First evidence for the Cenomanian–Turonian oceanic anoxic event (OAE2, 'Bonarelli' event) from the Ionian Zone, western continental Greece

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Abstract

Integrated biostratigraphic (planktonic foraminifera, calcareous nannofossils), chemostratigraphic (bulk C and O isotopes) and compound-specific organic geochemical studies of a mid-Cretaceous pelagic carbonate—black shale succession of the Ionian Zone (western Greece), provide the first evidence for the Cenomanian–Turonian oceanic anoxic event (OAE2, 'Bonarelli' event) in mainland Greece. The event is manifested by the occurrence of a relatively thin (35 cm), yet exceptionally organic carbon-rich (44.5 wt% TOC), carbonate-free black shale, near the Cenomanian–Turonian boundary within the Vigla limestone formation (Berriasian–Turonian). Compared to the 'Bonarelli' black-shale interval from the type locality of OAE2 in Marche–Umbria, Italy, this black shale exhibits greatly reduced stratigraphic thickness, coupled with a considerable relative enrichment in TOC. Isotopically, enriched $\delta^{13}C$ values for both bulk organic matter (−22.2‰) and specific organic compounds are up to 5‰ higher than those of underlying organic-rich strata of the Aptian-lower Albian Vigla Shale member, and thus compare very well with similar values of Cenomanian–Turonian black shale occurrences elsewhere. The relative predominance of bacterial hopanoids in the saturated, apolar lipid fraction of the OAE2 black shale of the Ionian Zone supports recent findings suggesting the abundance of N_2-fixing cyanobacteria in Cretaceous oceans during the Cenomanian–Turonian and early Aptian oceanic anoxic events.

Introduction

Oceanic anoxic events (OAEs), as originally conceptualized by Schlanger and Jenkyns (*1976*) and Jenkyns (*1980*), define periods during which much of the world's oceans became severely depleted in oxygen and widespread deposition of organic carbon-rich sediments took place. At least two major OAEs, i.e., the early Aptian 'Selli' event or OAE1a (e.g., Menegatti et al. *1998*) and the Cenomanian–Turonian 'Bonarelli' event or OAE2 (e.g., Arthur et al. *1988*; Hasegawa et al. *2003*; Tsikos et al. *2004a*), represent episodes of global perturbation in both the marine inorganic and the marine/terrestrial organic carbon reservoirs, due to excess burial of organic matter in the world ocean. Such perturbations are commonly manifested in the form of positive isotopic excursions in both inorganic and organic carbon, by up to 2.5 and 6‰, respectively. The driving mechanism behind OAEs is still subject to considerable controversy and suggested possibilities include, amongst others, increased primary biological production, expansion of the oxygen-minimum zone and water-column stratification, either singly or in combination (e.g., Parrish *1995*; Tyson *1995*; Sinninghe Damsté and Koster *1998*; Kuypers et al. *2002*; Pancost et al. *2004*). Large-scale volcanism and dissociation of gas hydrates may also be implicated, by adding excess CO_2 to the ocean–atmosphere system and thus raising global temperatures, accelerating the hydrological cycle and thereby increasing the flux of nutrients to the oceans (e.g., Jenkyns *1999*; *2003*; Larson and Erba *1999*; Jones and Jenkyns *2001*; Jenkyns et al. *2002*; Weissert and Erba *2004*).

The Ionian Zone of western Greece (Fig. 1) exposes Jurassic and Cretaceous pelagic, thrust-imbricated sediments that represent continental-margin sequences of the southern Tethyan ocean. Within these sequences, siliceous and organic carbon-rich sediments have been variously reported as commonly associated facies (e.g., Jenkyns *1988*; Karakitsios *1995*; Rigakis and Karakitsios *1998*; Neumann and Zacher *2004*). Recent studies have demonstrated that some of these organic-rich strata document OAEs of a supra-regional geographical distribution (i.e., the early Albian 'Paquier' event, or OAE1b; Tsikos et al. *2004b*) to global events (i.e., the early Toarcian OAE, Jenkyns et al. *2002*; the early Aptian 'Selli' event, or OAE1a, Danelian et al. *2004*). However, no evidence for organic-rich sediments representing the Cenomanian–Turonian OAE has hitherto been recorded from either the Ionian Zone, or elsewhere in mainland Greece. This paper presents, for the first time, integrated biostratigraphic, stable isotopic and molecular organic geochemical evidence suggesting that the Cenomanian–Turonian OAE is recorded in an isolated black shale within the stratigraphically uppermost part of the Vigla limestone formation of the Ionian Zone in western Greece.

