СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,
год. 85, кн. 1, 2024, с. 85–91

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,
vol. 85, part 1, 2024, p. 85–91

Paleo-depositional environment of carbonaceous mudstone bearing transformed organic matter, Troyanovo-3 Mine borehole, Mini Maritsa Iztok EAD, Bulgaria

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Условия на образуване на мъдстоуни с променено органично вещество от сондаж в рудник „Трояново-3“ („Мини Марица-изток“ ЕАД, България)

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Резюме. Ядкови проби от последователност на лигнити и мъдстоуни с вариации в зрелостта на органичното вещество от сондаж в рудник Трояново-3 („Мини Марица-изток“ ЕАД) са анализирани с цел изследване разпределението на елементите-следи. Всички елементи с изключение на Hg и Th показват един положителен връх в тяхното разпределение, но на различни дълбочини. Молибденът и Ni показват максимални стойности в дълбоките нива (52,6–53,0 m). Желязото, V, As, Hg, Zn, U и Th са с най-високи стойности при 29,3–29,5 m. Оловото и Cu също показват максимуми, но на малка дълбочина – 19,2–20,1 m. В сравнение с кларките за въглища нисък ранг и седиментни скали, всички измерени стойности са много по-високи, но в сравнение със стойностите за лигнитни въглища и черни глини от Източномаришкия басейн повечето елементи попадат в близък диапазон. Липсата на корелация между общия органичен въглерод и всички елементи-следи предполага, че геохимичното им поведение се различава от това на органично свързаните елементи. Силните положителни корелации на Fe с V, Ni, Cr, As и Mo предполагат включването им в железна сулфидна фаза. Силните положителни корелации на Al с Ni, Co, Mo и U и слабата корелация Al-V предполагат теригенна и/или сорбирана форма на присъствие. Връзката между живака и общия органичен въглерод, пепелта, сярата и урана не е еднозначна и потвърждава комплексния афинитет на Hg. Нашата хипотеза за повишена зрелост на ОМ в резултат на влиянието на възходящи хидросулфидни разтвори тук беше подкрепена от диференциацията на елементите-следи на различни дълбочини.

Ключови думи: разпределение и диференциация на елементи-следи, увеличена зрелост на органичното вещество, последователност от лигнити и мъдстоуни, сондажни образци от рудник „Трояново-3“, „Мини Марица-изток“ ЕАД.

Abstract. Drill core samples from a lignite-mudstone succession with variations in organic matter maturity from Troyanovo-3 Mine (Mini Maritsa Iztok EAD) were analyzed for trace element contents. All elements except Hg and Th show one positive spike in their distribution, located at different depths. Molybdenum and Ni peak at the deep level (52.6–3 m); Fe, V, As, Hg, Zn, U, and Th peak at 29.3–29.5 m; Pb and Cu peak at shallow depth – 19.2–20.1 m. All measured concentrations are much higher than the Clarke for low rank coal and sedimentary rocks and comparable with published data for black clays from Troyanovo-3 Mine. The lack of significant correlation between total organic carbon and all analyzed trace elements points to other hosts for the trace elements. The strong positive correlations found for Fe and V, Ni, Cr, As, and Mo suggest incorporation of these elements into Fe sulfide phase(s). The strong positive correlations for Al and Ni, Co, Mo and U, and a weak correlation between Al and V suggest a terrigenous and/or sorbed form of presence. The lack of

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https://bgd.bg/review-bgs
https://doi.org/10.52215/rev.bgs.2024.85.1.85

a strong correlation between mercury and total organic carbon, ash, sulfur and uranium confirms the well-known complex Hg affinity. Our previously outlined hypothesis for OM enhanced maturity as a result of ascended hydrosulfide injection is here further supported by the trace element differentiation at different depths.

Keywords: trace element distribution and differentiation, enhanced organic matter maturity, lignite-mudstone succession, Troyanovo-3 Mine core samples, Mini Maritsa Iztok EAD.

