Mineral Matter and Trace Elements in the Vulche Pole Coal, Bulgaria

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ABSTRACT: The phase-mineral and inorganic chemical composition of the Vulche Pole subbituminous coal and host rock samples were studied. The samples were taken from cross sections in natural outcrops. These minerals and inorganic phases established in the Vulche Pole coal include quartz, kaolinite, illite, gypsum, jarosite K-feldspar, albite, calcite, pyrite, Fe-oxide/hydroxides, etc. The contents, concentration trends, and modes of occurrence of 43 elements were also described. Some of the trace elements (Se, Ge, Mo, U, Cu, Pb, and B) show an affinity to organic matter, in particular to vitrain. Elements such as U, Mo, Pb, Ge, Se, S, Cu, Th, Be, V, Sc, Zr, Y, Ti, As, Ni, Ga, Cr, Hg, Co, Se, and others exceeded Clarke values to subbituminous coals.

KEY WORDS: coal, mineral matter, trace elements, Bulgaria.

Introduction

The coals continue to be an important energy resource in the world. They are also an alternative and attractive source for extraction of some trace metals (Seredin and Danilcheva 2001).

The major purpose of this paper is to characterize the concentration and mode of occurrence of some important industrial trace elements such as Ge, U, W, V, and others in the Vulche Pole coal, Bulgaria. The Vulche Pole coal deposit is small and without industrial significance. There has been established a vitrain lens with 7.75 % (in ash) content for Ge (Eskenazy 1994).

Geological setting

The Vulche Pole coal deposit is situated in the East Rhodopa Mountains, Bulgaria (Fig. 1). The coal-bearing sediments have Oligocene age and they fill a tectonic depression 25 km long in east-west direction and 3–4 to 10 km wide. The coal formation is not widespread everywhere in the area. Several well-developed coal seams are observed in the eastern part of the deposit near the Vulche Pole village. These coal seams become wedge-shaped in the west direction. There are four coal seams with thickness of 1 to 2.60 m (Kojuharov et al. 1995). The Oligocene sediments are divided in two horizons. The lower horizon in the most cases is overlied by the sediments of the upper horizon, and the former one is represented by andesites, rhyolite tuffs and limestones. Gneisses and amphibolites of Proterozoic age, as well as mollase-type sediments of Upper Eocene age, mostly conglomerates and sandstones form the lower horizon. The upper horizon is a mollase-type coal-bearing formation with a variegated lithological composition. The major sediments are

■ **Fig. 1.** Location of the Vulche Pole coal deposit according to Šiškov et al. (1988); (1) – Rhyolite complex with sediments (Oligocene–Miocene); (2) – Latite–trachyte complex with sediments and small intrusive bodies (Eocene- Oligocene–Miocene); (3) – Coal deposits.

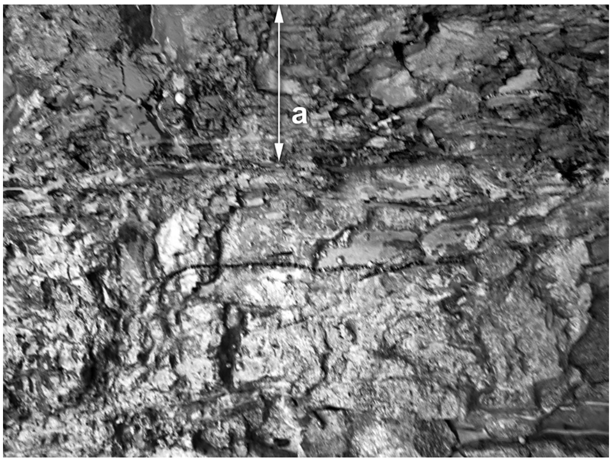
sandstones, sandy clays, conglomerates and clays. Interlayers of tuffs, thin coal seams and lenses are rarely observed in these sediments. Kaolinite-type clays are developed on the contact with the basal andesite horizon. The thickness of the Upper Oligocene horizon is 400–600 m (Minchev and Eskenazy 1966).

The coals are classified as subbituminous. The main characteristics of the coal by Minchev and Eskenazy (1966) are: 42–44 % V^{daf}, 35–55 % A^{d}, 4–8 % moisture, 1.5–2.5 % S^{daf}, 66–71 % C^{daf}, 7.7 % H^{daf}, 1.5–2.5 % S^{daf}, 0.44 % R_o.

