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Mineralogical characteristics of coal seams I^a, I and II^a from Bobov Dol Basin, SW Bulgaria

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Минераложка характеристика на въглищата от пластове I^a, I и II^a в Бобовдолския басейн, ЮЗ България

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Резюме. Минероложкият състав на кафявите въглища от долната част на въгленосната свита в Бобовдолския басен е изследван чрез оптична микроскопия, XRD и SEM-EDS анализи. Глинестите минерали (смектит, илит и каолинит) и кварц са доминиращи минерали. Техните характеристики показват преобладаващ теригенен произход и подсказват за преобладаващ привнос от базични до средни скали. Акцесорна епигенетична барит-целестинова минерализация, заместваща почти напълно окислени сидеритни кристали и сфероидни агрегати, свидетелства за циркулация на метеорни разтвори при отсъствието на други минерали, запълващи пукнатини. Микроскопични стъклени сфери от горната част на въглищен пласт I показват синхронна вулканична активност, като това не е повлияло на торфообразуването.

Ключови думи: Югозападна България, Бобовдолски басейн, кафяви въглища, минералогия.

Abstract. The mineralogical composition of Bobov Dol sub-bituminous coals from the lower part of the coal-bearing formation, was studied using optical microscopy, XRD and SEM-EDS analyses. Clay minerals (smectite, illite and kaolinite) and quartz, are the dominant minerals. Their characteristics indicate predominant terrigenous origin and argue for major detrital input from intermediate to mafic rocks. Accessory epigenetic barite-celestine mineralization, substituting almost completely oxidized siderite crystals and spheroidal aggregates, denotes circulation of meteoric aqueous solutions in the absence of other fracture-filing minerals. Finite glass spheres from the top of the coal seam I indicate synchronous volcanic activity, which did not influence peat formation.

Keywords: SW Bulgaria, Bobov Dol Basin, sub-bituminous coal, mineralogy.

Introduction

The Bobov Dol Basin contains the largest coal deposit in SW Bulgaria with over 200 Mt of remaining sub-bituminous coal resources (Jordanov et al., 2002). The deposit has been extensively mined at least since the late 19th century and the coals were essentially utilized for power generation and domestic heating. Due to its economic significance, various aspects of the geological settings (Kamenov, 1959; Yovchev, 1960), stratigraphy (Vatsev, 2014, 2015), major and trace element composition (Vassilev, 1994a; Vassilev et al., 2006; Kortenski, Zdravkov, 2008; Kostova et al., 2011), technological properties (Vassilev, 1994b; Kortenski et al., 2006; Vassilev et al., 2010), petrography (Konstantinova, 1956; Valčeva, 1985; Zdravkov, Kortenski, 2004; Zdravkov et al., 2024) and palynology (Černjavska, 1970, 1977; Ivanov, 1996; Palamarev et al., 1998; Bozukov et al., 2009) of the Bobov Dol coals were extensively studied. The mineralogical characteristics of the coals were previously studied by Vassilev et al. (1994, 1995) on coals of unknown location and seam assignment, feed coals and waste products from their combustion. In this short communication, we provide further insights into the mineralogical

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composition of Bobov Dol coals based on data from the lower part of the coal-bearing formation (seams I^a, I and II^a), using optical microscopy, XRD and SEM-EDS analyses.

Geological settings

The Bobov Dol Basin represents a NNW to SSE oriented graben basin, filled by up to 1.5 km thick Oligocene to Lower Miocene siliciclastic sediments (Vatsev, 2014, 2015). The basement and the catchment area of the basin are composed of denudated Vendian – Paleozoic metamorphic (green schists and metadiabase, Frolosh Fm.) and magmatic rocks (diorite-granodiorite, Strouma diorite Fm.), Permian–Lower Triassic siliciclastic red beds, Mid- to Upper Triassic carbonate rocks, Upper Cretaceous flysch and Upper Eocene flysch-like alternation of sandstone and mudstone (Kamenov, 1959; Vatsev, 2014). The coal-bearing Bobov Dol Fm. is up to 100 m thick and is distributed along the northern half of the graben. It contains up to 14 coal seams among which 6 (numbered I to VI from base to top) were considered economically significant (Kamenov, 1959). Seam I^a located beneath the first widespread coal seam (I) was locally also mined despite the poor quality of the coal. The sediments are extensively folded due to syn- to post-depositional compressional events related to the Savian tectonic phase.

