 267 starting from sample 34. This occurrence can be used
 268 at Kastelli to identify the NJT 6 nannofossil Zone. The

269 last occurrence of *Mitrolithus jansae* was observed in
 270 sample 71 (12.5 m). A single specimen of *Discorhab-*
 271 *dus ignotus* was encountered in sample 63 (12 m). The
 272 first occurrence of this species is fixed at the *tenu-*
 273 *icostatum/serpentinum* zonal boundary in central Italy
 274 (Mattioli & Erba, 1999), where it is considered to mark
 275 the end of the Early Toarcian OAE (Bucefalo Palliani &
 276 Mattioli, 1998; Mattioli *et al.* 2004), although in some
 277 areas an earlier occurrence of *D. ignotus* is recorded
 278 (Mattioli *et al.* 2008; Bodin *et al.* 2010).

5.a.2. Livartzi section 279

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

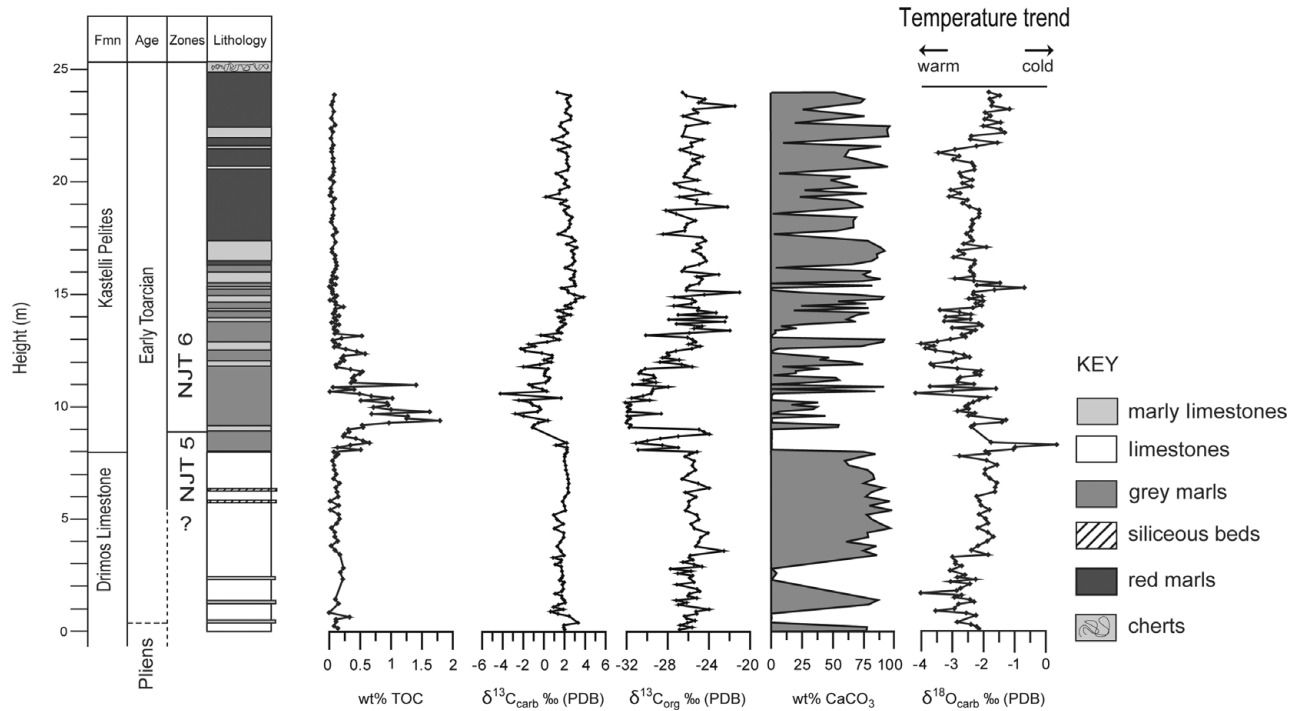


Figure 5. Lithostratigraphical log, bulk TOC, stable-isotope (C, O) and wt % CaCO₃ profiles through the Kastelli section. For a colour version of this figure see online Appendix at <http://journals.cambridge.org/geo>.

