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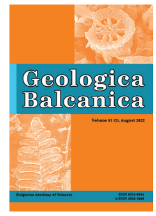

Preliminary data on critical element contents in lignite from the Maritsa East basin, Bulgaria

Mariana Yossifova[1], *Dimitrina Dimitrova*[1], *Milena Vetseva*[1], *Stoyan Georgiev*[1], *Yana Tzvetanova*[2]

[1] *Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 24, 1113 Sofia, Bulgaria; e-mails: mariana@geology.bas.bg; didi@geology.bas.bg; millena_vetseva@abv.bg; kantega@abv.bg*
[2] *Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 107, 1113 Sofia, Bulgaria; e-mail: yana.tzvet@gmail.com*

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Abstract. The studied samples include three composite coal, three lithotypes (lyptain, xylain, and fusain), and a black clay parting from the Troyanovo 1 and Troyanovo North mines in the largest Maritsa East lignite basin in Bulgaria. Mineral matter in composite coal samples, lithotypes, and clay is represented by clay minerals (montmorillonite, kaolinite, illite), quartz, pyrite, and gypsum in various quantities. A total of 66 elements were measured in all samples. The measured concentrations were compared to worldwide values of brown coal and upper continental crust and coefficients of enrichment (K1 and K2, respectively) were established. Most of the studied critical elements (REY, platinum-group metals, Li, Si, Mg, Ge, Ga, Nb, Sb, In, Co, Be, W) have low concentrations (K1 and K2 <2). The content of rare earth elements, yttrium, and scandium in the studied composite coal and lithotype samples is lower than concentration in world low-rank coal (65 ppm) and lower than in the studied black clay (145 ppm). The K1 and K2 coefficients of Pd and Pt, Te, Re, and Au are anomalously high. The mode of occurrence of most trace elements is mineral matter (sorbed in clay minerals, trace elements in pyrite, and as discrete phases). Some elements in low-ash samples (lithotypes) demonstrate affinity to organic matter: Te, Re, As, Mo, Ca, P, Au, Ba, Sr, Cd, etc. The lithotypes show enrichment in HREE (Gd–Lu) and Y in the following decreasing order: xylain > fusain ≫ liptain. The anomalously high contents of Te, Re, Pd, Pt, Au, Se, As, Mo, and others require further investigation.

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Keywords: coal and coal lithotypes, mineral matter, trace and critical elements, Maritsa East lignite basin, Bulgaria.

INTRODUCTION

For the past decade, the number of articles discussing the concentrations, mode of occurrence of critical elements in coal, combustion products (fly and bottom ash) and host rocks, and their potential as source for these elements has increased (Hower *et al.*, 1999, 2013, 2015; Dai *et al.*, 2003, 2010, 2011, 2012a, b, 2014, 2016, 2017a, b, 2018; Seredin and Finkelman, 2008; Seredin and Dai, 2012, 2014; Seredin *et al.*, 2013; Zhao *et al.*, 2015; Hower and Dai, 2016; Dai and Finkelman, 2018). Studies have shown that coal can be a source of valuable and trace metals; for instance, Ge is extracted from coal-derived fly ash in Russia (Seredin and Danilcheva, 2001) and China (Zhuang *et al.*, 2006;

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Dai *et al*., 2012a, 2015). Published data about critical elements in Bulgarian coal is given by Eskenazy (1987a, b; 1999), Vassilev (1994), Vassilev *et al*. (1995), Vassilev and Vassileva (1997), Kortenski (2011), Yossifova *et al*. (2007, 2011), Yossifova (2014), and others.

This paper presents preliminary data on the concentration and mode of occurrence of 66 elements in Bulgarian lignites. Among the considered elements are those that are critical for EC – HREE, LREE, platinum group metals, Li, Si, Mg, Ge, Ga, Nb, Sb, In, Co, Be, W (European Commission, 2014). The studied coals are from the Maritsa East lignite basin, which is the largest lignite basin in Bulgaria, occupying an area of 240 km^2 (Fig. 1).

GEOLOGICAL SETTING

The Maritsa East basin is a part of the Zagora depression, representing the easternmost part of the larger Late Alpine Upper Thrace depression (Boya-