Methods

The mineralogical composition of nine coal and carbonaceous shale samples originating from two galleries of the Bobov Dol underground mine and representing coal seams I^a, I and II^a, was studied. Sampling location and sample's position within the seams are presented by Zdravkov et al. (2024). Polished coal mounts, prepared according to ISO 7404-2 (2009), were studied under incident white light using Leica DM 2500P microscope. Each sample was further analyzed using Bruker D2 Phaser diffractometer (operated at 30kV/10mA), equipped with a Ni-filtered Cu cathode and LynxEye detector. Scanning was done in the 5–70° 2Θ range with step size of 0.014° and 1s per step. Crystallography Open Database (COD) was used for the identification of the crystalline phases. Quantitative determinations were obtained by Rietveld refinement using Profex frontend to BGMN software (Doebelin, Kleeberg, 2015). Refinement procedure included modelling of the complex background using a combination of broad generic peak to account for the organic matter's amorphous halo and Chebyshev polynomial function. Sample displacement, unit-cell parameters, and preferred orientation were also refined. Because of the chemical and structural variations between the studied and referenced mineral structures, however, the obtained phase amounts are considered semi-quantitative. The weighted profile R factor (Rwp) and the expected R factor (Rexp) were used to calculate the goodness of fit (GOF = Rwp/Rexp) in order to check the accuracy of the refinement in addition to the visual analysis of the residual pattern. Additionally, mineral characteristics were studied on polished coal blocks and coal chips using JEOL JSM 6010 PLUS/LA scanning electron microscope (SEM), equipped with an EDS analyzer (standardless) and operated at 15 kV under low and high vacuum modes.

Results and discussion

The amount of inorganic matter (ash yield) in the studied coal samples varies between 4.8 and 44.5 vol.% and reaches up to 73 vol.% in the carbonaceous shale samples (Table 1). The mineralogical composition of the studied coal seams is relatively uniform and comprise dominant clay-mineral assemblage and quartz, intimately disseminated within the organic matter in the low- to medium ash samples (Fig. 1a), or occurring as partings, lenses and microbands in the high-ash coals and the carbonaceous shales (Figs. 1c, d, 2a, c). Euhedral and framboidal pyrite (Figs. 1b, c, 2a, c) is also present in all samples, whereas other minerals such as feldspars, calcite, gypsum, and jarosite, were detected in minor amounts in part of the samples (Table 1). Trace amounts of bassanite are established by means of XRD only in two samples I^a_1 and I_6.

Apart from a low-ash coal sample (i.e., sample I^a_2), the bulk of the inorganic matter in Bobov Dol coal is predominantly composed of clay minerals (Table 1). An association of dominant smectite and subordinate illite/mica (2M1 and 1M/Md polytypes) and kaolinite, forming finely dispersed and microporous micro- to nanocrystalline mixtures of clay minerals, organic debris and quartz, was de-

Table 1
Semi-quantitative mineralogical composition (in % of crystalline pahses) of coal seams I^a, I and II^a from Bobov Dol Basin with probable origin of minerals: D = detrital; S = syngenetic; E = epigenetic; ● = dominant origin; ○ = subordinate origin; GOF = goodness of fit

Таблица 1
Полуколичествен минераложки състав на въглищни пластове I^a, I и II^a от Бобовдолски басейн с вероятен произход на минералите: D = детритен произход; S = сингенетичен произход; E = епигенетичен произход; ● = доминиращ; ○ = подчинен; GOF = коефициент на съответствие между измерената и калкулираната дифрактограма

Sample			I^a_1	I^a_2	I^a_4	I_5	I_6	I_8	I-1	II^a_2	II^a_4	Origin		
Coal seam			I^a			I				II^a		D	S	E
Ash yield [wt. %, db]			62.3	4.8	53.1	72.9	20.6	28.4	41.7	53.9	44.5			
GOF			1.12	1.99	1.39	1.10	1.26	1.25	1.10	1.13	1.29			
Minerals	Clay minerals	Kaolinite	22.1	–	11.7	12.7	7.7	5.6	26.3	13.3	22.4	●	○	
		Illite	22.2	–	13.8	14.9	7.2	20.9	24.5	18.2	20.3	●	○	
		Smectite	29.7	–	53.6	56.2	53.7	57.8	30.7	43.4	38.5	●	○	
	Quartz		9.4	61.9	8.4	9.9	9.5	8.8	7.2	14.7	10.2	●		
	Feldspars		3.0	–	5.2	2.5	–	2.6	6.7	5.2	3.7	●		
	Calcite		0.9	–	–	1.0	1.0	0.4	0.8	1.0	0.8		●	
	Pyrite		0.7	38.1	0.4	0.5	9.9	0.7	2.9	1.4	1.6		●	○
	Gypsum		1.6	–	3.0	1.9	1.1	1.9	0.6	2.8	2.6			●
	Bassanite		0.9	–	–	–	0.9	–	–	–	–			●
	Jarosite		9.3	–	3.2	–	9.2	1.3	–	–	–			●

