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MINERALOGICAL COMPOSITION AND SOME HAZARDOUS
TRACE ELEMENTS RELATED TO PYRITE IN COALS
FROM BELI BREG BASIN, BULGARIA

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Irena Kostova. MINERALOGICAL COMPOSITION AND SOME HAZARDOUS TRACE ELEMENTS
RELATED TO PYRITE IN COALS FROM BELI BREG BASIN, BULGARIA

The goal of the present investigation is to perform detailed mineralogical characterization of coals from Beli Breg basin, to determine size and morphology of minerals and mineral aggregates and to specify their formation. The other goal is to establish the concentration of some specific elements with environmental and human health concern, especially As, Se, Cd, Pb, Zn, Ni, Cu, Co and Mn in pyrite crystals and grains by using SEM-WDX electron microprobe elemental analyses. The proximate and ultimate analysis, optical microscopy, XRD and SEM-EDX and SEM-WDX analyses have been applied. The macerals from huminite group totally predominate. The minerals identified include illite, montmorillonite, kaolinite, quartz, calcite, pyrite, gypsum, jarosite and apatite. Quartz, clay minerals and calcite are the major minerals. The pyrite is also often observed in contrast with gypsum, jarosite and apatite, which are present in low amount. The close association among clay minerals, quartz, pyrite and organic matter was observed. The present study shows strong connection between pyrite and the presence of some environmentally sensitive trace elements. The data show that As is the most common minor constituent in studied pyrite from Beli Breg lignite with the highest concentrations in pyrite grains and masses. Obviously, the pyrite is the most important carrier of As, but also of a number of heavy metals like Cu, Co, Pb, Ni, Zn and Mn. Cadmium and selenium also present in very small quantities.

Key words: lignite, Beli Breg basin, mineral composition, trace elements in pyrite.

Ирена Костова. МИНЕРАЛЕН СЪСТАВ И СЪДЪРЖАНИЕ НА НЯКОИ ВРЕДНИ ЕЛЕМЕНТИ
ПРИМЕСИ В ПИРИТ ВЪВ ВЪГЛИЩА ОТ БАСЕЙН БЕЛИ БРЕГ, БЪЛГАРИЯ

Целите на настоящото изследване е да бъде извършена детайлна минераложка характеристика на въглищата от басейн Бели Брег, да бъде определен размерът и морфологията на минералите и минералните агрегати и да бъде установен техния произход. Друга цел, която изследването си поставя, е да бъде установено

съдържанието на някои вредни за околната среда и човешкото здраве елементи примеси (As, Se, Cd, Pb, Zn, Ni, Cu, Co и Mn) в пирита чрез прилагане на SEM-WDX. За характеризиране на пробите са извършени технически и елементен анализ, приложени са оптична и електронна микроскопия (SEM), рентгенодифракционни (XRD) и микросондови елементни анализи (SEM-EDS и SEM-WDX). Данните показват, че мацералите от групата на хуминита преобладават. Установени са минералите илит, монтморилонит, каолинит, кварц, калцит, пирит, гипс, ярозит и апатит. Кварцът, глинестите минерали, калцитът и пиритът се срещат в най-голямо количество, докато съдържанието на гипс, ярозит и апатит е минимално. Съществува тясна асоциация между глинестите минерали, кварца, пирита и органичното вещество. Данните от изследването показват несъмнена връзка между пирита във въглищата и съдържанието на някои важни за околната среда елементи примеси. Арсенът е с най-голямо съдържание и най-често срещаният елемент в пирита от лигнитите от Белобрещкия басейн. Очевидно той е основен носител на As, но също и на редица други тежки метали, като Cu, Co, Pb, Ni, Zn и Mn. В пирита се установяват още Cd и Se в минимално количество.

Ключови думи: лигнити, басейн Бели Брег, минерален състав, елементи примеси в пирит.

INTRODUCTION

The Beli Breg basin is situated in the in western part of Bulgaria and the distance from Sofia is about 50 km. Its comparatively small coal basin and gives 1.7% of the total lignite production in Bulgarian economy. The main use of the lignites from Beli Breg basin is to burn out in the Bobov Dol thermoelectric power plant (TPP) for energy production purposes. One of the basic mechanisms for entering of toxic compounds and elements into the atmosphere is coal combustion in TPPs on a large scale. Such processes are strongly connected with the type and content of mineral matter and with geochemical composition of burning coals, as well.

Detailed information regarding organic composition, biomarkers determination and environmental deposition characteristic of lignite from Beli Breg basin was reported by Zdravkov and Kortenski (2004) and Zdravkov et al. (2011). Some data regarding mineral and chemical composition of inorganic matter (Kortenski, 1993; Kortenski and Zdravkov, 2003; Markova et al., 2007) and iron disulphides precipitation stages in the coals (Kostova, 2006) have been also reported.

The goal of the present investigation is to perform detailed mineralogical study of inorganic matter of coals from Beli Breg basin, to determine textural and morphological features of minerals and their aggregates, to do some peculiarities about mineral formation and to define the presence of some hazardous trace elements in pyrite.