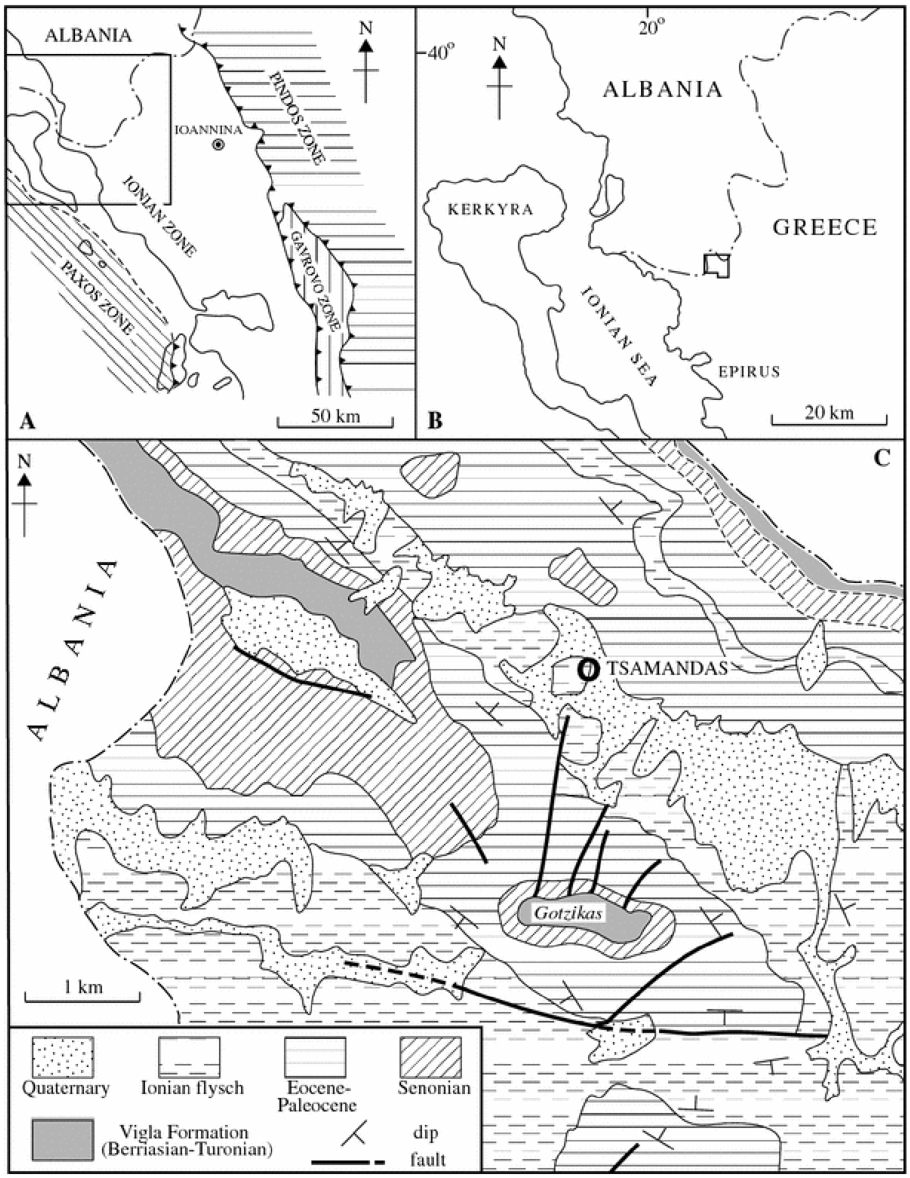

Fig. 1 a The zones of the northwestern Hellenides. b Location of the study area. c Simplified geological map of the study area (modified after Tsikos et al. *2004b*)

Regional geological framework

During the Early Jurassic, the Ionian Basin was characterized by deposition of platform-carbonate sediments (Pantokrator limestone formation) on a base comprising primarily Triassic evaporites. There followed a subsequent period of extensional stress and intense rifting (Pliensbachian–Tithonian), associated with the opening of the Neotethyan Ocean. Sedimentation during the rifting phase was partitioned into several discrete palaeogeographic units recording early regional subsidence and subsequent, internal syn-rift differentiation of the basin (Bernoulli and Renz *1970*; Karakitsios *1995*; Tsikos et al. *2004b*).

The lower Cretaceous (Berriasian–Turonian) Vigla limestone formation (Figs. 1, 2) represents a period of post-rift, pelagic-carbonate sedimentation across the entire Ionian Basin. The sequence is defined by a lower Berriasian unconformity at the base of the Vigla limestone formation, which largely obscures pre-existing syn-rift structures. In some cases, Vigla strata are seen to overly directly the Pantokrator limestone pre-rift sequence. This palaeogeographic configuration continued with minor off- and on-lap movements along basin margins until the Late Eocene, when orogenic movements and flysch sedimentation began. The evolution of the Ionian Basin constitutes a good example of inversion tectonics in a basin with an evaporitic base (Karakitsios *1995*).