tected in all samples (Figs. 1a; 2a–c). The observed herein XRD traces are very similar to the ones reported previously by Vassilev et al. (1995), but the semi-quantitative assessment of the mineralogical composition differs significantly, perhaps due to the different quantitation methods. For example, Vassilev et al. (1995) concluded that smectite is a common but rather rare component of the coals, while being more abundant in the carbonaceous shales. Our assessment, however, shows that smectite is the dominant clay mineral in all samples, although for one coal (i.e., I–1) and one carbonaceous shale (i.e., I^a_1) samples its contents are slightly reduced and are roughly equal to the amount of the other clay minerals (Table 1). This conclusion aligns with the observed increased wearing of the clay-rich particles during the preparation of the polished blocks, which is likely caused by the swelling properties of smectite. The basal 001 peak of smectite is always very broad and considering the shift of its position between ~6 and ~9 °2Θ within the individual samples, the presence of a turbostratically disordered interstratified mineral is more alike instead of a pure smectite. While the poor ordering of the structure renders its contents unreliable, the overall high iron concentration in the clayey matrix (FeO = 5.97–16.92) further supports the conclusion that iron-bearing smectitic and micaceous minerals comprise the dominant clay fraction.

Clay minerals are common weathering products, whose formation is largely controlled by the hydrological regime and the mineral and chemical composition of parent rocks. While kaolinite forms predominantly due to complete hydrolysis of the rock-forming minerals under humid and well drained acidic environments, the formation of smectite is favored by temperate/cool climate and mostly occur in poorly drained low-lying areas with high pH and abundance of basic cations (Wilson, 1999). Thus, the predominance of smectitic clays in Bobov Dol coals supports the available palynological data (Bozukov et al., 2009) and argue for peat formation under temperate climatic settings, perhaps with a well-established seasonality. Although certain amounts of neo-formed clay minerals due to the weathering of feldspar grains cannot be completely ruled out, especially those found in the cell structure of textinite (Fig. 2b), the broad basal peaks of all detected clay minerals denote their predominant detrital origin (Ward, 1989; Wilson, 1999). Thus, the different proportions of clay minerals detected in the studied samples might indicate changes in the weathering conditions and/or the peat forming environmental settings (e.g., pH conditions) due to changes in the