GEOLOGICAL SETTING AND LITHOLOGY OF THE SOURCE ROCKS

There are two different concepts about the geological development of Beli Breg basin. Zagorchev et al. (1995) and other authors based their view on the fact that all Neogene sedimentary basins in this region belong to the West Sredna Gora tectonic unit. They take into consideration the following facts – the geographic proximity, the identity of their lithologic properties, as well as the age of the rock sequences, and considered the Beli Breg basin and the other small basins in the region as a part of the greater Sofia basin. The other concept is based on the investigations of the area development, tectonic adherence, as well as the complete study of the stratigraphic sequences, their composition, structure, genesis and age considers the Beli Breg Neogene graben-basin as a separate basin (Vatsev and Zdravkov, 2004).

The coal beds occur within the Pliocene sediments of the Lozenetz Formation (Zagorchev et al., 1995). The sediments are represented by coarse and medium-grained gravel and sands, sandy clays, sandstones, lime and sandy clays. The coal-bearing sediments are deposited in graben structure, which is part of the Burrell fault zone (Gocev et al., 1970). These sediments are deposited discordantly over a denudated Jurassic and Early Cretaceous limestones and dolomites, and Late Cretaceous terrigenous and calcareous sediments, as well as the wide spread across this region volcano-clastic sediments and volcanic lavas. The volcanic rocks are represented by tuffs, agglomerates, thin layers of limestones and sandstones, along with volcanic lavas with andesite, latite, trachybasalt and basalt composition (Zagorchev et al., 1995).

The Beli Breg coal basin contains up to 5 coal seams, but only one of them has consistent thickness, occurrence and economic importance. The thickness of this coal bed is up to 35 m, with average thickness of 12.5 m. There are two economic districts in the framework of Beli Breg basin, but nowadays just in Nedeliste district coal mining activities take place.

SAMPLING AND METHODS

The Beli Breg open-pit mine was sampled. The sampling was carried out by the channel method from the top to the bottom of coal seam and represents the whole coal bed. Six coal samples were taken.

The proximate, ultimate, sulphur forms, optical microscopy, X-ray diffraction, SEM-EDS and SEM-WDX analyses of the samples were conducted in different laboratories. Macroscopically, coal is dull, brown to gray, hard and finely stratified. The carbonate minerals often form separate aggregations or coal lenses and layers and they often change the coal colour in gray.

The proximate and ultimate analyses were carried out in the Centre of Applied Energy Research in Kentucky, USA, using the appropriate ASTM International Standards. The total sulfur and sulfur forms is determined in Sofia University by Eshka (especially for pyrite S) and other standard chemical methods. The XRD analyses of the samples were conducted with Philips PW 3710 X-ray diffractometer at the Department of Mineralogy in the Natural History Museum in London.

The coal samples, which are rich in mineral matter, were selected for the scanning electron microscope analyses. Electron probe micro-analyses (EPMA) were conducted by using instrument Cameca SX100 Electron Microprobe with two types of detectors: 5 wavelength dispersive X-ray (WDX) spectrometers and Bruker AXS 4010 XFlash silicon draft energy dispersive X-ray (EDX) detector. The samples were covered with carbon before studying in both cases. The Cameca SX100 Electron Microprobe is located at the Department of Mineralogy in the Natural History Museum in London.

SEM study, equipped with EDS for elemental analyses, was used for morphological, textural and elemental determinations of selected coal samples. In order to determine the presence and content of some hazardous trace elements (different from Fe and S) in pyrite masses and crystals scattered among the coal matter, the SEM-WDX electron microprobe unattended overnight elemental analyses of coal samples in polished sections was carried out. The concentrations of the following metals (Mn, Co, Ni, Cu, Zn, Cd, As and Pb) and Se on seven pyrite spots (represented by pyrite masses, grains and crystals) has been investigated.

The organic coal petrography has been studied by optical microscopy using LEICA DM 2500 POL microscope with reflected white and blue excitation (fluorescent) light under oil-

immersion 50x objectives. The quantitative maceral analysis has been made by single scan method (Taylor et al., 1998) at 500 points measurement.

RESULTS AND DISCUSSIONS

COAL CHARACTERIZATION, SULFUR CONTENT AND MACERAL COMPOSITION

The proximate and ultimate analyses including moisture, ash, volatile matter, total S, pyrite S, sulfate S, organic S and main elements (C, H, N, S, O) contents were made on the coal samples. The data are given in Table 1. The moisture ranges between 8.7–12.1% (adb) with an average of 10.6%. The ash contents on dry basis vary from 17.9 to 34.8% with average of 24.7%. The average volatile matter is 67.2% and ranges between 62.2–72.4% (daf). As for the rank the Beli Breg coals, they should be considered as a transition from peat to lignite according to Zdravkov and Kortenski (2004).

The average total sulfur content of coals is 1.7 wt% and vary from 1.1 to 2.2 wt%. The pyrite sulfur (0.9%) predominates in comparison with organic (0.5%) and sulfate (0.4%) sulfur which is present in lower amount. These data show that Beli Breg basin have low to medium-sulfur coals. Chou (2012) and other authors indicated that lower sulfur content is inherent for coals formed in a fluvial environment, while high-sulfur coals deposited in the environment are affected by seawater. Environmental conditions and especially pH, appear to have a dramatic effect on pyrite content (Casagrande, 1987). The high pyrite content of coals also can be observed in calcium-rich environmental deposition (Taylor et al., 1998). It can be concluded that low to medium sulfur concentration in Beli Breg coals is result from the fluvial environment and calcium-rich conditions during their deposition.

