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Petrography, mineralogy and geochemistry of Balkan coals and their waste products

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ABSTRACT

The samples studied include raw coal from five mines, coal concentrate, coal slurry, associated rock, and waste water. Collodetrinite comprises the dominant portion in raw coals and waste products while collotelinite and telinite/cryptotelenite dominate in the CC. The $S_{sulphide}$, particularly that of a syngenetic origin, cannot be completely separated out after coal crushing and flotation. The major minerals are pyrite, quartz, and kaolinite; the minor minerals — illite, muscovite, plagioclase, K feldspar, gypsum, calcite, dolomite, and siderite; and the additional mineral species as gold, sulphur, $Fe_{1.24}S_{0.76}$, pyrrhotite, galena, hematite, magnetite, hercynite, Cr-spinel, Ti-bearing minerals, biotite, halloysite, zircon, apatite, stilbite, celestine, Mn-calcite, Fe-dolomite, $CaFe(CO_3)_2$, ankerite biogenic minerals, volcanic ash, and possible cosmogenic dust are present in the samples as accessory phases. The modes of occurrence of the authigenic minerals suggest that this coal has undergone a series of syngenetic, epigenetic, and exogenic mineralisation. The origin of the epigenetic framboidal pyrite and neoform phases of microbial activity and water treatment is also discussed. The elements Te, S, Cd, U, Cs, V, Mo, W, and Cr are enriched in the coal concentrate compared with worldwide Clarke values of hard coal. Most of the elements have a mixed mode of occurrence. The Br, S, U, and Ge display a strong affinity to organic matter, whereas the Al, K, Si, Rb, Li, Ti, P, and Se display a distinctly inorganic pattern of distribution. Certain of the trace elements (e.g., Sr, Ba, P, Mn, Mo, As, Pb, Sb, Tl, Li, Nb, Be, Y, Ti, Yb, and Cd) are present as impurities in various minerals, whereas other trace elements (e.g., La, Ba, Cu, Re, Pb, Gd, Nd, Sr, Sn, and Cr) are present as discrete phases. It is suggested that the main sources of the trace elements were mineral and mixed sea waters, the basement rocks, and the Sliven U-polymetallic ore deposit. It was also revealed that a number of elements (S, Li, Cs, F, Br, NH^{-}_{4}, NO^{-}_{3}, and V) in the Balkan coals are mobile in water and may pose certain environmental concerns. The coal slurry could be used as a form of fuel.

1. Introduction

As fundamental references concerning the petrology, mineralogy and geochemistry of coal can be cited the monographs of Yurovskii (1968), Gluskoter et al. (1977), Yudovich (1978), Finkelman (1980), Bouska (1981), Stach et al. (1975), Swaine (1990), Goodarzi (1995), Taylor et al. (1998), Yudovich and Ketris (2002, 2005, 2006), as well as numerous articles related to specific subjects and problems. In this case, the works of Lebedev et al. (1980), Shpirt (1986), and Shpirt et al. (1990) were used in studying waste products from coal preparation and their impact on the environment.

The Balkan coal basin is the biggest Bulgarian deposit for mining of bituminous coal. The annual quantities of the separated associated rock and coal slurry after the coal preparation are 230 000 t and 100 000 t, respectively. This paper follows on earlier work by Yossifova (1995) and presents a systematic petrographic, mineralogical, and geochemical characterisation of Balkan raw coals mined from five mines and the products generated from their flotation: coal concentrate, coal slurry, associated rock, and waste water. These complex investigations allow to be supposed the presence of a dominant H_2S environment in the basin.

Recently, Silva et al. (2011), Ribeiro et al. (2011), Dai et al. (2012b), Huggins et al. (2012), Misz-Kennan and Fabiańska (2012), and Oliveira et al. (2012) have published data, which associated with some sections of the present article.

