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# Biomarker evidence for intermittent photic zone euxinia in the Aptian–Albian organic sedimentary record from the Ionian Zone (Epirus, Greece)

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## ABSTRACT

New biomarker evidence is presented that constrains the conditions of deposition and preservation of sediments rich in extractable organic matter from the Aptian–Albian sedimentary record of the Ionian Zone in NW Greece. Analyses were specifically carried out on total lipid extracts from 12 organic rich samples from the Vigla Shale Member, two of which represent the regional record for the early Albian Paquier Event of OAE1b. In the aliphatic fractions, compound groups such as *n*-alkanes, isoprenoid alkanes, steroids, hopanoids and terpenoids were recognized, pointing to a mixed origin from algae and prokaryotes with an additional measurable contribution from terrigenous plant matter. These compounds suggest deposition of the primary organic sediments under conditions of decreased bottom water oxygen concentrations. Mass spectral evidence from the aromatic fractions of most samples reveal the variable presence of diagenetic and catagenetic derivatives of carotenoid pigments (including some with bound sulfur) that are characteristic of photoautotrophic sulfur bacteria. The presence of specific biomarkers originating from photosynthetic anaerobic microorganisms, similar to those in ancient and contemporary euxinic basins such as the Black Sea, suggest that photic zone euxinic conditions were intermittently operative in the Aptian–Albian stages of the Ionian Basin, but were not exclusively characteristic of the black shale representing the Paquier Event itself.

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## 1. Introduction

The term “euxinic” traditionally describes an environment of water column stagnation and limited circulation, or one where anoxic, anaerobic and sulfidic conditions are simultaneously present and thus conducive to the growth of photoautotrophic sulfur bacteria (PSB) (Repeta, 1993). This group of prokaryotic microorganisms comprises strictly anaerobic, photosynthetic bacteria which require hydrogen sulfide and light for their development, such as the green sulfur bacteria (green SB) of the family Chlorobiaceae (Imhoff, 1995); and the purple sulfur bacteria (purple SB) of the family Chromatiaceae, which exhibit a comparable physiology and ecology as the green SB (Brocks and Schaeffer, 2008). The light and hydrogen sulfide dependencies of PSB shown by their modern ecological data (Overmann et al., 1992; Repeta, 1993; van Gemerden and Mas, 1995) and the assumption of a physiological uniformitarianism for these bacteria, have permitted the detection of their specific biomarkers in Phanerozoic sediments, particularly those recording oceanic anoxic events (OAEs), to be interpreted as indicative of a euxinic water layer extending up to the photic

zone (Repeta, 1993; Sinninghe Damsté et al., 1993; Grice et al., 1996a). This is because green SB are restricted today to silled fjords and lakes with intense water stratification and anoxia (Repeta et al., 1989), conditions similar to those hypothesized for the oceans during OAEs (Jenkyns, 1980; Overmann et al., 1992; Repeta, 1993; van Gemerden and Mas, 1995; Sinninghe Damsté and Köster, 1998).

The diagenetic transformations of specific carotenoid pigments from PSB, belonging to the broader group of the geosphere tetra-terpenoids, have been the subject of intensive research efforts to identify traces of PSB in sediments deposited in ancient euxinic basins (Repeta, 1993; Schaeffer et al., 1997). These include particularly the isorenieratene biosynthesized exclusively by brown strains of green SB (Liaaen-Jensen, 1978a,b; Imhoff, 1995), chlorobactene biosynthesized by green strains of green SB (Imhoff, 1995; Brocks and Schaeffer, 2008) and okenone biosynthesized by purple SB (Brocks and Schaeffer, 2008). From these, the fossilization potential of the isorenieratene carbon skeleton is the one that has received the most attention (Schwark and Püttmann, 1990; Hartgers et al., 1994; Hoefs et al., 1995; Grice et al., 1996b; Koopmans et al., 1996a, 1997; Sinninghe Damsté and Koopmans, 1997).

Sulfurization of isorenieratene during diagenesis results in numerous sulfur-containing isorenieratene derivatives which can

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be, and have been, subsequently recognized in sediments (Koopmans et al., 1996a,b; Kok et al., 2000). Diagenetic and catagenetic isorenieratene derivatives have been found in organic carbon rich sedimentary rocks from many different palaeoenvironmental settings, ranging from Precambrian to Cenozoic age (van Kaam-Peters et al., 1995; Koopmans et al., 1996a; Bosch et al., 1998; Sinninghe Damsté and Köster, 1998; Passier et al., 1999; Schouten et al., 2000; Pedentchouk et al., 2004; Wagner et al., 2004; Bowden et al., 2006; Brocks and Schaeffer, 2008; Heimhofer et al., 2008). Stable carbon isotopes and molecular distribution patterns have also been used to document the source of PSB biomarkers (Ostroukhov et al., 1982; Summons and Powell, 1986, 1987; Schwark and Püttmann, 1990; Requejo et al., 1992; Hartgers et al., 1994). Green SB biomass, in particular, is known to be significantly more enriched in  $^{13}\text{C}$  compared to the algal biomass (Sirevåg and Ormerod, 1970; Quandt et al., 1977; Summons and Powell, 1987; Sinninghe Damsté et al., 1993; Hartgers et al., 1994; Koopmans et al., 1996a; Grice et al., 1996b; van der Meer et al., 1998; van Breugel et al., 2005).

Although the development of photic zone euxinic conditions was initially considered to be rare in the context of OAEs, several

studies have recently proved this to be otherwise (e.g. Sinninghe Damsté et al., 2001). Identification of isorenieratene derivatives in sediments recording OAEs has hitherto provided crucial information about water column redox conditions during organic matter accumulation; possible variations in PSB productivity; chemocline shifts; and/or role of anoxia in the preservation of organic matter (Demaison and Moore, 1980; Summons and Powell, 1986; Pedersen and Calvert, 1990; Sinninghe Damsté et al., 1993; Koopmans et al., 1996a; Pancost et al., 2002; Kuypers et al., 2002b; Kenig et al., 2004; Schwark and Frimmel, 2004).