282 samples show assemblages similar to those of the
 283 Kastelli section with poorly preserved and rare nano-
 284 fossils. The interval between samples 11 and 36
 285 (from 1.1 to 3.6 m) represents an exception, because
 286 samples are richer, with common *Schizosphaerella* and
 287 *M. jansae*. The stratigraphically highest specimen of
 288 *M. jansae* is recorded in sample 36 (3.6 m). However,
 289 we cannot confidently define this datum level as
 290 a last occurrence because the samples studied in
 291 the interval above are barren of nannofossils. This
 292 assemblage, and the presence in the assemblage of *L.*
 293 *sigillatus*, allows attribution of this interval to the NJT
 294 5b nannofossil Subzone (uppermost Pliensbachian to
 295 lowermost Toarcian).

296 5.b. Chemostratigraphy

297 5.b.1. Kastelli section

298 5.b.1.a. Organic carbon and carbonate profiles Chemo-
 299 stratigraphic data are illustrated in Figure 5. The
 300 total organic carbon (TOC) values are very low and
 301 stable in the lower part of the section where back-
 302 ground values are in the range 0.10–0.20 wt %. After the lowest
 303 7.5 m, the TOC values begin to rise gradually for 1.5 m
 304 defining a positive excursion to reach a maximum value
 305 of 1.79 wt %. At the top of this interval, values return
 306 to background levels.

307 The carbonate values do not follow any particular
 308 trend nor do they respond to the excursion. Up to the
 309 level where the TOC excursion begins, the percentage
 310 of CaCO₃ in the bulk rock fluctuates between 60 and
 311 100 %. When the excursion begins, there is a sudden
 312 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).

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

319 The carbon- and oxygen-isotope values in carbonate
 320 and the TOC of bulk rock are reported in Figure 5. The
 321 bulk carbonate carbon-isotope values record a small
 322 positive followed by a negative excursion in the lowest
 323 metre of the section. Above this small disturbance, val-
 324 ues are very stable within the next 7.5 m of the section,
 325 with background values of 2 ‰. Thereafter, δ¹³C_{carb}
 326 values begin to fall irregularly, reaching a minimum
 327 of -5 ‰. The negative excursion extends over the
 328 next 5 m before recovery takes place and back-
 329 ground values of ~2 ‰ are restored. What is remarkable is
 330 the polarity between the TOC profile and the carbonate
 331 carbon-isotope profile, with the two curves appearing as
 332 approximate mirror images of one another. The strati-
 333 graphical coincidence between the negative carbon-
 334 isotope excursion and relative TOC maximum is also
 335 observed in Toarcian black shales from northwestern
 336 Europe and central Italy (Jenkyns & Clayton, 1997;
 337 Jenkyns *et al.* 2002; Mattioli *et al.* 2004).

338 The organic carbon-isotope profile is slightly differ-
 339 ent from that of δ¹³C_{carb}. The first shift is recorded in
 340 the interval 8 to 9 m and records a drop from -25.15 ‰
 341 to -31.1 ‰; following this excursion, values return
 342 to -24.95 ‰. Above this level, values drop again, to
 343 -32.1 ‰, and remain low for approximately 2.5 m.
 344 Stratigraphically higher in the section, values become