Petrographic analyses of coal samples has been done. The maceral composition is totally dominated by the macerals from the huminite group (average content 89.1%). Attrinite (avg. 41.1%) and textinite (avg. 37.1%) are the most abundant macerals and represent about 80% of all macerals in Beli Breg coals. Macerals from the liptinite group were observed using fluorescent light. The total average amount of these macerals reach to 8%. Liptodetrinite,

Table 1

Main characteristic, chemical composition and sulfur forms of coals from Beli Breg basin

Samples	Depth (m)	Proximate analysis, wt %			Ultimate analysis (daf), wt %					Sulfur content (a), wt %			
		A ^d	W ^a	VM ^{daf}	C	H	N	S	O	S _{total}	S _{py}	S _{sulph.}	S _{org.}
BB1	11.2–12.6	17.9	10.3	62.2	47.7	5.0	0.9	1.3	37.2	1.8	1.0	0.6	0.2
BB2	12.6–13.4	22.1	12.1	66.5	37.1	3.8	0.8	1.3	31.4	2.2	1.4	0.7	0.1
BB3	13.4–14.5	25.0	10.7	67.6	39.6	4.4	1.2	1.3	29.0	1.8	0.4	0.6	0.8
BB4	14.5–15.7	34.8	8.7	–	32.7	3.3	0.6	0.2	30.1	1.1	0.3	0.2	0.7
BB5	15.7–17.0	19.0	11.2	72.4	41.9	4.4	1.0	1.3	24.5	1.2	0.9	0.2	0.2
BB6	17.0–19.5	29.6	10.3	–	50.3	5.2	0.8	1.5	30.8	2.2	1.1	0.2	0.9

A – ash; W – moisture; VM – volatile matter; py – pyrite; sulph. – sulphate; org. – organic; a – analytical basis; d – dry basis; daf – dry and ash-free basis.

fuorinite and resinite predominate, while suberinite, alginate and sporinite are present in smaller quantity. Inertinite macerals were established only in minor amount (average content 3.1%). Funginite although in small amount presents in all coal samples. The peat bog depositional system was determined as limnic-telmatic rheotrophic mire, characterized by intensive mineral influx (Zdravkov and Kortenski, 2004).

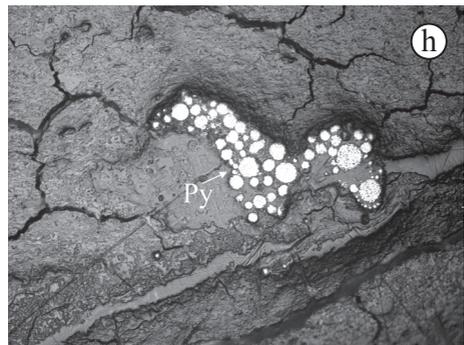
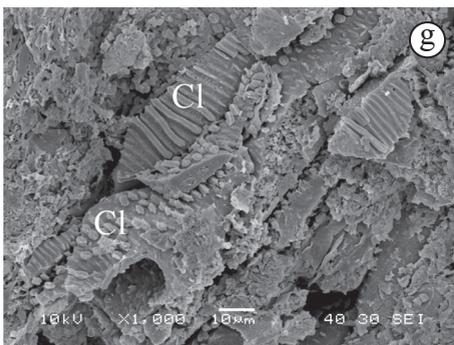
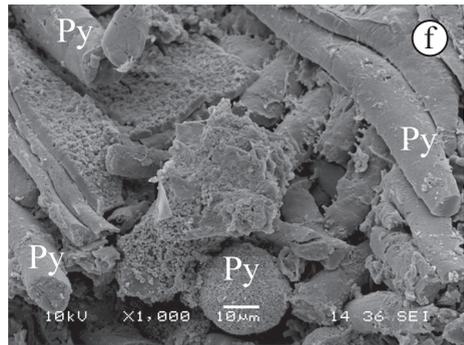
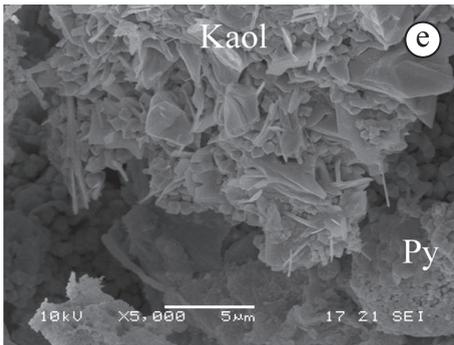
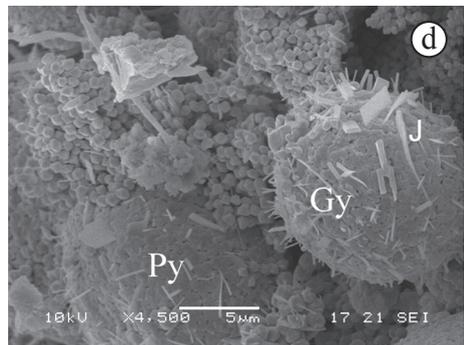
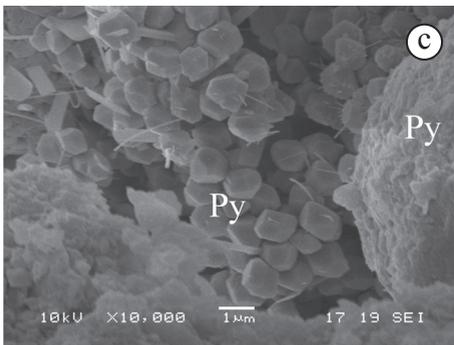
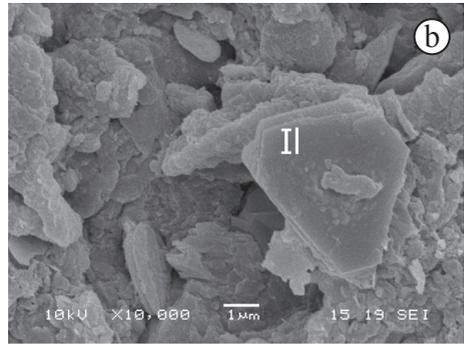
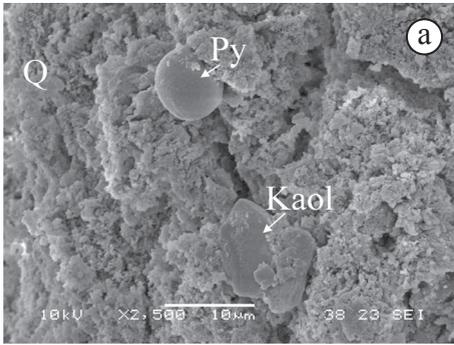
MINERALOGY

