Inorganic Chemical Chracterization of the Bitola, Oslomej, and Berovo Coals and their Waste Products from Burning, FYROM

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ABSTRACT: The coals are the main and dominant energy resource in FYROM. The mineral and inorganic chemical composition of two types of samples have been studied from the Oslomej, Bitola and Berovo lignite coals and their products generated from the Oslomej and Bitola thermo-electric power stations (TEPSs). They include low-grade coals (coals for TEPS) and solid wastes (fly ashes and bottom ashes). The minerals identified in the lignites include quartz, kaolinite, illite, K-feldspar, plagioclase, amphibole, smectite, pyrite, and others. The phase composition of waste products is represented by glass, quartz, albite, magnetite, gypsum. The concentration and behaviour of 43 elements have been also tested. All of the ash-forming elements (Si, Al, Mg, K, Ca, Fe, C, P, S, Ti, and Mn) are present in varying concentrations in the lignites and waste products. The trace elements enriched in coals (Mo, Sc, Pb, Cr, Y, Zr, Ti, Zn, and V) and waste products (Nb, Mn, Sb, Hg, Y, and Cd) normally have low over Clarke values. The data obtained is topical and pioneer for the former Yugoslav Republic of Macedonia.
KEY WORDS: coal, mineral matter, trace elements, waste products, FYROM.

Introduction

The Macedonian coals are lignites. The major coal deposites are "Suvodol", "REK Oslomej" and "Berovo–mine Brik". The coals have been mined in the open casts.

The *thermo-electric power stations* = TEPSs are energetic enterprises in FYROM. Both of them are the major "Bitola" and "Oslomej" TEPSs. The "Bitolia" TEPS has 1200 MW power capacity (3 units × 350 MW). It was built up with Russian equipments in 1978. The stack chimneys and cooling towers have heights of 250 and 120 m, respectively. This TEPS burns lignites originated from the open-cast "Suvo Dol". About 6 million tons of coal are burned annually in the "Bitolia" TEPS. The coal-combustion process is conducted at 900–1300 °C. The *bottom ash*=BA is highly abundant in unburned coal material and this product is combusted again in the boilers. The "Oslomej" TEPS use the Rek Oslomej coals for combustion.

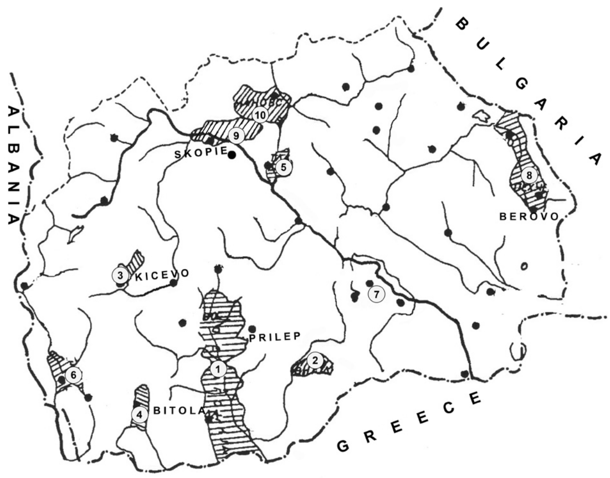
After sieving, the Berovo coal is used for: (1) coarse-grained fuel for domestic use, (2) medium-grained fuel for heating of public buildings; and (3) fine-grained fuel for briquettes.

The major purpose of this paper is to characterize the concentration of some trace elements such as Ge, U, W, V, and others in some Macedonian lignite coal deposits.

Geological setting

Macedonia lies within the Cenozoic Southern Balkan Extensional regime that forms the northern part of the more regional Aegean extensional regime (Dumurdzanov et al. 2004).

The first data for the „Suvodol" lignite were reported in 1965, however, the most significant investigations of this coal were conducted in the period 1971–1973. The present resource recovery potential of this lignite in the deposit was estimated at 175 million tons. Suvodol open coal deposit is a part of Pelagonian graben (Fig. 1). The graben is located in the Southern Macedonia and in the Northern Greece. It is ~100 km long and up to 25 km wide. The basal rocks in this coal basin are composed of Cambrian metamorphic rocks (mica schists, gneisses). The Pelagonian Formation consists of ~600 m of terrigenous coal-bearing strata that can be divided into three superimposed lithological units. The basal unit consists of gravel, sansdone and silty claystone. This unit is 150–200 m thick in the part of the graben around Prilep, and 400–500 m thick in the part around Bitola. The age of



■ **Fig. 1.** Location of the coal basins in Macedonia by Andreevski (1995). (1) Pelagonian basin; (2) Mariovo basin; (3) Kicevo basin; (4) Prespa basin; (5) Katlanovo basin; (6) Strumica basin; (7) Tikves basin; (8). Delcevo-Pehcevo-Berovo basin; (9) Skopje basin; (10) Kumanovo basin.