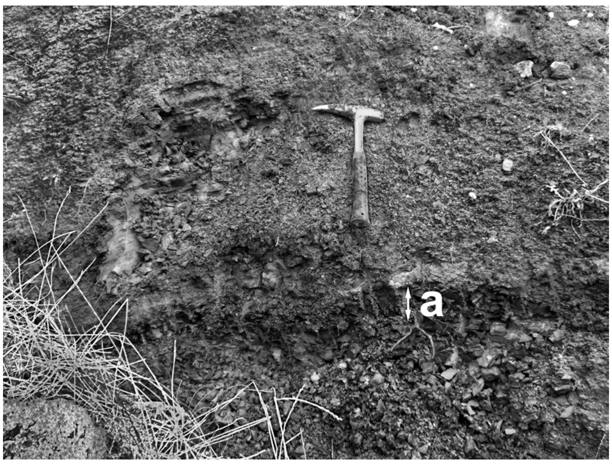
Material and methods

Subbituminous coal, coal argillites, partings, and host rock were tested (Figs. 2 and 3) The samples were collected from natural outcrops of the Vulche Pole deposit. Each sample with weight from 1.5 to 2.5 kg consists of six or seven individual samples. The samples had been broken to small pieces and dried at 40 °C.

The applied methods were: (1) Macroscopic observations; (2) Microscopic observation and hand isolation under an ordinary stereomicroscope; (3) SEM = *Scanning Electron Microscope*. Observations and semi-quantitative analyses had been performed with a JEOL JSM 6100 SEM coupled with an energy dispersive spectrometer EDS at 25 kV. Prior to analyses, a thin carbon layer had been sputter-coated on the sample; (4) EM = *Electron Microprobe*. The samples had been tested on polished sections. Spot analyses of organic matter had been performed using a Camebax SX50 EM with two stages analytical program. At the first stage C, Si and P were analyzed with a 10 kV acceleration voltage, a current beam of 20 nA and a 4–5 μm beam width. At the second stage Zn, S, Fe, As, Co, Ni, U, V, Ge, Sb, Cr, W had been analyzed with a 20 kV acceleration voltage and a current beam of 20 nA. Matrix corrections had been made with a ZAF computing program. The counting time was 10 s for major elements and 20 s for trace elements. Standards used included both well-characterized natural minerals and synthetic oxides. Matrix corrections had been made with a ZAF computing program. Detection limits were estimated for trace elements using the method described in Ancey et al. (1978): (in ppm) Zn 315, S 96, Fe 303, As 405, Co 202, Pb 437, Cu 250, Ga 149, Ni 221, U 566, V 196, Ge 124, Sb, 259, Cr 192 and W 343. (5) XRD = *Powder X-ray Diffraction*. XRD patterns were recorded on DRON 3M diffractometer with iron-filtered CoKα radiation and standard cylindrical specimen holder; (6) 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 were: inorganic C 0.05 %, total C 0.01 %, total S 0.01 %; SiO_2, Al_2O_3, 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; Ag 0.2 mg/kg. The high-temperature ashes had 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.



■ **Fig. 2.** Natural outcrop of the Vulche Pole coal; (a) Coal seam 40 cm thick.



■ **Fig. 3.** Natural outcrop of the Vulche Pole coal; (a) Coal seam 10 cm thick.

Results and discussion

Organic matter

The coals investigated (Bul 05–29) are black and mat, probably partly weathered. These coals are composed dominantly of clarain and vitrain. Vitrain stripes and lenses with thickness of 1 cm were found. The vitrain fragments show lamellar schistosity parallel to the stratification layers. Circular forms with halo of radial fan-shaped tracks were observed on the surface of the lamellas. The folds-forming layers, as well as colloform structures were observed in some coal fragments. The coals were thermally altered as a result of tectonic and hydrothermal processes. The clarain (Bul 05–30) is highly enriched in mineral impurities. The vitrain fragments included in clarain show fine strokes. The organic matter is also represented as: (1) brown and black plant fragments and vitrain lenses included in fine-grained clay sandstones and argillites (Bul 05–27 and Bul 05–42); (2) adsorbed in argillites and observed as dark colored pigmentation (Bul 05–26); (3) dark brown to black argillites with coal admixture .