The XRD and SEM-EDS analysis were applied in order to determine mineral matter in coal. The modes of mineral occurrence within the coal seam have been investigated mainly from optical and SEM study of coal particles and polished sections, with mineral identification based on EDS data at particular points in the relevant SEM images. Typical examples of the images of the key mineral occurrences are given in figures 1, 2 and 3. The minerals identified in the samples include illite, montmorillonite, kaolinite, quartz, calcite, pyrite, gypsum, jarosite and apatite. Quartz, clay minerals (illite, montmorillonite and rarely kaolinite) and calcite are the major minerals in the studied coal samples. The pyrite is also often observed in contrast with gypsum, jarosite and apatite, which are present just in low concentrations.

Clay minerals are very common in almost all coal samples. They occur in thin-layered and massive forms, as well as fine grains and crystals closely mixed with coal macerals and other mineral matter. The clay minerals are represented by illite and montmorillonite, but sometimes kaolinite can be observed also (Fig. 1b, e; Fig. 2b, c, e). Illite and montmorillonite are the most abundant clay minerals in the coals from the lower and upper parts of the seam section (Fig. 2c). In the middle of the seam, however, the mineral matter usually dominated by kaolinite (Fig. 2b, e). Irregular to ellipsoidal aggregates of kaolinite are found in some samples (Fig. 1e), especially in the middle part of the coal bed. Aggregates with similar shape, but consisting of illite and montmorillonite, instead of kaolinite, are also visible in some samples (Fig. 1b). The illite and other minerals are often relatively well crystallized, with individual flakes, well visible under the SEM (Fig. 1b). Distinguishing between illite and kaolinite is based on the presence of small peak due to K in the EDS specimen. The same is reported by Permana et al. (2013). The main part of the clay minerals and especially kaolinite and illite has terrigenous origin and the most possible source of these matter is the source province situated around the ancient peat bog. The modes of occurrence of some clay minerals in studied coals, however, implies that the smaller amount of clay minerals (mostly montmorillonite and partly kaolinite) might be authigenic and were formed during the peat generation.

Sub-angular to rounded quartz grains with very small size, usually between 1–2 and 20 μm and closely associate with clay minerals and organic matter, have been commonly observed during the SEM-EDS analyses (Fig. 1a; Fig. 2a, b, d, f). These quartz grains are mainly of detrital origin, introduced to the peat swamp during the transition from deposition of the underlying floor strata and from the surrounding area.

The high concentration of calcite in almost all samples makes an impression. Small amount of this mineral always present in the coals, but in the studied coals the calcite reach up to 33% of total chemical composition compared with average content of 11% in other coals (Zdravkov, 2011). The high concentration of calcite in the coals can be explained with the specific limestone rich surrounding peat bog source area in which the Beli Breg coals have been deposited. The calcite occur as fine-grained aggregates (Fig. 1g), as fine-grained disseminated micro-crystals (1–2 μm) among the huminite macerals (Fig. 1g), as filling of



← Fig. 1. SEM images and optical microscopy photo of Beli Breg coals
a – mixture between fine pyrite crystals and framboid, clay minerals, quartz and organic matter (SEM);
b – well crystallized flakes of illite (SEM); *c* – association between fine-grain and well-shaped pyrite crystals and pyrite framboid (SEM); *d* – association of euhedral and framboidal pyrite and well-shaped gypsum and jarosite crystals over the framboid (SEM); *e* – close association between small kaolinite and pyrite crystals (SEM); *f* – pyrite framboid and massive pyrite infilling cell lumens (SEM); *g* – organogenic calcite dispersed among organic matter (SEM); *h* – cluster of framboidal pyrite among humodetrinite (Optical Microscope).
Abbreviations: Q – quartz; Py – pyrite; Kaol – kaolinite; Il – illite; Gy – gypsum; J – jarosite; Cl – calcite

cell structure and partially replacing plant tissue. Rarely calcite occurs as fracture-fillings. The calcite usually is autogenic, but biogenic origin is also possible.