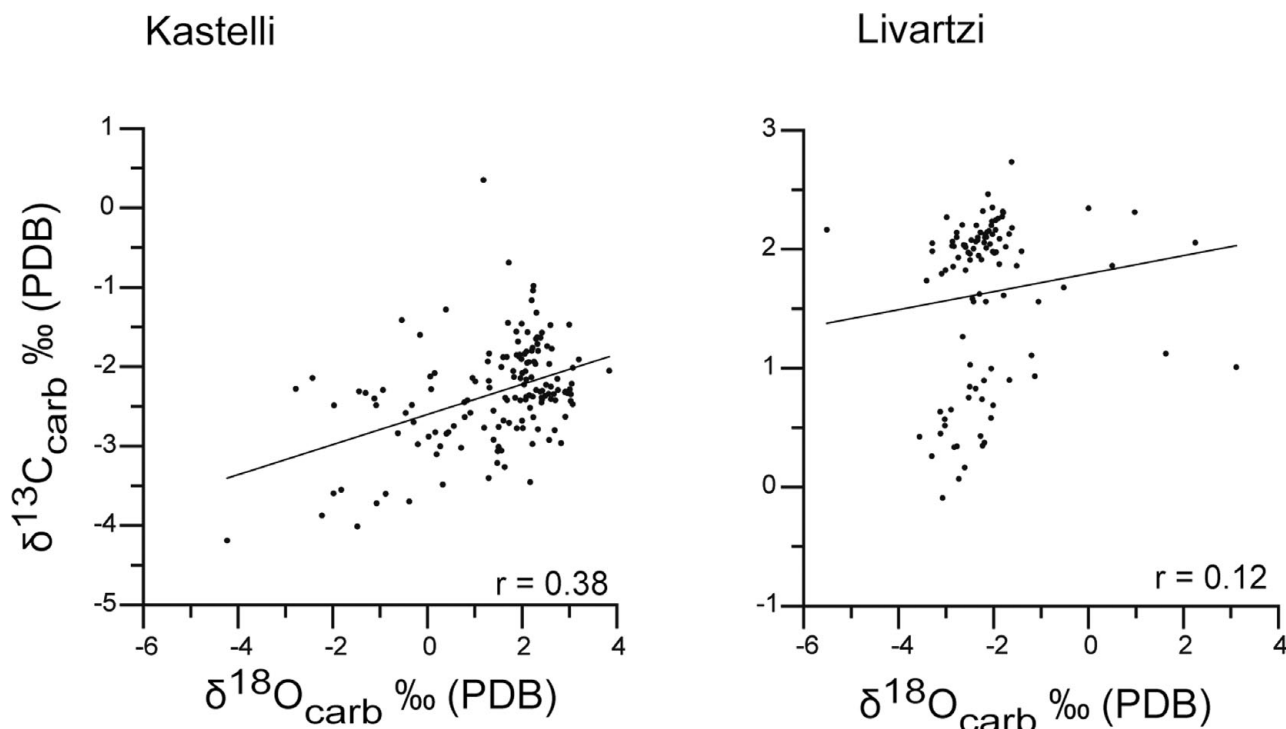


Figure 6. Cross-plot of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ data from the Kastelli and Livartzi sections. For a colour version of this figure see online Appendix at <http://journals.cambridge.org/geo>.

heavier and fluctuate around a background value of -25‰ .

Oxygen-isotope values are generally in the range of -2‰ (Fig. 5), which is a typical value for $\delta^{18}\text{O}$ 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. $\delta^{18}\text{O}$ 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 $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{18}\text{O}_{\text{carb}}$ 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 $\delta^{18}\text{O}$ values) would follow from an introduction of isotopically light carbon in the ocean-atmosphere system (as CH_4 or CO_2), some correlation between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ 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 $\delta^{13}\text{C}_{\text{carb}}$ in the Drimos Limestone Formation is very stable and constant at $\sim 2\text{‰}$. 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, $\delta^{13}\text{C}_{\text{carb}}$ values become higher.