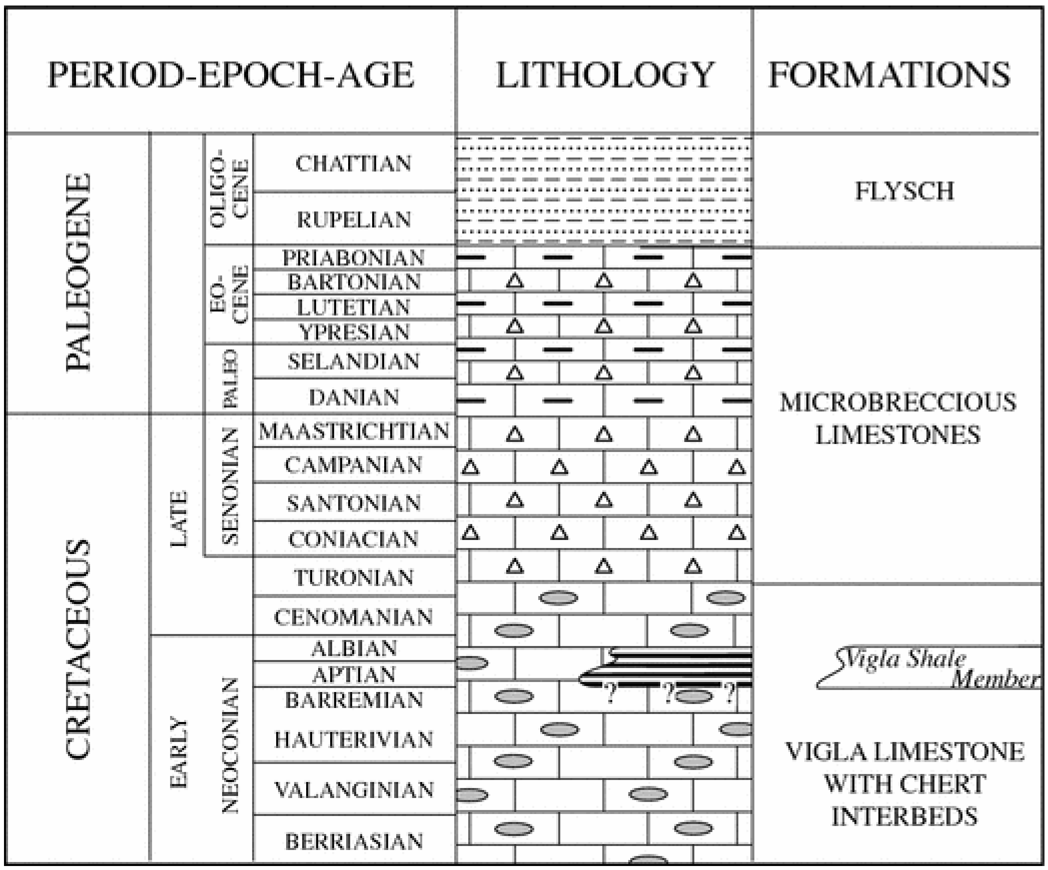

Fig. 2 Representative stratigraphic column of the Cretaceous–Paleogene of the Ionian Zone (modified after Karakitsios *1995*)

Field observations

The Vigla limestone formation (Fig. 2) comprises a thick succession of thin-layered (5–10 cm), sub-lithographic, pelagic limestones which contain abundant radiolaria and are rhythmically interbedded with centimetre- to decimetre-thick radiolarian chert beds. In its upper part, it contains a series of intercalated, organic C-rich marlstones and shales constituting the so-called Vigla Shale member (Fig. 2; Karakitsios *1995*; Tsikos et al. *2004b*). Recent studies on an outcrop section in Gotzikas, south of the village of Tsamandas in NW Epirus (Fig. 1c), have shown that the Vigla Shale Member spans the Aptian–lower Albian, and that a single isolated black-shale unit within the immediately overlying Vigla limestone contains isotopic and organic geochemical evidence for the early Albian 'Paquier' event (Tsikos et al. *2004b*).

We recently revisited the Gotzikas locality with the purpose of examining, in more detail, a 90 m-thick section of the stratigraphically uppermost part of the Vigla limestone formation. Optimal weather conditions and improved outcrop exposures allowed us to focus our field investigations on identifying any additional black-shale horizons stratigraphically above the lower Albian 'Paquier' black shale (Tsikos et al. *2004b*), that would potentially record the Cenomanian–Turonian OAE. We observed an additional 6, 5–15 cm-thick black-shale units within the first 20 m of the Vigla limestone formation above the 'Paquier' black shale. These units are finely laminated and lack any evidence for bioturbation, and thus exhibit macroscopic characteristics directly comparable to older black shales of the Vigla shale member. The stratigraphically higher parts of the Vigla limestone formation appear devoid of organic carbon-rich sediments, except for an isolated black-shale horizon observed approximately 40 m stratigraphically above the 'Paquier' black shale. This black shale has a total thickness of ca. 35 cm, and comprises two distinct, finely laminated sub-units separated by a thin, cherty layer in its middle part. No other black shales were recorded in the remaining portion of the examined section above, which comprises Vigla limestone formation overlain by Senonian limestone strata.

Methods

We undertook detailed biostratigraphic analyses of planktonic foraminifera and calcareous nannofossils, using both existing and new sample material collected from the Gotzikas section, in an effort to improve and expand our biostratigraphic resolution from previous studies (Tsikos et al. *2004b*). Representative samples were taken from the seven new organic carbon-rich units identified in the field, as well as from the uppermost part of the Vigla limestone formation, which had not been previously examined. Total organic-carbon (TOC) contents and corresponding $\delta^{13}C$ values were determined for all black shale samples collected, whereas carbonate samples were analyzed for bulk carbonate stable isotopes (C, O). The results have been combined with data from previous studies to provide a complete stratigraphic picture across the upper part of the Vigla limestone formation. Compound-specific geochemical and isotopic analyses on solvent-extractable organic matter were also conducted on two representative samples from the black-shale units.

