СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО, год. 80, кн. 3, 2019, с. 122–124
REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY, vol. 80, part 3, 2019, p. 122–124

Национална конференция с международно участие „ГЕОНАУКИ 2019“
National Conference with international participation "GEOSCIENCES 2019"

Mercury enrichments as a potential tracer for volcanism in sedimentary successions – examples from the Toarcian in Bulgaria

Повишени съдържания на живак като потенциален маркер за вулканизъм в седиментните последователности – примери от Тоарския етаж в България

Lubomir Metodiev[1], Tanya Stoylkova[2], Milena Georgieva[2], Elena Koleva-Rekalova[1]
Любомир Методиев[1], Таня Стоилкова[2], Милена Георгиева[2], Елена Колева-Рекалова[1]

[1] Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 24; 1113, Sofia, Bulgaria;
E-mails: lubo@geology.bas.bg, e_koleva@geology.bas.bg
[2] Sofia University "St. Kliment Ohridski", Department of Mineralogy, Petrology and Economic Geology,
15 Tzar Osvoboditel Blvd., 1504 Sofia, Bulgaria; E-mails: tstoilkova@gea.uni-sofia.bg, milena@gea.uni-sofia.bg

Keywords: mercury, Hg/TOC ratios, sedimentary successions, Toarcian, Bulgaria.

Introduction

The early Toarcian (183.6–181.4 Ma) was a time of Earth-scale warming, perturbations in the carbon cycle, the development of widespread anoxia, known as the early Toarcian Oceanic Anoxic Event (T-OAE), and a deep biotic crisis in marine ecosystems recognized as the early Toarcian Mass Extinction (T-ME) (e.g., Harries, Little, 1999; Jenkyns, 2010). Many studies link the T-OAE (and the T-ME, as a consequence thereof) to the massive CO_2 release and/or astronomically-paced methane hydrate dissociation, mercury emissions and thermal erosion of the cratonic lithosphere associated with the rapid magma emplacement and eruption of the vast Karoo–Ferrar flood basalt province in the southern hemisphere (e.g., Courtillot, Renne, 2003; Percival et al., 2015), and that is thought to have triggered a dramatic climatic perturbation. The volcanism-warming-anoxia-extinction link has been well established (Wignall, 2001, 2005), especially in the Northwestern European epicontinental sea areas, and continues to collect evidence, by exploring the stratigraphical variability of different isotopic and litho-geochemical tracers in numerous sites from around the world (see Jenkyns, 2010). In Bulgaria, the $\delta^{18}O$ record from diagenetically-screened belemnites have previously revealed a possible cooling event in the late Pliensbachian, a seawater warming at the Pliensbachian/Toarcian boundary time span and another warming in the early Toarcian, the latter being coincident with a broad positive $\delta^{13}C$ excursion (Metodiev, Koleva-Rekalova, 2008; Pugh, 2018; Pugh et al., 2019). The documented $\delta^{18}O$ and $\delta^{13}C$ shifts were interpreted as evidence of the T-OAE and implied that the seawater in the Moesian Basin has recorded global paleoceanographic conditions. In addition, a significant loss amongst bivalves was also evidenced in the lower Toarcian, suggesting in turn that benthic communities in the Moesian Basin have recorded the T-ME. However, both $\delta^{18}O$ and $\delta^{13}C$ profiles and the extinction levels are broadly not coincident with reduced oxygen conditions, since neither geochemical nor sedimentological data from the lower Toarcian strata support the prevalence of anoxic settings. The warming of the seawater in the Moesian Basin through the early Toarcian has been attributed to the eruption of the Karoo–Ferrar, as being associated with a prominent enrichment in mercury (Hg) recorded as a shift in sedimentary Hg/TOC (total organic carbon) values, synchronous with the positive $\delta^{13}C$ excursion (Pugh, 2018). The latter assumption was based on evidence obtained from a narrow stratigraphic interval, corresponding to the lower Toarcian Tenuicostatum and Falciferum ammonite zones, from the Teteven area (Central Fore-Balkan). Mercury concentrations have recently been used as a global-scale proxy for increased distal volcanism in the early Toarcian (e.g., Percival et al., 2015), assuming that the elevated Hg/TOC ratios are due to the enhanced atmospheric Hg availability, supplied exclusively from a volcanic activity. The aim of the present study is to extend the previous Bulgarian Hg-TOC data in other coeval stratigraphic intervals from the Toarcian in Bulgaria. Hence, it will become clear that the previously recorded increased Hg/TOC ratios in the lower Toarcian are more than local evidence, and it may be argued that the Jurassic sediments experienced an input from volcanic activity – a conspicuous feature, which has not been noted to date.