Intimate admixture of macerals and minerals within the coals and typical mineral assemblages mainly composed of illite, montmorillonite (rarely kaolinite), quartz and calcite, which are also finely mixed with organic coal matter, can be usually observed under the optical and scanning electron microscope.

Although the framboidal pyrite predominates in Beli Breg coals, a wide range of pyrite texture, including occurrence as small individual grains, disseminated inside the macerals, as spherical crystalline aggregates and coarser grained aggregates, as well as infilling plant cell structure and replacements of the organic components can be observed. The euhedral pyrite crystals are usually very small (up to 1 μm) (Fig. 1a, c, d, e; Fig. 2a, c) and the pyrite framboids can be seen as 15–20 μm in size (Fig. 1a, c, d, e, f, h; Fig. 2a). Anhedral pyrite masses, which infill opening cell structure can be seen on Figure 1f. These textural and morphological features indicate a syngenetic origin of pyrite. The absence of marcasite indicates the presence of neutral to alkaline swamp environment conditions during the coal depositional.

How the pyrite in the studied coals has been formed? During the early diagenesis in a reducing environment, ferric iron from fluvial clays is reduced to ferrous iron, possibly by sulfate-reducing bacteria that react with hydrogen sulfide to form iron monosulfide. Iron monosulfide [FeS] is transformed by reaction with elemental sulfur through several sulfide phases: from mackinawite [FeS_{0.9}] through greigite [Fe₃S₄] to framboidal pyrite [FeS₂] (Chou (2012). There are four steps in pyrite framboid formation: (1) precipitation of an iron sulfide; (2) reaction to form greigite; (3) aggregation of greigite microcrystals; (4) replacement of greigite by pyrite (Wilkin and Barnes, 1997). Disseminated single pyrite crystals may be formed by reaction of FeS with polysulfides (Luther, 1991). Framboidal pyrite originates late in the peat stage, but before the peat is strongly compacted.

Gypsum and jarosite, although in small amount, were also detected in the studied samples. Gypsum is represented by white powdered masses, small lenses and infilling fractions among coals. The gypsum crystals are usually long-prismatic (1–2 × 5–10 μm) but sometimes short-prismatic crystals (10 × 20 μm) and rounded grains (5 × 10 μm) also can be observed. The gypsum, like the most other sulfate minerals in coal, is considered to involve the interaction between the oxidation of sulfide (especially pyrite) and carbonate minerals and the breakdown of clays. The oxidation process occurs around pyrite masses surfaces, and gypsum and other sulfates are extruded from pores and grain boundaries within and marginal to the pyrite grains (Fig. 1d). Porous or spongy-textured pyrite is more appropriate for oxidation and sulfate formation than are well-crystallized pyrite masses (Kostova, 2005). The presence of clay minerals associated with the pyrite and high humidity conditions are important factors in the oxidation of pyrite. Jarosite and other Fe sulfate minerals are usually thought to rep-

resent oxidation of sulfide components, such as pyrite, during coal exposure or storage (Rao and Gluskoter, 1973; Kostova, 2005). Similarly, in this study jarosite can be derived from the oxidation of pyrite, and gypsum was probably produced from the result of the reaction between the calcite and the sulfuric acid derived from oxidation of pyrite. SEM-EDS analy-

