CHEMOSTRATIGRAPHY OF THE TOARCIAN OCEANIC ANOXIC EVENT FROM THE IONIAN ZONE, GREECE

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Abstract

A global perturbation in the carbon cycle has been recorded in the Early Toarcian (~ 183 Ma) and is marked by enhanced organic-carbon burial and mass extinction. It is also associated with high palaeotemperatures, both positive and negative excursions in carbon-isotope ratios, and the development of anoxic to euxinic conditions in marine environments: together these phenomena have been designated as constituting an Oceanic Anoxic Event. Here we provide a high-resolution, multi-proxy biostratigraphic and chemostratigraphic study from a section that belongs to the central Ionian Zone in Greece. Calcareous nannofossil distribution, as well as the TOC, δ\(^{13}\)C\(_{\text{carb}}\) and δ\(^{13}\)C\(_{\text{org}}\) have all been determined. The nannofossil zones NJT 5b, NJT 6 and NJT 7 have been recognized in the section. In the NJT 5b zone a small positive excursion in TOC and negative excursion in δ\(^{13}\)C\(_{\text{carb}}\) is recorded, tentatively assigned to the Pliensbachian/Toarcian boundary. In the NJT 6 zone, the main negative carbon-isotope excursion characteristic of this interval is developed, associated with a relative increase in TOC. The difference in this section, compared with sections from the Pindos Zone but in common with sections elsewhere, is the record of a positive excursion in the NJT 7 zone in both organic and carbonate carbon isotopes. This study offers new biostratigraphic and geochemical data for the Ionian Zone, and further illustrates the impact of Toarcian Oceanic Anoxic Event in the Tethyan region.

Key words: Jurassic, total organic carbon, carbon isotopes, biostratigraphy, geochemistry.
ανάλυσης μελέτη όπου συνδυάζονται βιοστρωματογραφικά και χημειοστρωματογραφικά δεδομένα, σε μια τομή της κεντρικής Ιόνιας Ζώνης. Στα πλαίσια της εργασίας, αναγνωρίστηκαν οι συναθροίσεις των ασβεστολιθικών ναννοαπολιωμάτων καθώς και οι συγκεντρώσεις του TOC, δ13C_carb και δ13C_org. Αναγνωρίστηκαν οι Ζώνες NJT 5b, NJT 6 και NJT 7. Στη Ζώνη NJT 5b παρατηρείται μια μικρή θετική μεταβολή στις συγκεντρώσεις του TOC και μια αρνητική μεταβολή στο δ13C_carb που οδηγούν στην αναγνώριση του ορίου Πλιενσβάχιο/Τοάρσιο. Στη Ζώνη NJT 6, αναπτύσσεται η κύρια αρνητική μεταβολή ή στα ισότοπα του άνθρακα, η οποία είναι χαρακτηριστική για το συγκεκριμένο επίπεδο, σε συνδυασμό με αύξηση των συγκεντρώσεων του TOC. Η διαφορά αυτής της τομής, σε σύγκριση με τη Ζώνη της Πίνδος, είναι η εμφάνιση θετικής μεταβολής και στα δύο ισότοπα του άνθρακα στη Ζώνη NJT 7. Αυτή η μελέτη δίνει νέα βιοστρωματογραφικά και γεωχημεία δεδομένα για την Ιόνια Ζώνη και διαφωτίζει περαιτέρω τον αντίκτυπο του Τοάρσιου Ωκεάνιου Ανοξικού Γεγονότος στην περιοχή της Τηθύος.

Λέξεις κλειδιά: Ιουρασικό, ολικός οργανικός άνθρακας, ισότοπα του άνθρακα, βιοστρωματογραφία, γεωχημεία.

1. Introduction

The Toarcian Oceanic Anoxic Event (T-OAE) constitutes one of the most profound environmental changes of the Mesozoic Era (Jenkyns, 1988). Marine depositional settings across the globe, show evidence for global warming (Bailey et al., 2003; Jenkyns, 2003; Suan et al., 2008), mass extinction (Little and Benton, 1995; Wignall, 2001) and probable ocean acidification (Hermoso et al., 2012; Hönisch et al., 2012; Trecalli et al., 2012). A major perturbation in the global carbon (Cohen et al., 2007) and sulphur cycle (Gill et al., 2011; Newton et al., 2011) during the Toarcian has been recorded. The carbon perturbation is marked by a negative excursion in carbon isotopes interrupting an overarching positive trend, that has been recorded in terrestrial wood (Hesselbo et al., 2000; Hesselbo et al., 2007; Al-Suwaidi et al., 2010), marine organic matter and carbonate (Jenkyns and Clayton, 1986; Suan et al., 2008; van Breugel et al., 2006; Woodfine et al., 2008).