The OAE1b spanning the Aptian/Albian boundary (113–109 Ma) represents a protracted interval of oceanic dysoxia with multiple discrete black shales deposited in regions across Mexico, the North Atlantic Basin (western Tethys) and the Mediterranean (eastern Tethys; Arthur and Premoli Silva, 1982; Bréhéret et al., 1986; Premoli Silva et al., 1989; Bralower et al., 1993; Leckie et al., 2002; Tsikos et al., 2004). The OAE1b comprises major phenomena of transition in mid-Cretaceous tectonics, sea level, climate, lithofacies and marine plankton populations (Leckie et al., 2002). A sea level fall near the Aptian/Albian boundary separates uppermost Aptian black shales (“Jacob Event” in the Vocontian Basin, and

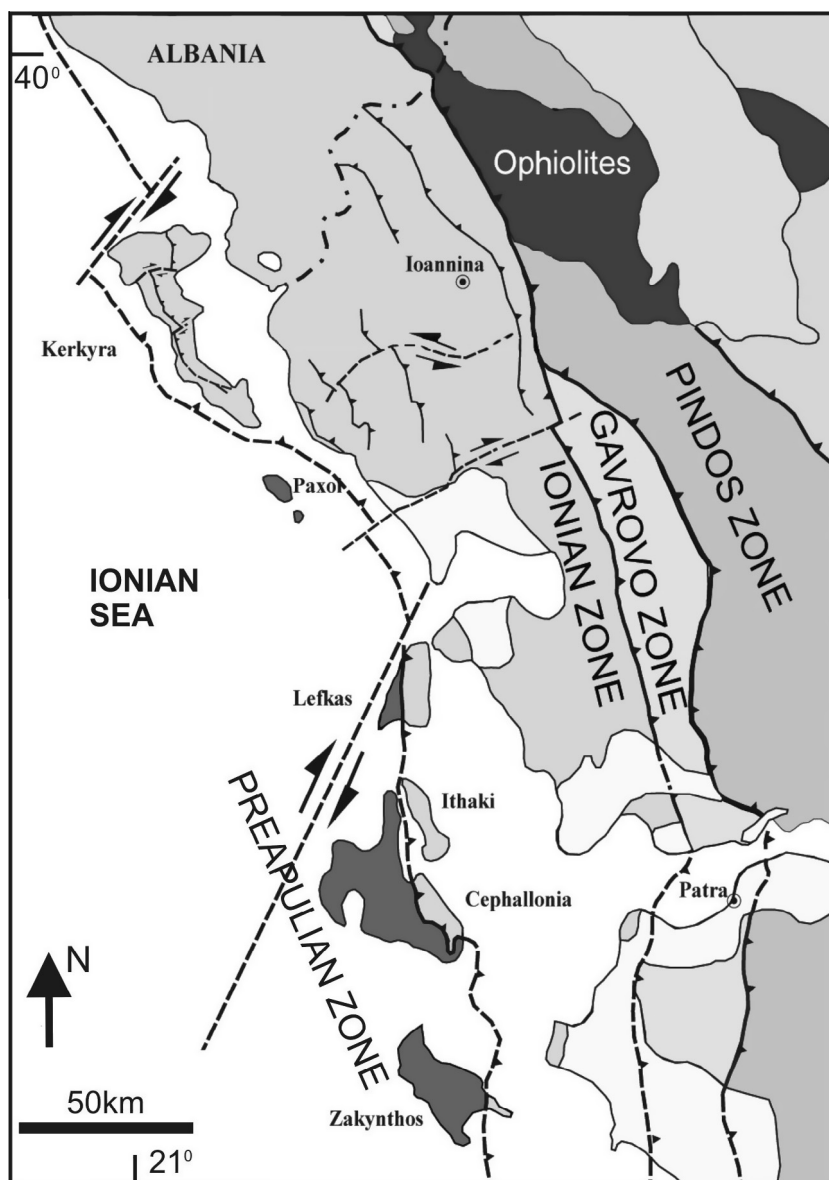


Fig. 1. The zones of the northwestern Hellenides (modified after Karakitsios and Rigakis, 2007).

“113 Event” in Umbria–Marche Basin, central Italy) from lower Albian black shales (“Paquier” and “Leenhardt” Events in the Vocontian Basin, and the “Monte Nerone” and “Urbino” Events in the Apennines of central Italy). Erbacher et al. (1998) note a significant difference between the uppermost Aptian Jacob Event of the Vocontian Basin as an OAE driven by detrital input and the lower Albian Paquier and Leenhardt Events as OAEs driven by productivity and rising sea level.

In this paper, we explore the Aptian–Albian biomarker record of organic rich horizons partly attributed to the Paquier Event of OAE1b from the Ionian Basin of NW Greece, following on from an earlier inter-disciplinary study on the same strata carried out by Tsikos et al. (2004). In this instance, we focus on assessing the same record with specific emphasis on biomarker evidence for photic zone euxinia and terrigenous detrital organic contributions before as well as during the Paquier Event of OAE1b, and the possible implications of these with respect to reconstructions of the depositional palaeo-environment and water column redox stratification.

## 2. Regional geological framework

The Ionian Zone of northwestern Greece (Epirus region) constitutes part of the most external zones of the Hellenides (Fig. 1). It corresponds to the Hellenic domain of the southern passive continental margin, associated with the early Mesozoic opening and the late Mesozoic–early Cenozoic closure of the Neotethyan Ocean (Karakitsios, 1992, 1995). Litho-stratigraphically, the Ionian Zone comprises Triassic evaporites at the base, followed by a Lower Jurassic to Eocene carbonate sequence with minor chert and shale contribution and capped by Oligocene flysch.