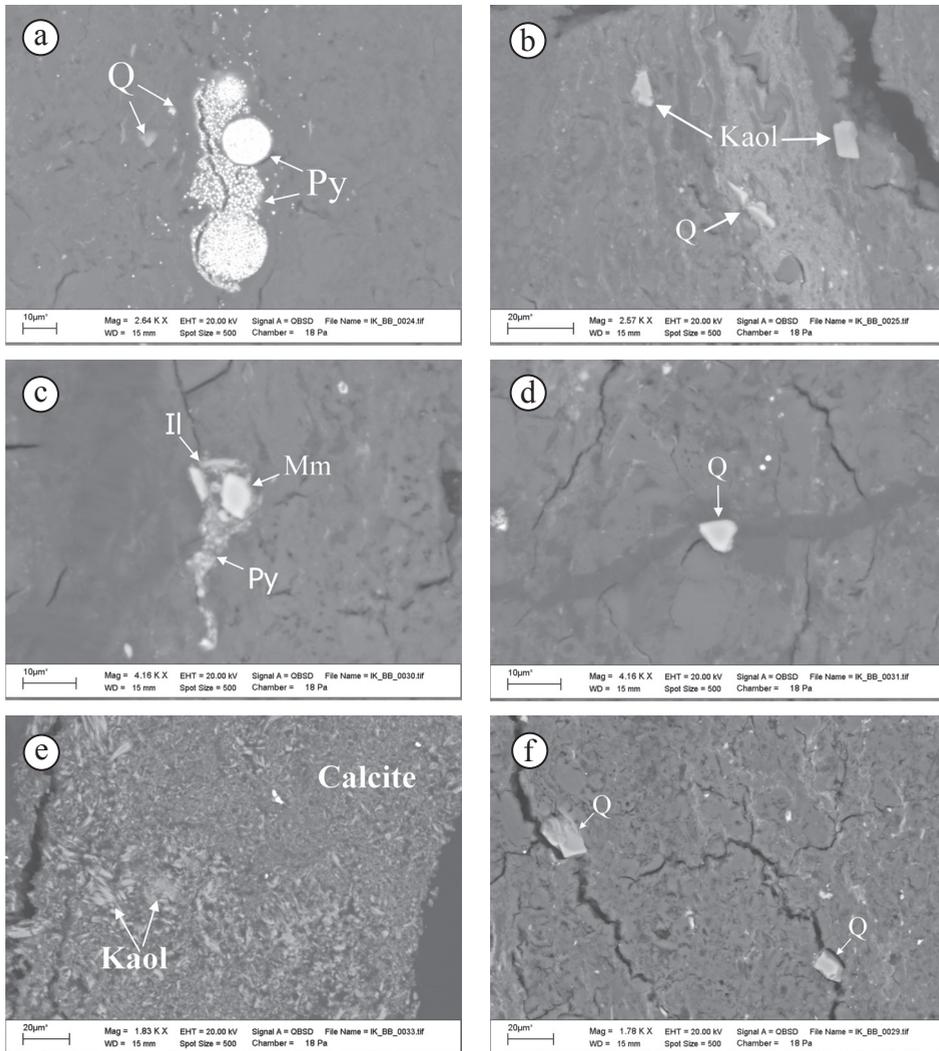


Fig. 2. SEM images of Beli Breg coals
a – cluster of framboidal and euhedral pyrite crystals and quartz grains dispersed among organic matter; *b* – kaolinite crystals and quartz grain dispersed among the organic matter; *c* – cluster of illite, montmorillonite and pyrite crystals; *d* – quartz grain; *e* – lens of well-ordered calcite and kaolinite crystals; *f* – quartz crystals among the organic matter. Abbreviations: Q – quartz; Py – pyrite; Kaol – kaolinite; Il – illite; Mm – montmorillonite

ses showed that pyrite framboids are usually surrounded by gypsum and jarosite minerals in places (Fig. 1d).

Apatite is rarely observed phosphorous mineral in Beli Breg coals and usually can be seen as infilling cell lumens, sometimes together with clay minerals (Fig. 3). Some fine-grained apatite may be present as a product from the interaction between phosphorus, released by decaying organic matter and Ca, Fe, Al and Sr in percolating solutions (Vassilev et al., 1994).

It have to be emphasized that SEM and optical microscopy studies show that a large amount of mineral matter occurs as finely dispersed particles within the organic components and especially in the pores and cell lumens of the most abundant huminite macerals. EDS analysis indicate that the minerals, infilling these spaces, are illite, kaolinite, calcite, quartz, pyrite and apatite. The same minerals, together with gypsum and jarosite, can occur either individually or as intimate mixtures with organic matter. Figure 1f and Fig. 3, for example, show pyrite and apatite infilling the cell lumens of macerals. These probably represent petri-

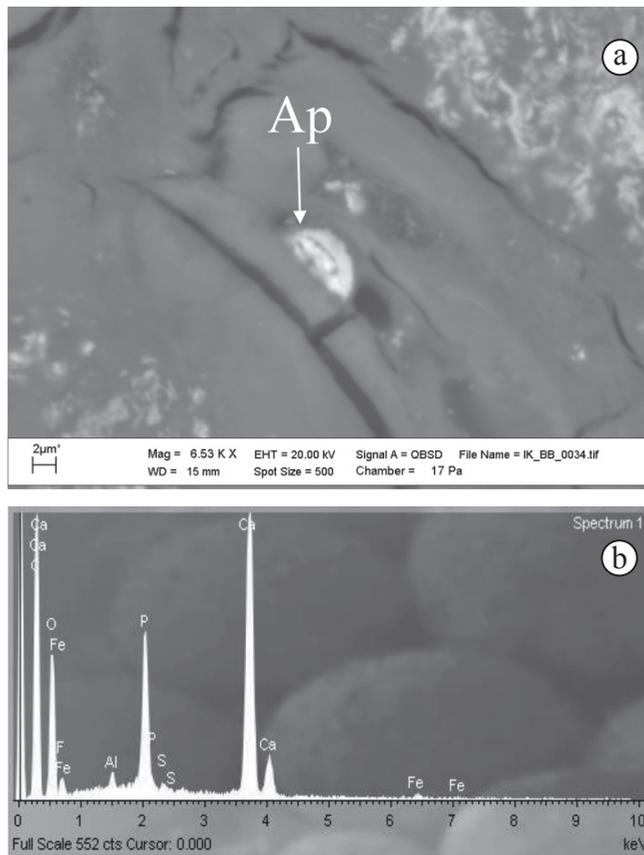


Fig. 3. SEM identification of apatite in Beli Breg coals
a – apatite (Ap) crystals which infilling plant cell structure; *b* – WDX data for apatite

fications of formed by precipitation from solution in the pores of the macerals after deposition but before compaction took place (Ward et al., 1999). The precipitation of kaolinite may be associated with changes from acid to more alkaline pH conditions within the peat. Low pH conditions under which Al becomes soluble, may have developed in parts of the peat, subject to oxidation. That would allow Al to be leached from any detrital mineral matter and transferred with the swamp water to other parts of the peat and deposit where less acid pH conditions were present. Precipitation of Al, accompanied by interaction with silica in solution, would then have allowed to form authigenic kaolinite (Spears, 1987). The apatite, which also is infilling cell lumens, may have been formed by similar process, involving interaction of Ca in solution with phosphorus, released from decomposition of the organic matter (Ward et al., 1999). Actually, the apatite may have been precipitated with the kaolinite from a pore-filling solution, containing a mixture of Al, Si, Ca and P components.

