

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

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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 Τοάρσιου 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-Αλβίου, 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-Τουρόνιο 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 Μεσοζωϊκών OAE στον Ελλαδικό χώρο.

Λέξεις κλειδιά: Ωκεάνια Ανοξικά Γεγονότα, Τοάρσιο, Άπτιο, Άλβιο, Κενομάνιο-Τουρόνιο, Ελληνίδες.

INTRODUCTION

Oceanic anoxic events (OAEs) were first described by SCHLANGER & JENKYN (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; DANIELIAN *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 CO₂ 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; JENKYN, 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; JENKYN, 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; PEPPIER, 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).

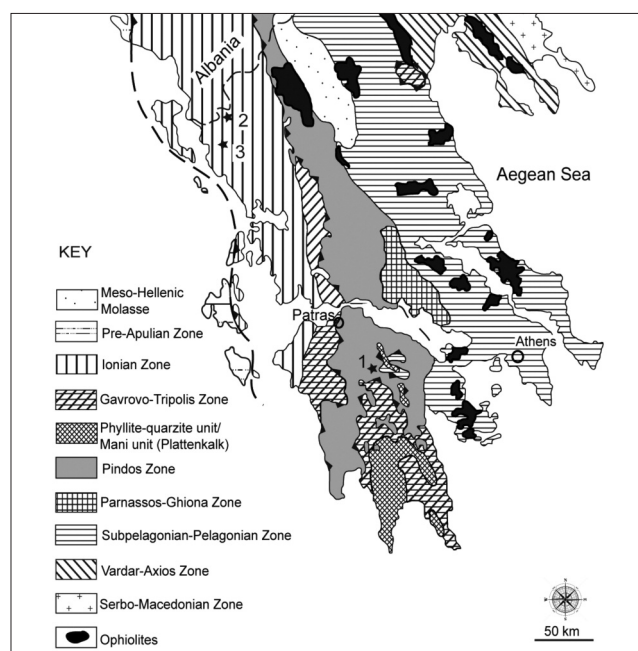


Fig. 1. Simplified geological map of Greece and localities of the studied outcrop sections discussed in the paper. 1: Kastelli, 2: Paliambela, 3: Gotzikas.

THE EARLY TOARCIAN OAE

The early Toarcian records a period of global warming (BAILEY *et al.*, 2003; JENKYN, 2003), accompanied by mass extinction events (WIGNALL *et al.*, 2006) and enhanced organic carbon burial (JENKYN, 1988; JENKYN *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 (JENKYN, 1988; RIGAKIS & KARAKITSIOS, 1998; JENKYN *et al.*, 2002; SABATINO *et al.*, 2009; JENKYN, 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