Bulk isotopic analyses were performed at the Departments of Earth Sciences and Archaeology, University of Oxford, using standard mass spectrometric methods as described elsewhere (Tsikos et al. *2004a*, *b*). Compound-specific organic geochemical investigations were conducted at the Royal Netherlands Institute for Sea Research (NIOZ) using analytical methods described in detail in Tsikos et al. (*2004b*).

Results and discussion

Biostratigraphy

Biostratigraphic results presented schematically in Fig. 3 suggest that the Vigla strata in the Gotzikas section span the Albian–Turonian interval. The black shale representing the 'Paquier' event in the lower portion of the section marks the lower to middle Albian (Fig. 3), as suggested by the presence of the calcareous nannofossil *Hayesites albiensis* in the limestone intervals 3 m stratigraphically below and 10 m above this horizon. The ca. 20 m-thick interval above the 'Paquier' black shale, which contains six of the newly observed black-shale horizons, spans the middle to upper Albian (Tsikos et al. *2004b*; see Fig. 3). This age assignment is suggested by the first occurrence of the calcareous nannofossil *Quadrum eneabrachium* and the presence of the planktonic foraminifer *Biticinella breggiensis* (middle Albian), followed by the presence of the planktonic foraminifera *Rotalipora appeninica* and *Planomalina buxtorfi* (late Albian) and of the nannofossil *Eiffellithus turriseiffelii* (late Albian–Maastrichtian) (Roth *1978*; Varol *1992*; Premoli Silva and Sliter *1995*). These black shales may correspond with some of the named organic-rich found in the Albian of the Vocontian Trough, south-east France (Bréhéret *1997*).

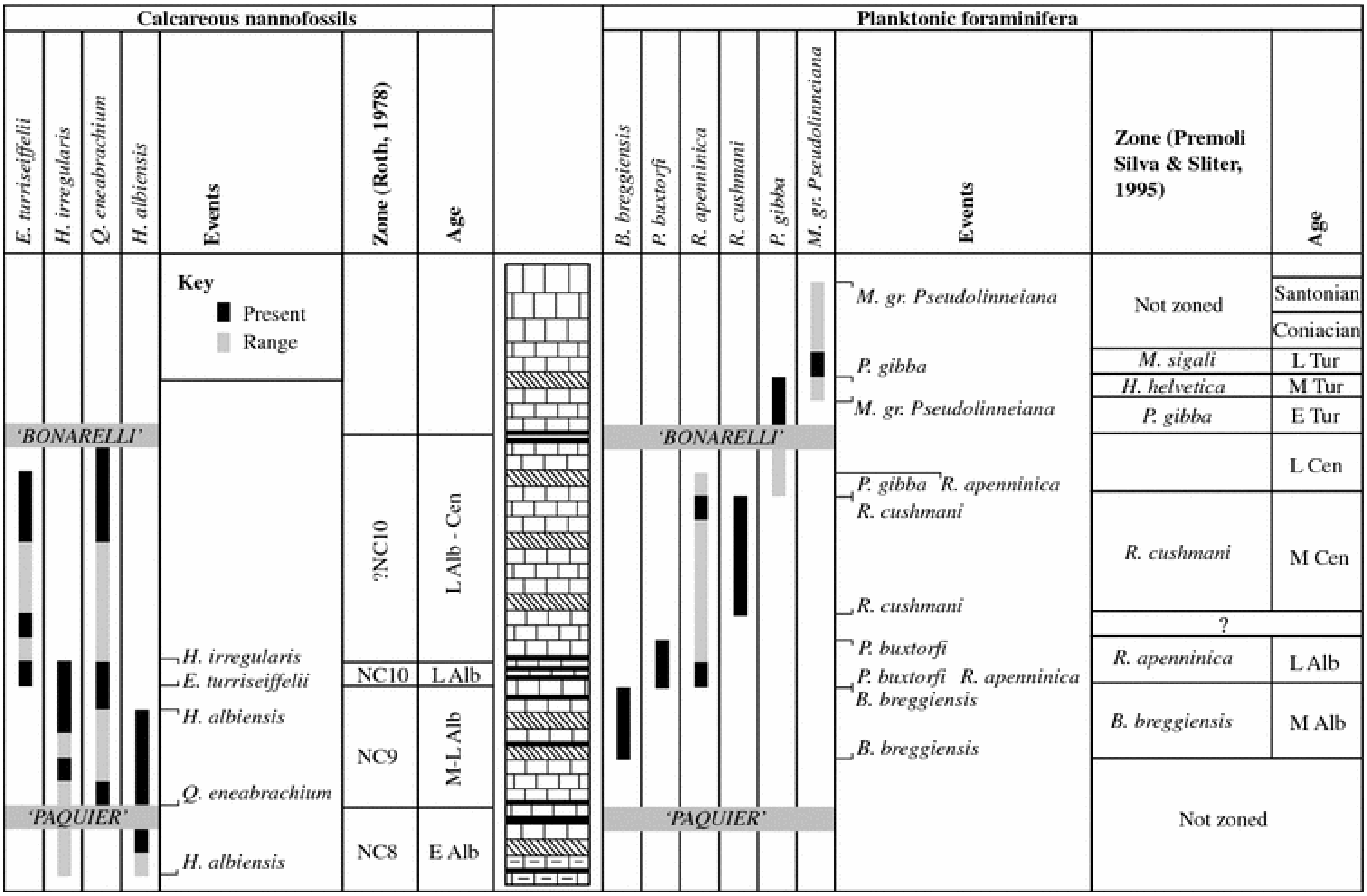

Fig. 3 Schematic representation of biostratigraphic data for the upper Vigla limestone formation across the Gotzikas section, based on observed distributions of planktonic foraminifera and calcareous nannofossils