There is strong connection between the mineral matter of Beli Breg coals and the mineral composition of sedimentary source rocks. Zdravkov et al. (2011) consider that the coals of Beli Breg basin were generated in a limnic-telmatic depositional environment, characterized by intensive mineral influx and a high density of mixed forests (coniferous and deciduous trees) and bushes, ferns, algae and grasses vegetation, under a temperature climate and possible rheotrophic conditions. The lithological composition of the sedimentary rocks from the feeding peat bog province is represented mainly by quartz, clay minerals and calcite and its very similar to the main mineralogical composition of Beli Breg coals, excepted with pyrite and other trace minerals, which have greater amount in coals.

SOME HAZARDOUS TRACE ELEMENTS RELATED WITH PYRITE

In order to determine the presence and concentrations of some trace elements, different from Fe and S, in pyrite masses, grains and crystals, electron probe micro-analyses altogether with 5 wavelength dispersive X-ray quantitative analysis (EPMA-WDX) for Mn, Co, Ni, Cu, Zn, Cd, As, Se and Pb have been applied on the seven pyrite spots in the studied polished coal samples. The results were obtained using instrument Cameca SX100 Electron Microprobe. Five framboidal pyrite masses, that predominate in studied samples, and two euhedral pyrite crystals have been analyzed.

The data from electron microprobe quantitative analyses are present in Table 2. Arsenic is the most common enriched minor constituent in the studied pyrite from Beli Breg lignite with the highest concentrations up to 0.2 wt%. The transition metals Cu, Co, Pb, Ni, Zn, Mn and Cd often present in the studied grains in smaller amount. Selenium also occurs in pyrite, but typically in very low concentrations (usually about 0.01 wt%).

The results of the study show that pyrite, one of the most abundant mineral in Beli Breg lignite, obviously represents important carriers of number of minor or trace constituents, the presence of which reflects substitution in the Fe disulfide crystal structures, for either S or Fe.

It considers that elements like As and Se substitute S in the pyrite structure, whereas metals, including transition metals, Pb, Zn, Cu, Co, Mn, Ni and Cd, are thought to substitute Fe. According to Abraitis et al. (2004) based on favorable size and charge characteristics, Co^{2+} , Ni^{2+} , Cu^{2+} and similar divalent cations undergo stoichiometric substitution for Fe^{2+} in six-fold coordination in the pyrite structure. Similarly, substitution of Se^{2-} for disulfide is stoichiometric. Like Se, As^{3-} (group V-A metalloids) shows geochemical affinity for sulfur, and the anion undergo non-stoichiometric substitution for S (Abraitis et al., 2004). Alternatively, it is been proposed that substitution for disulfide occurs as molecular ions, such as $(\text{As}_2)^{2-}$ or

Table 2
Electron microprobe trace elements determinations in Fe disulfides (pyrite) in Beli Breg coals and comparison with other worldwide coal (in weight % or in ppm) (after Kolker, 2012)

Mineral	Co	Ni	Cu	Zn	As	Se	Pb	Cd	Mn	Method/Ref.
Pyrite	dl-0.07	dl-0.05	0.03-0.09	dl-0.02	0.07-0.20	dl-0.01	dl-0.06	dl-0.05	dl-0.05	EPMA ^A
Pyrite	-	-	-	-	dl-1.5	dl-0.20	-	-	-	EPMA ^B
Pyrite	-	-	-	-	0.06-1.9	-	-	-	-	EPMA ^C
Pyrite	-	-	-	-	dl-3.5	-	-	-	-	EPMA ^D
Pyrite*	dl-2300**	dl-4500**	-	-	dl-4.9	dl-1000**	-	-	-	EPMA ^E
Pyrite*	dl-0.16	dl-0.16	dl-0.16	dl-0.04	dl-2.68	dl-0.06	dl-0.04	-	-	EPMA ^F
Pyrite	-	-	0.02-0.12	-	1.03-5.76	-	-	-	-	EPMA ^G
Pyrite	dl-0.29	0.03-1.37	dl-0.79	dl-0.05	dl-0.92	dl-0.14	-	-	-	EPMA ^H

* - Pyrite is dominated, but pyrite and marcasite are not distinguished; ** - in ppm; dl - concentration is at or below detection limit; ^A - data for studied Beli Breg coals.

Reference / Coals studied:

- Minkin et al., 1984^B - Upper Freeport coal, Pennsylvania;
 Ruppert et al., 1992^C - Upper Freeport coal, Pennsylvania;
 Ruppert et al., 2005^D - Fire Clay coal bed, Kentucky;
 Kolker et al., 1997^E - U.S. coals from Appalachian, Eastern Interior, and Powder River basins;
 Kolker and Huggins, 2007^F - Warrior field, Black Warrior Basin, Alabama, Springfield coal, Indiana, Pittsburgh coal;
 Ding et al., 2001^G - Southwestern Guizhou Province, China;
 Belkin and Luo, 2008^H - Lower Cambrian black shale (stone coal), Guizhou Province, China.

(AsS)²⁻ (Blanchard et al., 2007). Arsenic and selenium occupy the same structural location in pyrite by substituting sulfur.