Background and material

This work is based on the study of outcrop rock samples collected from three sections in the Western Balkan Mts area: Dobravitsa-1, Beledie Han and Bov. The former two sections have already been described in detail (Metodiev, Koleva-Rekalova, 2008), whereas the latter section is a newly studied sequence located near Bov Village. These sections refer both to the marlstone-shale-limestone sediments of the Bukorovtsi Member of the Ozirovo Formation, as well as to the iron ooidal limestones of the homogeneous Ozirovo Formation. The sections were sampled at a high biostratigraphic resolution supported by ammonites, with sampling density in the range of a few vertical centimeters, within the total thicknesses (and ammonite zonal extents), as follows: Dobravitsa-1 – 5 m (upper Pliensbachian Spinatum Zone–upper Toarcian Aalensis Zone); Beledie Han – 1 m (uppermost Pliensbachian–lower Toarcian Bifrons Zone); and Bov – 5 m (lower–upper Toarcian, Falciferum–Variabilis zones). Mainly marlstones and carbonaceous shales, but also decarbonated ooidal limestones, were selected for Hg and TOC measurements. A total of 47 whole-rock powders, from Dobravitsa-1 (28), Beledie Han (7) and Bov (12) sections, were analyzed. Mercury concentrations were determined on an Hg Analyzer RA 915 F coupled to a PYRO-915+ Pyrolizer (Lumex) at the University of Lausanne (Switzerland). Determination of the TOC was carried out by Rock-Eval 6, as well as by SSM-5000A TOC Analyzer at the University of Lausanne and the University of Bremen (Germany).

Results and discussion

Each of the examined sections shows enrichments in Hg concentrations (ppb) and excursions in Hg/TOC ratios (ppb/wt%), and Hg values closely follow the TOC record throughout the sampled intervals (Fig. 1). In the Dobravitsa-1 section, Hg and TOC values display a narrow trend through the upper Pliensbachian and the lowermost Toarcian, at around 22 ppb and 0.29wt %, respectively. A small increase of both Hg and TOC, to 39 ppb and to 0.64 wt%, was detected at the lower Tenuicostatum Zone. After a short decrease in Hg (to 10 ppb) and TOC (to 0.20 wt%), an increase and a stable level of values around 36 ppb for Hg and 0.40 wt% for TOC occur, from across the Tenuicostatum/Falciferum Zone boundary to the mid-Bifrons Zone. Following an interval of non-record (from the upper Bifrons Zone to the lower Fallaciosum Zone), Hg and TOC values remain relatively elevated throughout the upper Toarcian (av. 27 ppb for Hg and 0.65 wt% for TOC), but prominent peaks in both Hg (45 ppb) and TOC (1.25 wt%) were detected in the Pseudoradiosa Zone. The Hg/TOC ratios go along with the general trend of Hg, with lower values recorded in the upper Pliensbachian and the lowermost Toarcian (av. 62.3 ppb/wt%), increasing towards and across the lower Toarcian Falciferum–Bifrons zones interval (av. 91.5 ppb/wt%), but displaying a decrease through the upper Toarcian (av. 43.5 ppb/wt%).