Introduction

The current study is based on drill core samples from Troyanovo-3 Mine lignite-mudstone sequence. In this sequence, Milakovska et al. (2022) reported for the first time in the Maritsa Iztok lignite field (Bulgaria) variations in organic matter (OM) maturity. Elevated OM maturity in the lowermost sample (59.60 m depth) was evidenced by hopane distributions, i. e. Ts/(Tm + Ts), homohopane $H_{31\alpha\beta}$ index, hopane ratios ($H_{29\alpha\beta}/H_{30\alpha\beta}$ and $H_{27\beta}/H_{27\alpha}$). These variations are ascribed to interaction with hot ascending hydrosulfide fluids (Milakovska et al., 2022).

Trace elements (TE), and Hg in particular, have a strong affinity for OM, which is usually marked by significant TE and Hg enrichments in organic-bearing deposits in comparison to background sediments (Cherbonnier et al., 2020). While the effects of incipient weathering on sedimentary Hg have been investigated (Park et al., 2022), the impact of thermal maturation of organic matter on trace elements distribution in sedimentary basins has not been systematically studied (Indraswari et al., 2024). Here we explore the influence of thermal maturation on sedimentary TE using the core samples utilizing key inorganic geochemical proxies by whole-rock geochemistry. By investigating TE concentrations in addition to OM geochemical characteristics in a stratigraphically constrained interval in a bore-hole from Troyanovo-3 Mine, we examine the role of thermal maturation as a key factor in post-depositional TE mobility in the sediments. The new data additionally support our findings that hot reducing fluids that formed sulfide mineralization in fractures may have been responsible for the thermal alteration of the organic matter and the trace element enrichment.

Geological Setting

The Maritsa Iztok Basin (MIB) occupies the eastern part of the intraorogenic Thracian Basin (Dabovski, Zagorchev, 2010). The basin development and filling were coeval with Late Neogene extension that formed subequatorial Neogene–Quaternary pull-apart depressions (Burchfiel et al., 2000). The tectonic structure of the MIB comprises a pre-Miocene, highly disintegrated basement that is a fragment of a Meso-Alpine collisional orogeny, and a Upper Miocene–Pliocene cover (Boyanov, Goranov, 2001).

The Upper Miocene–Pliocene sedimentary infill of MIB consists from bottom to top of: the Upper Miocene Maritsa Formation (Fm.) (Kamenov, Panov, 1976), the Pliocene Gledachevska Fm. (Nedyalkov, Kojumdgieva, 1983; Nedyalkov, Rachev, 1990) and a Pliocene formation of dispersion clays (Nedyalkov, Kojumdgieva, 1983). The lignite-bearing sequence (Maritsa Fm.) comprises a coal basement of grey-black mudstone, fine- to coarse-grained sand, and three lignite seams separated by black clay-blended coal, coaly shale and mudstone.

The Troyanovo-3 (Tr-3) Mine has complex geological and engineering-geological features discovered with the progression of mining. Compared with the other two mines operating in the MIB, Tr-3 Mine has specific: (i) basement structure; (ii) position of coal in the sequence; (iii) ongoing active tectonic processes; and (iv) contoured areas where no coal seams were crossed during drilling. Other notable characteristics include mud volcanoes (Velchev, 1953), H_2S emission and hot underground water (Velchev, 1958; Nedyalkov, 1983). The sediments of Maritsa Fm. cover an uneven, most likely tectonically deformed and dismembered basement (Nedyalkov et al., 1982) as corroborated by the positive tectonic structures described by Vladislavov and Milakovska (2019). The basement consists of Paleozoic gneiss and gneiss-schist and Triassic limestone, dolostone, and low-grade metamorphosed conglomerate (Nedyalkov, 1983).