In this paper, we present biostratigraphical (calcareous nannofossils) and geochemical (wt% TOC, δ13C_carb, and δ13C_org) data from the Toarcian sediments of the central Ionian Zone (Petousi section), a marine basin that constituted part of the southern Tethyan margin (Bernoulli and Renz, 1970). Age equivalent deposits in Greece have recently been studied in Pindos Zone (Karakitsios et al., 2010; Kafousia et al., 2011), corresponding to a deep-sea ocean-margin basin that formed in the Triassic and the Jurassic.

2. Geological Setting

The Ionian Zone of NW mainland Greece is one of the most external Hellenides (Paxos Zone, Ionian Zone, Gavrovo Zone; Aubouin, 1959). This domain corresponds to the southern passive continental margin of the Neotethys Ocean. This Ocean’s opening started in Early Mesozoic while its closure took place during the Late Mesozoic–Early Cenozoic (Karakitsios, 1992, 1995; Laubscher and Bernoulli, 1977). The Ionian Zone constitutes of rocks that range from Triassic evaporites through a varied series of Jurassic to Upper Eocene mixed carbonate–siliciclastic–siliceous sediments, overlain by Oligocene flysch. During the Early Jurassic, northwestern Greece was covered by a vast carbonate platform (IGRS-IFP, 1966; Bernoulli and Renz, 1970; Karakitsios, 1992, 1995). In the Pliensbachian, extensional stresses that are related to the opening of the Neotethys Ocean, began to act in the area and caused the differentiation of the Ionian Zone from the adjacent Zones (Karakitsios, 1992, 1995). These Zones remained carbonate platforms, while the Ionian Zone became an area of strong subsidence and faulting with the development of pelagic conditions (Karakitsios, 1995). This palaeogeographic evolution is recorded in the pelagic
Siniais Limestone and the laterally equivalent Louros Limestones of Pliensbachian age (Karakitsios and Tsaila-Monopolis, 1988; Dommergues et al., 2002; Karakitsios, 1992). The initial formation of the Ionian Basin was followed by an internal differentiation into smaller sub-basins with half-graben geometry; in most cases these sub-basins did not exceed 5 km across (Karakitsios, 1995). This had as a result abrupt changes in thickness of the syn-rift formations, which take the shape of syn-sedimentary wedges. In the deeper parts of the half-grabens, these wedges include complete Toarcian-Tithonian successions, while in the elevated parts of the half-grabens; the succession is interrupted by unconformities (Karakitsios, 1992, 1995). The directions of syn-sedimentary structures (e.g. slumps and syn-sedimentary faults) indicate that deposition was controlled both by structures formed during extension related to the opening of the Neotethys Ocean and the halokinesis of evaporites at the base of the Ionian Zone succession (Karakitsios, 1992, 1995). In the Early Berriasian the post-rift sequence began with the pelagic Vigla Limestone, whose deposition was effectively synchronous throughout the Ionian Basin (Karakitsios et al. 1988; Karakitsios, 1992; Karakitsios and Koletti, 1992). The Vigla Limestone blankets the syn-rift structures and, in some cases, directly overlies pre-rift units (e.g. Pantokrator Limestone). As a consequence, the base of the Vigla Limestone represents the break-up unconformity of the post-rift sequence in the Ionian Basin (Karakitsios, 1992). Long-standing differential subsidence during the deposition of the Vigla Limestone, as shown by the marked variation in the thickness of this formation, was probably due to the continued halokinesis of the basal-Ionian Zone evaporites. This palaeogeographic configuration persisted with minor off- and onlap movements along the basin margin until the Late Eocene, when orogenic movements and flysch sedimentation began. The particular geometry of the restricted sub-basins that were formed during the syn-rift period of the Ionian Zone may have favored increased organic-matter burial during the Toarcian–Tithonian interval (Baudin et al. 1990; Karakitsios, 1995; Rigakis and Karakitsios, 1998; Karakitsios and Rigakis, 2007). Toarcian black shales in the Ionian Zone were described first by Renz (1910), who compared them with the Posidonienschiefere of Germany, and sedimentological details were given by Walzebuck (1982). In this paper we demonstrate that the Lower Toarcian organic-rich laminated black shales, deposited in the different palaeogeographic environments of the Ionian sub-basins, record a global rather than a local event.