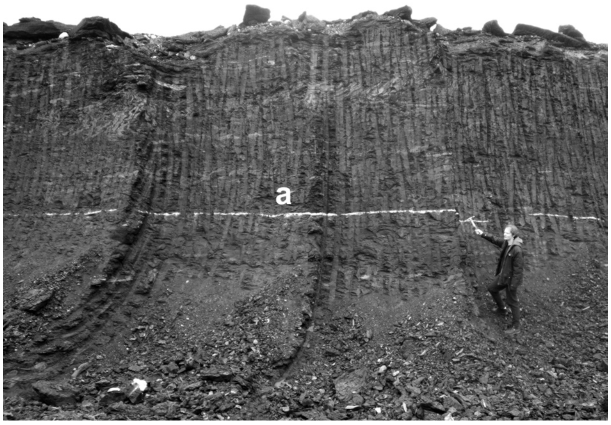
these strata is unknown. The coal-bearing unit consists of interbedded siltstone, silty claystone and a few coal bearing layers. In the Bitola area are two levels of coal-bearning strata, up to 58 m thick, with numerous coal layers. There is no direct evidence for the age of the strata, but correlation with the similar strata in the Kicevo, Tikves, Mariovo, and Skopje grabens suggests they are probably of Meotian age. The upper unit, consists of diatomite, siltstone, and claystone. Silicified sediments cover this seam as a result of activity of the "Kozuv" volcano. The roof part of the section is covered by Quarternary sediments (Dumurdzanov et al. 2004). The Pelagonian coal basin fills 1,500 km^2 area and is the largest in Macedonia (Andreevski 1995).

"Oslomej" open coal deposit is a part of the Kicevo graben (Fig. 1). The first investigations dated in 1957, while the industrial coal production started in 1973. The coal reserves in the eastern and western parts of the deposit are estimated at about 21 and 11 million tons, respectively. About 1.2 million tons were mined annually from the deposit. The Kicevo graben consists of two minor depressions. The basal rocks in the deposit are composed of Paleozoic schists. Lacustrine strata are horizontal and are of late Miocene, Pliocene, and Quaternary ages. The total sequence is 360 m thick. The Pelagonian Formation, typically known from the Pelagonian graben, consists of three superimposed lithological units. The lowest unit consists of 80 m of proluvial-alluvial gravels overlain by lacustrine sandstone and claystone. Age of the strata is unknown. The middle unit is composed of 50 m of coal-bearing claystone, siltstone, and few coal layers. The upper siltstone and claystone unit is ~100 m thick. In its lower part and in the siltstone below an upper coal layer, a diatomite flora is present (Dumurdzanov 1997, Dumurdzanov et al. 2004). It is very characteristic for the late Miocene (Ognjanova-Rumenova 2000). The roof sediments include aleurolites, thin coal layers without industrial significance, clays and Quarternary sediments (Dumurdzanov et al. 2004).

"Berovo" open coal cast is a part of the Delcevo-Pehcevo and Berovo grabens (Fig. 1). The grabens are located in the southeastern Macedonia. The filling of these grabens is very similar. The NE-SW-trending Berovo graben extend 15 km south from the Bukovik volcano that forms the boundary with the Decevo-Pehcevo graben. The sedimentary fill of the graben crops out across ~6 km width, but the sedimentary section near the "Brik"-Berovo coal mine and other smaller relicts of Neogene sediments to the south and west suggest that the area of the basin was much larger. The sedimentary section in the Berovo graben is more than 500 m thick and is composed of two formations and Quarternary sediments. The Pancarevo Formation is ~330 m thick and its stratigraphic section is similar to that of the same formation in the Delcevo-Pehcevo graben. Three superimposed lithological subunits are present in the Pancerevo Formation. The basal 125 m thick unit of gravel, sandstone, and claystone is very similar to the basal unit the Delcevo-Pehcevo graben. The middle coal-bearing unit is ~100 m thick and is composed of siltstone, grey and green-grey claystone, and 1–2 layers of coal developed at the SW margin of the basin at the "Brik" mine. The upper unit consists of ~100 m of interbedded sandstone, siltstone, and claystone. (Dumurdzanov et al. 2004). The uppermost part contains planktonic diatoms that belong to late Miocene (Ognjanova-Rumenova 2000). The presence of the kaolinitic claystone, diatomite, and rare occurrences of bituminous siltstone could be related to sedimentation following the activity of the Bukovik volcano, but the age of this volcano has not been determined (Dumurdzanov et al. 2004).