Until the early Lias, western Greece was part of an extensive carbonate platform. The Ionian Basin differentiated from the adjacent Apulian and Gavrovo platforms during the Lower Jurassic (Pliensbachian), as a result of persistent syn-sedimentary faulting and differential subsidence due to the opening of the Neotethyan Ocean, combined with halokinesis of the Ionian evaporitic base. Subsequently, internal syn-rift differentiation took place in the Ionian Basin creating several discrete, smaller palaeogeographic units (sub-basins). The sedimentation style in each of these sub-basins corresponds, in general, to half-graben geometry (Karakitsios, 1995).

The base of the Vigla Limestone Formation (Figs. 2 and 3) represents the break up unconformity of the post-rift sequence in the Ionian Basin which largely obscures the pre-existing syn-rift structures (Karakitsios, 1995). The Vigla Formation comprises a thick succession of thin layered (5–20 cm) sub-lithographic, pelagic limestones (white to grey micritic packstone with abundant radiolaria), in rhythmic alternations with centimeter to decimeter thick radiolarian chert beds containing rare shale intercalations. The Vigla Shale Member in the upper part of the Formation, is attributed to the Aptian–Cenomanian interval, and comprises marly limestone and chert beds interbedded with marlstone beds rich in organic matter, and dark greenish-grey shale (Karakitsios, 1992, 1995; Karakitsios and Koletti, 1992; Karakitsios et al., 2007).

Tsikos et al. (2004) have attributed the stratigraphically uppermost black shale horizon of the Gotzikas Section to the Paquier Event of the OAE1b, based on stable isotopic (C, O), biostratigraphic and organic geochemical data. Planktonic foraminiferal and calcareous nannofossil biostratigraphy indicates a lower to middle Albian age for the strata immediately above, and a lower Aptian age for the strata below the Paquier black shale. The latter is distinguished from the stratigraphically lower black shale horizons in the studied sequence by its very high TOC content (28.9 wt%) and Hydrogen Index (HI) (529 mg HC/g TOC) and much enriched  $\delta^{13}\text{C}_{\text{org}}$  value ( $-22.1\text{‰}$ ). It is also enriched in isoprenoidal compounds whose high isotopic values are indicative of an archaeal origin. This archaeal isotopic signature is characteristic of the Paquier Event of OAE 1b, as it is also replicated in broadly coeval organic-rich strata from SE France (Niveau Paquier of the Vocontian Basin, type locality for the Paquier Event; Vink et al., 1998) and from the North Atlantic (ODP Site 1049C; Kuypers et al., 2002a).

The Vigla Limestone Formation exhibits thickness variations due to continued halokinesis of the basal Ionian Zone evaporites and the resulting differential subsidence during their deposition. In some cases, Vigla strata are seen to directly overlie the Pantokrator Limestone pre-rift sequence (Karakitsios, 1995). This palaeogeographic configuration continued with minor off- and on-lap movements along the basin margins until the Late Eocene, when flysch sedimentation commenced (Karakitsios, 1995). Deposition of the Vigla Limestones was synchronous, from the beginning of the early Berriasian to Coniacian and their facies represent uniformity of depositional conditions over several hundred square kilometers across the Ionian Zone. Therefore, the Vigla Limestones blanket the entire seafloor pre-topography and represent the

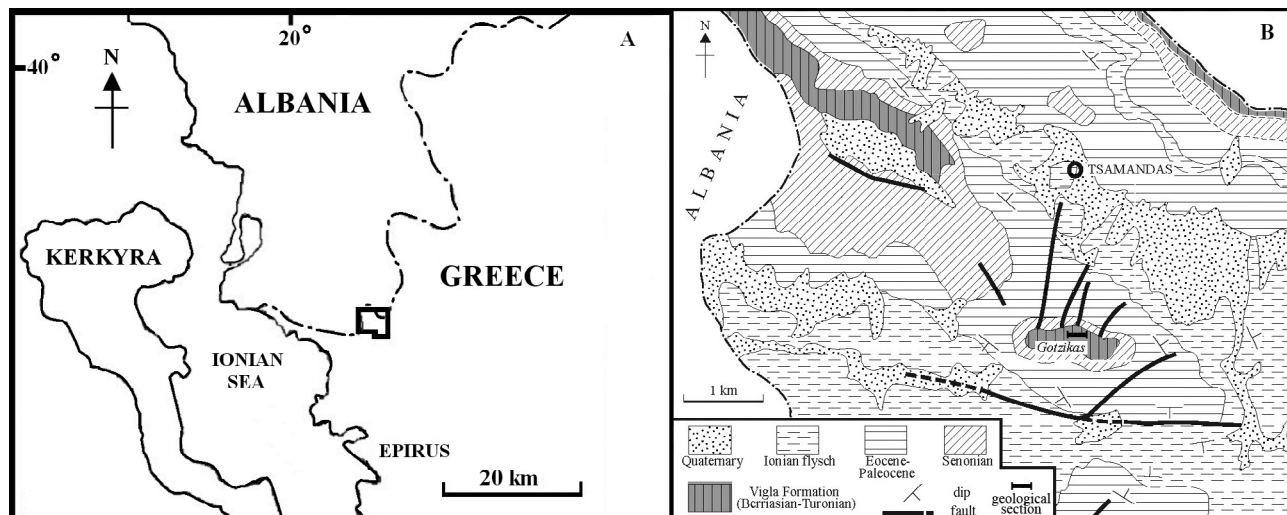


Fig. 2. (A) Location of the study area. (B) Simplified geological map of the study area (modified after Tsikos et al., 2004).

