Palaeogeography, Palaeoclimatology, Palaeoecology 409 (2014) 98–113

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

journal homepage: www.elsevier.com/locate/palaeo

# Paleoenvironmental conditions recorded by $^{87}$Sr/$^{86}$Sr, δ$^{13}$C and δ$^{18}$O in late Pliensbachian–Toarcian (Jurassic) belemnites from Bulgaria

Lubomir S. Metodiev [a], Ivan P. Savov [b,*], Darren R. Gröcke [c], Paul B. Wignall [b], Robert J. Newton [b], Polina V. Andreeva [a], Elena K. Koleva-Rekalova [a]

[a] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 24, 1113 Sofia, Bulgaria
[b] University of Leeds, School of Earth and Environment, Earth Science Department, Leeds LS2-9JT, UK
[c] Durham University, Department of Earth Sciences, Durham DH1 3LE, UK

ARTICLE INFO

*Article history:*
Received 11 October 2013
Received in revised form 29 April 2014
Accepted 30 April 2014
Available online 10 May 2014

*Keywords:*
Isotopes
Belemnites
Sedimentary
Ammonite Record
Lower Jurassic
Bulgaria

ABSTRACT

The late Pliensbachian–Toarcian (Jurassic) sedimentological, paleontological and geochemical (belemnite $^{87}$Sr/$^{86}$Sr, δ$^{13}$C and δ$^{18}$O) record is examined in two Eastern Tethyan (Bulgarian) locations. This interval contains the well-known early Toarcian ocean anoxic event (T-OAE) and its manifestation and temporal context is examined in Bulgaria. Many of the features seen in south-western Europe are identified: collapse of carbonate platform productivity at the Pliensbachian/Toarcian boundary, the T-OAE (a short pulse of euxinic deposition in the Falciferum Zone), an early Toarcian rapid warming event seen in the belemnite δ$^{18}$O record that peaked around the Falciferum/Bifrons Zone boundary. The long-recognized positive δ$^{13}$C excursion in the late Falciferum Zone is also seen but a precursor, sharp δ$^{13}$C negative excursion seen around the Tenuicostatum/Falciferum Zone boundary in most organic carbon records is not seen in the belemnite data, a curious absence noted from other belemnite records. Subsequent perturbations in $^{87}$Sr/$^{86}$Sr, δ$^{13}$C and δ$^{18}$O suggest that there may be more global isotopic excursions in the Early Jurassic. On the other hand, belemnite Sr isotope values from Bulgaria are in accord with those recorded in Western Europe and hence, demonstrating its value as a chronostratigraphic tool.

## 1. Introduction

The majority of studies on the biogeochemical cycles of the Early Jurassic have been devoted to investigations of the Pliensbachian–Toarcian time slice. During this time interval there is a wide range of paleontological, sedimentological and isotope evidence supporting the notion that a marine mass extinction event is associated with prominent δ$^{13}$C excursions, negative δ$^{18}$O shifts (i.e., warmer seawater temperatures or changes in the isotopic composition of seawater), a recognizable shift in the seawater $^{87}$Sr/$^{86}$Sr ratio, widespread anoxia, and substantial sea-level changes (e.g., Jenkyns, 1988; Jones et al., 1994; Sælen et al., 1996; Harries and Little, 1999; Hesselbo et al., 2000; McArthur et al., 2000; Jones and Jenkyns, 2001; Jenkyns et al., 2002; Bailey et al., 2003; Rosales et al., 2003, 2004; Kemp et al., 2005; Wignall et al., 2005; Gröcke et al., 2007; McArthur, 2008; Dera et al., 2009; Jenkyns, 2010; Suan et al., 2010; Dera et al., 2011). These major biogeochemical disturbances deeply affected both marine biota and global carbonate production in the shallow and deep ocean (Jones et al., 1994; Cecca and Macchioni, 2004; Tremolada et al., 2005; Dera et al., 2009; Morten and Twitchett, 2009; Al-Suwaidi et al., 2010; Jenkyns, 2010; Gröcke et al., 2011; Izumi et al., 2011). A major paleoceanographic phenomenon at this time – the Early Toarcian oceanic anoxic event (T-OAE) – may have been a consequence of some of these changes (Jenkyns, 1988; Jones et al., 1994; Jones and Jenkyns, 2001). Subsequently, global environmental conditions are considered to have remained relatively stable (Jenkyns, 1988; Jones et al., 1994; Jenkyns et al., 2002) although the upper Toarcian Variabilis Zone recorded minor, short-term δ$^{13}$C and δ$^{18}$O oscillations in some locations (e.g., Wales, Jenkyns and Clayton, 1997; Spain, Gómez et al., 2008; Bulgaria, Metodiev and Koleva-Rekalova, 2008; Morocco, Bodin et al., 2010). It is unknown if these events record further global paleoenvironmental changes and faunal turnover after the T-OAE and if they are discrete events or a consequence of the post-T-OAE stabilization (Gómez et al., 2008). Notably, there is evidence for turnover and abundance-diversity variations in late Toarcian fossil assemblages: these include the extinction of the ammonite subfamily Phymatoceratinae, the resurgence of the ammonite subfamily Harpoceratinae and the incoming in abundance of the ammonite subfamily Grammoceratinae and the family Hammatoceratidae (Bécaud et al., 2005; Dera et al., 2010), as well as the turnover of brachiopods and small benthic foraminifers (Alméras