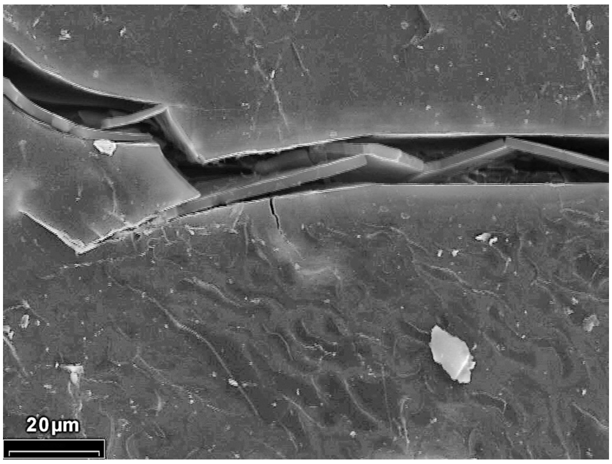
The maceral composition of the coal samples studied is represented by telinite with some collotelinite. The vitrinite shows high carbon content (79–86 wt %), consistent with a bituminous high to medium volatile coal rank. However, the vitrinite reflectance (R_o 0.30 %) and T_{max} (370 ° C) are low, rather indicating a subbituminous rank (Gouin, et al. 2007). This confirms that the coal are weathered or perhydrogenated (Jimenez et al. 1998, Gouin et al. 2007).

Mineral matter

The minerals identified in the coals studied are: (1) sample Bul 05–29 (vitrain). Quartz (minor mineral, 1–3 %) and accessory (< 1 %) illite, (Ag), (Cu > Zn), (Cu = Zn), Fe-oxide/hydroxides; (2) sample Bul 05–30. Gypsum and jarosite (major mineras > 3 %), kaolinite and quartz (minor minerals).

Silicates

Massive transparent quartz of epigenetic origin is observed in cracks parallel or across the stratification layers (Fig. 4). This quartz is characteristic of the samples both with lamellar schistosity and with prismatic cracking (Bul 05–30). In some cases it binders the fragmented coal particles. The clay minerals identified are: kaolinite, montmorillonite, and illite. They are mainly of an epigenetic origin. The kaolinite is the dominant clay mineral. It fills cracks in the coal fragments and has brown color. It also associates with jarosite, gypsum, quartz, and calcite. This association forms abundant fine-grained crusts on the surface of the coal and schist fragments or occurs in the cracks parallel to the layering (Bul 05–30 and Bul 05–43 argillites). Illite is an accessory mineral and it was found as scaly crystals containing of Fe, Ti, and Ca as impurities.



■ **Fig. 4.** SEM image of epigenetic quartz in vitrain cracks.

Oxides and hydroxides

Iron oxides/hydroxides were observed as individual lenses and crusts with size of several millimeters. These weathering products originated probably as a result of oxidation of authigenic pyrite.

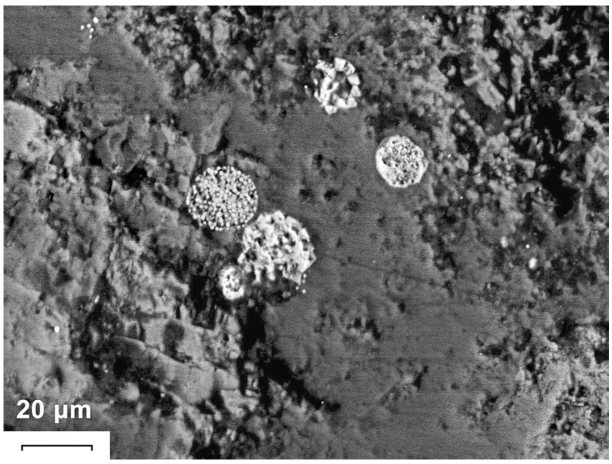
Sulphates

Gypsum was found as prismatic crystals forming aggregates on the surfaces of coal fragments. The origin of this mineral could be: (1) epigenetic and (2) weathering product in these coals. Jarosite was identified by XRD in association with gypsum, kaolinite and quartz. This epigenetic? mineral association of gypsum, jarosite and probably kaolinite imparts to the samples a citrine colour.

Other phases

Dispersed individual phases of (Ag), (Cu > Zn) and (Cu = Zn) were identified in the organic matter. They have detrital genesis (Ag) or some of them could also be products from the weathering of Cu- and Zn-bearing minerals. These phases are present as grain and irregular particles. The content of the element before the symbol (>) is above 50 wt %. The size of the phase (Cu = Zn) is 10 × 40 µm.

The mineral composition of the host rocks includes quartz, plagioclases, K feldspar + Na, mica, hydromica, amphibole, kaolinite, anorthoclase?, orthoclase, and the accessory minerals pyrite, calcite, gypsum, and barite. The detrital minerals are dominant (quartz, plagioclases, muscovite) among them. Minerals such as pyrite, calcite, gypsum, and barite have authigenic origin as some of them (gypsum, calcite?, and barite?) are also weathering products. Sulphide concretions with size about 1 cm in diameter were identified in sandstones (Bul 05–25 and Bul 05–40). They are composed of pyrite, which is partially substituted by goethite. Some zeolite mineralization was found as an association in these concretions. Additionally, crystalline pyrite (Bul 05–34, Bul 05–36, and Bul 05–38) and framboidal pyrite (Fig. 5) included in quartz and calcite were also identified (Bul 05–36). It may be supposed that the genesis of this sulphide mineralization is a result of infiltration of hydrothermal solutions. However, formation of the framboids in quartz is not clear at this stage. Their probable origin is a result of the activity of sulphur bacterium and penetrated organic matter in the quartz cracks.