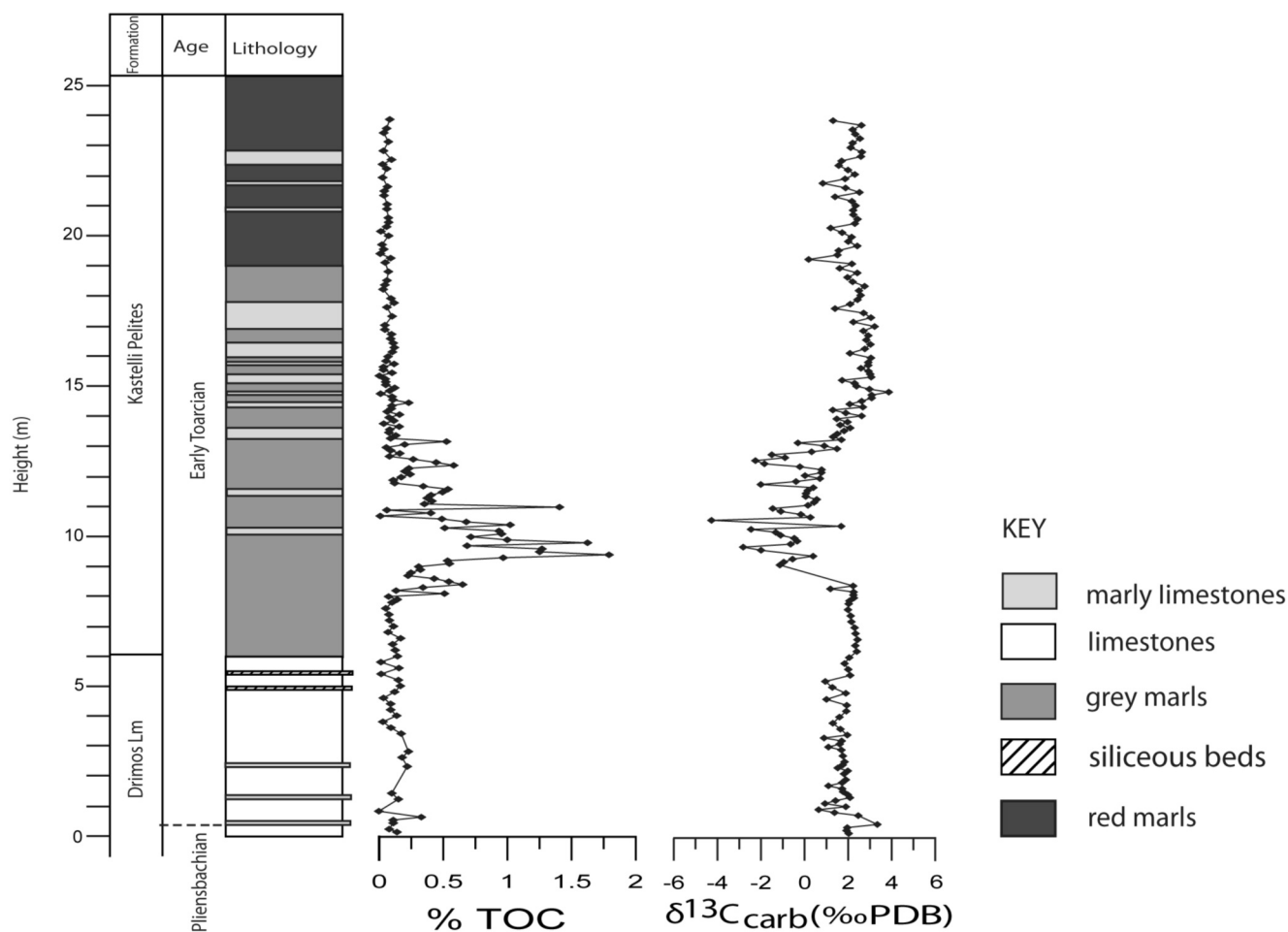


Fig. 2. Lithology, biostratigraphy and chemostratigraphy of the Early Toarcian OAE at the Kastelli section, Pindos Zone (from KAFOUSIA *et al.*, 2010).

interval up to 2 wt% is clearly visible. Across the same interval, a negative excursion of *ca.* 6‰ in bulk carbonate $\delta^{13}\text{C}$ 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 (JENKYN, 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; JENKYN, 1999; JENKYN, 2003; HEIMHOFFER *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, HEIMHOFFER *et al.*, 2004). Palaeotemperature data also suggest an abrupt in-

crease in SST of $\sim 8^\circ\text{C}$ 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; JENKYN, 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 (JENKYN, 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; JENKYN, 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