---

* Corresponding author. Tel.: +44 113 343 5199; fax: +44 113 343 5259.
*E-mail addresses:* lubo@geology.bas.bg (L.S. Metodiev), i.savov@see.leeds.ac.uk (I.P. Savov), d.r.grocke@durham.ac.uk (D.R. Gröcke), P.B.Wignall@leeds.ac.uk (P.B. Wignall), r.j.newton@leeds.ac.uk (R.J. Newton), polina_a@geology.bas.bg (P.V. Andreeva), e_koleva@geology.bas.bg (E.K. Koleva-Rekalova).

http://dx.doi.org/10.1016/j.palaeo.2014.04.025
0031-0182/© 2014 Elsevier B.V. All rights reserved.

et al., 1997; Ruget and Nicollin, 1997; Mailliot et al., 2009; Caruthers et al., 2013).

The marine $^{87}$Sr/$^{86}$Sr record is buffered against restricted and short-term fluctuations in ancient seawater due to the long residence time of Sr in the oceans (e.g., McArthur et al., 2000) and provides a record of major plate-scale events, linked to variations in the marine Sr input–output fluxes (e.g., Peterman et al., 1970; Elderfield, 1986; Veizer et al., 1997; McArthur et al., 2000; Jones and Jenkyns, 2001; Waltham and Gröcke, 2006; McArthur and Wignall, 2007). Jenkyns et al. (2002), among others, have shown that the Early Jurassic Sr-isotope curve has a well-defined shape. However, the late Toarcian portion of this curve is poorly defined and it is considered uneventful and of lesser use in evaluating paleoenvironments compared to the early Toarcian record (McArthur and Wignall, 2007). The same also holds true for the late Toarcian $\delta^{13}$C and $\delta^{18}$O records (i.e., Gröcke et al., 2007).

The history of the Early Jurassic isotopic and faunal events is thus well known, although much evidence has come from western European sections and most research effort has been focussed on the earliest Toarcian and its celebrated oceanic anoxic event. In order to assess the context of this interval both regionally and temporally we have undertaken a study in the relatively poorly known eastern Tethyan sections of Bulgaria and considerably expanded the interval to include the entire late Pliensbachian–late Toarcian interval. We use multiple lines of evidence from well-defined ammonite biostratigraphy, detailed facies analysis and have exploited belemnite rostra to decipher the variations of seawater $^{87}$Sr/$^{86}$Sr, $\delta^{13}$C and $\delta^{18}$O.

## 2. Geological setting

### 2.1. Background geology and stratigraphy

The Jurassic sediments of the Teteven region (Central Fore-Balkan, Bulgaria) have long been known for their abundant and very diverse fossils. This particularly applies to the exposures of the Lower Jurassic rocks, which have attracted much attention for more than a century now (e.g., Toula, 1881, 1889; Zlatarski, 1908; Cohen, 1931, 1932; Sapunov, 1961, 1968, 1969; Sapunov et al., 1971; Metodiev, 2008). Locally, these rocks are considered to be an integral part of the most elevated segments of the Teteven Arch (Bonchev, 1971), which is a prominent positive structure of the Balkan Zone of the Balkan orogenic system (Fig. 1a, b). Regionally, the Balkan orogenic system represents the northernmost part of the Alpine orogenic belt in Bulgaria that was created during multiphase collisional and extensional tectonic events in the late Palaeozoic to mid-Eocene (Zagorchev et al., 2009). According to Bonchev (1971), the Teteven Arch contains a basement of red Permian polymictic clastic sediments, associated with volcanoclastic rocks and acid tuffs, covered by dark-red polymictic clastic sediments of the Lower Triassic Petrohan Terrigenous Group. The Lower Triassic sediments are overlain by thick carbonates of the Middle Triassic Iskar Carbonate Group, which grade upwards into the regressive carbonate facies of the Upper Triassic Moesian Terrigenous-Carbonate Group. This variegated basement is covered unconformably by thick Jurassic successions that continue up to the Lower Cretaceous (Fig. 1b).