The first occurrence of the planktonic foraminifer *R. cushmani* ca. 6 m stratigraphically above the upper Albian interval, indicates the middle Cenomanian (Premoli Silva and Sliter 1995; Fig. 3). The last occurrence of *R. cushmani* and the presence of the planktonic foraminifera *R. appenninica* are recorded in the first 6 m of the limestone immediately underlying the stratigraphically uppermost, isolated black-shale unit, whereas the planktonic foraminifer *Praeglobotruncana gibba* (late Cenomanian–middle Turonian) occurs in the first 5 m of the immediately overlying limestone. These datum levels suggest that this black-shale horizon lies close to the Cenomanian–Turonian boundary (Fig. 3), and is therefore biostratigraphically correlative with the well-known uppermost Cenomanian black shale ('Bonarelli' level) of Marche–Umbria, Italy, representing OAE2 (see Tsikos et al. 2004a, and references therein). Stratigraphically higher, the occurrence of *Marginotruncana gr. pseudolinneiana* places a minimum upper age constraint for the examined section of late Turonian (Caron 1985; Perch-Nielsen 1985; Premoli Silva and Sliter 1995).

Bulk stable isotopes

Bulk stable isotope data and chemostratigraphic profiles across the Vigla Limestone Formation in the Gotzikas section are presented in Table 1 and Fig. 4, respectively. The carbonate carbon ($\delta^{13}C_{carb}$) isotope curve exhibits a first relative maximum of ca. 3.8‰, essentially coinciding with the level where the early Albian 'Paquier' event is recorded (Fig. 4; see also Tsikos et al. *2004b*). Thereafter, $\delta^{13}C_{carb}$ values decrease sharply to 2.5–3.0‰ over the middle–upper Albian portion of the section, and to 2.0–2.5‰ across the Cenomanian interval, with two relative maxima of around 3.0‰ around the lower–middle Cenomanian and immediately below the uppermost Cenomanian black-shale horizon. Complete lack of carbonate in the latter black shale results in the brief discontinuity of the $\delta^{13}C_{carb}$ record of Fig. 4. Stratigraphically higher, $\delta^{13}C_{carb}$ data are sparser, yet they record a "plateau" of increased values around 3.0‰ over the lower portion of the Turonian interval, progressively decreasing to values of ca. 2.5–2.6‰ in its upper part. Despite the relatively low sampling resolution employed in this study, the broad trends described above are consistent with similar isotope curves from Cenomanian–Turonian strata of Marche–Umbria, Italy (Scaglia Facies) but somewhat less so with those from the English Chalk (cf. Jenkyns et al. *1994*; Tsikos et al. *2004a*; see Fig. 4).

Table 1 Bulk-rock stable isotope data of the uppermost Vigla limestone formation

Sample	$\delta^{13}C_{TOC}$ (‰)	$\delta^{13}C_{carb}$ (‰)	$\delta^{18}O_{carb}$ (‰)
1		2.64[a]	−1.50[a]
2		2.75[a]	−1.59[a]
3		2.73[a]	−1.44[a]
4		3.00[a]	−1.90[a]
5		2.91[a]	−1.93[a]
6		3.02[a]	−2.14[a]
7		2.52[a]	−1.77[a]
8	−22.21[a]		
9		2.60[a]	−1.83[a]
10		2.70	−2.04
11		2.99	−1.87
12		2.53	−2.09
13		2.40	−2.11
14		2.42	−2.05
15		2.37	−2.07
16		2.31	−2.05
17		2.55	−1.94
18		2.29	−2.10
19		2.25	−2.14
20		2.38	−1.99
21		2.39	−2.01
22		2.48	−1.72
23		2.64	−1.63

Sample	$\delta^{13}C_{TOC}$ (‰)	$\delta^{13}C_{carb}$ (‰)	$\delta^{18}O_{carb}$ (‰)
24		3.07	−1.81
25		3.04	−1.89
26		2.30	−1.94
27		2.14	−1.81
28		2.81	−1.87
29	−25.78[a]	ND	ND
30	−26.33[a]	ND	ND
31		2.74	−1.74
32	−26.12[a]	ND	ND
33		2.76	−1.67
34	−26.49[a]	ND	ND
35		2.63	−1.77
36		2.78	−1.55
37	−26.40[a]	ND	ND
38		2.81	−1.49
39		2.61	−1.44
40		2.81	−1.27
41	−26.86[a]	ND	ND
42		2.62	−0.78
43	−22.14	2.92	−1.32
44		2.97	−1.42
45		3.79	−0.70
46		3.39	−0.72
47		2.07	−0.75
48	−26.61	2.23	−1.21

All data in stratigraphic order shown in Fig. 4, normalized versus VPDB (Vienna Pee Dee Belemnite)
ND not determined, *TOC* total organic carbon; *carb* carbonate
[a]This study; all remaining data from Tsikos et al. (*2004b*)