Material and methods

The tested samples are original and they include: lignite coals, *fly ash* = FA, BA, and partings (Figs. 2 and 3). The samples were collected from natural disclosures and storages. Each composite sample (weight from 3 to 5 kg) consists of 10 or 15 individual samples. The coarse samples have been broken to small pieces. Each sample has been dried at 40 °C. The applied methods were: (1) Macroscopic observations; (2) *Powder X-ray diffraction* = XRD. XRD patterns were recorded on DRON 3M diffractometer with iron-filtered CoKα radiation and standard cylindrical specimen holder; (3) Chemical analyses. The concentrations of major and trace elements of the bulk rocks had been determined by ICP-AES and ICP-MS after tri-acid digestion of each sample in HNO_3-HF-$HClO_4$. Inorganic carbon was measured by a volumetric method. Total carbon and total sulphur were measured by combustion method. Detection limits of elements are: inorganic C – 0.05 %, total C – 0.01 %, total S – 0.01 %, SiO_2, Al_2O_3,



■ **Fig. 2.** Suvodol open mine.(a) Thin (15–20 cm) white seam in the coal layers.

■ **Fig. 3.** Oslomej open mine.

Fe_2O_3, CaO, and MgO – 1 %; K_2O – 0.5 %; MnO and TiO_2-0.01 %; P_2O_5 – 100 mg/kg (ppm); Ga, Ge, Hg, Th and U – 0.1 mg/kg; Sc, and Se – 0.01 mg/kg; Li, B, V, Cr, Sn, Sb, Ba, Ce, W, Pb, Ni and Bi – 10 mg/kg; Co, Cu, Zn, Sr, and Mo – 5 mg/kg; Be and Cd – 2 mg/kg; As, Y, Nb, La, and Zr – 20 mg/kg; A – 0.2 mg/kg. The high-temperature ashes have been produced from coal combustion at 450 °C. The analyses had been done in laboratories of BRGM (Orleans, France) with the exception of the XRD. The powder X-ray diffraction had been done in the Central Laboratory of *Mineralogy and Crystalography – Bulgarian Academy of Sciences* = CLMC-BAS in Sofia, Bulgaria.

Results and discussion

Organic matter

Bitola,"Suvodol" lignites. The mined lignite is mixed preliminary to produce homogeneous fuel mixture of 1,000–l,100 kcal/kg. The lignite has ash yield about 51 % and the contents of S_{total} are 0.25–0.60 % (according to oral reports). The macroscopic observations show that this lignite has brown, black and yellow colors and reveal an initial stage of coalification. According to ICCP, 1993 in Taylor et al. (1998) for lithotype classification, the Bitola lignite could be characterized as matrix coal. The heterogeneous lithotypes as humoclarain and liptain as well as the homogeneous lithotypes as xylain and semifusain/fusain (Šiškov and Valčeva 1983, Šiškov 1997) have been recognized in the lignite. Clay minerals and some plant remains have been also observed as inclusions in the fuel.

"REK Oslomej" lignites. The major coal characteristics include 16–18 % A^d, 48–50 % W^a, 0.25 % S_{total} (by oral reports). This fuel has been used for combustion in the "Oslomej" TEPS. The macroscopic observations show that these mat coals are of brown, dark brown and yellow colors and the individual lithotypes are unrecognizable. They are in an initial stage of coalification and they could be classified as matrix coal (Taylor et al. 1998). Grass and reed marks from lake-swamp plants have been identified on the stratigraphic layer surfaces when the coal samples were fragmented. The coal fragments have beige-brown color and are similar to xylain (Šiškov and Valčeva 1983). Fine stripes of branch remains with thickness of several millimetres had been also observed. They note an initial stage of vitrainization.

"Berovo" lignites. The macroscopic observations show that these lignites are matrix coal (Taylor et al. 1998). They are of gray-black, brown and yellow colors. Coarse wood fragments with well-preserved cellular structures had been observed in the coals. The homogenous lithotypes as xylain, humovitrain and fusain/semifusain as well as the heterogeneous lithotypes as humoclarain and liptain (Šiškov and Valčeva 1983, Šiškov 1997) have been recognized in the coal. An initial stage of vitrainization has been also recognized. Some of the established humovitrain lenses have high hardness and high brittleness. It could be supposed that these lenses are thermally influenced (Yossifova 2007, Yossifova et al. 2007) or these changes originated as a result of a perhydrogenation (Suárez-Ruiz et al. 1994). The semifusain and fusain, 1–2 cm thin, have been established to form lenses and layers.