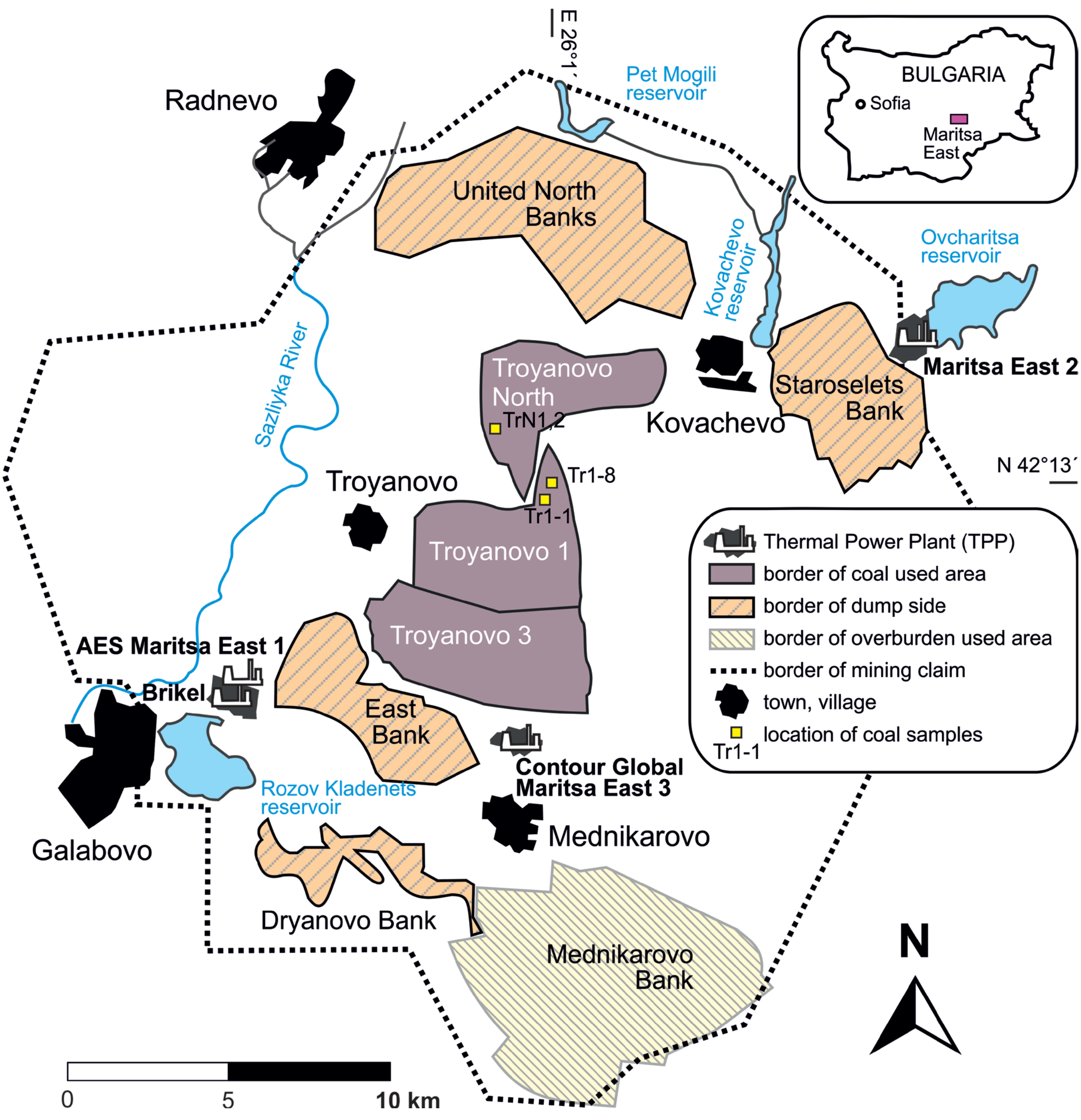

Fig. 1. Location of the Maritsa East basin, modified scheme published by Mini Maritsa Iztok EAD.

nov and Goranov, 2001). The structure has a complex pre-Paleogene basement and Paleogene–Quaternary basin fill (Fig. 2).

Basement

The pre-Paleogene basement is represented by fragments of older rock units: pre-Middle Ordovician schists, gneisses, and amphibolites, Carboniferous–Permian Sakar granite batholith, Triassic quartz-mica and garnet schists, Triassic calcite and dolomite marbles, Late Cretaceous Granitovo-Chernozem and Monastery Height plutons (Boyanov *et al.*, 1993; Kozhoukharov *et al.*, 1994; Kamenov *et al.*, 2000; Georgiev *et al.*, 2012; Bonev *et al.*, 2019). This basement is transgressively overlain by middle to upper Eocene basal breccias (diluvial and proluvial clayey sands and gravels, breccias, and con-

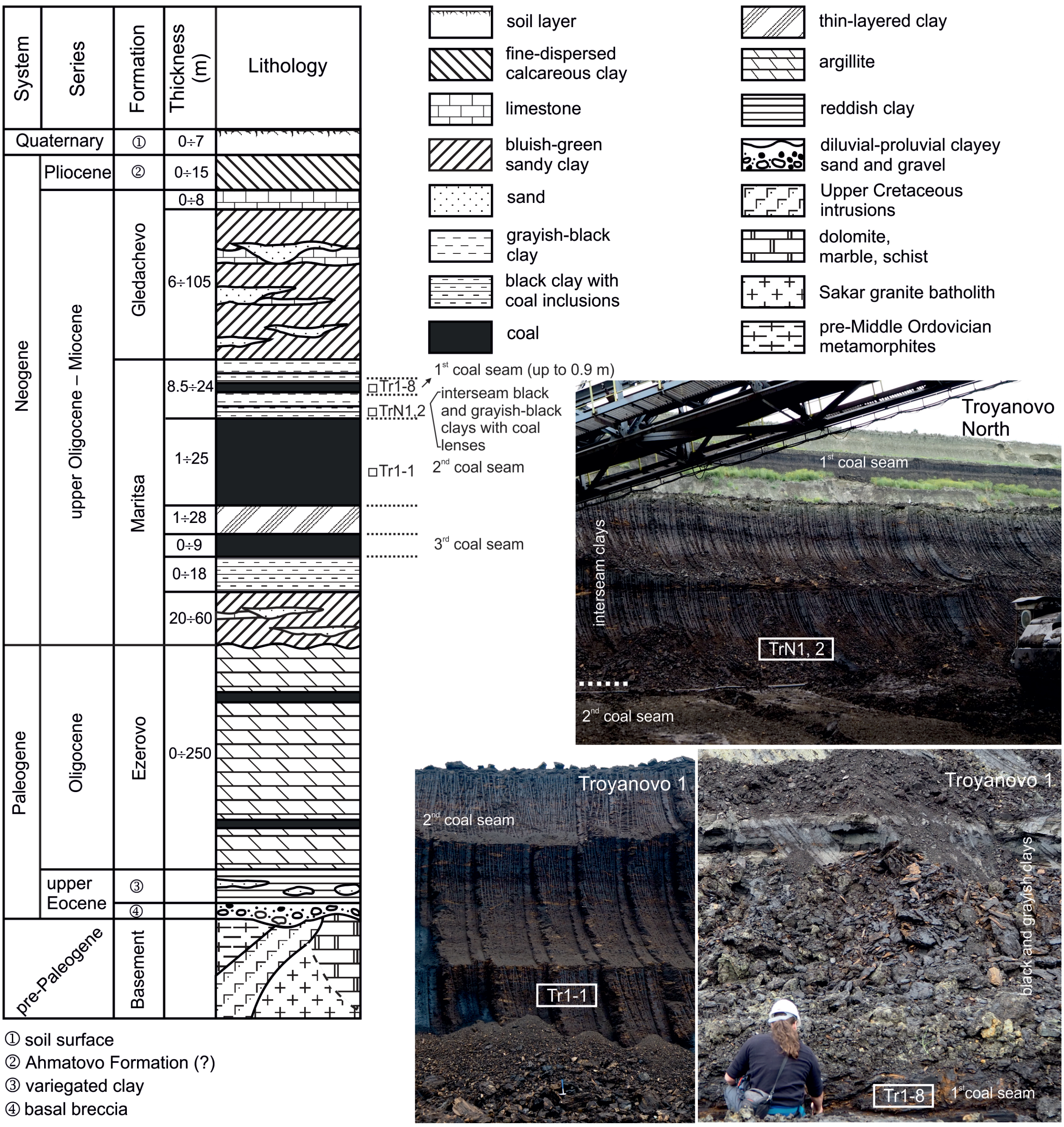

Fig. 2. Stratigraphic column of the Maritsa East basin (modified after Nedyalkov, 1985, Nedyalkov and Kojumdgieva, 1983, and Panov, 1982) and photographs of sample locations.

glomerates) and variegated clays (reddish and gray-green clays and sands) (Nedyalkov, 1985), which in turn are transgressively overlain by the sediments of the Oligocene Ezerovo Formation (gray and gray-green argillites and marls) (Kamenov and Panov, 1976; Panov, 1982).