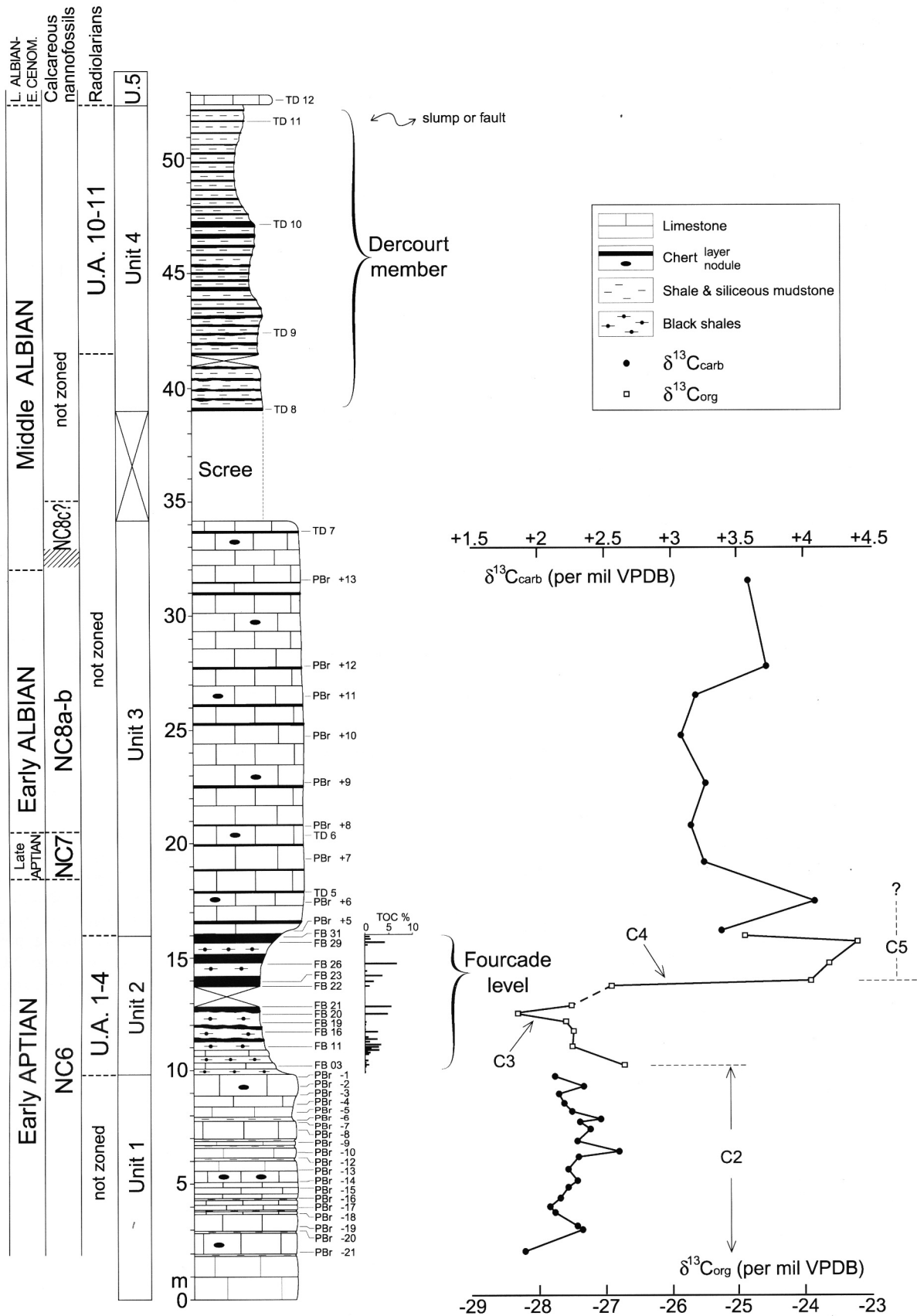


Fig. 3. Lithology, biostratigraphy and carbon isotope stratigraphy of the Early Aptian OAE at Paliambela section, Ionian Zone (modified after DANIELIAN *et al.*, 2004).