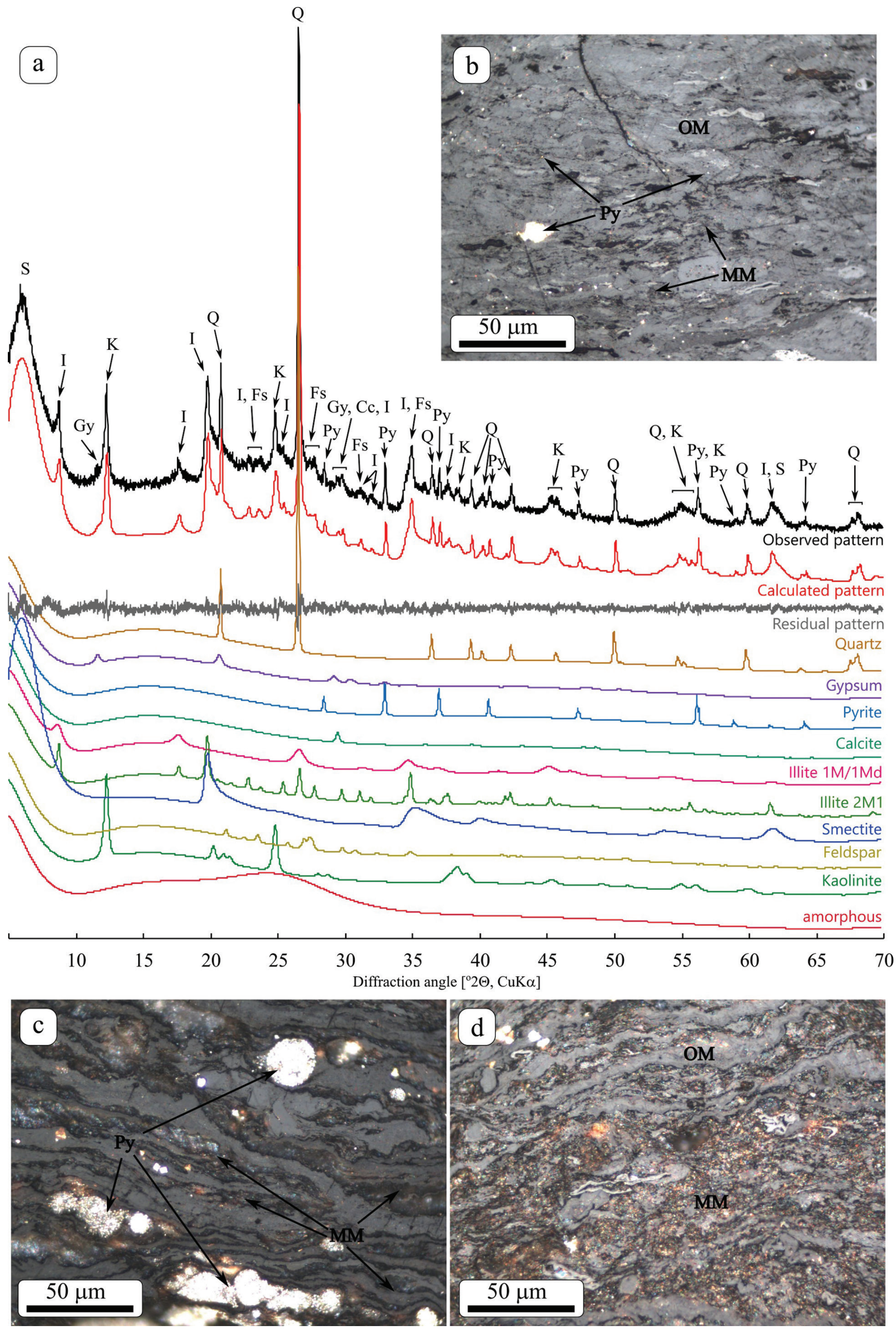

Fig. 1. Mineralogical composition of Bobov Dol coal: *a*) Example of Rietveld refined XRD pattern (sample II$^a_4$, GOF = 1.29), showing the difference between the acquired and the calculated pattern and the peak curves of the individual minerals; I, illite, K, kaolinite, S, smectite; Q, quartz, Fs, feldspar, Gy, gypsum, Py, pyrite; *b–d*) Microphotographs of typical minerals in low- (sample I$^a_2$) and high-ash (samples I^{a}4 and II$^a_4$ in *c* and *d* respectively) coals: MM, clay-rich muddy matrix, Py, pyrite, OM, organic matter

Фиг. 1. Минерален състав на въглища Бобов дол: *a*) Пример за Rietveld рафинирана рентгенограма (проба IIa4, GOF = 1,29), показваща разликата между измерената и изчислената дифрактограми, както и пиковите криви на отделните минерали; I–илит, K–каолинит, S–смектит, Q–кварц, Fs–фелдшпат, Gy–гипс, Py–пирит, OM–органично вещество; *b-d*) Микроснимки на типични минерали в ниско- (проба I^{a}2) и високопепелни (проби I$^a_4$ и II$^a_4$ в *c* и *d* съответно) въглища: MM, глинести минерали, Py, пирит