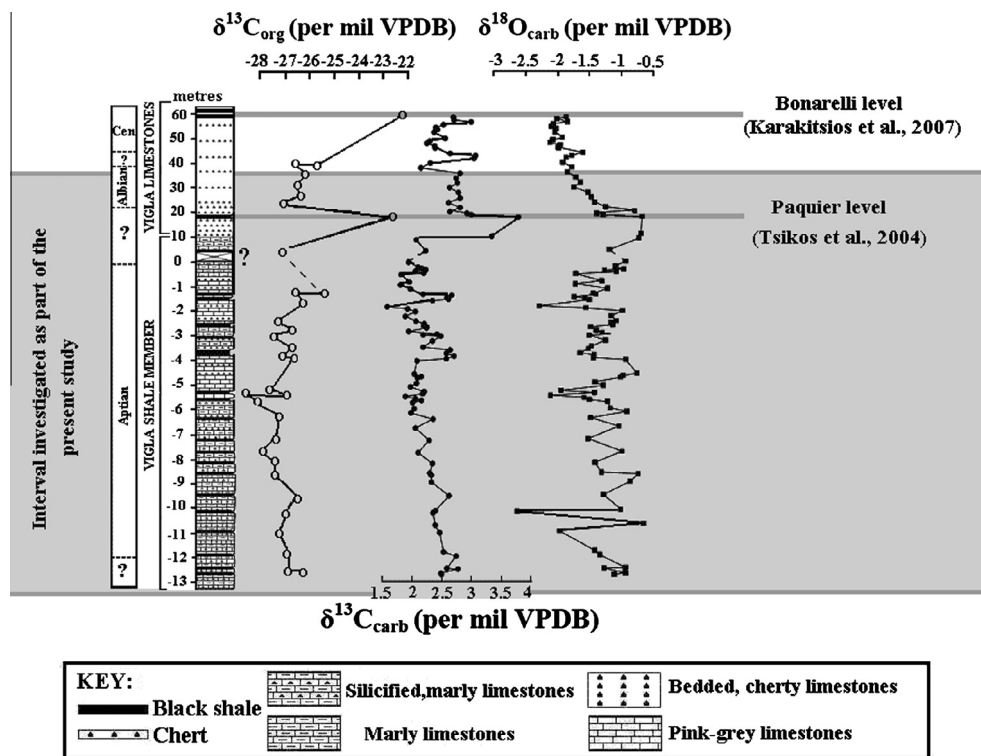


Fig. 3. Lithostratigraphic log and bulk carbon and oxygen stable isotope profiles through the Gotzikas Section. The interval investigated as part of the present study is highlighted. Note the different scales used for the portions of the section above and below the observation gap (modified after Tsikos et al., 2004; Karakitsios et al., 2007).

beginning of the Ionian Basin post-rift period (Karakitsios, 1992, 1995; Karakitsios and Koletti, 1992). The Gotzikas Section constitutes a highly representative profile for the post-rift stratigraphy of the Ionian Basin.

### 3. Materials and methods

The samples on which this study is based were originally collected in May 2001 from outcrops of the Vigla Shale Member in the Gotzikas valley, south of the village of Tsamandas in NW Epirus (Fig. 2). They were used in an earlier isotopic, biostratigraphic and organic geochemical study which carried special emphasis on the recognition of the OAE1b Paquier Event in the Vigla Shale Member (Tsikos et al., 2004). Following this earlier work, unprocessed portions of 12 organic carbon rich samples were chosen for this study, including two sub-samples representing the Paquier OAE1b Event itself (Figs. 3 and 4). Our analyses were conducted with utmost care in order to prevent contamination and exclude any possibility of an exogenous source for the identified biomarkers. An allochthonous source for carotenoids and particularly for isorenieratene in our samples can also be ruled out, as these compounds are relatively sensitive to degradation and are unlikely to survive during transport over long distances or during re-deposition (Sinninghe Damsté and Koopmans, 1997). During sub-sampling, special care was also given in preventing contamination effects from weathering surfaces, locally intense silicification and secondary carbonate veining.

Preparation for the gas chromatographic–mass spectrometric (GC–MS) analysis was conducted separately for each sample to prevent cross contamination. A small quantity (2–6 g) of rock was dried, powdered in an agate mortar, and extracted in an ultrasonic bath (Branson 3510) with dichloromethane (Sigma–Aldrich, Chromasolv, HPLC Grade). The total lipid extracts (TLE) were filtered through a Pasteur pipette plugged with clean cotton filter

into a pre-cleaned amber vial. Desulfurization of the extracts included TLE treatment with acid-activated copper wire to remove elemental sulfur which could interfere with the gas chromatographic analysis (Forster et al., 2004), followed by re-filtering over a clean cotton filter-plugged Pasteur pipette into a pre-cleaned amber vial to remove any traces of copper.

The first solvent (dichloromethane, DCM) was evaporated to complete dryness and each dried extract was dissolved in 2 ml hexane (Merck, Lichrosolv, LC Grade). This process was followed by the separation of the extracted compounds according to their polarity through column chromatography, over a glass Pasteur pipette plugged with clean cotton filter and filled with suitably prepared adsorption material (SiO<sub>2</sub> Sigma–Aldrich, 100–200 mesh, 75–150 mm, pore diameter 30 Å). Hexane was used for pre-elution of the chromatographic column. Fractions of increasing polarity were collected from each extract through sequential elution with 4 ml of hexane (aliphatic fraction); 4 ml of DCM:hexane (1:1) (aromatic fraction); and 4 ml of DCM (polar fraction). The eluates were collected in clean amber vials, the elution solvents were evaporated and the eluted fractions of each extract were dissolved in hexane. This process was followed by filtration over a Pasteur pipette plugged with clean cotton wool to remove components insoluble in hexane. The fractions were then transferred into the autosampler vials of the GC system.

Analyses were carried out on a Thermo Finnigan, Trace GC Ultra 2.0 gas chromatograph coupled with a Finnigan Trace DSQ II 2.0.1 mass spectrometer. Electron Impact (EI) mass spectra were acquired at an ionization energy of 70 eV in full scan mode (scan range from  $m/z = 27$ –800). Helium (He) was used as the carrier gas and its flow was maintained constant during the entire analysis. The GC–MS system was equipped with a capillary column Restec, RXi 35-Sil MS (fused silica, medium polarity, equivalent to 35% phenyl methylpolysiloxane), 30 m × 0.25 mm,  $df = 0.25 \mu\text{m}$  (i.e. length 30 m, diameter 0.25 mm and thickness of film coating

0.25  $\mu\text{m}$ ). A quantity of 2  $\mu\text{l}$  of each sample was injected through an auto-injector AI 3000 (split/splitless). Samples of the two solvents used in the preparation of the extracts (i.e. DCM and hexane) were analyzed as blanks. The compound *trifluralin* [ $\text{C}_{13}\text{H}_{16}\text{F}_3\text{N}_3\text{O}_4$ , benzenamine, 2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)-] was added in the samples and blanks as an internal standard and was eluted from the gas chromatographic column at 16.45 min.