■ **Fig. 5.** SEM image of framboidal pyrite. Matrix form quartz and calcite.

Geochemistry

Element content

The detected concentrations of elements in the coal samples studied had been compared to the respective Clarke values for 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 had been compared to the respective Clarke values for shales and sediment rocks (Beus and Grigorian 1975, Vinogradov 1962). The *ratio* = K between the contents (ash basis) of elements in low-ash coal samples to high-ash coal samples or shales had been also calculated for comparison (Yudovich 1978, Yudovich 2002). Reason of this calculation had been to determine the affinity of each element to the organic matter of the samples studied.

The contents of 43 elements and their *enrichment/depletion factor* = EDF, based on the respective Clarke value are listed in Tables 1 and 2.

The chemical investigations were conducted for 7 samples (Tables 1 and 2). Two of them are coal samples, while the rest of the samples are host rocks with inclusions of organic matter and argillites with coal admixture. The coal samples have ash yields of 9.4 % (Bul 05–29) and 44.8 % (Bul 05–30). The first sample is represented by vitrain and the genesis of the inorganic matter in this sample is dominantly infiltrated type. The second sample is composed of clarain, which is highly abundant in mineral impurities, as some of them exhibit epigenetic origin. The major elements in sample Bul 05–29 are C, Si, and S. Mostly authigenic quartz contributes the occurrence of Si in this sample. The major elements in sample Bul 05–30 are Al, K, C, Si, S, and Fe, while Ti was detected as minor element.

Elements higher than Clarke values are listed in the Table 3. The sample Bul 05–29 contained the less number of elements higher than Clarke values and these elements also showed relatively low enrichment. Only five of them have EDF >5 (U, Pb, Ge, Mo and Se).

The sample Bul 05–30 shows the most elements (22) higher than Clarke values and they have the highest EDFs, especially for $U_{75.2}$, $Mo_{30.5}$, $Se_{12.1}$ and Th_{10}. Germanium also reveals over Clarke concentration in the sample. These element enrichments are probably a result of: (1) fine vitrain inclusions in the clarain;

Element[1]	Clarke[2]	Bul 05–29 Coal	Bul 05–29 Ash	EDF[3] Coal	Bul 05–30 Coal	Bul 05–30 Ash	EDF[3] Coal
Lithophilic elements							
Li	20±7	<10			29	65	1.5
Be*	1.2±0.1	3	32	2.5	11	25	9.2
Mg**	1.50 %	<0.6 %			<0.6 %		
Al**	8.65 %	<0.5 %			5.6	12.4 %	
K**	2.7 %	<0.4 %			1.1 %	2.4	
Ca**	2.0 %	<0.8 %			<0.8 %		
Sr	130±24	35	372		66	147	
Y	7.0±1	<20			25	56	3.6
Zr	30±3	<20			249	556	8.3
Nb	1.0±0.4	<20			<20		
Mo*	2.1±0.2	15	160	7.1	64	143	30.5
Ba	120±18	81	862		112	250	
La**	92	<20			30	67	
Ce**	59	34	362		75	167	1.3
W	2–6	<10			<10		
Radioactive elements							
Th*	3.8±0.2	10	106	2.6	38	85	10.0
U*	2.1±0.3	33	351	15.7	158	353	75.2
Non-metals							
B*	56±3	16	170		<10		
C** total	1.2%	59.8 %		49.8	32.9 %		27.4
C (min.)		<0.0 5%			<0.05 %		
C (org.)							
Si**	27.5 %	2.9%	31.31%		8.4 %	28.0 %	
P*	220±30	52	553		209	466	~1.0
S** total	0.24 %	1.4 %		5.8	2.7 %		11.3