The pyrite in coal has a several stages of formation history, which include early diagenetic, coalification, and post-coalification events, and substitution of minor constituents is a function of processes operative during each stage. Kolker (2012) reported that for early-formed Fe disulfides, such as framboidal pyrite, substitution of minor constituents may be controlled by bacterial mediation together with the suitability of precursor monosulfide crystal structures for elemental substitution. The presence of transition metals, that usually accommodate in Fe disulfides, is consistent with complexing of metals in anoxic sediments and derivation of framboidal pyrite from greigite (Fe₃S₄), an Fe monosulfide precursor to framboidal pyrite, having the thio-spinel structure (Kolker, 2012). The framboidal pyrite is the most common pyrite form in Beli Breg lignite and might be the elements Pb, Zn, Cu, Co, Mn, Ni and Cd, that have been detected in its crystal structure, are adopted during the early diagenesis of coal and framboidal pyrite formation according to the model, described by Kolker (2012).

The similar data for the presence of some of the elements in pyrite in coals from all over the world are given in Table 2. In comparison with other reported data, the concentrations of Se, Co, Ni, Cu and Zn in pyrite from Beli Breg basin are lower and the concentrations of As and Pb are on the same level or bigger than the others.

The presence of detected minor and trace elements in the crystal structure of pyrite have attitude to all aspects of coal utilization and especially with entering of hazardous elements into the atmosphere during coal combustion in power plants and with the oxidation and self-heating processes that pass in coals. Substitution of impurities for Fe or S influences the electrical properties of pyrite and is causing defects in the crystal structure that result in positive or negatively charged entities (Abraitis et al., 2004). Lehner and Savage (2008) report that even small amounts of impurities can influence the electrical properties of pyrite, which in turn influence the rate of pyrite oxidation. Thus, substitution of minor elements in pyrite not only influences the releasing of elements considered as hazardous air pollutant after coal combustion, it also accelerates the oxidation of Fe disulfides in coal and coal waste products, thereby releasing in the environment acidic drainage and substituted minor constituents. Additionally, pyrite oxidation reactions are exothermic, and together with associated heat-generating oxidation reactions in coal, contribute to self-heating that may result in spontaneous combustion of coal in storage, waste piles and mines (Nalbandian, 2010).

It can be concluded that pyrite is one of the most abundant and widespread mineral in Beli Breg lignite and it exerts considerable control over the elements present, including many elements of environmental interest, such as As, Se, Cd, Pb, Zn, Cu, Ni, Mn and Co.

CONCLUSIONS

The lignite from Beli Breg basin has medium to high ash content and is with low to medium sulfur concentration. Petrographic analyses show that macerals from huminite group totally dominate (average content 89.1%), represented mainly by attrinite and textinite and macerals from liptinite and inertinite groups present in rather smaller amount. The minerals identified in the samples includes illite, montmorillonite, kaolinite, quartz, calcite, pyrite, gypsum, jarosite and apatite. Quartz, clay minerals and calcite are the major minerals in the studied coal samples. The pyrite is also often observed in contrast with gypsum, jarosite and apatite which are present in low concentrations. Clay minerals occur in thin-layered and massive forms, as well as fine grains and crystals closely mixed with coal macerals and

other mineral matter. The clay minerals are represented by illite and montmorillonite, but sometimes kaolinite can be observed also. Most clay minerals and especially kaolinite and illite have terrigenous origin, but the modes of occurrence of some clay minerals, however, implies that the smaller amount of clay minerals (mostly montmorillonite and partly kaolinite) are may be authigenic.

Quartz grains with very small sizes are closely associated with clay minerals and organic matter. They are mainly of detrital origin. High concentration of calcite (up to 33%) in almost all samples was observed. It can be explained with the specific limestone rich surrounding peat bog source area in which the Beli Breg coals have been deposited. The calcite occurs as fine-grained aggregates, as fine-grained disseminated micro-crystals among the huminite macerals, as filling of cell structure and partially replacing plant tissue. The calcite usually is autogenic, but biogenic origin is also possible. Framboidal pyrite predominates, but a wide range of pyrite texture, including occurrence as small individual grains disseminated inside the macerals, as spherical crystalline aggregates and coarser grained aggregates, as well as infilling plant cell structure and replacements of the organic components, can be observed also. Gypsum and jarosite, although in small amount, were also detected. Gypsum is represented by white powdered masses, small lenses and infilling fractions among coals. Jarosite usually occurs as infilling cell lumens. Apatite is rarely observed phosphorous mineral and usually can be seen as infilling cell lumens, sometimes together with clay minerals.

Intimate admixture of macerals and minerals within the coals and typical mineral assemblages mainly composed of illite, montmorillonite (rarely kaolinite), quartz and calcite, which are also finely mixed with organic coal matter can be usually observed.

Backscattered electron imaging, altogether with quantitative analyses by electron microprobe for Mn, Co, Ni, Cu, Zn, Cd, As, Se and Pb have been applied on the seven pyrite spots. The data show that As is the most common enriched minor constituent in the studied pyrite from Beli Breg lignite, with the highest concentrations and at the weight percent level on a grain scale. Obviously, the pyrite is the most important carrier of As, but also of a number of heavy metals like Cu, Co, Pb, Ni, Zn and Mn. Cadmium and selenium also present in very small amount in some studied pyrite grains.

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