Some coal layers that underwent spontaneous combustion (clinker and paralava) were also identified in some areas of the coal basin.

Mineral matter

The dominant identified minerals in Macedonian coal belong to silicates (Table 1). The phase composition of the FA and BA is represented by original lignite minerals and newly formed min-

Samples	Minerals/Phases
Mac 05-7. Feed coal for TEPS. Suvodol coals.	quartz, pyroxene (M); plagioclase, kaolinite[1] (m); gypsum (A).
Selected coal pieces.	amourphous phase – organic matter.
White seam in the coal layers (Fig. 2).	plagioclase, amourphous phase – glass? (M).
Mac 05-2. FA and BA. Bitola TEPS.	
1) FA.	quartz, albite, diopside (M); magnetite (m).
2) BA.	quartz, amourphous phase – glass (M); albite (m).
Mac 05-22. Feed coal for TEPS. Oslomej coals.	quartz, kaolinite, illite (M); K-feldspar (m).
Host rock.	quartz (M); muscovite, albite, chlorite (m).
Mac 05-23. FA from the Oslomej TEPS (the sample was taken from the conveyor belt).	quartz, amourphous phase – glass (M); albite (m); magnetite (A).
FA sample, taken from the storage.	quartz (M); albite (m); gypsum (A).
Mac 05-24. Composite sample of the Berovo coal.	–
Mac 05-35. Host rock.	–

M – *major mineral* > 3 %; m – *minor mineral* 1–3 %; A – *accessory mineral* < 1 %; [1] – fine dispersed phase

■ **Tab. 1.** Mineral composition of the Macedonian lignites, waste products and partings by X-ray data (%).

erals and phases generated during the combustion process (glass, magnetite, diopside?) or storage of FA (gypsum).

Yossifova and Valčeva (2008) found out that the dominant minerals in the Berovo coals and host rock are: kaolinite, quartz, pyrite, plagioclase, amphibole, smectite/halloysite and accessory opal. The opal, probably of syngenetic origin, was established in xylain and liptain lithotypes. High-temperature and fumarolic phases such as crystobalite, tridymite, maghemite, cordierite, opal-crystobalite-tridymite, and others newly formed phases were established in the clinker and paralava.

Geochemistry

The detected concentrations of elements in the coal samples studied have been compared to the respective Clarke values for lignite and subbituminous coals (Yudovich et al. 1985, Yudovich and Ketris 2005). The detected contents of elements in the coal samples with ash yield >50 %, coal shales and samples highly enriched in mineral matter have been compared to the respective Clarke values for shales and sediment rocks (Beus and Grigorian 1975, Vinogradov 1962).

The contents of 43 elements and their *enrichment/depletion factor* = EDF, based on the respective Clarke value are listed in Tables 2, 3 and 4.

Bitola coals

The lignite sample Mac 05-7 with ash yield of 35.7 % was studied. Major elements (> 1 %) are Al, Ca, C, Si and Fe, whereas minor elements (1–0.1%) are K, S and Ti in the sample. Eighteen elements (C, Mo, Mn, Sc, Zn, Cr, Ti, S, Be, Zr, Ba, Th, U, V, Co, Ga, P, Cu, and Ni) were found higher than Clarke concentrations (Table 2). However, only four trace elements have EDF > 2. The highest enrichments shows the element Mo (5.7).

The sample studied, namely Mac 05-2, is a composite sample of BA and FA. The bulk fly ash sample includes portions collected from each of the forth-electrostatic precipitators. Major elements (> 1 %) are Mg, Al, K, Ca, C, Si, and Fe, whereas minor elements (1– 0.1 %) are P, S, Ti, and Mn. It was found that four trace elements (Nb, Mo, Cr, and Sc,) in this sample were found higher than Clarke values but they show relatively low enrichments with an exception of Nb (Table 5).

REK Oslomej coals

The coal sample Mac 05-22 with ash yield of 33.6 % was studied. Major elements (> 1 %) are C, Si, Ca, Al and Fe, whereas minor elements (1–0.1 %) are K, S and Ti. It was found that 19 elements higher than Clarke values (Table 3). Elements such as C, Pb, Sc, S, Cr, Y, Zr, Ti, Mn, Zn, V, Ni, Co, Ba, and Cu have EDF > 2 as the most enriched trace elements are Pb, Sc, Cr, Y, and Zr.