Figure 1 – A: structural map of Greece, B: geological map of the Petousi section.

2.1. Petousi Section

The Petousi section (39°30′N, 20°35′E), was first described by Karakitsios (1992). It is located around 2 km WSW from Petousi village, south of the Petousi–Paramithia road, in Thesprotia prefecture. The studied outcrop is of excellent quality even though it is locally covered by vegetation.
The section begins with the uppermost metres of the Siniais Limestone: white to grey limestones, with thin layers of black shales intercalations. It continues with the Undifferentiated Posidonia Beds, which begins with 10 m of black shales followed by a yellow-green chert rich in Posidonia (Bositra buchi).

Figure 2 – Petousi section.

3. Materials and Methods

A total of 139 samples from Petousi, were analysed for their wt% TOC using a direct combustion and automatic titration method through a Strohlein Coulomat 702 analyser. Duplicate samples were used; one of them was roasted at 420ºC overnight to remove organic carbon. Both samples were then combusted at 1220ºC to decompose the calcium carbonate. The gaseous products of combustion are released (a Urea Peroxide tablet is removing SO2) and fed to barium perchlorite solution at stable temperature 10ºC and pH 10 with resultant change in pH. An electrolytically titration is bringing the pH back to the original value. The quantity of electricity needed for this purpose gave an absolute determination of the amount of carbon present. The difference between the samples that had (Ca) and had not (Cb) been roasted at 420ºC gave a measure of the value of TOC. Reproducibility of the samples was usually better than 0.1%. The result was given in counts and the following formula was used for the final result.

\[
\%C = \frac{\text{counts} \times 0.2}{\text{weight (mg)}} \\
\%TOC = \%Ca - \%Cb
\]

Equation 1

For carbonate carbon-isotope composition, 211 bulk sediment samples were analysed. The powdered samples were cleaned using 10% H2O2 followed by acetone ((CH3)2CO) and then dried at 60ºC for at least 30 minutes. Samples were then reacted with purified orthophosphoric acid at 90ºC and analysed on-line using a VG Isogas and Prism II mass spectrometer. Corrections were applied and the results are reported through the \( \delta \) notation, in % deviation from the Pee Dee Belemnite (PDB) standard. The calibration of the PDB was performed via the laboratory standard that was calibrated against NBS19 and Cambridge Carrara marble. Reproducibility of replicate analyses of the standards was usually better than 0.1‰.

\[
\delta X = \frac{R_s - R_t}{R_t} \times 1000
\]

Equation 2

For 97 samples organic carbon-isotope composition was calculated. The samples were decarbonated using 3 M HCL for the removal of CaCO3 and put in a warm surface for the removal of the rest CO3 for 8 hours. Samples were then rinsed with distilled water, centrifuged and rinsed again until pH was neutral and then dried in an oven at 60ºC. A quantity of 4 to 50 mg (depending on the amount of organic carbon) was weighed out into a 8x6 mm tinfoil cup and placed in an Europa Scientific Limited CN biological sample converter connected to a 20–20 stable isotope gas ratio mass spectrometer. Carbon isotope ratios were measured against a laboratory nylon standard (\( \delta^{13}C = -26.1 \pm 0.2\% \) and) and expressed relative to Peedee belemnite (PDB) and reported through the \( \delta \) notation. Reproducibility is better that 0.2‰. All the above analyses were undertaken at the University of Oxford.
A set of 24 samples was investigated for the content of calcareous nannofossils. Smear-slides were prepared from the powdered rock according to the technique described in Bown & Young (1998), then analyzed in an optical polarizing Leitz microscope at x1250. Nannofossils were counted for each sample in a surface area of the slide varying between 2 and 3 cm$^2$ at the Laboratoire de Géologie de Lyon, Université Claude Bernard.