Duration for total analysis of each sample was 78.5 min. During sample injection, the oven temperature of the GC system was set at 70 °C and held constant for the next 1 min. Then, it increased to 130 °C at a rate of 20 °C/min, maintained at that level for 2 min, and then increased to 320 °C at a rate of 4 °C/min, where it was held for 25 min. The temperature of the transfer line between sample injector and detector was set at 280 °C, while the temperature of the detector ion source was maintained at 230 °C.

Analytical data were acquired and processed by Xcalibur software (version 2.0.7). Compounds were identified by their relative retention times and through comparison of their mass spectra with those reported in the literature. For this purpose, the NIST 2008 mass spectral database and the corresponding NIST MS Search v.2.0 were also used.

#### 4. Results

Normal alkanes, ranging from  $n\text{-C}_{13}$  to  $n\text{-C}_{35}$ , were identified in the aliphatic fraction of all samples analysed, with a dominant presence of compounds with shorter carbon chain length; this is commonly used as an indicator of organic matter of marine algal and cyanobacterial origin (Tissot et al., 1975). No strong even or odd carbon number predominance was observed. The isoprenoid alkanes pristane, phytane and crocetane were also identified, with pristane in much lower concentration than phytane. This is variously interpreted as an indication of an anoxic depositional environment (Didyk et al., 1978; Volkman and Maxwell, 1986). Crocetane was identified only in the two Paquier OAE1b samples and is considered to have derived from anaerobic methanotrophic archaea, though its origin can only be further verified through compound-specific isotopic analyses which were not employed here.

The isoprenoids 2,6,10-trimethyl dodecane, 2,6,10-trimethyl tridecane, 2,6,10-trimethyl tetradecane and 2,6,10-trimethyl pentadecane were recognized in the aliphatic fractions of all samples and probably have the same origin as that of pristane and phytane (Volkman and Maxwell, 1986). The isoprenoid 2,6,10-trimethyl dodecane (farnesane), however, is considered to be derived from bacteriochlorophyll *e* of green SB, therefore, its presence may be correlated with photic zone euxinic conditions during deposition. Branched alkanes with quaternary carbon atoms (BAQCs), ranging from  $n\text{-C}_{17}$  to  $n\text{-C}_{22}$ , were also recognized in most samples. However, uncertainties concerning the precise origin of

these compounds (Kenig et al., 2005) and the possibility that they may even represent contaminants derived from plastic lab-ware during analysis (Grosjean and Logan, 2007), renders them as unsuitable for further discussion in this paper.

Several steroids were recognized in the aliphatic fractions of all samples with varying structures, 26–27 carbon atoms and mostly saturated. The geosteroids, abundant in sedimentary organic matter, derive from sterols which are structural components of the cell membranes of eukaryotic organisms (Volkman, 1986).  $\text{C}_{27}$  sterols occur mostly in animals and in the red lineage of algae, hence the presence of  $\text{C}_{27}$  steranes and sterenes in sediments constitutes evidence of marine depositional palaeoenvironments. Numerous  $\text{C}_{26}$  steranes, belonging to the groups of 24- and 27-norcholestanes, were also identified. The possible precursor compounds of 24-norcholestanes are known to occur, in low concentrations, in marine invertebrates and some algae, diatoms and dinoflagellates (Moldowan et al., 1991), whilst one of the 27-norcholesterol isomers has been isolated from sponges. The bacterial degradation of  $\text{C}_{27}$  sterols before early diagenesis is possibly responsible for the presence of 27-norcholestanes in sediments (Moldowan et al., 1991).

Various diagenetic transformations in steroid structures depend on the conditions prevailing after deposition of the host sediments and their recognition indicates the nature of the diagenetic conditions (MacKenzie et al., 1982). In most of the analyzed samples, saturated and unsaturated hopanoids were identified. During diagenesis, the bacteriohopanepolyols (structural and functional components of bacterial cell membranes, with potentially relevant functions to eukaryotic sterols) undergo various transformations into saturated, unsaturated and aromatic hopanoids (Ourisson et al., 1979). Hopanoids, belonging to the group of pentacyclic triterpenoids, have been isolated from several aerobic prokaryotes and amphiaerobic photosynthetic bacteria (Ourisson et al., 1979; Rohmer et al., 1979).

In the aliphatic fraction of the two Paquier OAE1b samples, terpenoid compounds were identified which can be attributed either to the influx of terrigenous plant material in the sedimentary environment (Ageta and Arai, 1983; Simoneit, 1986; Hazai et al., 1988; Otto and Wilde, 2001; Samuel et al., 2010; Dutta et al., 2011) and/or to pronounced microbial activity under anoxic conditions (Ourisson et al., 1982; Moldowan et al., 1983; Huang et al., 2008). In the aromatic fraction of the same samples, a number of tetraterpenoids were recognized, mostly diagenetic isorenieratene derivatives that can be correlated with the presence of green SB in the sedimentary environment (Koopmans et al., 1996a). In the two Paquier OAE1b samples and in those collected from the black shale horizons of the lowermost 4.5 meters of the studied section, these derivatives were on a greater variety of structures and in higher concentrations, as compared to samples from the intermediate part (Table 1, Fig 4, Supplementary Figs. A1 and A2, Supplementary

**Table 1**  
Summary of bulk geochemical and stable isotope data of the samples selected for this study as published elsewhere (Tsikos et al., 2004), including corresponding PSB biomarker contents resulting from the present study. PSB biomarker numbers refer to compounds in Supplementary Table B1.