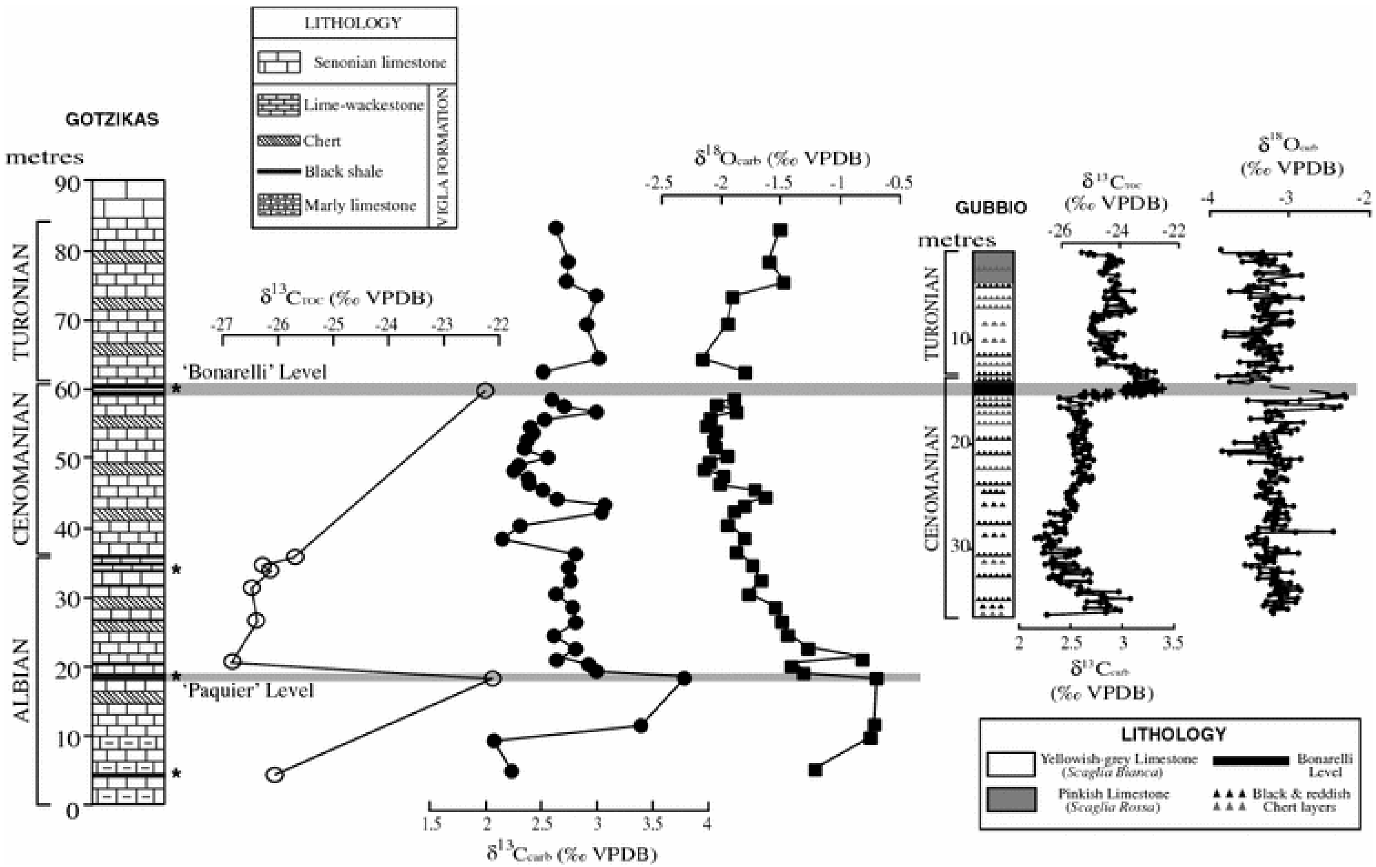

Fig. 4 Bulk stable (C, O) isotope profiles through the upper part of the Vigla limestone formation (Albian–Turonian). Similar profiles across the Cenomanian–Turonian Scaglia formation (carbonate isotope data shown as *dots*) and enclosed 'Bonarelli' black shales ($\delta^{13}C_{TOC}$ data shown as *crosses*) from Gubbio in Marche-Umbria, Italy, are shown for comparison (modified from Tsikos et al. 2004a). The four black-shale samples on which detailed molecular organic geochemical analyses were performed, are also highlighted with *asterisks*

Carbonate $\delta^{18}O$ data (Fig. 4) record a smooth, progressive decline in values from above −1‰ in the lower–middle Albian, to below −2‰ over the upper Cenomanian–lower Turonian, followed by a relative increase up to ca. −1.6‰ in the uppermost part of the section (upper Turonian). Assuming that the $\delta^{18}O$ data have not been greatly affected by diagenetic overprinting, the above stratigraphic trend could indicate a general warming trend during the Albian–Cenomanian, followed by gradual cooling in the Turonian. Such patterns conform to global trends (Jenkyns et al. 1994; Clarke and Jenkyns 1999).