Coal-bearing unit

The lower boundary of the coal-bearing Maritsa Formation is discordant and transgressive with the pre-Paleogene basement and the Eocene sediments, and smoothly transitional with the Ezerovo Formation (Panov, 1982; Nedyalkov, 1985). The lignite-bearing Maritsa Formation comprises a coal basement of black clays and sandstones, containing carbonaceous plant detritus and three coal seams (Troyanovo coal-bearing level) interbedded with layers of gray, grayish-green, and black clays and shales with various thicknesses, some of them containing abundant coal matter and fossils. The total thickness of the coal-bearing level is estimated to about 35–45 m. The second lignite seam (15–28 m thickness), which is deposited throughout the area of the basin, has economic value. The lower (third) coal seam (2.0–2.8 m to 9.0 m) is unevenly deposited, mostly in the central part of the basin. The upper (first) coal seam (0.7–0.9 m) has a random distribution and is overlain by black, grayish-green and grayish-black clays with various thickness (up to 10 m) that mark the upper boundary with the overlying Gledachevo Formation.

Overlying sediments

The Gledachevo Formation (Fig. 2) is represented by grayish-green, bluish-green, and ocher-yellow dense clays; fine- to coarse-grained sands; sandstones; and limestones with varying thickness (up to 100 m) throughout the basin (Panov, 1982; Nedyalkov and Kojumdgieva, 1983; Nedyalkov, 1985). The sands and sandstones occur as paleo-riverbeds within the claystones, providing evidence for water current and muddy flows in the basin. Fine-dispersed calcareous clays of Pliocene age and Quaternary sediments outcrop in the uppermost part of the basin.

General information

The age of the Maritsa Formation is considered to be late Oligocene–early to middle Miocene (freshwater mollusk; Sapundgieva and Kojumdgieva, 1973; Panov, 1982), whereas the age of the Gledachevo Formation is middle–late Miocene to Pliocene (freshwater mollusk and ostracod; Nedyalkov and Kojumdgieva, 1983). Several fault structures are present within the area of the Maritsa East lignite basin. Their predominant direction is NNE–SSW, NW–SE and W–E with mostly vertical movements. Paleo-landslides along faults and mud volcanoes have been described within the Troyanovo coal-bearing level (Nedyalkov, 1985). The coal is lignite (Šiškov, 1997) with varying contents of S_t (3.8–8.0%) and ash yield (A_d 28.0–34.7%) (Yossifova and Dimitrova, 2017).

SAMPLES AND METHODS

Samples

A total of seven samples collected from outcrops in the Troyanovo 1 and Troyanovo North mines were studied in order to obtain preliminary data for their trace element composition: three composite samples of coal, three coal lithotypes (liptain, xylain, and fusain), and one clay sample. Sample description and location are shown in Table 1 and Figs 1, 2.

Methods

Sample preparation

All coal samples were dried at room temperature and then were crushed, quartered, and 50-g portions of each were pulverized by a Fritsch planetary ball mill using agate grinding bowls and balls. Pressed pellets of coal/coal lithotype samples and fused pellets with lithium tetraborate of clay sample were prepared for trace element analyses by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

Analytical procedures

Mineral and phase composition was determined by binocular stereomicroscope and X-ray diffractometry (XRD) on powdered sample using D2 Phaser – Bruker AXS (Institute of Mineralogy and Crystallography, BAS) using Cu Kα radiation and Ni filter, in the 3–70° 2θ range with a scan step of 0.05. The XRD patterns were processed using PowderCell v.2.4. The mineral phases were identified against the PDF-2 database patterns (ICDD).

Major element contents (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, MnO, TiO_2, P_2O_5, and SO_3) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) at Aquaterratest Ltd. The moisture and ash yield were measured prior to ICP-OES analysis. In Bureau Veritas mineral laboratories were determined total sulfur

Table 1
Sample location and description

Sample No. in Figs 1, 2	Sub-sample	Mine	Description	Location
TrN1	total	Troyanovo North	Composite lignite coal sample	Lignite coal lense within interseam black clays over the top part of the second coal seam (stripping horizon)
	xylain		Xylain lithotype	
TrN2	black clay		Black clay	Interseam black clays with coal lenses over the top part of the second coal seam (stripping horizon)
Tr1-1	total	Troyanovo 1	Composite lignite coal sample	Second coal seam (stripping horizon; ~ 4m above the bottom of the coal seam)
	a, liptain		Liptain lithotype	
	b, fusain		Fusain lithotype	
Tr1-8	total	Troyanovo 1	Composite lignite coal sample	Upper (first) coal seam (0.3 m thick in this outcrop)

using LECO instruments, mercury by cold vapor flow injection mercury system (CV-FIMS), and measurement of trace elements by ICP-MS in the clay sample digested with aqua regia.

LA-ICP-MS using a PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser system was used to measure the trace element content in coal samples. The analyses were carried out in four 100-μm diameter spots in each pressed pellet at the following laser operation conditions: 6-Hz repetition rate and 60% energy with homogeneous 6.0 J/cm^2 energy density on the sample. The oxide production rate in ICP-MS was tuned to <0.5% ThO. The following isotope masses were chosen to avoid typical interferences formed in the argon plasma and measured throughout the experiment by ICP-MS: ^{7}Li, ^{9}Be, ^{23}Na, ^{25}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{34}S, ^{39}K, ^{42}Ca, ^{45}Sc, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, $^{63/65}$Cu, ^{66}Zn, ^{71}Ga, ^{73}Ge, ^{75}As, ^{77}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{103}Rh, ^{105}Pd, ^{107}Ag, ^{111}Cd, ^{115}In, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{182}W, ^{185}Re, ^{195}Pt, ^{197}Au, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{238}U. ICP-MS software input correction of isobaric interferences was performed during the measurement. The same conditions and set of isotope masses were applied during the analysis of the clay sample. A NIST SRM 610 glass was used as external standard and was analyzed repeatedly during the experiment. Data reduction of LA-ICP-MS analyses was done using SILLS ver. 1.1.0 software (Guillong *et al*., 2008) and Si as internal standard. The reported concentrations for each sample are no ash average values from the four measurements done on the pellet.