Element[1]	Clarke[2]	Bul 05–29 Coal	Bul 05–29 Ash	EDF[3] Coal	Bul 05–30 Coal	Bul 05–30 Ash	EDF[3] Coal
Siderophilic elements							
Sc	2.0±0.4	2	21	1.0	9	20	4.5
Ti	500±30	60	659		1800	4012	3.6
V*	22±2	38	404	1.7	174	388	7.9
Cr*	15±1	<10			30	67	2.0
Mn*	100±5	80	853		80	155	
Fe**	4.80 %	<0.7 %			2.4 %	5.5 %	
Co*	4.2±0.3	<5			8	18	1.9
Ni*	9.0±0.9	<10			21	47	2.3
Chalcophilic elements							
Cu*	14±1	47	500	3.4	129	288	9.2
Zn*	18±1	7	74		39	87	2.2
Ga	7±1	2.1	22		16	36	2.3
Ge	1.5±0.3	13	138	8.7	3.5	8	2.3
As*	7.4±1.4	<20			25	56	3.4
Se*	1.1±0.15	7.4	78.7	6.3	13.3	29.7	12.1
Cd*	0.24±0.03	<2			<2		
Sn	1±0.2	<10			<10		
Sb*	0.82±0.06	<10			<10		
Hg*	0.1±0.01	<0.1			0.2	0.4	2.0
Pb*	6.7±0.4	75	798	11.2	31	69	4.6
Bi*	0.92±0.09	<10			<10		
Noble metals							
Ag	0.3±0.1	<0.2			<0.2		
Ash yield (%)		9.4			44.8		

[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. 1.** Element concentration (ppm) inVulche Pole coals. The Clarke value and EDF are also given.

Element[1]	Clark[2]	Bul 05–43	EDF[3]	Bul 05–44	EDF[3]	Bul 05–42	EDF[3]	Bul 05–26	EDF[3]	Bul 05–27	EDF[3]
Lithophilic elements											
Li	66	40		42		39		29		24	
Be	3.0	5	1.7	9	3.0	8	2.7	9	3.0	7	2.3
Mg	1.50 %	<0.6 %		<0.6 %		<0.6 %		<0.6 %		<0.6 %	
Al	8.65 %	9.4 %	1.1	10.2 %	1.2	10.2 %	1.2	9.9 %	1.1	8.5 %	1.0
K	2.70 %	2.0 %		2.8 %	1.0	2.7 %	1.0	2.6 %	1.0	2.6 %	1.0
Ca	2.00 %	<0.7 %		<0.7 %		<0.7 %		0.8 %		0.8 %	
Sr	300	50		59		64		186		235	
Y	26	20		42	1.6	41	1.6	42	1.6	30	1.2
Zr	160	191	1.2	226	1.4	247	1.5	335	2.1	229	1.4
Nb	16	23	1.4	33	2.1	38	2.4	34	2.1	28	1.8
Mo	2.6	9	3.5	12	4.6	7	2.7	5	1.9	5	1.9
Ba	580	105		174		207		459		4828	8.3
La	92	37		65		65		61		46	
Ce	59	69	1.2	147	2.5	145	2.5	133	2.3	100	1.7
W	1.8	<10		<10		<10		<10		<10	
Radioactive elements											
Th	12	29	2.4	43	3.6	43	3.6	41	3.4	33	2.8
U*	3.2	14	4.4	41	12.8	27	8.4	15	4.7	13	4.1
Non-metals											
B	100	24		<10		<10		<10		<10	
C total	1.2 %	10 %	8.3 %	5.6 %	4.7	4.5 %	3.8	1.51 %	1.3	0.84 %	
Cmin.		<0.05%		<0.05%		<0.05%		<0.05 %		<0.05 %	
C org.											
Si	27.5 %	25.6 %		26.6 %	1.0	28.4 %	1.0	28.7 %	1.0	28.0 %	1.0
P	700	128		176		168		237		278	
S total	0.24 %	0.51	2.1	1.43	6.0	0.17		0.05 %		0.2 %	
Siderophilic elements											
Sc	13	5		8		9		9		8	
Ti	3800	2455		2695		3054		3300		2335	
V	130	56		99		75		74		58	
Cr	90	28		35		34		50		40	
Mn	800	78		78		78		155		233	
Fe	4.8 %	1.0 %		1.9 %		1.1 %		1.9 %		1.9 %	
Co	19	<5		11		9		9		10	
Ni	68	<10		21		<10		24		14	
Chalcophilic elements											
Cu	45	14		33		18		29		17	
Zn	95	28		46		72		108	1.1	66	
Ga	19	23	1.2	26	1.3	26	1.3	25	1.3	23	1.2
Ge	1.6	4.5	2.8	2.4	1.5	5.6	3.5	3.5	2.2	3.0	1.9
As	13	<20		186	14.3	<20		<20		<20	
Se	0.5	1.9	3.8	2.8	5.6	1.4	2.8	1.5	3.0	<0.1	
Cd	0.3	<2		<2		<2		<2		<2	
Sn	6.0	<10		<10		<10		<10		<10	
Sb	1.5	<10		<10		11	7.3	11	7.3	11	7.3
Hg	0.66	0.1		0.3		<0.1		<0.1		0.1	
Pb	20	93	4.7	77	3.9	73	3.7	64	3.2	50	2.5
Bi*	0.01	<10		<10		<10		<10		<10	
Noble metals											
Ag	0.07	<0.2		<0.2		<0.2		<0.2		<0.2	
Ash yield (%)		79		86.8		88.1		92.12		92.57	

[1] – Mineralogical classification of elements (Solodov et al. 1987)

[2] – Clarke for shales (Beus and Grigorian 1975)

[3] – Enrichment/depletion factor, ratio of the element content in coal to the Clarke value.