The sample Mac 05-23 composes FA. Major elements (>1 %) are Mg, Al, K, Fe, Ca and Si, whereas minor elements (1–0.1 %) are C, P, S and Ti. This composite sample has 17 elements with over Clarke contents as 7 elements from them have EDF >2. The elements that reveal the highest enrichment in the sample are Nb, Sb, and Hg. It should be noted that Hg also shows significant enrichment, namely 3.4 times higher than the Clarke value (Table 5).

Berovo coals

The coal sample Mac 05-35 with ash yield of 19.6 % was studied. Major elements (> 1%) are Al, Ca, C, Si, Fe and S, whereas minor elements (1-0.1%) are Mg, P and Ti (Table 4). It was found that eleven elements in this sample (C, Pb, P, S, Mn, Cr, Ti, Ba, Co, V, and Ni) are higher than Clarke values (Tables 4 and 5). Three trace elements have EDF > 2 as Pb (17.8) and P (9.9) are much higher than Clarke values.

The sample Mac 05-24 with ash yield of 97.09 % was also studied. Major elements (> 1 %) are Mg, Al, Ca, Si, and Fe, whereas minor elements (1–0.1 %) are K, C, P, S, Ti and Mn. The concentration of elements in this sample had been compared to Clarke values for shales (Beus and Grigorian 1972). It was found that sixteen elements (Cd, As, P, Fe, Ca, Ag, Mn, Co, Ti, Sn, Y, Mg, Sc, V, Cr, and Ge) have over Clarke contents in this sample. Four of them have EDF > 2 as Cd, As, P, and Fe shows the highest enrichment (Table 5).

Probably the dominant phases are Fe oxide/hydroxide and silicates in the sample Mac 05-24. It could supposed that some of the elements such as Cd, As, P, Ag, Mn, Co, Ti, Sn, Cr are impurities in the Fe oxide/hydroxide phase/mineralization.

Conclusion

The silicate minerals as quartz, pyroxene, plagioclase, clay minerals, mica and others are dominant in Bitola, Oslomej and Berovo lignite coals and their host rocks. These minerals are detrital as it concerns the coal genesis but for some of them it could be supposed having autigenic origin (quartz) or they are a product of weathering (mica). The clay minerals are represented by abundant kaolinite and less common illite for Bitola and Oslomej coals, while smectite/halloysite mineralization is dominant in Berovo coals. Probably their origin is both detrital and autogenic. Kaolinite characterizes an acidic environment in Bitola and Oslomej basins, while the occurrence of a more alkaline environment in the Berovo coal basin could be indicated by smectite presence.

All of the ash-forming elements (Si, Al, Mg, K, Ca, C, Fe, P, S, Ti, and Mn) are present in varying concentrations in the Macedonian lignite and combustion waste products. According to sulphur contents, the coals studied could be characterized as low-sulphur coal (Oslomej and Bitola coals). Berovo coals are characterized by higher contents of total sulphur (1.51 %) as a result from the pyrite presence.

Trace elements such as Mo, Sc, Zn, Cr (Bitola coals); Pb, Sc, Cr, Y, Zr, Ti, Zn, V, Ni, Co, Ba, and Cu (Oslomej coals); as well as Pb, P, Cr, and Ti (Berovo coals) exceed Clarke concentration more than two times. The trace elements enriched in waste products are: (1) Nb, Mn, P, Mo, and Ti for FA and BA from "Bitola" TEPS; and (2) Nb, Sb, Hg, Y, Ti, Zr, Sc, Cu, Cr, Mn, V, Zn, Th, Ni, Ga, Co, and Pb for FA from "Oslomej" TEPS. The REK Oslomej coals and their wastes are described with the greatest number of trace elements higher than Clarke values.

