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Redox levels of deposition across the lower Toarcian – trace element data from Bulgaria

Редукционни обстановки на седиментация в долния Тоарски подетаж – данни по микроелементи от България

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

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Introduction

The Jurassic sequences in Bulgaria include widespread shelf sediments that often contain organic-rich strata. The bulk of these rocks comprise dispersed organic components covering a wide range of amount and composition. However, a defined number of stratigraphic intervals correspond to sedimentary rocks with elevated organic carbon contents and denote sedimentary accumulations under oxygen-deficient conditions. The organic-rich shelf deposits of the Lower Jurassic in Bulgaria mainly correspond to the transgressive mudrock lithologies of the Ozirovo Formation. It is known that in these strata the fade of the oxygen bottom deficiency accumulation settings concurs around with the Pliensbachian/Toarcian boundary. It is also known that most of them do not correspond to typical black shale facies, as being relatively coarse-grained and often with scarce organic carbon contents. Both their lithologies and fossil biofacies indicate frequent intervals of seafloor oxygenation (e.g., Sapunov et al., 1988), without constant steady-state conditions (*sensu* Arthur, Sageman, 1994; Wignall, Newton, 2001). Recently, we reported a positive Hg/TOC excursion through the lower Toarcian, from two stratigraphic sections of the West Balkan Mts region, extending from the upper Tenuicostatum ammonite Zone to the mid-Bifrons ammonite Zone (Metodiev et al., 2019). This shift was found to be in accordance with the data previously recorded from other coeval intervals from Bulgaria (Pugh et al., 2019) and, by analogy, we assumed that Hg/TOC enrichments in the Bulgarian sections could be indicative of far-field volcanism and the early Toarcian Oceanic Anoxic Event (T-OAE), as suggested for other European sections where similar anomalies have been discovered. However, we did not have supporting data to specify whether these anomalies occurred under conditions of bottom anoxia. Herein, we evaluate the redox levels of previously measured sequences from the West Balkan, by using the ratios of a few informative trace elements derived from bulk samples: V/Cr, V/(Ni+V), Ni/Co and Th/U. This work is based on the ongoing study of the Dobravitsa-1 and Bov sections, by analyzing samples from the upper Pliensbachian–lower Toarcian interval, on which TOC measurements have previously been made (for the background, see Metodiev et al., 2019). Trace element values were determined by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Geological Institute of the Bulgarian Academy of Sciences.

Results and discussion

Estimating the obtained values of the selected elements and our earlier TOC data, we found that the observed levels of TOC enrichments throughout the lower Toarcian also contain increased sediment V/Cr, V/(Ni+V), Ni/Co and Th/U ratios (Fig. 1*a*–*c*). These ratios have been proposed as valuable redox indices for identifying the level of oxygenation of