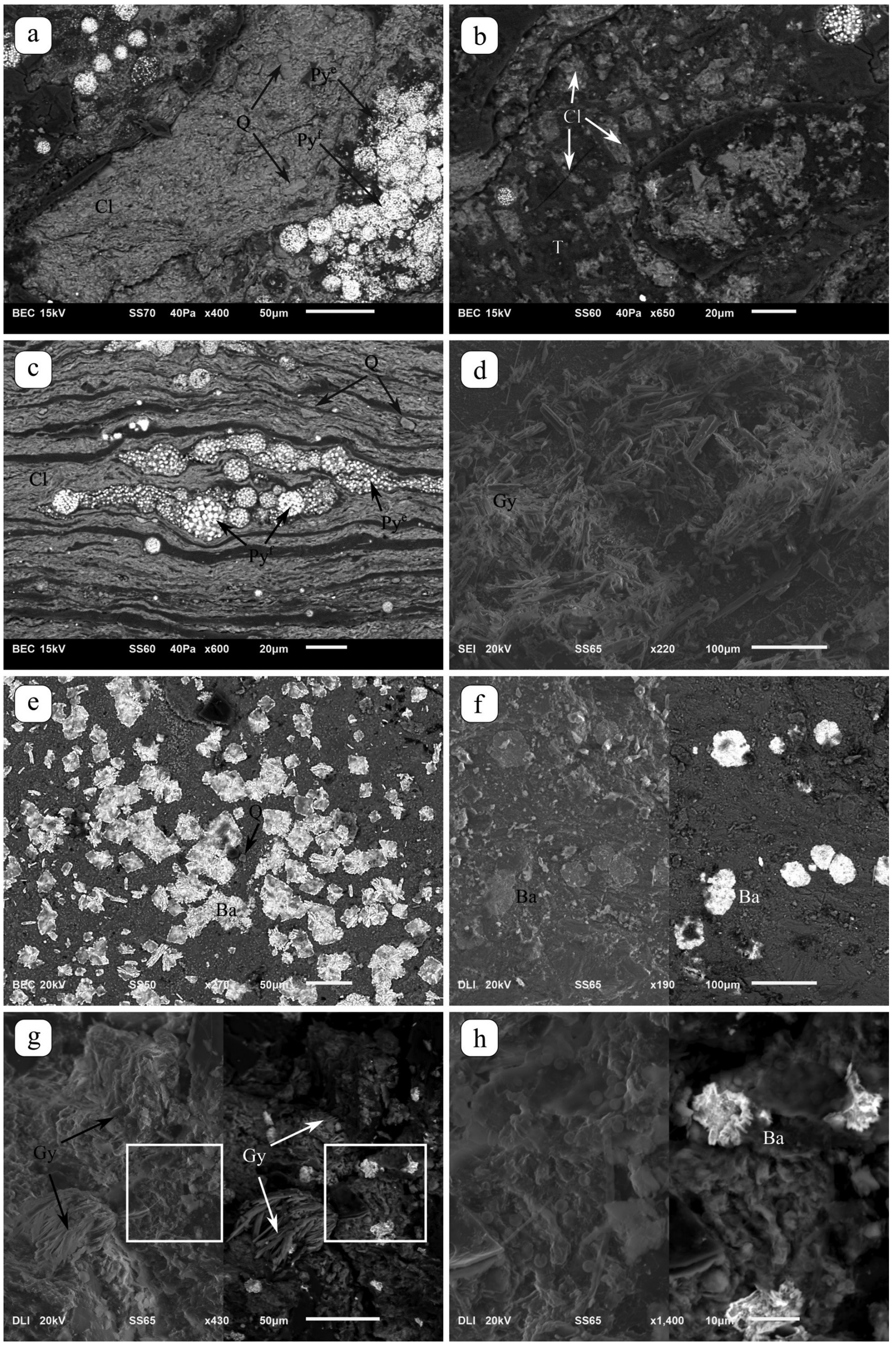

Fig. 2. SEM microphotographs of Bobov Dol coal: *a–c*) Backscatter electron images (BEC) of clay-rich (Cl) mineral bands and lenses (*a, c*), clay cell infillings in textinite (T; *b*), and abundant framboidal (Py^f) and euhedral (+) pyrite, polished block of sample I^a_4; *d*) Secondary electron image (SEI) of randomly oriented gypsum (Gy) crystals, coal chip from sample I^a_2; *e*) BEC image of abundant barite-celestine (Ba) microcrystals substituting oxidized siderite rhombohedral crystals and irregular aggregates, polished block of sample I^a_1; *f*) Split SEI/BEC image of barite/celestine microcrystals substituting former spheroidal siderite, polished block of sample I_8; *g–h*) Split SEI/BEC images of barite/celestine (Ba) aggregates, associating with numerous glass spheres and gypsum (Gy) crystals, coal chip of sample I_8. Image *h* represents an enlarged inset of image *g*.

Фиг. 2. Микрофотографии от сканиращ електронен микроскоп на въглища от Бобовдолския басейн: *a–c*) Образи в обратно отразени електрони (BEC) на богати на глина (Cl) минерални ивици и лещи (*a, c*), глинест пълнеж на клетки в текстинит (T; *b*) и множество пиритни фрамбоиди (Py^f) и евхедрални кристали (Py^e), полиран препарат от проба I^a_4; *d*) Образи във вторични електрони (SEI) на произволно ориентирани гипсови (Gy) кристали, въглищен къс от проба I^a_1; *e*) BEC изображение на множество барит-целестинови (Ba) микрокристали, заместващи окислени сидеритни ромбоедрични кристали и неправилни агрегати, полиран препарат от проба I^a_1; *f*) Разделено SEI/BEC изображение на микрокристали от барит/целестин (Ba), заместващи сфероидални сидеритови агрегати, полиран препарат от проба I_8; *g–h*) Комбинирани SEI/BEC изображения на агрегати барит/целестин (Ba), свързващи се с множество стъклени сфери и гипсови (Gy) кристали, въглищен къс от проба I_8. Изображение *h* представлява увеличен кадър на изображение *g*.

hydrological regime. The high iron contents of the clay matrix further suggests that the most probable sources of the clay minerals are mafic to intermediate rocks, and therefore, the green shists and diorites from the southern and eastern basin margins seem likely candidates.