Samples and methods

Powdered aliquots of seven non-ashed drill core mudstones from Troyanovo-3 Mine (Table 1) used in our previous study (Milakovska et al., 2022) were analyzed here for Fe and Al using a Varian Vista MPX Simultaneous apparatus, and for selected

Table 1
TOC, mineral content and hopane distributions in the studied core samples from Troyanovo-3 Mine (from Milakovska et al., 2022)

Таблица 1
Съдържание на органичен въглерод, минерален състав и разпределение на хопаните в изследваните ядкови образци от сондаж в рудник „Трояново-3“ по Milakovska et al. (2022)

Sm. №	Mudstone*	Depth (m)	TOC (wt %)	XRD data	Biomarker parameter		
					$H_{31\alpha\beta}$ S/(S+R)**	Ts/(Ts+Tm)	$H_{27\beta}$/$H_{27\alpha}$
Tr-3-1	mudstone	12.7–12.9	nd	I/S, kaol, quartz	nd	nd	nd
Tr-3-4	coaly mudstone	18.4–18.5	31.13	Chl, I/S, kaol, quartz	0	0	11.0
Tr-3-5	carbonaceous mudstone	19.2–20.1	5.13	I/S, I/Ms, kaol, quartz	0	0	7.4
Tr-3-8	mudstone	24.1–24.3	1.31	I/S, kaol, Py	nd	nd	nd
Tr-3-15	carbonaceous mudstone	29.3–29.5	10.01	I/S, kaol, quartz, Py	0	0	10.6
Tr-3-38	carbonaceous mudstone	52.6–53.0	16.27	I/S, chlorite, kaol, quartz	0	0	15.1
Tr-3-38s	sulfide veinlet	53.20	0	quartz, Py, marcasite (tr.)	nd	nd	nd
Tr-3-43	carbonaceous mudstone	59.1–59.2	3.31	quartz, I/S, kaol, Py	0	0	10.2
Tr-3-44	mudstone	59.5–59.7	0.77	I/Ms, quartz, Py, gypsum	0.3	0.29	2.0
Tr-3-45	sulfide veinlet	60.20	0	I/Sm, kaol, Py, quartz	nd	nd	nd

TOC: total organic carbon; H: hopane; Ts: 18_{α}(H)22,29,30-trisnorneohopane; Tm: 17_{α}(H)22,29,30-trisnorhopane; nd, not determed; Chl, chlorite; I/S, illite/smectite; I/Ms, illite/muscovite; kaol, kaolinite mineral; Py, pyrite; tr, traces
* Mudstone term is according to the “Nomenclature and Description Guidelines” introduced by Lazar et al. (2015)
** $H_{31\alpha\beta}$ S/(S+R) = Homohopane index (HomoH)

TOC: общ органичен въглерод; Biomarker parameter – биомаркерен параметър
H: хопан; Ts: 18_{α}(H)22,29,30 – триснорнеохопан; Tm: 17_{α}(H)22,29,30 – триснорнеохопан; nd – неопределян; Chl – хлорит; I/S – илит/смектит; I/Ms – илит/мусковит; kaol – каолинитов минерал; Py – пирит; tr – следи
* мъдстоун – терминът е използван съгласно Насоките за номенклатура и описание, публикувани от Lazar et al. (2015)
** H31αβ S/(S+R) – хомохопанов индекс

trace elements (As, Pb, Cu, Zn, Mo, Cr, Ni, Co, V, U, Th) using a LA-ICP-MS on pressed rock powder pellets. The LA system in the Geological Institute at Bulgarian Academy of Sciences consists of a 193 nm ArF excimer laser (ATLEX-LR, Germany) linked to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma mass spectrometer. Additionally, we measured the Hg content in nine non-ashed drill core mudstones and two ~5-mm-thin pyrite-bearing veinlets (Table 1) crossing the mudstones. Mercury abundances were measured using a Dual-cell Double beam DMA-80 Evo direct mercury analyzer (Milestone, Inc.) in the Geological Institute at Bulgarian Academy of Sciences; the analytical setup and method details are given in Georgiev and Bidzhova (2023). Enrichment coefficients (EC) according to Ketris and Yudovich (2009) were calculated to estimate the enrichment or depletion of particular elements.