The bulk organic-carbon isotope data ($\delta^{13}C_{TOC}$) of Fig. 4 are very few and thus are of little use in terms of chemostratigraphic application. As expected, however, markedly high TOC and $\delta^{13}C_{TOC}$ values are observed for the black shale corresponding biostratigraphically to the Cenomanian–Turonian OAE (44.5 wt%, −22.2‰), in a similar fashion to the 'Paquier' black shale (28.9 wt%, −22.1‰). Similarly high TOC and enriched bulk $\delta^{13}C_{TOC}$ isotopic values also characterize the black shales of the 'Bonarelli' Level, the type locality of the Cenomanian–Turonian OAE in the Italian sections (Fig. 4), as well as other coeval organic-rich sediments elsewhere in the world (e.g., Arthur et al. 1988; Tsikos et al. 2004a). It should be noted, however, that the type 'Bonarelli' black-shale interval exhibits almost twice the thickness and considerably lower TOC contents than those recorded in the upper Cenomanian black shale of the Ionian Zone, evidently due to dilution of the former by abundant, interlayered radiolarian sands. The Albian black-shale units presented in Fig. 4 exhibit much lower TOC contents (1.5–2.5 wt%) and substantially lower $\delta^{13}C_{TOC}$ values (between −27 and −25‰), and thus compare very well with all organic-rich beds of the Vigla Shale member occurring stratigraphically lower in the section, that is, below the 'Paquier' black shale (Tsikos et al. 2004b).

Molecular organic geochemistry

Compositional information is presented in Fig. 5 for the saturated, apolar lipid fractions of four black shale samples from the Vigla limestone formation, namely the two black-shales representing the Early Albian ‘Paquier’ (OAE1b) and Cenomanian–Turonian ‘Bonarelli’ (OAE2) events, one black shale sample (sample 32, Table 1) representative of the six black-shale units occurring within the middle to upper Albian stratigraphic interval, and the uppermost black shale sample from the underlying Aptian–lower Albian Vigla shale member (sample 48, Table 1). Generally, all samples contain compounds belonging to four main compound groups, namely *n*-alkanes, acyclic isoprenoids (e.g., pristane, phytane), steroids and hopanoids, in variable relative amounts. As reported in Tsikos et al. (*2004b*), the sample representing the ‘Paquier’ event contains, in addition to the above compounds, substantial concentrations of isotopically heavy (up to −15‰), monocyclic isoprenoids of archaeal origin. The selected upper Albian black shale (Fig. 5) exhibits compositional characteristics which are very similar to the black shales of the Vigla shale member (Tsikos et al. *2004b*), except for its very low relative abundance of hopanoids. In marked contrast to the above, the upper Cenomanian black shale contains considerably increased relative amounts of hopanoids (Fig. 5). Furthermore, approximately 17% of the total abundance of hopanoids is made up by 2-methyl hopanes, suggesting a substantial contribution of pelagic cyanobacteria (relative to other bacteria) to the hopanoids (Summons et al. *1999*). This feature is in line with recent findings from organic-matter rich sediments representing Cretaceous OAEs such as OAE1a (early Aptian) and OAE2 (Cenomanian–Turonian), whereby N_2-fixing cyanobacteria are believed to have become dominant under conditions of prolonged ocean stratification, increased rates of organic-carbon accumulation and high nutrient-N depletion (Ohkouchi et al. *1997*; Kuypers et al. *2004*).