Sample	TOC (wt%)	$\text{CaCO}_3$ (wt%)	$\delta^{13}\text{C}_{\text{TOC}}$ (‰)	$\delta^{13}\text{C}_{\text{carb}}$ (‰)	$\delta^{18}\text{O}_{\text{carb}}$ (‰)	Depth (m)	PSB biomarkers (present study)
1	28.87	23.25	-22.14	2.92	-1.32	14.80	1, 2, 3, 4, 6, 9, 10, 11, 12, 16, 19, 20, 22
2							1, 2, 5, 7, 8, 9, 10, 12, 16, 17, 20, 21, 22
3	3.35	61.67	-26.83	2.48	-1.53	-3.10	10
4	3.19	72.92	-27.59	2.15	-1.52	-5.69	10
5	4.42	67.83	-26.84	2.28	-1.55	-7.29	13
6	3.61	53.35	-26.75	2.29	-1.34	-8.64	11, 14, 18, 16, 20
7	-	-	-	-	-	-9.60	-
8	2.43	81.30	-25.96	2.62	-1.31	-10.05	3, 6, 7, 16, 17, 18, 19, 20, 21, 22
9	1.77	20.00	-26.37	2.35	-2.66	-10.72	2, 4, 5, 6, 7, 11, 16, 19, 20
10	2.29	84.50	-26.20	2.74	-1.37	-12.47	2, 10, 11, 16, 19, 22
11	6.33	59.92	-26.20	2.77	-1.30	-12.99	3, 4, 5, 6, 7, 10, 19, 21
12	2.77	81.12	-25.63	2.49	-1.14	-13.22	5, 15, 16, 19, 20, 21, 22

Table B1). A C<sub>18</sub> aromatic isoprenoid was also identified which, according to Brocks and Schaeffer (2008), most likely derives from diagenetic cyclization of the compound okenone and is therefore a specific biomarker for the PSB of the family Chromatiaceae.

Compounds of a possible bacterial origin such as indenyltrimanes (Killops, 1991), benzohopanes and aromatic secohopanoids were also detected in the aromatic fractions of the samples. The presence of benzohopanes probably suggests diagenetic cyclization and aromatization of the side chain of hopanes (Hussler et al., 1984; Rohmer et al., 1993; van Kaam-Peters et al., 1995), whereas aromatic secohopanoids would have arisen from bacteriohopanepolyols through diagenetic cyclization, aromatization, ring fission and cleavage of the side chain (Oba et al., 2008). Aromatic terpenoid compounds were recognized especially in the Paquier OAE1b samples (Supplementary Fig. A3, Supplementary Table B2), possibly indicating input from terrestrial plants to the sedimentary environment (Stout, 1992). Two aromatic lycopane derivatives of enigmatic origin (Zhang et al., 2007) were also identified in one of the Paquier OAE1b samples. Finally, although maleimides were recognized in the polar fractions, it was not possible to identify methyl-isobutyl maleimide which is a specific biomarker for green SB.

## 5. Discussion

As indicated in the introductory sections of this paper, this study focuses on biomarker evidence derived mainly from the aromatic fraction of the studied samples. It therefore builds on the work of Tsikos et al. (2004) which concentrated on the aliphatic fraction and specifically on molecular and isotopic evidence for an archaeal contribution in the organic matter of the Paquier black shale interval. To this end, the presence of the isoprenoids crocetane, itself of possible archaeal origin, and farnesane (of possible origin from PSB), in the aliphatic fraction is compatible with both the results of previous studies (i.e. Tsikos et al., 2004), and also those of the analysis of the aromatic fraction which constituted the main objective of the present work. Identification of molecular fossils in the aromatic fraction of our samples was based mainly on the results of Koopmans et al. (1996a), who reported the discovery of several and previously unknown diagenetic and catagenetic isorenieratene derivatives in Phanerozoic sediments from many different areas.

### 5.1. Molecular evidence for photic zone euxinia

The recognition of isorenieratene derivatives in our samples is consistent with previous studies of Cretaceous OAEs (Kuypers et al., 2002b) and can be taken as a strong indication for the existence of at least intermittent photic zone euxinia (PZE) in the palaeoenvironment of the studied succession. The occurrence of photic zone euxinic conditions during OAE1b is not considered a typical feature of this event, contrary to other, more widely researched OAEs, such as OAE1a (e.g. Danelian et al., 2004; Pancost et al., 2004). Intense oceanic thermohaline stratification has been considered to be the main causative factor leading to the onset of OAE1b (Erbacher et al., 2001; Kuypers et al., 2001; Meyers, 2006), whereas its termination has been associated with deep-water oxygenation and attendant elimination of water column stratification (Kuypers et al., 2001).

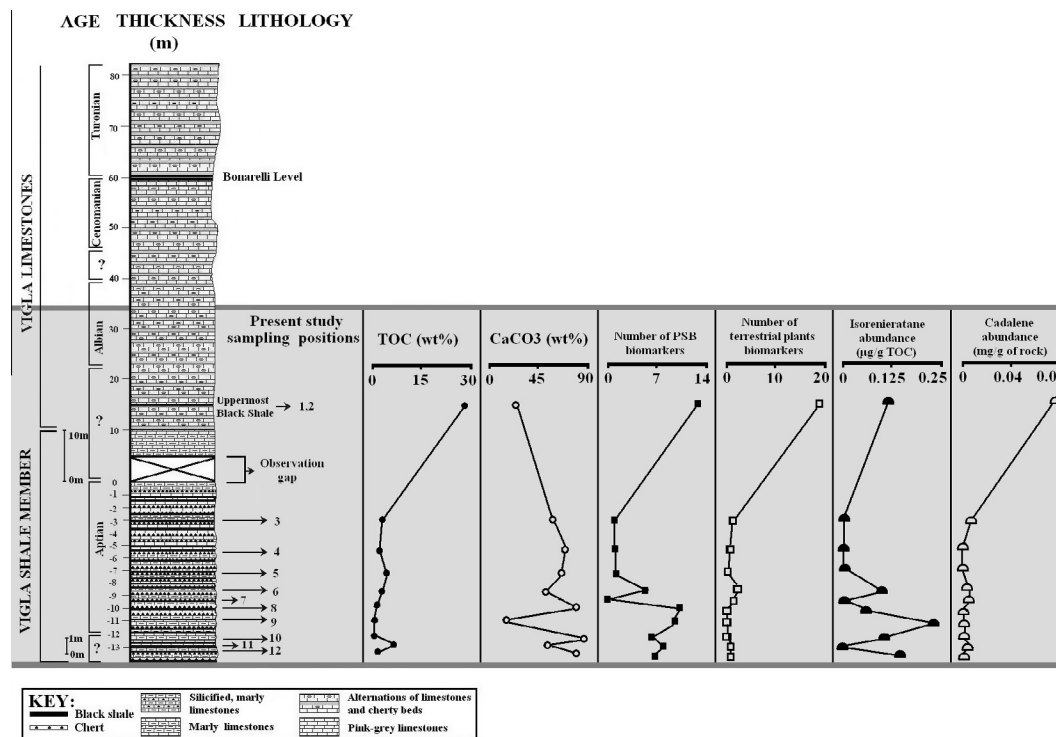
According to Erbacher et al. (2001) there are commonalities between the factors that led to deposition of OAE1b black shales and to that of Quaternary Mediterranean sapropels. The partial tectonic isolation of certain basins of the Atlantic and Tethys, the low sea level and the establishment of warm global climatic conditions may have been important favorable factors in causing oceanic stag-