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

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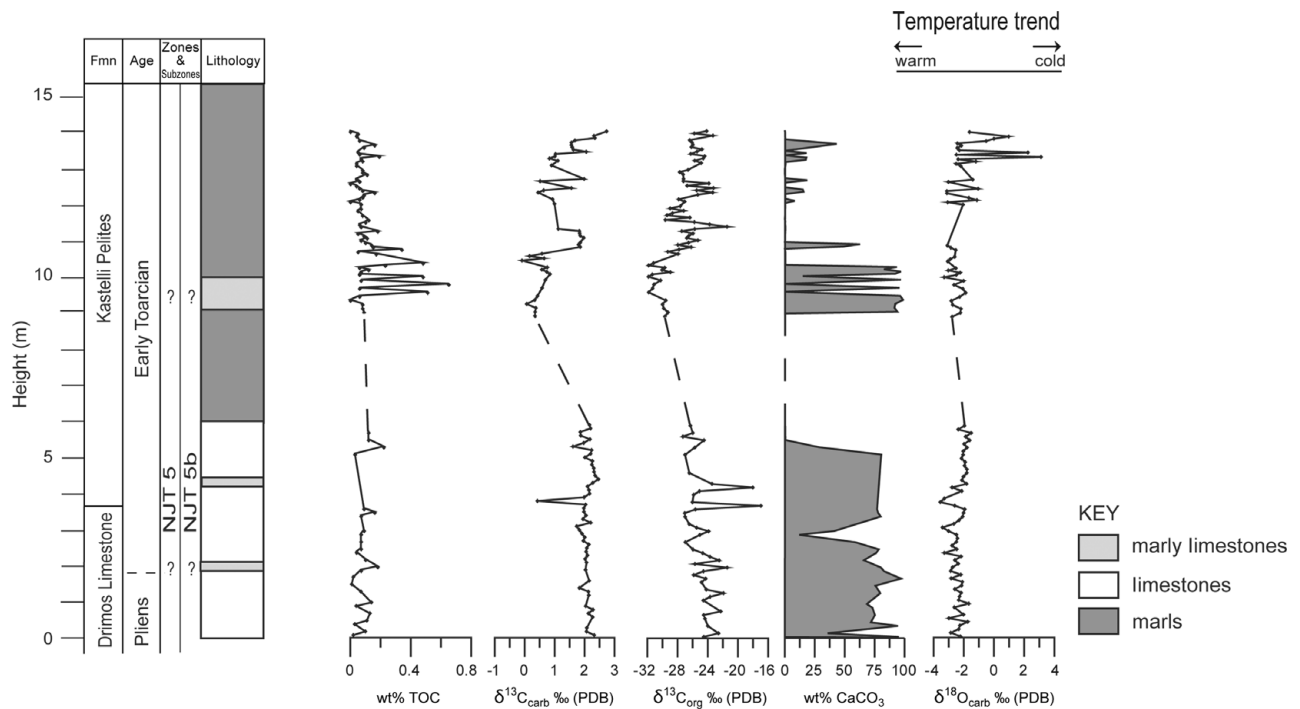


Figure 7. Lithostratigraphical log, bulk TOC, stable-isotope (C, O) and wt % CaCO₃ profiles through the Livartzi section. The dashed line represents a sampling gap. For a colour version of this figure see online Appendix at <http://journals.cambridge.org/geo>.

409 the section. In the upper part of the section the $\delta^{13}\text{C}_{\text{org}}$
410 values fluctuate around -25‰ .

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

427 6. Discussion

428 6.a. New biostratigraphic data based 429 on calcareous nannofossils

430 In spite of the paucity of calcareous nannofossil
431 assemblages recorded in the two studied sections,
432 some significant biostratigraphic results are presented
433 in this work that allow direct dating of the
434 carbon-isotope curves from Kastelli and Livartzi in
435 addition to correlation with biostratigraphically well-
436 dated $\delta^{13}\text{C}$ records from elsewhere. Although the
437 standard chronostratigraphy of the Jurassic is based
438 upon ammonite biostratigraphy, an increasing number
439 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).