Results

The abundances of the analyzed elements have an overall homogeneous depth profile. However, specific TE are notably elevated in certain samples (Fig. 1). For example, Mo and Ni are enriched in sample Tr-3-38 (52.6–53.0 m); Fe, V, As, Hg, Zn, U, and Th in sample Tr-3-15 (29.3–29.5 m); Pb and Cu in sample Tr-3-5 (19.2–20.1 m). The Hg content is also relatively high in sample Tr-3-4 (18.4–18.5 m) and Th content – in sample Tr-3-5 (19.2–20.1 m). Compared with the Clarke values for low rank coal and sedimentary rocks (Ketris, Yudovich 2009), all measured TE concentrations are notably higher. However, most values fall in the same range as in previously reported trace element contents in black clays (Yossifova et al., 2018) from Troyanovo-3 Mine. Mercury contents are higher than previously reported Hg contents for black clays from Troyanovo-3 Mine and Maritsa Iztok lignite (Yossifova et al., 2017) and from the average Hg value of 300 ppb for Bulgarian high-sulphur coal (Kostova et al., 2020). Mercury in pyrite bearing veinlets (323–476 ppb) is similar to the lower Hg values (400 ppb) reported by Dimitrova et al. (2023) for pyrite in blue silty clay from the bottom part (109.4 m) of the Troyanovo-North Mine bore-hole (Mini Maritsa Iztok EAD).

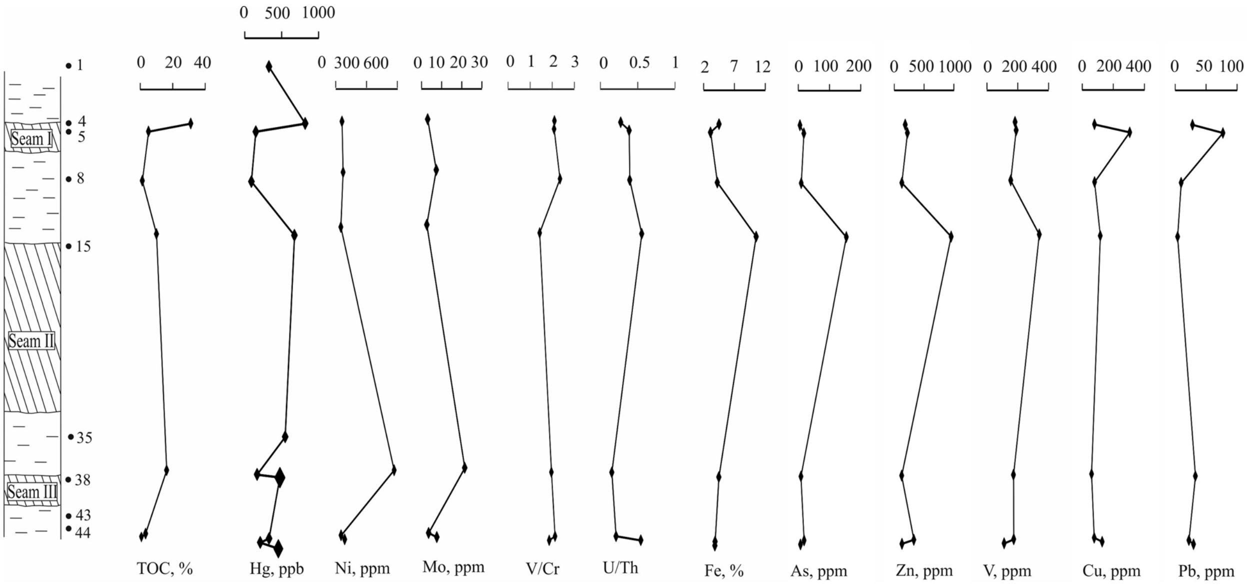

Fig. 1. Trace element depth distribution in the core samples from the Trojanovo-3 Mine borenole (Mini Maritsa Iztok EAD, Bulgaria. Data for samples position and TOC are from Milakovska et al. (2022). Coarser diamonds in Hg log represent Hg content in pyrite veinlets.