nation during OAE1b. The development of euxinic conditions is a typical situation in cases of significant increase in biological productivity, though according to Erbacher et al. (2001), this is not thought to have been a major controlling factor for OAE1b. Euxinic conditions may also be the result of loss in connectivity between restricted basins and sub-basins, although geological data from the Ionian Basin seem to exclude this possibility (Karakitsios, 1992).

The prevalence of anoxic conditions across large parts of the water column during the Paquier Event of OAE1b may be plausibly linked to the massive expansion of chemoautotrophic archaea (Kuypers et al., 2001). According to Kuypers et al. (2001), there is evidence of a significantly increased contribution by archaea (probably from planktonic chemoautotrophic Crenarchaeota) to organic matter deposited during Paquier OAE1b. The predominant presence of a dense archaeal population in the water column has been isotopically confirmed by a number of studies among which is that of Tsikos et al. (2004) who provide supporting evidence in this respect from the study area, based on the high concentrations of several <sup>13</sup>C enriched, monocyclic isoprenoids of putative archaeal origin. Adaptation of some groups of hyperthermophilic Crenarchaeota to low temperature marine environments during the Paquier Event of OAE1b, has been associated with increased hydrothermal activity in the Early Albian oceans, expansion of the oceanic crust, significant changes in oceanic chemistry, prominent stratification and water column anoxia (Kuypers et al., 2001).

The detection of traces of green SB in the black shale horizons of the Vigla Shale Member as presented here, provides a first evidence for the co-existence between chemoautotrophic archaea and photoautotrophic bacteria in a euxinic oceanic environment during the Paquier Event. This is potentially very important from a palaeoecological point of view, as the massive expansion of Crenarchaeota probably was influenced by the presence of PSB in the photic zone, although the exact ecological relationships developed in the early stages of this coexistence cannot be conclusively discussed on the basis of the present results alone. This type of biotic association is, however, observed in contemporary anoxic basins. The coexistence of archaea and PSB have been studied in the profundal anoxic sediments of the subtropical Lake Kinneret of Israel (Schwarz et al., 2007) and in the water column of the coastal saline meromictic Lake Faro of Messina, Italy (Lentini et al., 2012). The distribution of various groups of prokaryotic organisms was studied using fluorescence microscopy as well as molecular techniques. The various groups of prokaryotic organisms (green SB, sulfate reducing bacteria, cyanobacteria, purple SB and archaea of the groups Crenarchaeota and Euryarchaeota) exhibit characteristic vertical distribution in accordance with water column stratification. Their densest populations have been observed in the chemocline. The bacterial abundance has been found to decline from the surface to the bottom whereas the abundance of archaea increases with depth (Lentini et al., 2012). Green SB dominate at the chemocline where they have an important role as primary producers in the biogeochemical cycling of carbon, contribute as sulfide oxidizers in the sulfur cycle and oxidize sulfides to less toxic compounds for organisms living in the upper parts of the water column. The purple SB of the species *Chromatium okenii* which generally are less abundant than the green SB, are seen throughout the water column, reaching their highest abundance at the chemocline (Lentini et al., 2012).

From the two archaeal groups, the abundance of Crenarchaeota in oceans and lakes increases with depth, in contrast to Euryarchaeota which are dominating in the upper layers. It is therefore evident that the coexistence of PSB and chemoautotrophic Crenarchaeota in euxinic basins is feasible, since the two groups of organisms occupy different ecological niches. In theory, this may also have happened during the Paquier Event of OAE1b when



**Fig. 4.** Stratigraphic anatomy of the Aptian–Albian interval of the Gotzikas Section, showing sample locations for the present study; stratigraphic records for TOC and bulk carbonate content in wt% of sediment (modified after Tsikos et al., 2004); and similar profiles of quantitative data for selected PZE and terrigenous input parameters. The studied interval is highlighted in grey. Note the different scales used for the portions of the section above and below the observation gap.

there were large populations of planktonic chemoautotrophic archaea (Crenarchaeota) throughout the water column and fairly dense populations of PSB in the habitats created at the sites where the photic zone overlapped with euxinic water layers.

## 5.2. Quantitative considerations and implications

As part of our further data evaluation, we carried out quantitative analysis of our new results in conjunction with selected bulk geochemical profiles as published for the same samples by Tsikos et al. (2004), with a view to providing insights into stratigraphic fluctuations of selected organic parameters, their possible causes and implications. This involved quantification of GC–MS data through standard chromatographic peak integration methodology, using the *Xcalibur* software (version 2.0.7). All results are presented in the diagrams of Fig. 4. The new parameters included in our considerations are the total number of PSB and terrigenous plant biomarkers detected in the samples, as well as the relative concentrations of two highly specific biomarkers: isorenieratane as an index of PZE and cadalene as an index of the land plant material input into the sedimentary environment. The number of PSB biomarkers which were identified in 11 of 12 samples, range from 1 to 13. The number of terrigenous plant biomarkers which were identified in eight of the 12 samples, range from 1 to 19.