454 A preceding negative excursion of 2‰ below the
455 main carbon-isotope excursion has been recorded
456 in Peniche (Portugal) and constitutes a chemostrati-
457 graphic marker for the Pliensbachian/Toarcian bound-
458 ary (Hesselbo *et al.* 2007). In the Kastelli section, the
459 carbonate carbon-isotope profile starts with a positive
460 excursion of $\sim 1\text{‰}$, and follows with a negative excu-
461 sion of the same range. This negative excursion is not
462 clearly dated by calcareous nannofossils in the Kastelli
463 section, but it lies just below an interval assigned to the
464 NJT 5 Zone, spanning the Late Pliensbachian–Early
465 Toarcian interval. This negative excursion resembles
466 those also observed at the stage boundary in Yorkshire
467 (NE England), Valdorbria, (Marche–Umbria, Italy) and
468 the High Atlas of Morocco, as recorded by Sabatino
469 *et al.* (2009), Littler, Hesselbo & Jenkyns (2010) and
470 Bodin *et al.* (2010). Given the occurrence of this feature
471 in the Pindos Zone, this isotopic feature, as proposed
472 by Hesselbo *et al.* (2007) as at least a regional marker,
473 is likely be of global significance.

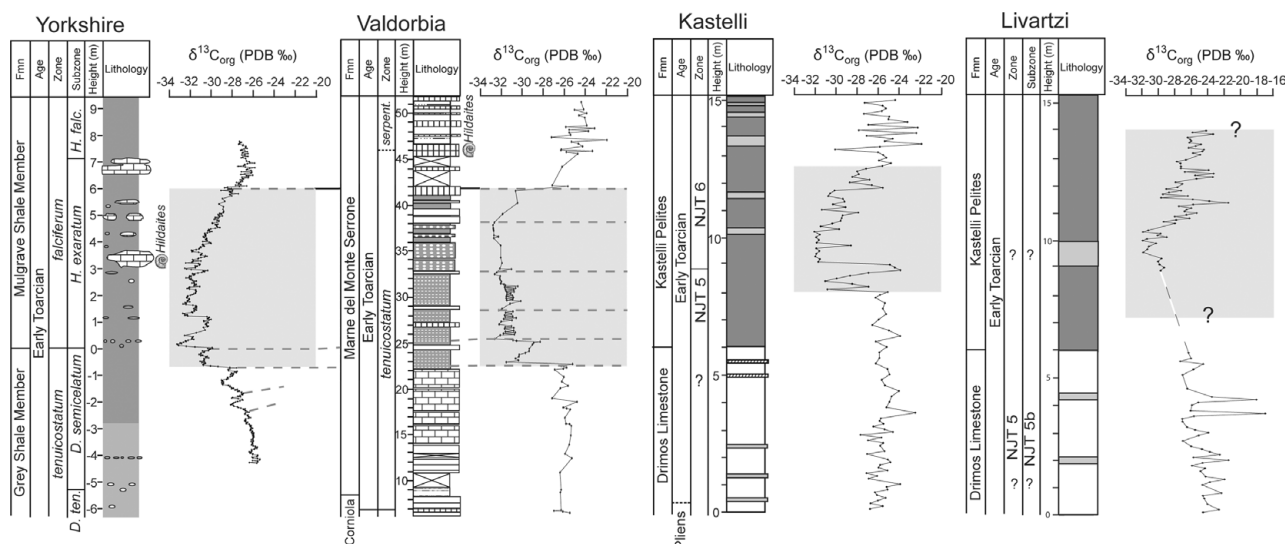


Figure 8. Comparison between the $\delta^{13}C_{org}$ data from Yorkshire, UK (Kemp *et al.* 2005), Valdorbria, Italy (Sabatino *et al.* 2009), and Kastelli and Livartzi, Greece. For a colour version of this figure see online Appendix at <http://journals.cambridge.org/geo>.