Both Hg and TOC from the Bov section displayed elevated values relative to the background values from the coeval strata of the Dobravitsa-1 section. In this sequence, Hg and TOC values vary throughout the lower Toarcian Falciferum and lower Bifrons zones, between 62 ppb and 213 ppb, and from 1.55 wt% to 2.82wt%, respectively, gradually reducing up-section to 24 ppb and to 0.6 wt% in the upper Toarcian Variabilis Zone. The Hg/TOC ratios follow the same trend, from 114 ppb/wt% at the very base of the lower Toarcian Falciferum Zone to 70 ppb/wt% at the mid-Bifrons Zone, to 40 ppb/wt% at the top of the Variabilis Zone. Despite being a shallow-water section, comprising ironstones that are likely to have both too little Hg and TOC present, the Beledie Han section yielded enough organic carbon content, and the values of Hg and Hg/TOC ratios were found to be much higher in comparison with those of both the Dobravitsa-1 and Bov sections. Low Hg and TOC values (of around 33 ppb and 0.2 wt%) in the upper Pliensbachian interval of this section are comparable to the low values of the same interval in the Dobravitsa-1 section, but the Hg/TOC ratio is higher (166 ppb/wt%). A rapid subsequent positive shift in Hg values (from 50 ppb to 222 ppb), as well as in TOC values (from 0.5 wt% to 1.5 wt%), was recorded through the lower Toarcian Tenuicostatum and Falciferum zones, having both maxima at the base of the Falciferum Zone. This shift is followed upwards by a decline in Hg and TOC values to 33 ppb and to 0.6 wt%, from the upper Falciferum Zone to the mid-Bifrons Zone. The same trend is observed in the Hg/TOC ratios, with a rise from around 100 ppb/wt% to 230 ppb/wt%, but the Hg/TOC record, however, shows elevated values throughout, from the lower Tenuicostatum Zone to the very base of the Bifrons Zone.

As evident from the above stated data, a positive Hg/TOC excursion persists through the lower Toarcian, extending from the upper Tenuicostatum Zone to the mid-Bifrons Zone. This shift is in accordance with, and enhances, that derived from the data previously recorded from Bulgaria (Pugh, 2018; Pugh et al., 2019). Overall, Hg and Hg/TOC values are akin to those reported in previous studies using Hg as a volcanic tracer in equivalent Northwest European intervals (Percival et al., 2015), although the

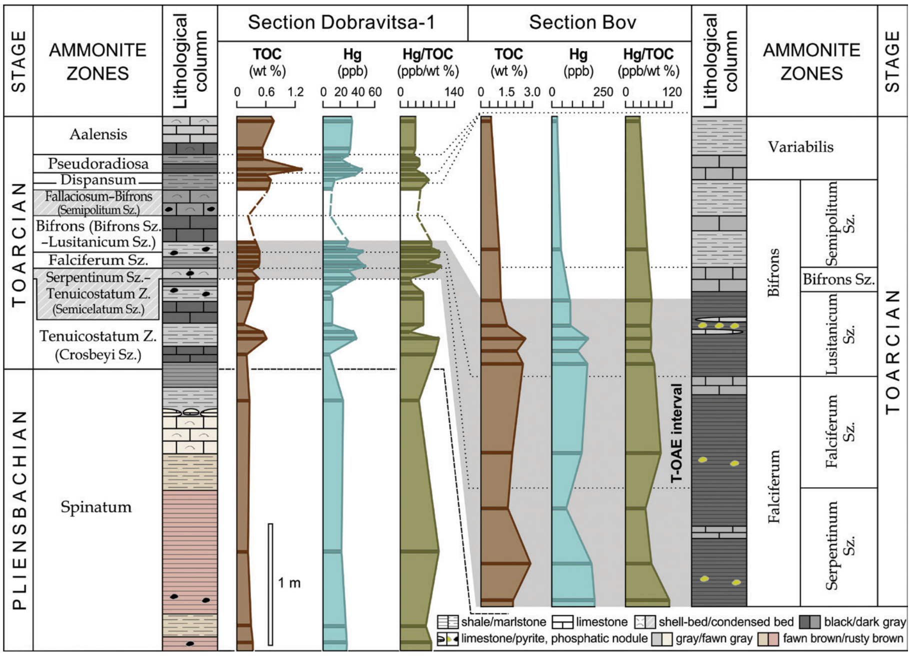

Fig. 1. Geochemical data (Hg, TOC and Hg/TOC) plotted stratigraphically for the Dobravitsa-1 and Bov sections (the data from the Beledie Han section are not shown; see text for details). The T-OAE interval is shown as gray shaded area.