Element[1]	Clarke[2] Coal	Coal ash	Mac 05-2 FA and BA	EDF[3]	Mac 05-7 Coal	EDF[3]	Mac 05-7 Coal ash
Lithophilic elements							
Li	20±7	80±15	50		21	1.0	59
Be*	1.2±0.1	6.7±0.5	5		2	1.7	6
Mg**	1.50 %		2.0 %		<0.6 %		
Al**	8.65 %		9.5 %		3.5 %		9.9 %
K**	2.70 %		1.4 %		0.7 %		1.9 %
Ca**	2.0%		7.8 %		1.4 %		3.8 %
Sr	130±24	1100±310	685		131	1.0	367
Y	7.0±1	37±6	29		<20		
Zr	30±3	160±20	157		52	1.7	146
Nb	1.0±0.4	5.0±4.0	31	~1.0	<20		
Mo*	2.1±0.2	14±1	21	6.2	12	5.7	34
Ba	120±18	890±220	594	1.5	209	1.7	585
La**	92		43		<20		
Ce**	59		100		39		109
W	2-6		<10		<10		
Radioactive elements							
Th*	3.8±0.2	19.±1	17		6.5	1.7	18
U*	2.1±0.3	15±1	8.5		3.5	1.7	10
Non-metals							
B*	56±3	410±30	91		12		34
C** (total)	1.2 %		1.6 %		9.82 %	8.2	
C (min.)			0.16 %		<0.05 %		
C (org.)			1.44 %				
Si**	27.5 %		22.3		7.6		21.2
P*	220±30	1200±100	2050	1.7	310	1.4	880
S**(total)	0.24 %		0.54 %		0.43 %	1.8	
Siderophilic elements							
Sc	2.0±0.4	15±2	17	1.1	6	3.0	17
Ti	500±30	2600±300	4000	1.5	1000	2.0	3800
V*	22±2	140±10	144	1.0	38	1.7	106
Cr*	15±1	82±5	105	1.3	37	2.5	104
Mn*	100±5	520±30	2790	5.4	465	4.7	1320
Fe**	4.80 %		4.9 %		1.7 %		4.7 %
Co*	4.2±0.3	27±1	21		7	1.7	20
Ni*	9.0±0.9	53±5	50		12	1.3	34
Chalcophilic elements							
Cu*	14±1	72±4	70	~1.0	20	1.4	56
Zn*	18±1	110±10	86		51	2.8	143
Ga	7±1	36±4	29		11	1.6	31
Ge	1.5±0.3	9±3.7	2.9		1.1		3.0
As*	7.4±1.4	49±8	22		<20		
Se*	1.1±0.15	9.3±0.7	<1.0		<1.0		
Cd*	0.24±0.03	1.0±0.14	<2		<2		
Sn	1±0.2	4.1±2.8	<10		<10		
Sb*	0.82±0.06	4.4±0.4	<10		<10		
Hg*	0.1±0.01	0.58±0.06	<0.1		<0.1		
Pb*	6.7±0.4	39±2	11		<10		
Bi*	0.92±0.09	5.7±0.7	<10		<10		
Noble metals							
Ag	0.3±0.1	1.0	<0.2		<0.2		
Ash yield (%)			97.99		35.7		

[1] Mineralogical classification of elements (Solodov et al. 1987)
[2] Clarke for lignite and subbituminous coals (Yudovich et al. 1985)
[3] Enrichment/depletion factor, ratio of the element content in coal to the Clarke value
* Clarke for lignite and subbituminous coals (Yudovich and Ketris 2005)
** Clarke for shales (Beus and Grigorian 1975)

■ **Tab. 2.** Element concentration (ppm) in Bitola, Suvodol coals and their wastes from the combustion. The Clarke value and EDF are also given

Element[1]	Clarke[2] Coal	Clarke[2] Coal ash	Mac 05-23 FA	EDF[3]	Mac 05-22 Coal	EDF[3]	Mac 05-22 Coal ash
Lithophilic elements							
Li	20±7	80±15	58		14		42
Be*	1.2±0.1	6.7±0.5	5		<2		
Mg**	1.50 %		1.7 %		<0.1 %		
Al**	8.65 %		14.1 %		3.5 %		9.9 %
K**	2.70 %		2.5 %		0.7 %		2.2 %
Ca**	2.0 %		1.9 %		1.4 %		4.3 %
Sr	130±24	1100±310	152		49		146
Y	7.0±1	37±6	117	3.2	28	4.0	83
Zr	30±3	160±20	421	2.6	121	4.0	360
Nb	1.0±0.4	5.0±4.0	38	7.6	<20		
Mo*	2.1±0.2	14±1	12		<5		
Ba	120±18	890±220	853	1.0	298	2.5	887
La**	92		115		26		77
Ce**	59		293		64	1.1	190
W	2-6		<10		<10		
Radioactive elements							
Th*	3.8±0.2	19.±1	29	1.5	6.3	1.7	19
U*	2.1±0.3	15±1	5.3		1.5		4
Non-metals							
B*	56±3	410±30	10		<10		
C** (total)	1.2%		0.95 %		39.2 %	32.7	
C (min.)			0.07 %		0.05 %		0.14 %
C (org.)			0.88 %		39.15 %		116.9 %
Si**	27.5%		22.0		7.2		21.4
P*	220±30	1200±100	1062		284	1.3	845
S**(total)	0.24 %		0.31 %		0.98 %	4.1	
Siderophilic elements							
Sc	2.0±0.4	15±2	37	2.5	9	4.5	27
Ti	500±30	2600±300	7300	2.8	1980	4.0	6000
V*	22±2	140±10	243	1.7	68	3.1	202
Cr*	15±1	82±5	150	1.8	65	4.3	193
Mn*	100±5	520±30	930	1.8	390	3.9	1160
Fe**	4.80 %		5.0 %		1.7 %		5.0 %
Co*	4.2±0.3	27±1	33	1.2	11	2.6	33
Ni*	9.0±0.9	53±5	70	1.3	27	3.0	80
Chalcophilic elements							
Cu*	14±1	72±4	139	1.9	35	2.5	104
Zn*	18±1	110±10	191	1.7	61	3.4	182
Ga	7±1	36±4	47	1.3	11	1.6	33
Ge	1.5±0.3	9±3.7	4.3		1.1		3.0
As*	7.4±1.4	49±8	41		<20		
Se*	1.1±0.15	9.3±0.7	2.1		<1.0		
Cd*	0.24±0.03	1.0±0.14	<2		<2		
Sn	1±0.2	4.1±2.8	<10		<10		
Sb*	0.82±0.06	4.4±0.4	26	5.9	<10		
Hg*	0.1±0.01	0.58±0.06	2.0	3.4	<0.1		
Pb*	6.7±0.4	39±2	47	1.2	144	21.5	429
Bi*	0.92±0.09	5.7±0.7	<10		<10		
Noble metals							
Ag	0.3±0.1	1.0	<0.2		<0.2		
Ash yield %			99.26		33.6		