Quartz is also a common mineral in the studied coal with contents of about 10% being roughly equal between the samples (Table 1). The low-ash coal sample from seam I[a], in which quartz and pyrite are the only detectable minerals, is an exception with quartz contents of up to 60%. In all samples the mineral is of detrital origin and occurs as angular to sub-angular grains, ~5 – 10 µm in size, scattered throughout the clay matrix (Fig. 2a, c). The XRD patterns of most samples further indicate the presence of minor amounts (3–7%; Table 1) of feldspar minerals (probably a mixture of K-feldspar and plagioclase). In coals, these are commonly of detrital origin although neo-formed feldspars can also occur in particular cases. Since no feldspars were detected during the SEM studies, their origin in the studied coal samples cannot be clearly resolved.

Pyrite is present in varying amounts (0.4–38%) in all samples. It is mostly occurring as euhedral crystals, either isolated throughout the organic groundmass (Fig. 1b), or most often clustered within the inorganic matter together with pyritic framboids (Figs. 1c; 2a, c). The latter are typically composed of relatively evenly distributed equal-sized pyritic microcrystals (~1 µm) and considering the well-shaped octahedral, pentagon dodecahedral or cubic crystals associating with clay minerals in the interstices, inorganic origin can be presumed. Under the microscope pyrite appears unaltered with only rare framboids having yellowish to orange-reddish discolorations as a result of partial weathering. However, the XRD patterns of most samples indicate the presence of gypsum (mostly long prismatic crystals and sometimes gypsum roses; Fig. 2d) and locally bassanite and jarosite (Table 1) denoting that a certain amount of pyrite has already been degraded.

Traces of calcite (<1%) were detected in most of the samples. These coincide with the presence of inorganic carbon in Bobov Dol coal (Zdravkov et al., 2024) and most probably occur as syn-/diagenetic calcite microcrystals intermixed with the clay minerals, as no evidence for the presence of carbonate nodules, nor epigenetic fracture-filling mineralization were detected during the petrographic and SEM analysis.

The accessory minerals in the studied samples are essentially represented by a series of barite-celestine aggregates with highly variable chemical composition ($Ba_{0.02–0.67}Sr_{0.0–0.71}SO_4$), identified in samples I^a_1 and I_8 from the base of seam I[a] and the top of seam I. The minerals substitute partially or fully an iron-bearing mineral, which based on the rhombohedral crystals and locally spheroidal aggregates (Fig. 2e, f) is likely to be siderite. However, the EDS data (low vacuum mode) do not indicate the presence of carbon atoms, so the mineral appears to be fully oxidized and transformed into iron oxide/hydrooxide (FeO = 80.7–95.9%, avg. 91.60%; CaO =1.9–10.27, avg. 8.42%). Due to the absence of other fracture-filling minerals, hydrothermal origin of the barite-celestine aggregates seems less alike. This coincides with the fact that no change in huminite reflectance can be detected (Zdravkov et al., 2024). Moreover, considering the almost complete oxidation of the siderite, it can be presumed that the barium and strontium were more probably introduced by oxidizing meteoric water solutions. Furthermore, the research of Eskenazy (1988) and Eskenazy and Minčeva (1989) indicate that both Ba and Sr are present in Bobov Dol coal and remobilization from the coal itself cannot be ruled out. However, in sample I_8 the barite-celestine mineralization co-occur with micrometer-sized glass spheres (~ 2 µm; Fig. 2g, h), composed of (avg. %) SiO_2 – 57.14, Al_2O_3 – 27.49, FeO – 3.31, MgO – 2.18, Na_2O – 1.20, K_2O – 1.58, P_2O_5 – 4.14, SO_3 – 2.95, and therefore, volcanic origin of Ba and Sr (introduced by volcanic ash particles) cannot be excluded too. Research on products from modern volcanic eruptions and laboratory experiments (Heiken, 1972; Wadsworth et al., 2017; Genareau et al., 2019) indicate that similar glass spheres commonly form trough melting of particulate volcanic ash due to high temperatures related to volcanism-induced lightnings. It can, therefore, be presumed that the occurrence of the glass spheres in Bobov Dol coal can be linked to synchronous volcanic activity. This conclusion coincides with the data from Vassilev et al. (1994, 1995) who also found the presence of individual glass spheres, volcanic ash particles and sanidine crystals. However, the XRD characteristics of the clay minerals assemblage, together with the single occurrences of these volcanic-related particles in the studied coal denote for a long distance from the volcano. During the Oligocene, numerous volcanoes were active within the Balkan Peninsula