* – Clarke for Sediment rocks (clays and shales) (Vinogradov 1962)

■ **Tab. 2.** Element concentration (ppm) in Vulche pole argillites, partings, and host rock. The Clarke value and EDF are also given.

Sample	Ash yield %	Orders of concentration
Coals		
Bul 05–29 quartz (m)	9.4	$C_{49\,8} > U_{15.7} > Pb_{11.2} > Ge_{8.7} > Mo_{7.1} > Se_{6.3} > S_{5.8} > Cu_{3.4} > Th_{2.6} > Be_{2.5} > V_{1.7} > /Sc_{1.0}/$
Bul 05–30 gypsum, jarosite (M); kaolinite, quartz (m)	44.8	$U_{75.2} > Mo_{30.5} > C_{27.5} > Se_{12.1} > S_{11.3} > Th_{10.0} > (Be = Cu)_{9.2} > Zr_{8.3} > V_{7.9} > Pb_{4.6} > Sc_{4.5} > (Y = Ti)_{3.6} > As_{3.4} > (Ni = Ga = Ge)_{2.3} > Zn_{2.2} > (Cr = Hg)_{2.0} > Co_{1.9} > Se_{1.8} > Li_{1.5} > Ce_{1.3} > /P_{1.0}/$
Argillites, host rock and partings		
Bul 05–43 jarosite, quartz (M); kaolinite, plagioclase (m)	79.0	$C_{8.3} > Pb_{4.7} > U_{4.4} > Se_{3.8} > Mo_{3.5} > Ge_{2.8} > Th_{2.4} > S_{2.1} > Be_{1.7} > Nb_{1.4} > (Zr, Ce, Ga)_{1.2} > Al_{1.1}$
Bul 05–44 quartz, calcite, albite (M); kaolinte, mica (m)	86.8	$As_{14.3} > U_{12.3} > S_{6.0} > Se_{5.3} > C_{4.7} > Mo_{4.6} > Pb_{3.9} > Th_{3.6} > Be_{3.0} > Ce_{2.5} > Nb_{2.1} > Y_{1.6} > Ge_{1.5} > Zr_{1.4} > Ga_{1.3} > Al_{1.2}$
Bul 05–42 quartz, kaolinite (M), albite, K-feldspar (m)	88.1	$U_{8.4} > Sb_{7.3} > C_{3.8} > Pb_{3.7} > Th_{3.6} > Ge_{3.5} > Se_{2.8} > (Be, Mo)_{2.7} > Ce_{2.5} > Nb_{2.4} > Y_{1.6} > Zr_{1.5} > Ga_{1.3} > Al_{1.2}$
Bul 05–26 quartz, albite, kaolinite (M); K-feldspar (m)	92.12	$Sb_{7.3} > U_{4.7} > Th_{3.4} > Pb_{3.2} > (Be, Se)_{3.0} > Ce_{2.3} > Ge_{2.2} > (Zr, Nb)_{2.1} > Mo_{1.9} > Y_{1.6} > Ga_{1.3} > C_{1.3} > Al_{1.1}$
Bul 05–27 quartz, K-feldspar (M); albite, montmorillonite (m)	92.57	$Ba_{8.3} > Sb_{7.3} > U_{4.1} > Th_{2.8} > Pb_{2.5} > Be_{2.3} > (Mo, Ge)_{1.9} > Nb_{1.8} > Ce_{1.7} > Zr_{1.4} > (Y, Ga)_{1.2}$

■ **Tab. 3.** Orders of the elements with enhanced Clarke concentration in Vulche Pole coals, argillites, host rock and partings. Index value = EDF. The *major* = M and *minor* = m minerals (%) are also given.

(2) high sorption capacity of the clarain lithotype; (3) intensive syngenetic mineralization; and (4) abundant epigenetic mineralization (jarosite, calcite, kaolinite) which is characteristic for some other coal samples. On the other hand, this sample shows high ash content and the Clarke values for argillites could also be used for comparison. In this case the higher content than Clarke elements would have EDF comparable with the other samples.