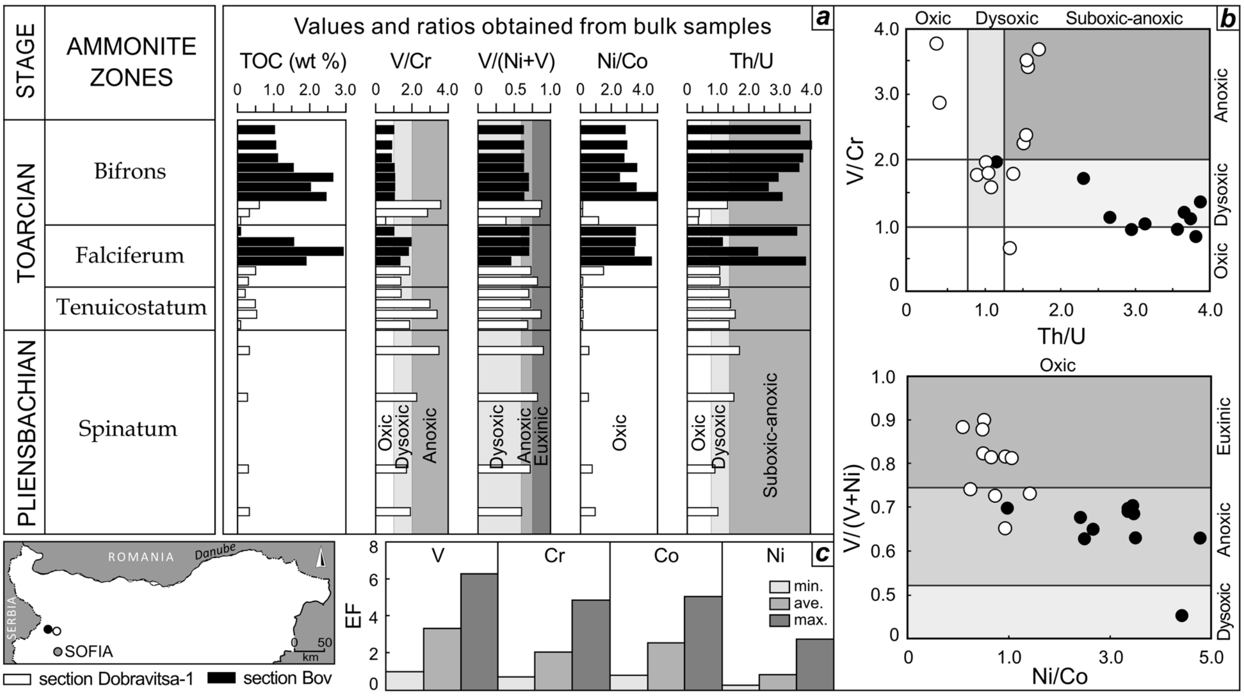

Fig. 1. *a*, redox sensitive ratios (V/Cr, V/(Ni+V), Ni/Co and Th/U) and TOC (total organic carbon) data plotted stratigraphically for the Dobravitsa-1 and Bov sections; *b*, V/Cr *vs.* Th/U and V/(V+Ni) *vs.* Ni/Co diagrams; *c*, Enrichment Factor (EF) column diagram for the approximate order of enrichment of V, Cr, Co and Ni in sediments. Redox levels (taken from Jones, Manning, 1994; Hatch, Leventhal, 1992; Wignall, Newton, 2001) denote temporal fluctuations of seafloor oxygenation through the Pliensbachian/Toarcian interval of studied Bulgarian successions.

bottom waters since they usually attain elevated values in oxygen-depleted marine environments owing to authigenic enrichments or delivery in sediments in association with organic matter (e.g., Hatch, Leventhal, 1992; Jones, Manning, 1994; Tribovillard et al., 2006). In our case, the elements used for calculation of these ratios yielded appreciable concentrations, showing different heights of enrichment. Enrichment factors (EF) for V, Cr, Ni and Co were determined by normalizing each element to aluminum, which is assumed to represent the detrital influx of the sediments. Using the approach of Rimmer (2004), the obtained enrichments were compared to those for "typical" shale. Based on the EF values, we found that the approximate order of enrichment is: V (*av*. 126 ppm, EF_{range}: 0.92–6.28); Cr (*av*. 79 ppm, EF_{range}: 0.71–4.84); Co (*av*. 54 ppm, EF_{range}: 0.8–2.45); and Ni (*av*. 50 ppm, EF_{range}: 0.27–2.75). We also found that the stratigraphic enrichments of V and Ni are approximately concomitant with that of TOC. Both Co and Cr exhibited little TOC dependence and their abundances are probably tied to the abundance of some inorganic clastic phase (cf., Tribovillard et al., 2006). Hence, we obtained V/Cr ratios ranging from 0.66 to 3.77 and, excluding a few samples that contain the lowest ratios, the remainder of the dataset generated V/Cr ratios >1, some of which have values above 2. The whole-rock V/(Ni+V) ratios are in the range between 0.40 and 0.90. The Ni/Co ratios produced values ranging from 0.12 to 4.77, assuming that both Ni and Co are not coming from diagenetic pyrite (Jones, Manning, 1994). All samples contributed with detectable values of Th and U (3.37–18.5 ppm for Th and 2.11–37.7 ppm for U), covering the entire data set. These values produced Th/U ratios that vary between 0.96 and 4.12. Both Th and U abundances were obtained from levels with elevated TOC contents, but the uranium displayed a weak correlation relative to the organic carbon ($r = 0.20$), thus hinting at low bacterial activity and low intensity of sulfate reduction activity or deficiency of reactive organic matter into the sediments (Tribovillard et al., 2006).

Jones and Manning (1994) suggested that values of V/Cr ratios above 2 imply anoxic, whereas values below 1 are indicative of oxic depositional conditions, reflecting an oxygen-hydrogen sulphide interface within the sediments. According to Hatch and Leventhal (1992), high V/(Ni+V) ratios (0.84–0.89) indicate strongly stratified (euxinic) water column, whereas intermediate ratios (0.54–0.82) and low ratios (0.46–0.60) indicate less-strongly stratified (anoxic) and weakly stratified (dysoxic) water column, correspondingly. The Ni/Co ratios in mudstones <7 are thought to be indicative of dysoxic conditions (Jones, Manning 1994), whereas Th/U ratios <2 generally coincide with dysaerobic environments (Wignall, Newton, 2001). Except for the Ni/Co ratios that indicate generally oxic environments, the remaining indices denote temporal fluctuations of seafloor oxygenation, from oxic-dysoxic to suboxic-anoxic and even euxinic conditions (see Fig. 1). The V/Cr values revealed a limited deposition beneath a relatively oxic water column in the uppermost Bifrons Zone, while, for the remaining segments of sections, these ratios suggest dysoxic conditions, with short-term transitions to anoxic conditions around the Pliensbachian/Toarcian boundary and at the base of the lower Toarcian Bifrons Zone. The Th/U ratios indicate dominantly dysoxic to suboxic-anoxic settings, the latter usually corresponding to elevated uranium concentrations. According to the V/(Ni+V) ratios, the studied sequences were deposited mainly under dysoxic to anoxic water column conditions, with a short-term settlement of euxinic environments recorded around the Pliensbachian/Toarcian boundary, as well as in the lower Falciferum and Bifrons zones. In summary, the depositional environments corresponding to the rocks of sampled Bulgarian sections appear to have been dysoxic and moderately dynamic, with periodic excursions of anaerobic conditions above the sea bottom. However, additional evidence, such as from pyrite morphology, Fe-pyrite chemistry data and systematic data on the organic geochemistry of the host rocks are required to determine whether this depositional pattern is a consequence of truly oxygen-restricted environments.

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