[1] Mineralogical classification of elements (Solodov et al. 1987)
[2] Clarke for lignite and subbituminous coals (Yudovich et al. 1985)
[3] Enrichment/depletion factor, ratio of the element content in coal to the Clarke value.
* Clarke for lignite and subbituminous coals (Yudovich and Ketris 2005)
** Clarke for shales (Beus and Grigorian, 1975)

■ **Tab. 3.** Element concentration (ppm) in "REK Oslomej" coals and their wastes from the combustion. The Clarke value and EDF are also given.

Element[1]	Clarke[2] Coal	Clarke[2] Shales**	Mac 05-24 Host rock	EDF[3]	Mac 05-35 Coal	EDF[3]	Mac 05-35 Coal ash
Lithophilic elements							
Li	20±7	66	25		<10		
Be*	1.2±0.1	3.0	2		<2		
Mg**	1.50%		2.1 %	1.4	0.7 %		3.4 %
Al**	8.65%		5.0 %		1.2 %		6.2 %
K**	2.70%		0.6 %		<0.4 %		
Ca**	2.0%		5.9 %	3.0	1.9 %	1.0	9.8 %
Sr	130±24	300	168		95		485
Y	7.0±1	26	38	1.5	<20		
Zr	30±3	160	121		30	1.0	153
Nb	1.0±0.4	16	<20		<20		
Mo*	2.1±0.2	2.6	<5		<5		
Ba	120±18	580	572		198	1.7	1010
La**	92		<20		<20		
Ce**	59		40		15		77
W	2-6		<10		<10		
Radioactive elements							
Th*	3.8±0.2	12	4.7		1.6		8
U*	2.1±0.3	3.2	2		0.5		3
Non-metals							
B*	56±3	100	24		36		184
C** (total)	1.2 %		0.3 %		47.9 %	39.9	
C (min.)			<0.05		0.05		
C (org.)							
Si**	27.5 %		17.1 %		3.1 %		15.7 %
P*	220±30	700	3520	5.0	2170	9.9	1110
S**(total)	0.24%		0.14 %		1.51 %	6.3	
Siderophilic elements							
Sc	2.0±0.4	13	18	1.4	2	1.0	10
Ti	500±30	3800	6300	1.7	1200	2.4	6100
V*	22±2	130	155	1.2	32	1.5	163
Cr*	15±1	90	104	1.2	39	2.6	199
Mn*	100±5	800	2260	2.8	300	3.0	1500
Fe**	4.80%		19.2 %	4.0	1.3 %		6.4
Co*	4.2±0.3	19	50	2.6	7	1.7	36
Ni*	9.0±0.9	68	61		11	1.2	56
Chalcophilic elements							
Cu*	14±1	45	42		12		61
Zn*	18±1	95	101	1.0	17		87
Ga	7±1	19	16		2.7		14
Ge	1.5±0.3	1.6	1.8	1.1	0.3		2.0
As*	7.4±1.4	13	67	5.2	<20		
Se*	1.1±0.15	0.5	<1.0		<1.0		
Cd*	0.24±0.03	0.3	4	13.3	<2.0		
Sn	1±0.2	6.0	10	1.7	<10		
Sb*	0.82±0.06	4.4±0.4	<10		<10		
Hg*	0.1±0.01	0.58±0.06	<0.1		<0.1		
Pb*	6.7±0.4	39±2	<10		119	17.8	607
Bi*	0.92±0.09	5.7±0.7	<10		<10		
Noble metals							
Ag	0.3±0.1	0.07	0.2	2.9	<0.2		
Ash yield %			97.09		19.6		