The rest of the samples (Bul 05–43, Bul 05–44, Bul 05–42, Bul 05–26 and Bul 05–27) have high ash yields in the range of 79 % and 92.57 % (Table 3). They have similar number of elements higher than Clarke values (12–14) as the highest enrichments (EDF > 5) show: As, U, and Se for sample Bul 05–44; U and Sb for sample Bul 05–42; Sb for sample Bul 05–26; Ba and Sb for sample Bul 05–27. Germanium also reveals over Clarke values in these samples.

The affinity of elements to the organic matter was calculated by the *ratio* = K of element content in sample Bul 05–29 (ash basis) to sample Bul 05–26 (ash basis). The latter sample was chosen due to the absence of epigenetic mineralization in it. The calculation shows that the order of organic affinity of elements is: K: $B > C_{39.6} > S_{28.0} > Se_{4.9} > Ge_{3.7} > Mo_{3.0} > U_{2.2} > Cu_{1.6} > Pb_{1.2}$.

Germanium reveals the highest content in sample Bul 05–29 and this element also exhibits organic affinity. The Ge content decreases considerably in the coal samples with high ash yield. The above order calculated by Minchev and Eskenazy (1966) was as follows: $As_{107} > Ge_{100} > U_{33} > Sb_{28.9} > Ga_{21.5} > Mo_{18} > Co_{17.7} > Ni_{14} > Cr_{13.8} > Sc_{9.5} >$ V, $Be_{8.5} > Cu_{8.2} > Yb_{5.4} > Zn_{4.6} > Y_{4.3} > Mn_{3.5} > Pb_{1.9}$. The range 0÷400 ppm of Ge concentration in vitrain lenses (Bul 05–29; Bul 05–31) was established by microprobe analyses (Gouin et al. 2007).

Most of the elements studied also show an affinity to the mineral matter. For example, some elements were detected in:

- pyrite – Zn, Sb, As, Co, Pb, Cu, Cr, Ga, U, Ni, Mn, V, based on EM (Table 4);
- proper phases – Cu, Zn;
- association of gypsum, jarosite, kaolinite, and quartz – U, Mo, Se, Th, Be, Cu, Zr, V, Pb, others;
- association of jarosite, quartz, and kaolinite – Pb, U, Se, Mo, others;
- association of quartz, calcite and kaolinite – As, U, Se, Mo, Pb, Th, others;
- organic matter and montmorillonite – Ba, Sb, U, Th, Pb, others.

The high concentrations of Sb and W determined by electron microprobe analyses (Table 4) are probably related to their enrichment in: (1) organic particles?; (2) silicates?; (3) proper phases?. For example Vassilev et al. (1994) published data about the stolzite/respite ($PbWO_4$) in a lens from Vulche Pole coal deposit.

Conclusion

It was found that the coals studied undergone thermal transformations as a result of probable tectonic activity and influence of epigenetic low-temperature hydrothermal solutions. Such changes are typical of the contact zones between the organic matter and epigenetic mineralization in coal. (Yossifova et al. 2007). The epigenetic mineralization for the Vulche Pole coal deposit can be divided into two generations: (1) quartz; and (2) jarosite-kaolinite-quartz and sulphides.

The investigations established that the organic matter, in particular vitrain, is a concentrating phase of elements with dis-