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 $\delta^{13}\text{C}$ spike that typifies the lower portion of OAE 1a black shales in Italian sections and elsewhere is faithfully re-produced in bulk or-

ganic 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

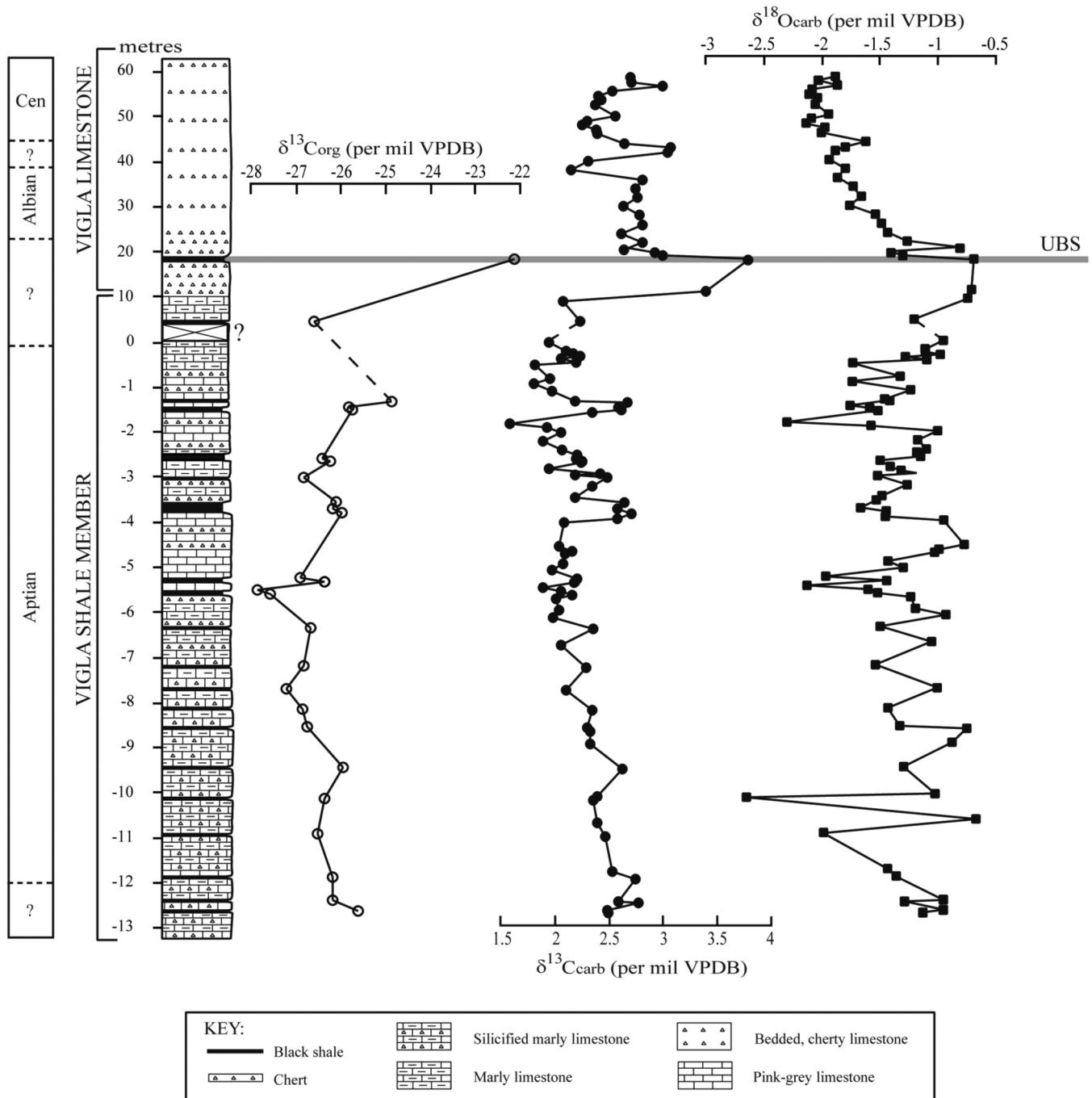


Fig.4. Lithostratigraphy and stable isotope profiles through the Vigla section in the Gotzikas section of the Ionian Zone (modified after TSIKOS *et al.*, 2004b). The OAE1b ("Paquier") black shale is highlighted. Note the different scales used for the portions of the section above and below the observation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

recorded this event across much of the Tethyan-Atlantic region, including ODP drilling sites (LECKIE *et al.*, 2002; JENKYN, 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) (JENKYN, 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 phytoplanktonic source (KUYPERS *et al.*, 2002, 2004; TSIKOS *et al.*, 2004b; JENKYN, 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 pres-

ence 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 & JENKYN, 1976; JENKYN, 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 (JENKYN *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 (JENKYN *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