RESULTS

The XRD study revealed the presence of the following major minerals in various quantities in coal samples: pyrite, quartz, illite, montmorillonite, kaolinite, and gypsum. Pyrite mostly occurs as framboids. Gypsum (epigenetic) is present as prismatic crystals and aggregates. Montmorillonite, kaolinite, and quartz were identified in the clay sample.

The measured concentrations of 66 elements were compared to average concentrations for brown and US coal (Finkelman, 1993; Ketris and Yudovich, 2009) and the upper continental crust (UCC) (Rudnick and Gao, 2014), respectively (Table 2). The coefficients K1 and K2 are introduced, revealing the respective values larger or equal to 2. Data is given in order of decreasing ash content in samples.

Sample Tr1-8 total: this sample has highest ash yield (A$_d$) 39.27%, total sulfur (S$_t$) 12.94% and Fe 11.84%. Mineral matter is presented by pyrite, montmorillonite, and quartz.

K1: Te$_{128}$ > Re$_{41}$ ≫ Co$_{18}$ > As$_{14}$ > Ni$_{13}$ > (Au, Mo)$_{10}$ > (Fe, Cu)$_9$ > Zn$_8$ > (S, V)$_7$ > Cd$_5$ > (Mg, Se, Rb)$_4$ > (Na, Hg, Cr, Ge, Cs, Fe)$_3$ > (Al, K, Ca, Si, In, Pb, Ag, Li, Ti, Mn, Pd, Be, Sb, U, Ga)$_2$;

K2: S$_{208}$ > Re$_{205}$ > Te$_{128}$ > Pd$_{50}$ > Se$_{42}$ > As$_{23}$ > (Au, Mo)$_{20}$ > Cd$_{14}$ > Hg$_7$ > Cu$_5$ > (Co, Ag, Ge)$_4$ > Fe$_3$ > (V, Ni, Zn, Bi, U)$_2$.

Sample TrN1 total: A$_d$ = 24.98%, S$_t$ = 2.39%, and Fe = 2.79%. Mineral matter is presented by quartz, montmorillonite, kaolinite, pyrite, and gypsum.

K1: Re$_{510}$ > Te$_{64}$ > S$_7$ > (Au, V)$_5$ > Cu$_4$ > (Rb, Ni, Hg)$_3$ > (Al, K, Ca, Fe, Cs, Li, As, Mo, Pd, Cr, Zn, Ge)$_{2.0}$.

Table 2

Element concentrations (in ppm, unless indicated otherwise) in coal. Concentrations of elements given in % were determined by ICP-OES, contents of elements in ppm were determined by LA-ICP-MS, and Hg – by CV-FIMS. Contents of Li, Rb, Re, Cd, Ag, Te, and Pt in TrN2 were determined by ICP-MS with aqua regia digestion

Elements[a]	Average element contents in brown coal[b]	Upper continental crust[c]	Samples						
			Tr1-1a total	Tr1-1a liptain	Tr1-1b fusain	Tr1-8 total	TrN1 total	TrN1 xylain	TrN2 clay
Lithophile elements									
Li	10	21	9.23	1.10	6.66	20.67	23.01	3.46	17
Be	1.2	2.1	0.57	0.51	1.74	2.19	1.21	0.41	27.3
Na, %	0.08[d]	2.426	0.24	0.16	0.22	0.22	0.24	0.15	0.32
Mg, %	0.11[d]	1.496	0.37	0.13	0.47	0.42	0.38	0.11	0.82
Al, %	1.5[d]	8.15	1.78	0.27	1.03	3.15	3.35	0.56	13.37
K, %	0.18[d]	2.32	0.21	0.03	0.11	0.40	0.38	0.06	1.20
Ca, %	0.46[d]	2.56	1.88	0.62	2.72	0.92	0.99	0.37	0.60
Rb	10	84	19.87	2.93	9.39	36.45	34.35	5.22	148.10
Sr	120	320	216.60	90.12	317.57	129.66	60.45	31.48	146.49
Y	8.6	21	5.34	1.78	7.26	6.90	11.44	3.24	19.075
Zr	35	193	18.14	5.11	8.81	27.35	18.63	3.62	77.89
Nb	3.3	12	1.90	0.94	0.82	2.51	2.33	0.62	9.51
Mo	2.2	1.1	11.90	5.73	8.54	21.79	4.94	0.67	2.56
Cs	0.98	4.9	1.52	0.21	0.75	2.52	2.38	0.38	8.87
Ba	150	624	269.34	96.38	527.08	167.00	92.50	26.07	375.7
La	10	31	5.68	2.47	6.55	6.41	7.56	4.32	27.54
Ce	22	63	11.57	5.94	13.52	13.56	14.89	6.49	46.69
Pr	3.5	7.1	1.38	0.66	1.63	1.48	1.73	0.87	6.41
Nd	11	27	5.18	2.51	6.59	5.96	6.75	3.41	24.76
Sm	1.9	4.7	1.08	0.50	1.52	1.34	1.54	0.74	5.06
Eu	0.5	1	0.24	0.10	0.35	0.32	0.39	0.17	0.95
Gd	2.6	4	0.88	0.37	1.33	1.26	1.56	0.65	4.25
Tb	0.32	0.7	0.14	0.05	0.20	0.20	0.26	0.09	0.53
Dy	2	3.9	0.89	0.30	1.29	1.23	1.67	0.55	3.44
Ho	0.5	0.83	0.18	0.06	0.26	0.27	0.37	0.11	0.74
Er	0.85	2.3	0.52	0.15	0.72	0.77	1.03	0.30	1.9
Tm	0.31	0.3	0.08	0.02	0.11	0.12	0.16	0.04	0.36
Yb	1	1.96	0.54	0.13	0.75	0.78	0.98	0.26	1.64
Lu	0.19	0.31	0.08	0.02	0.10	0.11	0.14	0.04	0.35
Hf	1.2	5.3	0.46	0.14	0.23	0.73	0.51	0.11	2.13
Ta	0.26	0.9	0.14	0.06	0.05	0.17	0.13	0.04	0.58
W	1.2	1.9	0.24	0.12	0.15	1.76	0.73	0.26	2.31
Re	0.001[f]	0.000198	0.02	0.03	0.03	0.04	0.51	0.01	0.003
ΣREY			33.79	15.08	42.18	40.71	50.46	21.26	145.0
Non-metals									
Si, %	2.7[d]	31.145	3.03	0.44	1.85	5.95	5.16	0.87	22.39
P	200	654.7	101.03	166.30	44.75	94.13	68.95	29.36	0.02
S_t, %	1.8[d]	0.0621	2.99	2.47	1.94	12.94	2.39	1.34	0.24
Siderophile and chalcophile elements									
Sc	4.1	14	3.88	0.72	4.15	6.03	6.24	1.33	25.25
Ti	720	3832	683.67	221.87	359.50	1738.03	882.12	280.53	3957