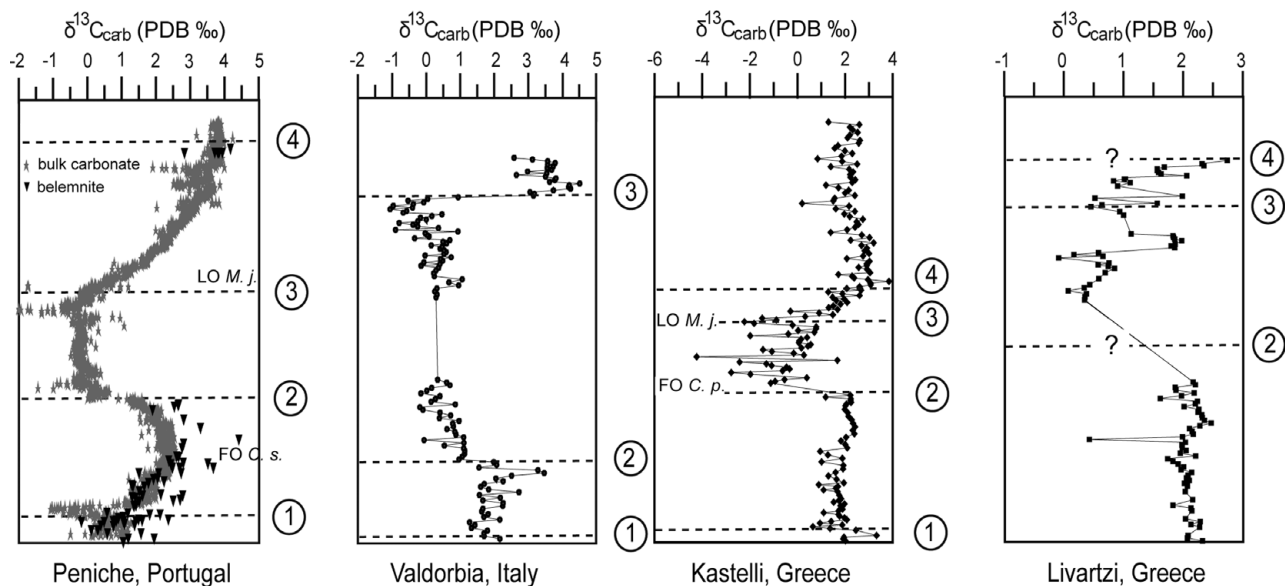


Figure 9. Comparison between the $\delta^{13}C_{carb}$ data from Peniche, Portugal (Hesselbo *et al.* 2007), Valdorbria, Italy (Sabatino *et al.* 2009), and Kastelli and Livartzi, Greece. For a colour version of this figure see online Appendix at <http://journals.cambridge.org/geo>.

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, Valdorbria, Kastelli and Livartzi, whereas in Figure 9, correlation is based mostly on the $\delta^{13}C_{carb}$ data from Peniche, Valdorbria, 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 Valdorbria profiles are based on $\delta^{13}C_{org}$ data and their spectral analyses, whereas the comparison between these two sections and the Greek sections is based only on the shape of the

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carbon-isotope excursion. In all four compared sections, the negative carbon-isotope excursion has a similar range of values, but each profile differs in detail. The Greek sections have a relatively small negative excursion in $\delta^{13}\text{C}_{\text{org}}$ of $\sim -5\%$, after which values return to background values ($\sim -25\%$). 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, Valdorbja 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 superbis* and *Carinolithus poul nabronei* (Mailliot *et al.* 2007). The nannofossil zone of *C. superbis* (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. poul nabronei*, whose first occurrence is stratigraphically very close to that of *C. superbis* (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 Valdorbja is where $\delta^{13}\text{C}_{\text{carb}}$ 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 $\delta^{13}\text{C}$ 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 Valdorbja, 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 Valdorbja, 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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