(Harkovska et al., 1989) and some of them might have been responsible for the presence of ash particles in the coal. However, since no direct comparison with the chemical composition of the Oligocene volcanic rocks can be made because of the possibility that melting likely have changed the mineral/chemical composition of the volcanic glass, the link to a specific volcano or volcanic event cannot be clearly established.

Conclusions

The mineralogical composition of Bobov Dol coal is relatively simple and mostly dominated by clay minerals (smectite, illite/mica and kaolinite) and quartz. The predominance of smectitic minerals, together with the poor crystallinity of the clays and the angular to sub-angular quartz grains suggests predominant detrital origin of the minerals and indicate that the Paleozoic granodiorite and the low-grade schists from the southern and south-eastern basin margins might have been the detrital source. The occurrence of epigenetic barite-celestine mineralization, substituting almost completely oxidized siderite crystals and spheroidal aggregates, denote circulation of meteoric aqueous solutions, whereas the presence of glass spheres at the top of seam I indicate synchronous volcanic activity.

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References

Bozukov, V., T. Utescher., D. A. Ivanov. 2009. Late Eocene to early Miocene climate and vegetation of Bulgaria. – *Rev. Palaeobotany and Palynology*, *153*, 360–374.

Černjavska, S. 1970. New spore and pollen species from coal-bearing Paleogene sediments in Bulgaria. – *Rev. Bulgar. Geol. Soc.*, *1*, 33–39.

Černjavska, S. 1977. Palinological studies on Paleogene deposits in South Bulgaria. – *Geologica Balc.*, *7*, 3–26.

Doebelin, N., R. Kleeberg. 2015. Profex: a graphical user interface for the Rietveld refinement program BGMN. – *J. Appl. Cryst.*, *48*, 1573–1580.

Eskenazy, G. M. 1988. On the geochemistry of barium in coal. – *C. R. Acad. Bulg. Sci.*, *41*, 2, 95–98.

Eskenazy, G. M., E. Minčeva. 1989. On the geochemistry of strontium in Bulgarian coals. – *Chem. Geol.*, *74*, 265–276.

Genareau, K., K. L. Wallace., P. Gharghabi., J. Gafford. 2019. Lightning effects on the grain size distribution of volcanic ash. – *Geophys. Res. Lett.*, *46*, 3133–3141.

Harkovska, A., Y. Yanev., P. Marchev. 1989. General features of the Paleogene orogenic magmatism in Bulgaria. – *Geologica Balc.*, *19*, 37–72.

Heiken, G. 1972. Morphology and petrography of volcanic ashes. – *Geol. Soc. Am. Bull.*, *83*, 1961–1988.

International Organization for Standardization. 2009. ISO 7404-2:2009. *Methods for the* Petrographic *A*nalysis *of* C*oals. Part 2: Methods for* Preparing C*oal Samples*, 12 p.

Ivanov, D. A. 1996. Pollen analysis of the Tertiary sediments from the Bobovdol coal basin. – *Phytologia Balc.*, *2*, 38–42.

Jordanov, J., J. Kortenski., H. Kazandgiev. 2002. Energy potential of coal basins in Bulgaria. – In: *Intern. Conf. "Corporate Finance Management in Mining Industry",* Varna, 7–11.10.2002.

Kamenov, B. 1959. Die Geologie des Bobowdoler Braunkohlenbeckens. – *Ann. Direct. générale des rech. géol., Ser. A*,*8*, 1–26.

Konstantinova, V. 1956. Petrographic description of the coal at Bobov dol. – *Ann. Direct. générale des rech. géol., Ser. 6*, 281–317.

Kortenski, J., A. Zdravkov. 2008. Occurrence and distribution of major elements in coals from Bobov Dol Basin, Bulgaria. – *Annual Univ. Mining and Geol. "St. Ivan Rilski," 51*, 34–40.

Kortenski, J., A. Zdravkov., D. Pinalova. 2006. Applying the International classification of in-seam coals and the International codification system to the coals from Pernik Province. – *Annual Univ. Mining and Geol. "St. Ivan Rilski," 49*, 41–46.