Table 2 (continued)

Elements[a]	Average element contents in brown coal[b]	Upper continental crust[c]	Samples						
			Tr1-1a total	Tr1-1a liptain	Tr1-1b fusain	Tr1-8 total	TrN1 total	TrN1 xylain	TrN2 clay
V	22	97	38.63	21.19	34.15	160.56	117.40	32.55	212.7
Cr	15	92	22.47	9.02	15.79	44.25	29.26	7.42	114.7
Mn	100	774.6	196.16	52.65	257.55	212.78	95.68	23.20	77
Co	4.2	17.3	3.50	1.39	1.84	75.45	4.91	0.81	6.45
Ni	9.0	47	16.93	3.60	9.41	115.28	26.92	3.36	27.3
Cu	15	28	18.62	6.24	39.61	133.86	56.59	5.60	106
Zn	18	67	7.40	2.53	7.71	144.81	36.08	5.15	138.1
Ga	5.5	17.5	4.50	1.27	2.84	8.89	8.34	1.61	29.9
Ge	2.0	1.4	0.79	0.76	0.77	5.49	3.13	1.23	na
As	7.6	4.8	17.66	18.52	11.81	109.54	17.17	5.33	5.52
Se	1.0	0.09	1.84	1.10	1.40	3.78	1.48	0.42	2.56
Cd	0.24	0.09	0.11	0.13	0.12	1.24	0.21	0.06	0.68
In	0.021	0.056	0.02	0.01	0.01	0.05	0.03	0.01	0.18
Sn	0.79	2.1	0.59	0.13	0.30	1.51	0.95	0.19	3.29
Sb	0.84	0.4	0.37	0.25	0.37	1.49	0.41	0.08	1.21
Te[e]	0.01	0.01	1.47	1.93	0.31	1.28	0.64	0.29	0.05
Hg	0.1	0.05	0.4	0.09	0.42	0.33	0.25	0.07	2.06
Tl	0.68	0.9	0.17	0.06	0.14	0.70	0.44	0.06	0.93
Pb	6.6	17	3.05	0.50	3.16	15.10	8.34	1.48	23.25
Bi	0.84	0.16	0.10	0.03	0.08	0.35	0.23	0.03	1.59
Radioactive elements									
Th	3.3	10.5	2.52	0.55	1.84	3.30	3.64	0.98	14.33
U	2.9	2.7	1.53	0.34	1.75	4.89	3.10	0.47	6.59
Noble elements									
Rh[e]	0.011	0.011	0.01	<0.013	0.01	<0.016	0.01	<0.003	<0.26
Pd	0.013	0.00052	0.03	<0.016	0.04	0.03	0.03	0.01	<0.46
Ag	0.09	0.053	0.03	<0.017	0.02	0.21	0.07	0.01	0.16
Pt	0.065	0.0005	<0.020	<0.031	0.01	<0.047	<0.029	0.01	<0.002
Au	0.003	0.0015	0.01	0.03	0.01	0.03	0.01	0.01	0.078
A_d, %			16.23	3.54	13.19	39.27	24.98	4.74	
M_{ad}, %			12.53	5.33	24.38	6.71	20.9	15.08	
LOI, %									16

[a] Element arrangement according to Solodov *et al*. (1987); [b] Average element concentrations in world brown coal (Ketris and Yudovich, 2009); [c] Element concentrations in upper continental crust (UCC) (Rudnick and Gao, 2014); [d] Average element concentrations in US coal (Finkelman, 1993); [e] Average element concentrations in clay and shales (Grigoriev, 2009); [f] Background Re concentration in UCC (Yudovich and Ketris, 2006); A_d, ash yield on dry basis; M_{ad}, moisture on air-dry basis.

K2: $Re_{2576} > Te_{64} > Pd_{55} > S_{38} > Se_{16} > Au_{10} > Hg_5 >$ $(Mo, As)_4 > (Cd, Ge, Cu)_2$.

Sample Tr1-1 total: A_d = 16.23%, S_t = 2.99%, and Fe = 1.48%. Mineral matter is represented by quartz, illite, and pyrite.

K1: $Te_{147} > Re_{16} > (Mo, Au)_5 > (Ca, Hg)_4 > (Na, Mg)_3 > (Pd, As, Rb, Mn, Ni, Sr, Ba, Se, V)_{2.0}$;

K2: $Te_{147} > Re_{78} > Pd_{61} > S_{48} > Se_{20} > Mo_{11} > Au_9 > Hg_8 > As_4$.

Sample Tr1-1b fusain/semifusain: A_d = 13.2%, S_t = 1.94%, and Fe = 0.95%. Quartz and pyrite were identified in the sample.

K1: $Te_{31} > Re_{27} > Ca_6 > (Mg, Hg, Mo, Ba)_4 > (Na, Pd, Mn, Sr, Cu)_3 > Au_2$

K2: $Re_{139} > Pd_{85} > (S, Te)_{31} > Se_{16} > Pt_{15} > (Hg, Mo)_8 > Au_4 > As_2$.