2. Geological setting

The Balkan coal basin is located in the southeastern part of the central Balkan Range and occupies its highest parts (Fig. 1A,B), where the slopes are steep and deeply incised. The coal basin is 75-km long east–west and 5- to 20-km wide (Mihailov, 1981; Vassilev, 1945). The basin was formed in a coastal lagoon environment (Minchev, 1958), and a subsequent Cenomanian marine transgression resulted in the drowning of three river valleys (Nikolov, 1979). The Subhercynian, Laramide, and Pyrenean orogenic phases resulted in the structural

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development of the basin (Vassilev, 1945). The igneous rocks (andesites, diorites, and monzodiorites) in the south of the basin comprise part of the Alpine-Mediterranean mountain system and the Tetthyan Eurasian metallogenic belt (TEMB) (Dabovski and Zagorchev, 2009). This belt extends from the Apuseni Mountains and Banat in Romania through the Timok region and the Ridanj-Krepolin belt in the Sredna Gora Mountains (Sredan Gora Volcanic Arc), Serbia, and continues farther east across the southern Black Sea area in the Pontides and Small Caucasus Ranges. The ages of the igneous rocks along the boundaries of this belt vary widely, but the latest data for the rocks in the Sredna Gora Mountains, Bulgaria, suggest an age of Late Cenomanian to approximately Early Campanian, whereas certain plutonic bodies in the Rhodope Mountains, Bulgaria, also date to the Maastrichtian (Dabovski and Zagorchev, 2009). The earliest andesitic volcanism was represented by tuffs associated with an Upper Cenomanian marl formation in the vicinity of the village of Tranak (Fig. 1A) (Kanchev, 1966). The Tranak syncline is located 60-km southeast of the town of Kotel and 80-km southeast of the town of Sliven.

The lithology and stratigraphy of the Balkan basin are shown in Fig. 1C. The Balkan coal-bearing sediments are divided into three units: the Basal, Coal-bearing and Marl Formations. The Basal Formation (0–200-m thick) lies transgressively and nonconformably on Paleozoic (gneisses, amphibolites, granitoids), Triassic, and Jurassic sedimentary rocks and includes conglomerates, sandstones, and argillites. The argillites contain limestone fragments, siderite spherulites and pyrite grains. The Coal-bearing Formation (20–100 m) consists of dark to black argillites, including siderite concretions, clay marls, sandstones, and coal. Due to thrusting, this unit is repeated two to three times in the exposed tectono-stratigraphic sequence. Only three to six of the eight coal seams are economically significant. The ages of the coal-bearing sediments have not been determined completely, but an Early Cenomanian age has been accepted (Dabovski and Zagorchev, 2009). Natural coke is present in the western part of the basin and is a result of a local heat from the Lutetian basalt dikes (Kanchev, 1962; Vassilev, 1945). The coals were formed primarily from an angiosperm and gymnosperm