Kostova, I. J., C. G. Vassileva., J. Hower., M. Mastalerz., S. V. Vassilev., N. Nikolova. 2011. Mercury in coals and fly ashes from Republika and Bobov dol thermoelectric power plants. – *C. R. Acad. Bulg. Sci.*, *64*, 253–262.

Palamarev, E., D. A. Ivanov., G. Kitanov. 1998. New data about the fossil flora from Bobovdol basin and its biostratigraphic significance. – *Rev. Bulg. Geolog. Soc.*, *59, 2–3, 13–21.*

Valčeva, S. 1985. Petrology and geochemistry of the Bulgarian coal basins and deposits. Petrological characteristics of coals from Bobov dol Basin. – *Ann. Univ. de Sofia "St. Kliment Ohridski," 79*, 55–69.

Vassilev, S. V. 1994a. Trace elements in solid waste products from coal burning at some Bulgarian thermoelectric power stations. – *Fuel*, *73*, 367–374.

Vassilev, S. V. 1994b. Phase-mineralogical studies on solid waste products from burning of Bobov Dol coal at "Bobov Dol" thermo-electric power plant. – *Ann. Univ, de Sofia "St. Kliment Ohridski," 84*, 85–108.

Vassilev, S. V., M. G. Yossifova., C. G. Vassileva. 1994. Mineralogy and geochemistry of Bobov Dol coals, Bulgaria. – *Intern. J. Coal Geol.*, *26*, 185–213.

Vassilev, S. V., M. G. Yossifova., S. Valceva. 1995. Petrographic, mineral and chemical composition of coal and waste products from the central processing factory "Bobov dol". II. Mineral and chemical composition. – *Ann. Univ. de Sofia "St. Kliment Ohridski," 87*, 103–123.

Vassilev, S. V., N. Lihareva., C. G. Vassileva. 2006. Sequential leaching behaviour of some elements during chemical treatment of Bobov Dol coal fly ash. – *C. R. Acad. Bulg. Sci.*, *59*, 645–650.

Vassilev, S. V., C. G. Vassileva., D. Baxter., L. K. Andersen. 2010. Relationships between chemical and mineral composition of coal and their potential applications as genetic indicators. Part 1. Chemical characteristics. – *Geologica Balc.*, *39*, 21–41.

Vatsev, M. 2014. Contribution to the stratigraphy of the Oligocene–Lower Miocene sediments of the Bobovdol coal-bearing Basin (South-Western Bulgaria). Part 1 – Lithostratigraphy of the Rupelian sediments. – *Rev. Bulg. Geol. Soc.*, *75*, 1–3, 47–62.

Vatsev, M. 2015. Contribution to the stratigraphy of the Oligocene–Lower Miocene sediments of the Bobovdol coal Basin (South-Western Bulgaria). Part 2 – Lithostratigraphy of the Chattian–Lower Miocene sediments. – *Rev. Bulg. Geol. Soc.*, *76*, 1, 5–21.

Wadsworth, F. B., J. Vasseur., E. W. Llewellin., K. Genareau., C. Cimarelli, D. B. Dingwell. 2017. Size limits for rounding of volcanic ash particles heated by lightning. – *J. Geophys. Res.: Solid Earth*, *122*, 1977–1989.

Ward, C. R. 1989. Minerals in bituminous coals of the Sydney basin (Australia) and the Illinois basin (U.S.A.). – *Intern. J. Coal Geol.*, *13*, 455–479.

Wilson, M. J. 1999. The origin and formation of clay minerals in soils: past, present and future perspectives. – *Clay Miner.*, *34*, 7–25.

Yovchev, Y. 1960. *Raw Material Deposits of the People's Republic of Bulgaria. Coal and Bituminous Shale*. Tehnika Publishing House, Sofia, 167 p. (in Bulgarian).

Zdravkov, A., J. Kortenski. 2004. Petrology and depositional environment of the coals from Bobov dol basin, Bulgaria. – *Annual of the University of Mining and Geology "St. Ivan Rilski," 47*, 101–108.

Zdravkov, A., A. Bechtel., D. Groβ., I. Kojić., K. Stojanović., D. Životić. 2024. Paleovegetation and environment during deposition of the Late Oligocene sub-bituminous coal in the Bobov Dol Basin (SW Bulgaria) as deduced from petrographic and geochemical characteristics. – *Intern. J. Coal Geol.*, *285*, 104489; https://doi.org/10.1016/j.coal.2024.104489.

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