Sample TrN1 xylain: A_d = 4.74%, S_t = 1.34%, and Fe = 0.48%.

K1: $Te_{29} > Re_{14} > Au_2$.

K2: $Re_{69} > Te_{29} > S_{22} > Pd_{20} > Pt_{16} > Se_5 > Au_4$.

Sample Tr1-1a liptain: A_d = 3.54%, S_t = 2.47%, and Fe = 0.25%.

K1: $Te_{193} > Re_{32} > Au_9 > Mo_3 > As_2$;

K2: $Te_{193} > Re_{164} > S_{40} > Au_{18} > Se_{12} > Mo_5 > As_4 > Hg_2$.

Sample TrN2 black clay: LOI = 16%, S_t = 0.24%, and Fe = 3.68%.

K2: $Au_{52} > Re_{15.2} > Be_{13} > Bi_{10} > Cd_{7.6} > Hg_{6.6} > Te_{5.0} > St_{3.9} > Cu_{3.8} > In_{3.2} > Sb_{3.0} > Ag_{2.9} > U_{2.4} > Mo_{2.3} > V_{2.2} > Zn_{2.1}$.

In this study, in comparison to US coal (Finkelman, 1993), lignite samples with $A_d \geq 13.2\%$ have higher contents of Al, K, Ca, Na, Mg, as well as Fe and S.

The content of rare earth elements, yttrium, and scandium in the studied composite coal and lithotype samples is lower than concentration in world low-rank coal (ΣREY = 65 ppm) (Ketris and Yudovich, 2009) and lower than the studied black clay (ΣREY = 145 ppm) (Table 2). Comparison to concentrations in upper continental crust (Taylor and McLennan, 1985) (Fig. 3, Table 3) reveals two types REY enrichment according to Seredin and Dai (2012): 1) L-type: $La_N/Lu_N > 1$ – Tr1-1a liptain and TrN1 xylain; 2) H-type: $La_N/Lu_N < 1$ – Tr1-1 total, Tr1-1b fusain, Tr1-8 total, TrN1 total, and TrN2 (clay). Although relatively clear weak positive Eu/Eu* anomalies can be noted in all coal and lithotype samples, excluding TrN2 (clay) (Fig. 3, Table 3), the relatively high Ba contents and high Ba/Eu ra-

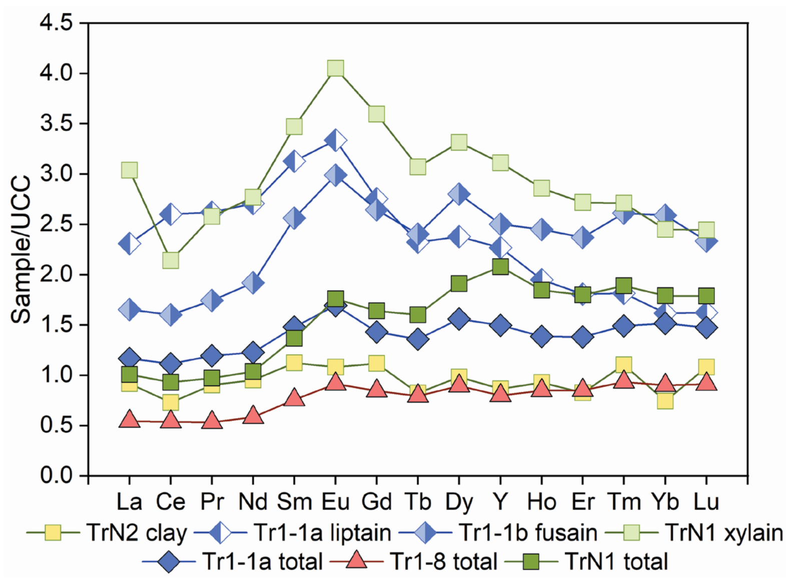

Fig. 3. REY patterns of distribution in coal, coal lithotypes, and black clay (ash basis). REY concentrations are normalized to upper continental crust (Taylor and McLennan, 1985).

Table 3
Selected element anomalies and ratios in coal, coal lithotypes, and black clay normalized to upper continental crust (Taylor and McLennan, 1985)

Element ratios	Tr1-1a total	Tr1-1a liptain	Tr1-1b fusain	Tr1-8 total	TrN1 total	TrN1 xylain	TrN2 clay
Ce/Ce*	0.94	1.05	0.94	1.00	0.94	0.76	0.80
Eu/Eu*	1.18	1.17	1.19	1.19	1.22	1.21	1.06
Gd/Gd*	1.02	1.06	1.08	1.08	1.08	1.12	1.21
Y/Y*	1.02	1.05	0.95	0.91	1.11	1.01	0.91
La_N/Lu_N	0.79	1.42	0.71	0.60	0.56	1.24	0.85
La_N/Sm_N	0.79	0.74	0.65	0.72	0.74	0.87	0.82
Gd_N/Lu_N	0.97	1.70	1.13	0.93	0.92	1.47	1.03

tio ≥ 1000 (Dai *et al*., 2016, 2017b) in Tr1-1 total, Tr1-1a liptain, and Tr1-1b fusain support the existence of interference of $^{135}Ba^{16}O^{+}$ species on the ^{151}Eu mass during measurement by quadrupole ICP-MS and thus on the estimated Eu contents. However, the impact of such interference on ^{151}Eu in TrN1 xylain, TrN1 total, and TrN2 (clay) is expected to be considerably lower (Ba/Eu = 154–394), thus the positive Eu/Eu* anomaly is more reliable. The influence of the interference in Tr1-8 is moderate (Ba/Eu=528). Such weak positive Eu/Eu* anomalies have already been reported for clays in the Maritsa East basin (Yossifova *et al*., 2018) at low Ba/Eu < 1000 (210–473) and have been explained by Eu scavenging from basin water by clay minerals. Ce/Ce* anomaly is almost non-existent or weakly negative in TrN1 xylain and TrN2 (0.76 and 0.80, respectively), which can be explained with the influence of source provenance and redox conditions during diagenesis. The same applies for Y/Y* and Gd/Gd* anomalies.