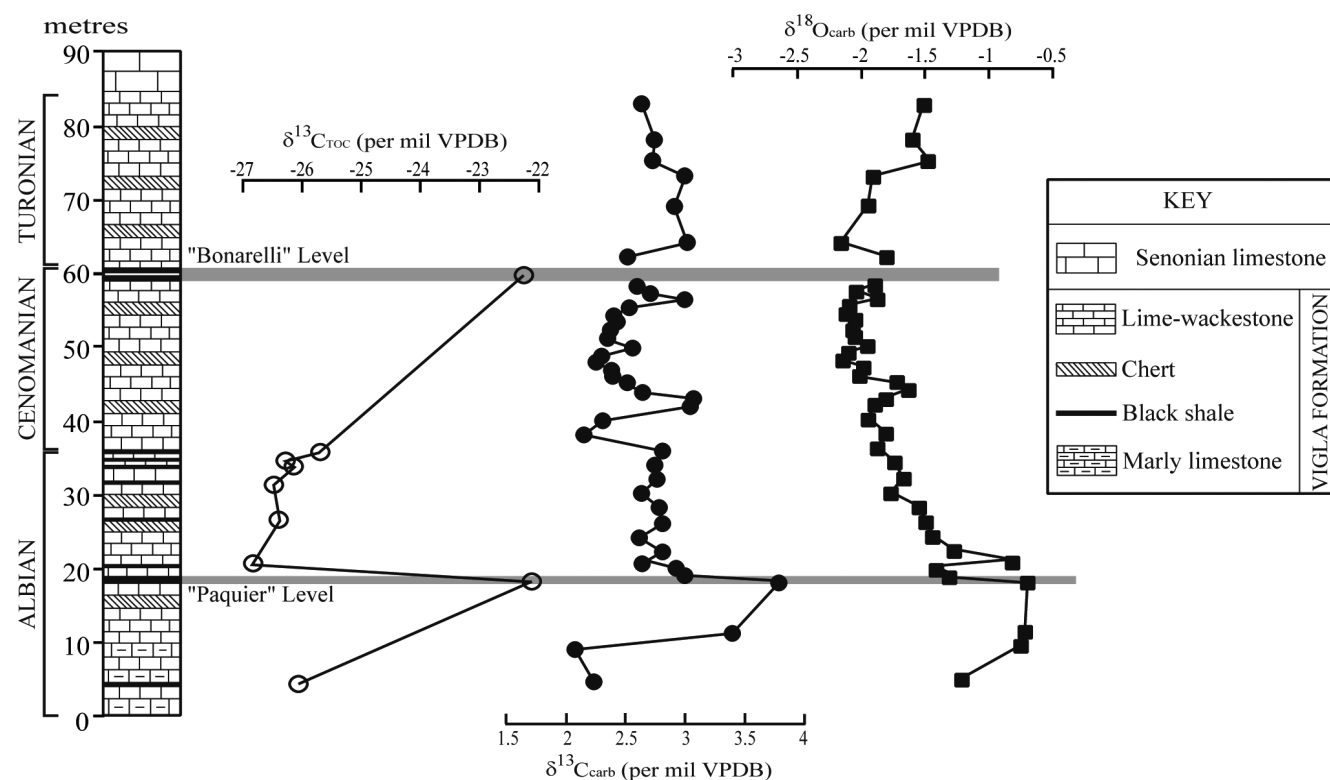


Fig. 5. Bulk stable (C, O) isotope profiles through the upper part of the Vigla Limestone Formation in the Gotzikas section, which includes the Bonarelli-equivalent, OAE 2 black-shale horizon (modified after KARAKITSIOS *et al.*, 2007b).

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 $\delta^{13}\text{C}$ 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; JENKYN *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.

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