Фиг. 1. Разпределение на елементите-следи в изследваните ядкови проби от сондаж в рудник „Трояново-3“ („Мини Марица-изток“ ЕАД, България). Данните за положението на пробите и общото съдържание на органичен въглерод са по Milakovska et al. (2022). По-едрите ромбове в разпределението на живака представят съдържанието на живак в пиритните жилки.

The calculated enrichment coefficients defined as “TE concentration compared to Clarke for sedimentary rocks” (Ronov et al., 1990 in Ketris, Yudovich, 2009) reach maximum values of 12 for Hg, 14 for Mo, 20 for As, and 22 for Zn.

Discussion

Based on inorganic proxies like low Mo (<50 ppm) and V (<200 ppm) contents; U/Th ratio between 0.15–0.55 (<0.75) and V/V+Ni ratio between 0.015–0.034 (<0.45) (Jones, Manning, 1994; Mouro et al., 2017), the depositional conditions for the sediments are characterized as oxic. However, according to the V/Cr ratio (close to 2) and the elevated values for redox-sensitive trace elements like U, V, Th, Ni, Zn, and Pb our samples indicate an oxic/dysoxic environment. On the other hand, the samples fall in the anoxic to euxinic area on a U/Th *vs*. V/V+Ni plot.

No significant correlation was found between the following redox sensitive elements and ratios: Th/U and Ni/Co *vs*. V/Cr; Mo and Th/U *vs*. V/V+Ni; Th/U, Hg and Mo *vs*. TOC (total organic carbon). TOC is not correlated with other trace elements, pointing to additional trace element host next to the organic matter. Strong positive (higher than 0.80 at 95% level) correlation between Fe and V, Ni, Cr, As, and Mo suggest incorporation of these elements into Fe sulfide phase(s), whereas a less pronounced correlation between Fe and Al hints to some of the Fe being present in alumosilicate minerals. The strong correlation between Al and Ni, Co, Mo and U, and a weaker one between Al and V point to a terrigenous source and/or sorbed form for these metals. The absence of notable correlation between Al and Pb, Cu, Zn, Cr, Th, and As indicates that they are not primarily controlled by the amount of clay minerals, even if some of these trace elements are probably adsorbed onto clays. The maximum values for TOC and Hg coincide only for Sm. Tr-3-18.40. Not all samples with high TOC have consistently elevated mercury concentration, but generally, the samples with the lowest TOC have low Hg content. The overall lack of significant correlation between TOC and Hg suggests that at least some of the mercury can be attributed to an inorganic source, or that Hg is unevenly enriched only in specific organic compounds and is therefore not correlated to the bulk TOC. The lack of significant correlations between uranium, ash and sulfur supports the latter hypothesis. The variations in the relationship between mercury and TOC in the samples studied confirm the known complex Hg affinity (e.g. Grasby et al., 2013; Percival et al., 2018), presumably a function of the type of the organic compounds in addition to the available sulfides and clays with which mercury can be deposited.

The "discrepancies" found using established geochemical proxies and correlations for most samples could be explained by variations in the OM compounds, by the substantial clay content of the rocks, by alternating oxic-dysoxic depositional conditions and/or by post-depositional epigenetic processes.