DISCUSSION

Concentration trends and modes of occurrence of trace elements

Organic matter

The ratio (Cf) between elements (on ash basis) in coal lithotypes to non-coaly sedimentary rocks is indirect approach to evaluate whether a certain element has an organic affinity (Yudovich, 1978). With respect to Cf, the elements are arranged into two groups: *1*) Cf>5 – elements with strong affinity to organic matter and minerals intimately associated with organic matter; and *2*) 2 ≥ Cf ≥ 5 – elements with moderate affinity to organic matter and minerals intimately associated with organic matter. Samples are arranged according to ash yield (A_d) (Table 4). All studied lithotypes have common number of elements with affinity to organic matter (Cf). Liptain has most elements with strong affinity Cf > 5 (highest Cf). REY elements have moderate affinity to organic matter (2 ≥ Cf ≥ 5). The low ash content samples (in this study lithotypes) demonstrate tendency to concentrate HREE (Gd-Lu) and Y in the following decreasing order: xylain > fusain ≫ liptain (Fig. 3, Table 4) similarly to Eskenazy (1987a).

Mineral matter

The sum of REY+Sc contents is higher in the samples with high ash yield and mineral occurrence (clay minerals), *e.g.*, composite coal samples and fusain (Table 2). The order of REY enrichment in lithotypes, as well as decrease of A_d, is fusain → xylain → liptain, and corroborate with the statement of Eskenazy (1987b) (Table 5). The enrichment of fusain with REY could be explained with its capacity of physical sorption (Eskenazy, 1987b). Moreover, ΣREY contents have not well manifested positive correlation with ash yield (r = 0.73) at critical values for r = ±0.81 and significance level (α) 0.05 for six coal samples, which may imply mixed modes of occurrence. However, the relatively moderate positive correlation with K (r = 0.78), Si (r = 0.80), Al (r = 0.83), and Mg (r = 0.83) (Fig. 4*a*) could suggest that they are mostly related with mineral matter, such as clay minerals and probably accessory zircon (?) (with Zr r = 0.68). A variation of REY contents in coal and coal lithotypes in the Maritsa East basin is observed with comparison with data reported by Eskenazy (1987b). Lithium shows strong positive correlation with Al (r = 0.99), K and Rb (r = 0.98), Sc (r = 0.94), Cs (r = 0.97), REY (r = 0.84), and A_d (r = 0.91), which suggests association with clay minerals, plagioclase, and K feldspar.

Table 4
Elements with moderate to strong affinity to organic matter (Cf)

Samples	2 ≥ Cf ≥ 5	Cf > 5
Tr1-1a Liptain	$Mg_{4.4}$, $Ni_{3.7}$, $Ce_{3.6}$, $Eu_{3.1}$, $Pr_{2.9}$, $(V, Nb, Nd, Sm, Tb, Ta)_{2.8}$, $Y_{2.6}$, $(La, Gd)_{2.5}$, $Dy_{2.4}$, $(Cr, Er, Yb)_{2.2}$, $Ho_{2.1}$	Te_{1083}, Re_{305}, As_{95}, $Mo_{63.2}$, Ca_{29}, P_{24}, Mn_{18}, $(Sr, Mo)_{17}$, Na_{14}, Se_{12}, St_{10}, $Au_{9.8}$, $Ba_{7.2}$, $Co_{6.1}$, $Sb_{5.7}$, $Cd_{5.3}$
TrN1 Xylain	$Sr_{4.5}$, $Li_{4.3}$, $(Eu,Tb)_{3.7}$, $Y_{3.6}$, $(Se, Dy)_{3.4}$, $(La, Er, Yb)_{3.3}$, $(P, V, Gd)_{3.2}$, $(Sm, Ho)_{3.1}$, $(Ce, Pr, Nd)_{2.9}$, $Mg_{2.8}$, $(Fe, Co)_{2.7}$, $Ni_{2.6}$, $Tm_{2.5}$, $W_{2.4}$, $Lu_{2.3}$, $Ti_{2.1}$	Te_{124}, Re_{97}, $As_{20.4}$, Ca_{13}, Na_{10}, Mn_{8}, $S_{5.6,}$ $Mo_{5.5}$
Tr1-1b Fusain	$Mg_{4.3}$, $Se_{4.1}$, $Li_{3.0}$, $(Y, Tb, Dy, Er)_{2.9}$, $(Cu, Eu)_{2.8}$, $(Ni, Ho)_{2.6}$, $Yb_{2.5}$, $(Gd, Tm)_{2.4}$, $(Sb, Sm)_{2.3}$, $(Co, Ce, Lu)_{2.2}$, $(Nd, U)_{2.0}$	Re_{69}, Te_{47}, Ca_{34}, Mn_{27}, $Mo_{25.3}$, $(As, Sr)_{16}$, Ba_{11}, $Stot_{8.1}$, $Na_{5.3}$

Note: The numbers after the elements are Cf.

Table 5
Established content of selected REY (Y, La, Ce, Sm, Eu, Tb, Yb, Lu) in coal and coal lithotypes in this study compared to published data from the Maritsa East basin by Eskenazy (1987b) (no ash basis)

Sample No.	Eskenazy (1987b)									This study					
	278	278 xylain	280	280 xylain	596	596 liptain	544 liptain	701	701 fusain	Tr1-1a total	Tr1-1a liptain	Tr1-1b fusain	TrN1 total	TrN1 xylain	Tr1-8 total
A_d, %	37.7	5.0	36.6	3.8	46.7	3.7	2.4	69.9	44.5	16.2	3.5	13.2	25.0	4.7	39.3
ΣREY	45.1	13.9	58.9	5.3	39.2	5.2	1.4	129.8	161.0	24.7	11.0	30.2	37.2	15.3	29.6