The relative abundance of isorenieratane which was identified in seven samples was expressed as a proportion of the calculated amount of isorenieratane in sediment samples (in micrograms) to the amount of total organic carbon in the samples (TOC, expressed in grams). Isorenieratane abundances, range from  $6.2 \times 10^{-2}$  to  $22 \times 10^{-2} \mu\text{g/g TOC}$ . The relative concentration of cadalene which was identified in five from the 12 samples analyzed, was expressed in milligrams per gram of processed sediment. Cadalene concentrations range from  $5.2 \times 10^{-4}$  to  $7.7 \times 10^{-2} \text{ mg/g of sediment}$ .

The results of such an exercise must, however, be treated with caution for two main reasons: firstly, our quantitative estimations were derived from total lipid extracts of small quantities of starting sample material, resulting in very low isorenieratane abundances that are intrinsically difficult to quantify very accurately. Secondly, our sample resolution is arguably rather small, which leads to a statistically low degree of robustness of our quantitative data. Nevertheless, the ensuing profiles provide some interesting trends and relationships against stratigraphic depth:

- (1) A clear upward increase in the accumulation of terrigenous input with stratigraphic height is recorded, both in terms of total number of terrigenous biomarker species and in terms of cadalene abundance. By contrast, only minimal terrigenous input is seen in samples collected from lower stratigraphic levels of the studied interval (Fig. 4; see also Supplementary Fig. A3; and Supplementary Table B2). We tentatively attribute this feature to a relatively increased continental run off during the Paquier OAE1b, coupled with a rise in marine primary productivity due to elevated nutrient supply, and resultant expansion of the oxygen minimum zone. As mentioned in earlier sections of this paper, due to the homogenization of sedimentation conditions during the post-rift period in the Ionian Zone and specifically during the Berriasian–Coniacian interval (which includes the Aptian–Albian interval studied in this paper) the findings of the Gotzikas Section are representative of the much wider palaeogeographic area of the Ionian Zone. During that time, the Ionian Basin was surrounded by extended shallow-water carbonate banks of the Apulia and Gavrovo-Tripolitza platforms. The Apulia platform to the west was periodically exposed to subaerial conditions at this time due to fluctuating sea level, as manifested by several bauxite horizons and evidence for Milankovitch cyclicity in the platform

successions which bear several exposure surfaces. Similar evidence is also recorded in the Gavrovo platform adjacent to the Ionian Zone, and is supported from palaeontologic, stratigraphic and sedimentologic data (Fleury, 1980; Bosellini, 2002). The increased terrigenous flux during Paquier times would thus have coincided with one of those periods of sub-aerial exposure under accelerated hydrological conditions.

- (2) The relative abundance of PZE biomarkers and of isorenieratane in particular as an index of PSB biomass contribution to the TOC, is variable across the entire studied profile, and lacks a maximum peak at the Paquier level. This is in stark contrast to the clear maximum at the latter level in terms of terrigenous biomarker abundance and also its correspondingly strong archaea-derived biomarker signal as highlighted in earlier studies (Tsikos et al., 2004). The fact that evidence for increased terrigenous supply is essentially confined to the Paquier OAE1b black shales whilst biomarker evidence for PZE is not, intuitively suggests that the latter would have developed independent of broad-scale tectonic and associated hydrological processes. Our results also seem to collectively conform, at least in part, with similar new data on the occurrence of PZE in the Vocontian Basin during the Paquier Event based on the detection of the compound chlorobactane, and increased terrigenous supply over the same interval based on the respective terrigenous plant biomarker record (Takuto et al., 2012). However, Kuypers et al. (2001) provide no records of isorenieratene derivatives or other similar molecular evidence for PZE in Paquier sediment samples from the ODP Site 1049C. This, in combination with the fact that biomarker evidence of PZE is not exclusive to the Paquier level of the studied section but extends also to stratigraphically lower black shale horizons as well, implies that PZE conditions should not be considered as a key diagnostic feature of the Paquier Event of OAE1b, especially in the absence of any supporting compound-specific isotopic information.

## 6. Conclusions

The presence of PSB biomarkers in organic rich samples of Aptian–Albian age from the Ionian Basin documented in this paper permits the conclusion that euxinic conditions occurred periodically in the primary depositional environment of these deposits that extended right through to the photic zone. Evidently, such conditions characterised the deposition of a number of such organic rich accumulations, including the horizon recording the Paquier OAE1b in the uppermost part of the studied section. This adds to the few published reports that hitherto document molecular organic geochemical evidence of PZE for OAEs in general and the OAE1b in particular.

Combination of previously published biomarker results with those presented in this study point to a mixed origin of sedimentary organic matter derived from autochthonous as well as allochthonous (terrigenous) sources. With specific regard to the uppermost organic rich horizon recording Paquier OAE1b, the increased supply of terrigenous organic matter from adjacent emerged platforms would have triggered increased marine primary productivity and expansion of the oxygen minimum zone. This would have progressively led to de-oxygenation of sea floor and development of euxinic conditions in the water column, creating suitable habitats for anaerobic organisms such as marine chemoautotrophic archaea and PSB, which have left recognizable biomarker traces in the studied sediments. Although the relative primary contribution of these groups of organisms to the sedimentary organic matter remains unclear, PZE conditions were evidently not exclusive to the Paquier Event of OAE1b, but occurred intermittently during earlier periods of organic carbon

deposition as well. Therefore, we contend that PZE should not be considered diagnostic of the Paquier Event itself, unless biomarker and corresponding isotopic data from other coeval sections elsewhere provide further unequivocal evidence.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orggeochem.2013.08.013>.

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