The potential mechanisms forming the TE peaks in the sequence (Fig. 1) could be: i) fluid remobilization; ii) volcanism; iii) remobilization of sedimentary TE due to wildfires; or iiii) changes in the weathering environment. In our case, a hypothesis that changes in local bioproductivity and/or OM flux to a water body strongly influenced rates of TE accumulation, evidenced by positive correlation between TE and total OM, may be valid only for the maximum TOC and Hg values for sample Tr-3-4 (18.4–18.5 m). Only for this sample, a predominant organic association of Hg is likely. The lack of Al-Hg correlation precludes significant Hg absorbance onto clay minerals in the water column. Although there is no notable Fe-Hg correlation in the studied mudstones, sample Tr-3-15 (29.3–29.5 m) has elevated Fe, Mo, V, As, Zn, Cr, Ni and Hg contents, suggesting euxinic conditions caused local TE and Hg drawdown (Cherbonnier et al., 2020). The sorption capacity of fusain could not be an additional source of TE enrichment, because the Hg content in fusain (200 ppb), even though the highest among the different coal lithotypes from MIB (Yossifova et al., 2017), is lower than the Hg content that exceed 500 ppb in samples Tr-3-4 (18.4–18.5 m), Tr-3-15 (29.3–29.5 m) and Tr-3-35 (49.2–49.3 m).

For sample Tr-3-15 (29.3–29.5 m) a predominant inorganic (sulfide) association followed by an organic association of TE could be outlined. Samples Tr-3-43 (59.1–59.2 m) and Tr-3-44 (59.5–59.7 m) with thermally affected OM have elevated, but not anomalous, values for Mo, Zn, Pb and Cu and high enrichment coefficients (EC) for Hg, Mo, Cu and Zn. Sample Tr-3-38 (52.6–53.0 m) interpreted by Milakovska et al. (2022) as affected by OM mobilization, transport and fractionation as a result of wash-out processes has elevated values for Ni, V and Mo and low EC probably due to TE remobilization.

Our hypothesis for TE transport and enrichment in the studied mudstones from Troyanovo-3 Mine is based on enhanced OM maturity (Sm. Tr-3-43, Tr-3-44) found by hopane distributions (Milakovska et al., 2022), and on pyrite formation in veinlets at the deeper levels and TE differentiation, in the present study. The described features together with the mud volcanoes, H_2S emission and hot underground water mentioned by Milakovska et al. (2022) are related to the specific tectonic position and basement structure of Troyanovo-3 Mine. All the factors lead to pre-, intra- and post-basinal tectonic activities that generated faults, fractures and ascending hot reductive fluids infiltration. According to Abarghani et al. (2020), remineralization and decomposition of OM with thermal maturity could release sulfur as a source of thermogenic H_2S, which could accelerate pore water/rock interaction and authigenic Fe-sulfides formation. The accompanying H_2O, CO_2, and H_2S generation from both the organic matter and clay phases might also play a role in TE mobility and deposition. TE differentiation and deposition at different levels was probably temperature dependent. Mercury differentiation from the other TE can also be favored by the declining temperature of the fluids, as Barnes et al. (1967) experimentally found that cinnabar solubility in the hydrosulfide solution passes through a maximum somewhat above 100 °C, and the hydrothermal separation of Hg from Zn, Cu, and Pb is nearly complete, probably as a consequence of very low solubility of the sulfides of the latter metals.

Conclusions

In this study, we report the first elevated TE (including Hg) contents in an altered carbonaceous mudstone succession from a borehole of Troyanovo-3 Mine in Maritza-Iztok coal field. Our results support the hypothesis of Milakovska et al. (2022) for hot fluid injection as a possible trigger of the OM thermal alteration and TE mobility and enrichment. In constraining the effect of thermal alteration on specific trace elements distribution the authors will add TE data on a denser sample dataset, and search for establishing the main host phases of TE and Hg in the sediments.

Acknowledgements: The study was performed with financial support of projects KP 06-H64/5-2022 – TE analyses, and KP 06-H64/2-2022 – Hg analyses, Bulgarian National Science Fund, Ministry of Education and Science, Bulgaria. The authors sincere thanks are due to the reviewer Mariana Yossifova.

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Постъпила на 20.06.2024 г., приета за печат на 10.07.2024 г.
Отговорен редактор Йоцо Янев