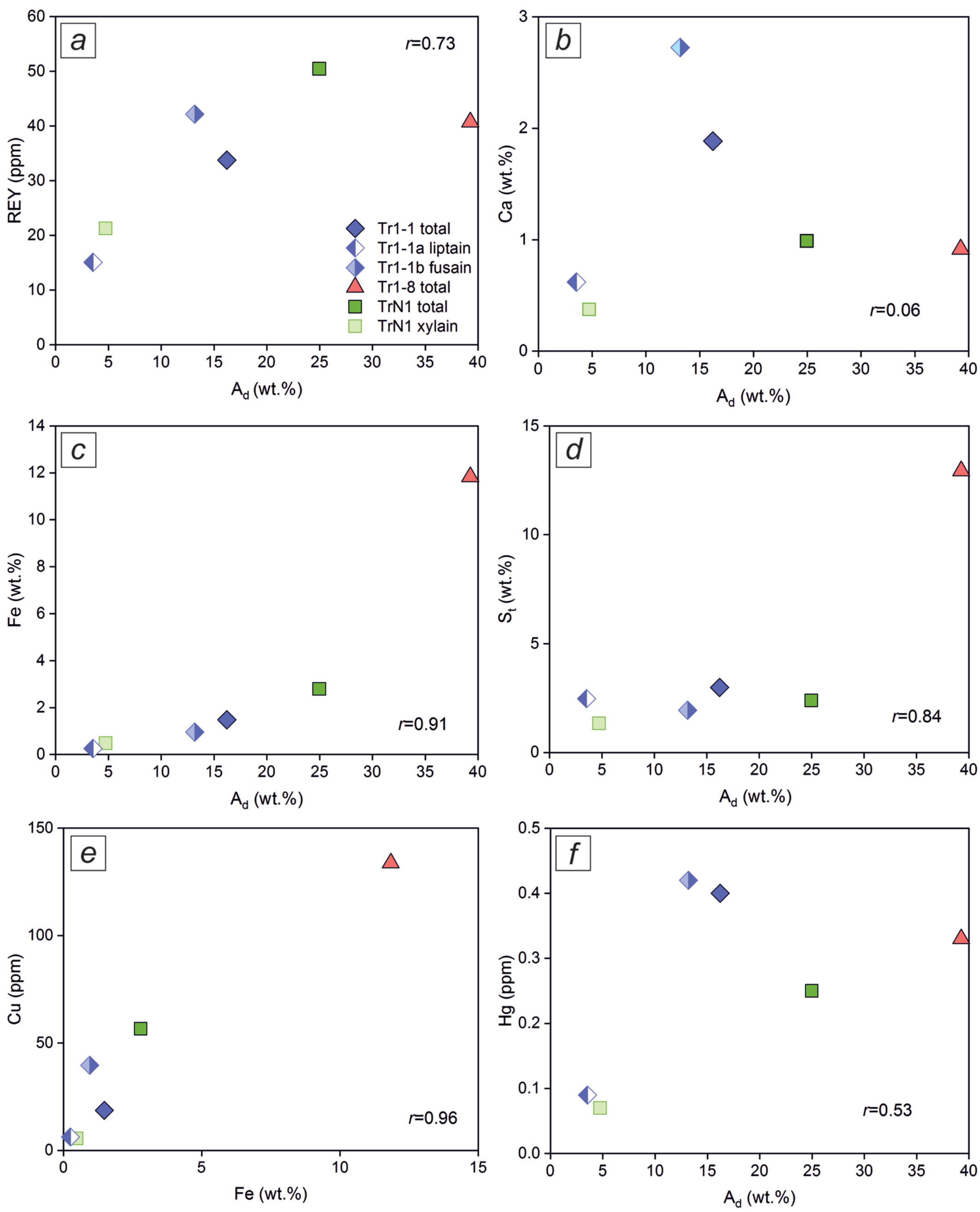

Fig. 4. Correlation coefficients of some elements vs. ash yield (A_d, %) and Fe: *a)* REY vs. A_d; *b)* Ca vs. A_d; *c)* Fe vs. A_d; *d)* S vs. A_d; *e)* Cu vs. A_d; *f)* Hg vs. A_d.

Calcium, Sr, and Ba do not show any correlation (positive or negative) to A_d (*r* = 0.05–0.06) (Fig. 4*b*). This could be explained as dual relation of these elements to both organic and inorganic matter (Table 4). On the other hand, Fe and S exhibit strong positive correlation with A_d (*r* = 0.91 and 0.84, respectively; Fig. 4*c*, *d*), which is mostly explained with the abundant pyrite occurrence. This is particularly visible in Tr1-8 total sample, with highest Fe and S content, as well as, highest contents of the following elements: Ti, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, Mo, Ag, Cd, In, Sn, Pb, Tl, Bi, Au, As, Se (Table 2, Fig. 4*e*), which are probably related to the presence of framboidal pyrite and other sulfides. The possible mode of occurrence of Hg is related to pyrite (low positive correlation with Fe, S, and A_d (*r* = 0.53); Table 2, Fig. 4*f*). Tellurium shows high enrichment (K1, K2) compared to average content of brown coal and upper continental crust. Its uncertain relation to A_d (*r* = 0.04), very low positive correlation to S and Se (*r* = 0.30), and relatively distinct positive correlation to Ag and Au (*r* = 0.52 and *r* = 0.80, respectively) could suggest presence of discrete Ag-Au selenides/tellurides, already reported by Yossifova (2014). On the other hand, Te could be related to organic matter, because it has highest concentration in Tr1-1a liptain. Rhenium also exhibits anomalously high coefficient of enrichment compared both to average world contents in brown coal and UCC. However, its mode of occurrence is not clear, because its positive correlation to A_d is negligible (*r* = 0.30) and low with other lithophile elements (REY, Al, K, *r* = 0.50–0.70), thus implying a relation to clay minerals (as sorbed species) or discrete phases. Platinum group elements (Pd and Pt) were detected in some samples with high K1 and K2. It might be assumed that their presence is related to clay minerals. Based on mineral and chemical composition, the other critical elements might occur in: 1) association with clay minerals (Li, Be, Nb, Sc, Ga, Ge, W); 2) related to sulfides (Ge, In, Co, W); 3) associated with fusain (Li, Sc); and 4) associated with xylain (Ge) (Table 2, Table 4).

CONCLUSIONS

REY and Sc, as well as other critical elements (Li, Si, Mg, Ge, Ga, Nb, Sb, In, Be, W), have low contents in the studied samples. They occur mostly as mineral matter (sorbed in clay minerals or associating with pyrite). The low-ash content samples (lithotypes) concentrate HREE (Gd–Lu) and Y in the following decreasing order: xylain > fusain ≫ liptain. Mercury has high contents compared to average values in brown coal and UCC. Since it is a toxic element, the combustion of coal might pose a threat to the environment. Especially interesting is the enrichment in Pd and Pt (critical), Te, Re, and Au compared to UCC and average values in brown coal, but their mode of occurrence is still not well established.

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