4. Results

4.1. Biostratigraphy

The samples that were studied from Petousi section show a diverse and relatively rich nannofossil assemblage, although preservation is moderate to poor. Schizosphearaella, *M. jansae* and some small Lotharingius (*L. hauffi* and *L. frodoi*) are the dominant forms in the assemblage. In the base of the section, corresponding to the Siniais Limestone, NJT 5b Subzone was identified based on the presence of *Calyculus* spp. and *L. sigillatus*. This zone spans the Pliensbachian/Toarcian boundary (Mattioli & Erba, 1999). Higher in the section, the NJT 6 Zone is identified; starting at 5.4 m with the FO of *C. superbus* and ending at 9.8 m with the FO of *D. striatus* that marks the onset of the NJT 7 Zone.

![Figure 3](image-url)

Figure 3 – Calcareous nannofossil biostratigraphy of Petousi section. Relative abundance per square surface unit was estimated. Four abundance classes were defined: rare, frequent, common and abundant. These classes are represented by a different size of black dots.

4.2. Chemostratigraphy

4.2.1. Wt% Total Organic Carbon (TOC)

TOC values in the Siniais Limestone begin at very low values, ~ 0-1 wt%. In the basal Undifferentiated Posidonia Beds, where there are black shales, TOC values begin to rise marking a positive excursion that reaches values up to 4.86 wt% over a 2-metre interval. Higher in the section, values are lower and fluctuate between ~ 0 and 3 wt%.
4.2.2. Carbon-Isotope Ratio

In Figure 3 it can be seen that both carbonate and organic-carbon $\delta^{13}C$ profiles show a small disturbance at the 2-metre level of the section. This, together with the small excursion in the TOC data and the biostratigraphy, designate that this is the Pliensbachian/Toarcian boundary. Up-section, isotopic values of bulk carbonate remain stable around 1.3‰. The values show a marked ~1‰ decrease, that spans less than 1 m, half a metre above the NJT 5b/NJT 6 boundary. Above this level and for 11 metres, values increase recording a positive excursion of only ~1‰. Higher in the section, values decrease again.

Above the Pliensbachian/Toarcian boundary $\delta^{13}C_{\text{org}}$ fluctuates around a background value of -29‰. At the NJT5b/NJT6 boundary, values fall and define the negative excursion that spans 2 metres of the section where values drop to -33‰. Following this excursion, values begin to rise reaching values up to -30‰. Up-section, values go up and down until the 9.5-metre level of the section. At this point a positive excursion that lasts for 2 metres and reaches values up to ~ -26‰ is recorded. Above this level, $\delta^{13}C_{\text{org}}$ attains background values (~~-29‰) to the top of the section.

5. Discussion

Calcareous nannofossil analysis from the Petousi section reveals the age of the studied formations. The Upper part of the Siniais Limestone belongs to Subzone NJT 5b *Lotharingius sigillatus*, spanning the Late Pliensbachian–basal Toarcian interval (Mattioli and Erba, 1999; Mattioli et al., 2009). The small negative followed by a small positive excursion in carbonate carbon-isotopic data in the same formation, confirms that there is the Pliensbachian–Toarcian boundary. The small negative
carbon-isotope excursion probable represent a global event, since it has been recorded in many areas (Bodin et al., 2010; Hesselbo et al., 2007; Kafousia et al., 2011; Littler et al., 2010; Sabatino et al., 2009).

The lower part of the overlying stratigraphic formation (Undifferentiated Posidonia Beds) belongs to the Nannofossil Zone NJT 6 Carinolithus superbus. This Zone is encapsulated in the ammonite zones polymorphum/tenuicostatum and levisoni/serpentinus in Tethyan sections where ammonite biostratigraphy is available (Mattioli and Erba, 1999; Mattioli et al., 2009).

Total organic carbon values in the Petousi section from the Ionian Zone are comparable with coeval Tethyan sections. TOC values over the interval of the negative carbon-isotope excursion reach values up to ~ 5%. These values are similar to those in certain pelagic sections from the Southern Alps of Italy (Jenkyns, 2010; Jenkyns et al., 2001; Pancost et al., 2004).

In the Petousi section the negative carbon-isotope excursion and the increase in TOC, that are the main characteristics of the Toarcian Oceanic Anoxic Event, take place in the NJT 6 zone. The difference in this section, compared to sections from the Pindos Zone (Kafousia et al., 2011), is that in the NJT 7 zone is recorded a positive excursion, in both organic and carbonate carbon isotopes.

All the above data indicate that the Toarcian Oceanic Anoxic Event took place in the Ionian Zone but sedimentation and the geochemistry of seawater has been affected by local palaeoenvironmental conditions.

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7. References


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