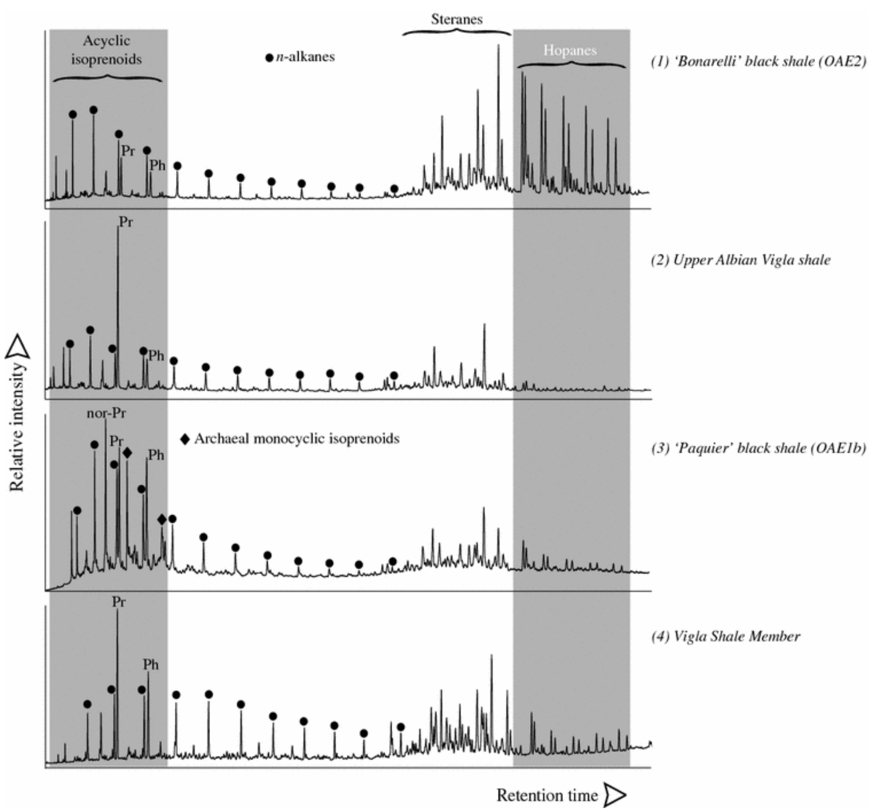

Fig. 5 Total ion currents of the saturated apolar fractions of four black-shale samples from the Gotzikas section, namely: (1) the upper Cenomanian black shale (Cenomanian–Turonian OAE, sample 8, this study); (2) one of the six black-shale units from the middle-upper Albian interval (sample 32, this study); (3) the lower Albian ‘Paquier’ black shale (sample 43, data from Tsikos et al. *2004b*); and the uppermost sample from the Aptian Vigla shale member (sample 48, data from Tsikos et al. *2004b*). Major compounds and compound groups are *highlighted*. Note the relative predominance of hopanoids in the upper Cenomanian black shale (*Pr* pristane; *Ph* phytane; *nor-Pr* norpristane)

The compound-specific carbon-isotope data of Table 2 provide further evidence for the manifestation of the Cenomanian–Turonian OAE in the Gotzikas section. The ca. 4‰ shift in $\delta^{13}C_{TOC}$ observed between the upper Albian (−26.1‰) and upper Cenomanian (−22.2‰) black-shale horizons is coupled with respective positive shifts of around 5‰ for phytane and pristane, 3‰ for C29-steroid, and up to 9‰ for C31-hopane (22S + 22R). This relative enrichment in ^{13}C is typically the case with black shales that record the Cenomanian–Turonian OAE, because global-scale, positive carbon $\delta^{13}C_{TOC}$ shifts caused by increased burial of organic matter are reflected in respective shifts in individual lipid compounds derived from primary algal and/or bacterial biomasses (e.g., Kuypers et al. 2002; Tsikos et al. 2004a).

Table 2 Mean, compound-specific $\delta^{13}C$ data (‰ vs. VPDB) for the four black shale samples from the Vigla limestone formation shown in Figs. 4 and 5

Sample	Pristane (‰)	Phytane (‰)	C29-steroid (‰)	C31-hopane (22S + 22R) (‰)
8 ($n = 4$)	−27.4	−26.8	−26.4	−20.3
32 ($n = 4$)	−32.4	−31.5	−29.1	−29.0
43 ($n = 3$)[a]	−20.5	−18.1	−27.8	−25.4
48 ($n = 2$)[a]	−32.1	−32.0	−30.3	−29.8

[a]From Tsikos et al. (2004b)

Summary and conclusions

Our paper presents, for the first time, integrated biostratigraphic, isotopic and organic geochemical evidence for the Cenomanian–Turonian OAE (OAE2, 'Bonarelli' event) in the Ionian Zone of north-western Greece. The OAE is manifested in the form of a 35cm-thick black-shale unit within the stratigraphically uppermost portion of the lower Cretaceous (Berriasian–Turonian) Vigla limestone formation. This black-shale interval constitutes a stratigraphically "condensed" equivalent to coeval strata from the type-locality of upper Cenomanian black shales in Marche–Umbria, Italy (i.e., 'Bonarelli' level) and shares common organic geochemical and stable isotopic characteristics not only with the latter but also with other Cenomanian–Turonian black shales elsewhere. These include the relatively enriched $\delta^{13}C$ values for both TOC (−22.2‰) and specific organic compounds (i.e., acyclic isoprenoids, steranes and hopanes), as well as the substantial relative abundances of 2-methyl hopanoids that are indicative of cyanobacterial derivation.

In a local geographical context, the upper Cenomanian black shale of the Ionian Zone is a stratigraphically discrete lithologic unit which, like the lower Albian black shale representing the 'Paquier' event, appears to be unrelated to the Vigla shale member spanning the Aptian–lower Albian (Tsikos et al. 2004b). The Vigla shale member is known to contain a series of at least 20, decimetre-thick organic-rich marly units, which despite having relatively low TOC contents (1–6 wt%) are volumetrically clearly more significant than the two black shales representing OAEs (see also Katz et al. 2000, for a similar situation in Italian sections). Nevertheless, on the grounds of TOC contents alone, one cannot underestimate the exceptionally enriched character of the two OAE black shales in the Ionian strata and, by extension, their source-rock potential for substantial petroleum generation in the wider area (Rigakis and Karakitsios 1998).

In conjunction with our previously published work on the Ionian Zone (Tsikos et al. 2004b; Danelian et al. 2004), our present study also concludes a comprehensive documentation of the sedimentary record of organic-carbon sequestration events across the lower Cretaceous of southern Tethys. This record has evidently resulted from a confluence of palaeoceanographic and biogeochemical processes, operating on geographical scales ranging from regional (Vigla shale member) to supra-regional ('Paquier Event', OAE1b) to unequivocally global ('Selli' Event, OAE1a; 'Bonarelli' Event, OAE2). In this context, our paper stresses once again the importance of integrated isotopic, biostratigraphic and organic geochemical studies in elucidating the stratigraphy and palaeoenvironmental evolution of ancient pelagic domains. Crucially, it also demonstrates that organic geochemical data at a molecular level can provide not only reliable—as well as reproducible—records of distinct palaeobiological phenomena associated with OAEs but also potentially useful markers for stratigraphic correlation of sedimentary strata recording such events, on a variety of scales.

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