In the vicinity of the town of Teteven, the Jurassic strata form a spectacular landscape on the northern slope of the Beli Vit River valley and provide a continuous depositional record of the Jurassic (e.g., Sapunov, 1961, 1968, 1969; Shopov, 1970; Sapunov et al., 1971; Sapunov and Tchoumatchenco, 1989 and references therein) (Fig. 1c). Mixed shallow- to medium-depth transgressive carbonates and siliciclastic sediments represent the Lower–Middle Jurassic rocks of this area. These deposits largely correspond to the Ozirovo and the Etropole Formations that span the Early Sinemurian to the Early Bajocian (Fig. 1d) (Sapunov and Tchoumatchenco, 1989).

The Ozirovo Formation is subdivided into three members, in ascending order: the Teteven, Dolni Loukovit and Boukorovtsi Members. The Teteven Member is a regionally extensive shallow-marine sequence of Early Sinemurian to early Pliensbachian age, composed of a 10–30 m thick succession of alternating sandy bioclastic limestones, calcareous sandstones and silty marls with abundant bivalves, common brachiopods and scarce belemnites. The Dolni Loukovit Member is a 30–80 m thick succession of ferruginized sandy bioclastic limestones, of Early Sinemurian to late Pliensbachian age. Above this the Boukorovtsi Member is a 20–40 m thick hemipelagic, irregular shale–marl–limestone alternation of late Pliensbachian to late Aalenian age. The uppermost Pliensbachian and the Toarcian segments of the Boukorovtsi Member are the most fossiliferous (mainly ammonites and belemnites) and notably ooid-bearing. The rest of the Boukorovtsi Member is a monotonous Aalenian sequence with scarce fossils but common *Zoophycos* burrows.

The Ozirovo Formation is sharply overlain by 150 m thick poorly fossiliferous, deeper-water shales and siltstones of the Etropole Formation that span the late Aalenian to the middle Bajocian (Sapunov and Tchoumatchenco, 1989). The Lower–Middle Jurassic sedimentary succession of the Teteven area displays uneven depositional rates that were highest in two intervals: the Sinemurian to Pliensbachian and the Aalenian to middle Bajocian, with a markedly condensed Toarcian portion (Fig. 1d), reflecting an often interrupted sedimentary influx (Metodiev, 2008). The scarcity of Toarcian fossils prevents a high-resolution biostratigraphic subdivision and thus correlation with other coeval strata from elsewhere. In this study, we adopt the recently proposed Toarcian ammonite zonation for Bulgaria (Metodiev, 2008) that can be correlated with the NW European chart of Elmi et al. (1997) (Fig. 2).

### 2.2. Paleogeography

The Lower–Middle Jurassic rocks in the Teteven area represent inner shelf sediments deposited into an epicontinental basin of strait-like configuration (Zagorchev et al., 2009). It developed on the Moesian Platform due to an Early Jurassic extension and normal faulting, proximal to the southern Eurasian passive continental margin (Bassoulet et al., 1993; Fourcade et al., 1995). This basin was part of the wide NW Peritethyan epicontinental sea, at a paleolatitude between 33°N and 38°N (Dera et al., 2009 and references therein).

## 3. Materials and methods

This work is based on the study of petrographic samples, belemnite rostra, and ammonite specimens, which are part of the Bulgarian Geological Institute collections (Coll. No. F. FSR.SR.2012.1). Twenty-three samples of the host rocks were taken for facies analysis and 48 belemnites (mostly *Dactyloteuthis* and *Acrocoelites*, and less commonly *Passaloteuthis* and *Gastrobelus*) were chosen for isotopic measurements. Thin sections were studied using conventional microscopy and represent each rock type identified in the field. In general, the sampling density of the belemnites was in the range of a few vertical centimeters, depending on the amount and the density of occurrence of their rostra. For the purposes of our study, we also collected 230 ammonites in order to achieve the best possible biostratigraphic subdivision and to supplement the available biochronostratigraphic database (Sapunov, 1968; Sapunov et al., 1971; Metodiev, 2008). Before the isotope measurements, belemnite rostra were carefully screened under plane polarized light and cathodoluminescence for evidence of preservation, recrystallization, and luminescence characteristics. From each belemnite, a polished thick-section was prepared for a cathodoluminescence study and microsampling. After the assessment from cathodoluminescence, only the non-luminescent areas of the rostra interior were chosen and the sampling was carried out by using a dentist drill, avoiding rostra periphery, apical lines, portions of non-homogeneous pattern, small veins and fractures filled with secondary calcite and borings.

Approximately 50 μg calcite powder was collected for $^{87}$Sr/$^{86}$Sr measurements and a minimum of 150 μg was used for $\delta^{18}$O and $\delta^{13}$C