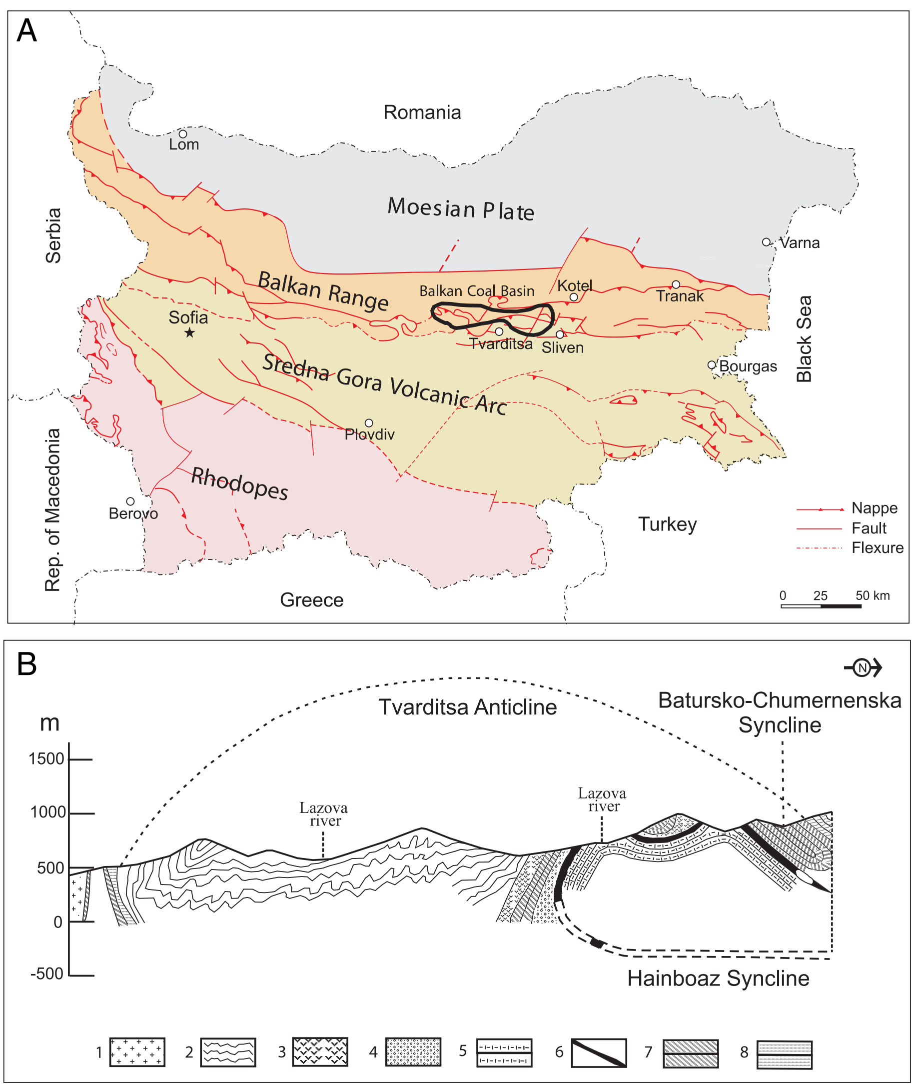

Fig. 1. A — Tectonic map of Bulgaria (adapted to Dabovski and Zagorchev, 2009) and location of the Balkan coal basin. B — Profile of the Tvarditsa anticline (Kanchev, 1962). (1) granites; (2) schists; (3) quartz porphyries; (4) conglomerates; (5) marls; (6) coals; (7) Trassiac sediments; (8) Jurassic sediments. C — Lithological column of the Balkan area (by Kanchev, 1962, 1995; Kanchev et al., 1995). *Precambrian – Paleozoic*: (1) and (2) gneisses and amphibolites; (3) biotite plagiogranites; (4) granodiorites and granites. *Mesozoic, Triassic*: (1) — sandstones, conglomerates, and silty claystones; (2) — dolomites; (3) — limestones and argillites; (2*) —dolomites; (4) — limestones. *Jurassic*: (1) — sandstones; (2) — limestones; (3) — black argillites with siderite and marcasite concretions; (4) — sandstones and silty claystones; (5) — conglomerates, sandstones, and marls. *Cretaceous, Early Cretaceous*: (1) — marls, sandstones and conglomerates; (2) — marls and sandstones; (*) — conglomerates, sandstones and marls. *Late Cretaceous*: Basal Formation; Coal-bearing Formation; Marl Formation; (1) — quartzites, argillites and conglomerates; (2) — marls and sandy-aleurolitic; (3) — sandstones and conglomerates; (4) — argillaceous-sandy flysch; (5) — marls, limestones and sandstones; (6) — limestones with flint, breccia-conglomerate, and sandstone. *Cenozoic, Paleogene*: (1) — biodetrital limestones with flint concretions; (2) — sandy aleurolites to fine sandstones; (3) — white sandstones; (4) — clayey marls and calcareous clays; (5) — sandstones, clayey-aleorolitic marls, and aleurolitic clays; (6) — polygenic conglomerates; (7) — black clays and coals; (8) — sapropelic argillites; (9) — conglomerates, sandstones and clays. *Quaternary* — proluvial, deluvial, eluvial, and alluvial sediments.