TOC values in Bulgarian sections are notably lower than those from NW Europe. Hence, it can be assumed that Hg and Hg/TOC enrichments in the Bulgarian sections could be indicative of far-field volcanism and the T-OAE, as suggested for other Toarcian sections where similar anomalies have been discovered. The elevated values in Hg and Hg/TOC documented after the T-OAE interval through the upper Toarcian may have been controlled by other environmental or diagenetic factors acting on a local scale. It is worth noting that the Bulgarian sections yielded close temporal relationships between Hg and TOC, but with variable degrees of positive correlation, ranging from 0.28 to 0.79, and thus showing that the TOC-content of the sediments was not the only controlling factor on Hg sequestration. Further work should be done to the organic matter and other bulk-rock proxies to understand changes in continental weathering rates in the Moesian Basin. This would allow further understanding of the links between volcanism, weathering and climate that have been driven the environmental changes.

Acknowledgements. This work was carried out through the National Science Program's "Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters", approved by the Resolution of the Council of Ministers № 577/17.08.2018 and supported by the Ministry of Education and Science of Bulgaria (Agreement № DO-230/06-12-2018). Special thanks go to Prof. Thierry Adatte (University of Lausanne, Switzerland) for doing the Hg and TOC measurements, as well as to Dr Autumn Pugh (Government Office for Science, UK) for allowing us to use her data from Bulgaria.

References

Courtillot, V. E., P. R. Renne. 2003. On the ages of flood basalt events. – *C. R. Geoscience*, *335*, 113–140.

Jenkyns, H. C. 2010. Geochemistry of oceanic anoxic events. – *Geochem., Geophys., Geosyst.*, *11*, Q03004, doi:10.1029/2009GC002788.

Harries, P. J., C. T. S. Little. 1999. The early Toarcian (Early Jurassic) and the Cenomanian–Turonian (Late Cretaceous) mass extinctions: similarities and contrasts. – *Palaeogeogr., Palaeoclimatol., Palaeoecol*, *154*, 39–66.

Metodiev, L., E. Koleva-Rekalova. 2008. Stable isotope records ($\delta^{18}O$ and $\delta^{13}C$) of Lower–Middle Jurassic belemnites from the Western Balkan Mountains (Bulgaria): palaeoenvironmental application. – *Appl. Geochem.*, *23*, 2845–2856.

Percival, L. M. E., M. L. I. Witt, T. A. Mather, M. Hermoso, H. C. Jenkyns, S. P. Hesselbo, A. H. Al-Suwaidi, M. S. Storm, W. Xu, M. Ruhl, 2015. Globally enhanced mercury deposition during the end-Pliensbachian extinction and Toarcian OAE: A link to the Karoo-Ferrar Large Igneous Province. – *Earth and Planet. Sci. Lett.*, *428*, 267–280.

Pugh, A. 2018. *Palaeoenvironmental and Biotic Change through the Lower Jurassic in Bulgaria*. Unpublished PhD Thesis, University of Leeds, Earth Surface Science Institute, School of Earth and Environment, 383 p.

Pugh, A., C. T. Little, I. P. Savov, L. Metodiev, P. B. Wignall, R. J. Newton, J. Riding. 2019. The early Toarcian extinction event and associated Pliensbachian-Toarcian palaeoenvironmental perturbations in Bulgaria. – *PeerJ Preprints*, 7:e27948v1 https://doi.org/10.7287/peerj.preprints.27948v1.

Wignall, P. B. 2001. Large igneous provinces and mass extinctions. – *Earth-Sci. Rev.*, *53*, 1–33.

Wignall, P. B. 2005. The link between large igneous province eruptions and mass extinctions. – *Elements*, *1*, 293–297.