1 Mineralogical classification of elements (Solodov et al. 1987)
2 Clarke for lignite and subbituminous coals (Yudovich et al. 1985)
3 Enrichment/depletion factor, ratio of the element content in coal to the Clarke value
* Clarke for lignite and subbituminous coals (Yudovich and Ketris 2005)
** Clarke for shales (Beus and Grigorian, 1975).

■ Table 4. Element concentration (ppm) in Berovo coals and partings. The Clarke value and EDF are also given

Sample	Ash yield, %	**Orders of concentration**
Bitola, Suvodol		
Mac 05-7 coal	35.7	$C_{8.2} > Mo_{5.7} > Mn_{4.7} > Sc_{3.0} > Zn_{2.8} > Cr_{2.5} > Ti_{2.0} > S_{1.8} > (Be = Zr = Ba = Th = U = V = Co)_{1.7} > Ga_{1.6} > (P = Cu)_{1.4} > Ni_{1.3} > /(Li = Sr)_{1.0}/$
Mac 05-2 FA and BA	97.99	$Nb_{6.5} > Mn_{5.4} > P_{1.7} > (Mo = Ti)_{1.5} > Cr_{1.3} > Sc_{1.1} > /(Zr = V = Cu)_{1.0}/$
REK Oslomej		
Mac 05-22 coal	33.6	$C_{32.7} > Pb_{21.5} > Sc_{4.5} > S_{4.1} > Cr_{4.3} > (Y = Zr = Ti)_{4.0} > Mn_{3.9} > Zn_{3.4} > V_{3.1} > Ni_{3.0} > Co_{2.6} > (Ba = Cu)_{2.5} > Th_{1.7} > Ga_{1.6} > P_{1.3} > Ce_{1.1}$
Mac 05-23 FA	99.26	$Nb_{7.6} > Sb_{5.9} > Hg_{3.4} > Y_{3.2} > Ti_{2.8} > Zr_{2.6} > Sc_{2.5} > Cu_{1.9} > (Cr = Mn)_{1.8} > (V = Zn)_{1.7} > Th_{1.5} > (Ni = Ga)_{1.3} > (Co = Pb)_{1.2} > /Ba_{1.0}/$
Berovo		
Mac 05-35 coal	19.6	$C_{39.9} > Pb_{17.8} > P_{9.9} > S_{6.3} > Mn_{3.0} > Cr_{2.6} > Ti_{2.4} > (Ba = Co)_{1.7} > V_{1.5} > Ni_{1.2} > /(Ca = Zr = Sc)_{1.0}/$
Mac 05-24 Host rock	97.09	$Cd_{13.3} > As_{5.2} > P_{5.0} > Fe_{4.0} > Ca_{3.0} > Ag_{2.9} > Mn_{2.8} > Co_{2.6} > (Ti = Sn)_{1.7} > Y_{1.5} > (Mg = Sc)_{1.4} > (V = Cr)_{1.2} > Ge_{1.1} > /Zn_{1.0}/$

■ **Tab. 5.** Orders of the elements with enhanced Clarke concentration in Suvo dol, REK Oslomej and Berovo lignites, their wastes, and host rocks. Index value = EDF.

Some of the trace elements (Mo, Mn, Sc, Zn, Cr, Pb, Sc, Y, Zr, Ti, V, Ni, Co, Ba, Cu, and P) show an affinity to organic matter and phases intimately associated with organic matter.

The main factors responsible for the concentration of the trace elements in Bitola, Oslomej, and Berovo coal are: water and hydrothermal solutions; influence of the volcanic activity; lithological features; feed areas; and tectonic features.

About 50 % of the fly ashes are utilized in the industry. Most of the trace elements studied (Sr, Sb, U, Cr, Hg, Be, Mn, and Th) in the combustion waste products from Macedonian TPSs exhibit potential toxic or toxic characteristics. Such elements may contribute to some environmental and health problems in the country.

It should be stated that the data for trace element concentrations in the Macedonian coals are reported for the first time in this paper.

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