Sample	Elements
Bul 05-34 (argillites) (1) Pyrite	Fe: 45.955 ÷ 46.150 and S: 52.521 ÷ 53.121 Zn: 0.000 ÷ 0.050; Sb: 0.000 ÷ 0.020; As: 0.015 ÷ 0.026; Co: 0.000 ÷ 0.019; Pb: 0.097 ÷ 0.147; Cu: 0.000; Cr: 0.000; Ga: 0.000 ÷ 0.071; U: 0.000 ÷ 0.133; Ni: 0.000 ÷ 0.004; Mn: 0.000 ÷ 0.010; Ge: 0.000; V: 0.000 ÷ 0.020.
(2) Quartz, K-feldspar, anorthoclase	Fe: 0.094 ÷ 23.540; S: 0.012 ÷ 29.944; Zn: 0.000 ÷ 0.014; Sb: 0.008 ÷ **0.527**; As: 0.000 ÷ 0.055; Co: 0.000 ÷ 0.035; Pb: 0.000 ÷ 0.059; Cu: 0.000 ÷ 0.012; Cr: 0.000 ÷ 0.012; Ga: 0.000 ÷ 0.028; U: 0.000; Ni: 0.000 – 0.003; Mn: 0.000 ÷ 0.020; Ge: 0.000 ÷ 0.057; V : 0.000 ÷ 0.018.
number of analyses – 8	
Bul 05–36 (silicated argillites) 1) Pyrite	Fe: 45.282 ÷ 46.142 and S: 53.094 ÷ 53.596 Zn: 0.000 ÷ 0.020; Sb: 0.000; As: 0.021 ÷ 0.050; Co: 0.000 ÷ 0.043; Pb: 0.036 ÷ 0.120; Cu: 0.000 ÷ 0.019; Cr: 0.000; Ga: 0.000 ÷ 0.030; U: 0.000 ÷ 0.162; Ni: 0.000 ÷ 0.006: Mn: 0.000 ÷ 0.021: Ge: 0.000; V : 0.000 ÷ 0.026; W: 0.000 ÷ 0.033.
2) Quartz, kaolinite, K-felspar, albite, anorthoclase	Fe: 0.000 ÷ 0.756; S: 0.00 ÷ 747; Zn: 0.000 ÷ 0.005; Sb: 0.000 ÷ **0.493**: As: 0.000 ÷ 0.020; Co: 0.000 ÷ 0.032; Pb: 0.000 ÷ 0.078; Cu: 0.000 ÷ 0.020; Cr: 0.000 ÷ 0.001; Ga: 0.000 ÷ 0.034; U: 0.000 ÷ 0.149; Ni: 0.000 ÷ 0.005; Mn: 0.000 ÷ 0.005; Ge: 0.000 ÷ 0.024; V: 0.000 ÷ 0.022; W: 0.025 ÷ **1.061**.
number of analyses – 23	
Bul 05–38 (argillites) 1) Pyrite	Fe: 45.672 ÷ 45.759 and S: 53.048 ÷ 53.863 Zn: 0.000; Sb: 0.000; As: 0.029 ÷ 0.045; Co: 0.000 ÷ 0.016; Pb: 0.016 ÷ 0.160; Cu: 0.000 ÷ 0.015; Cr: 0.000 ÷ 0.004; Ga: 0.000; U: 0.050 ÷ 0.094; Ni: 0.000 ÷ 0.008; Mn: 0.000; Ge: 0.000; V: 0.00 ÷ 0.011; W: 0.003 ÷0.010.
2) Quartz, kaolinite, K- feldspar, albite	Zn: 0.000 ÷ 0.008; Sb: 0.000 ÷ **0.485**; As: 0.000 ÷ 0.045; Co: 0.000 ÷ 0.012; Pb: 0.000 ÷ 0.062; Cu: 0.000 ÷ 0.012; Cr: 0.000 ÷ 0.005; Ga: 0.000 ÷ 0.045; U: 0.000 ÷ 0.041; Ni: 0.000 ÷ 0.008; Mn: 0.000 ÷ 0.008; Ge: 0.000 ÷ 0.017; V: 0.000 ÷ 0.016; W: 0.346 ÷ **0.819**
number of analyses – 12	

■ **Tab. 4.** Element content in Vulche Pole coal by EM (wt %).

tinctive geochemical behavior. It was found that some element concentrations Pb-75 ppm, Cu-47 ppm, U-33 ppm, Mo-15 ppm, Ge-13 ppm, Th-10 ppm, Se-7.4 ppm were higly enriched. On the other hand, the ratio between the concentrations of the above elements in coals and their respective host rocks is also from several times.

A great number of elements such as U, Mo, Th, Be, Cu, Zr, V, Pb, Sc, Y, Ti, As, Ni, Ga, Ge, Zr, Cr, Hg, Co, Se, Li, and Ce exceed Clarke values in high ash coals as well as Pb, U, Se, Mo, Th, As, S, C, Ce, Nb, Y, Be, Ba, Ge, others in host rocks studied.

The Ge content decreases considerably in the coal samples with high ash yield. However, the Ge concentrations are highly variable in the coal samples. Clarke values of Ge are also characteristic of argillites with coal admixture and host rocks (in the interval of 2.4–5.6 ppm), however their values are normally lower than those of coal samples.

Trace elements such as: Zn, Sb, As, Co, Pb, Ga, U, Mn, V and W were found to occur in pyrite; Cu and Zn as detrital or authigenic proper phases; U, Mo, Th, Be, Cu, Zr, V, Pb, Se, Th, Ba, Sb, and others in sulphates/clay minerals; As, U, Se, Mo, Pb, Th in carbonates and clay minerals.

Some elements as Se, Mo, U, Cu, and Pb show affinity to both organic matter and mineral matter, while B shows a strong affinity to organic (vitrain) matter.

The main factors responsible for the concentration of the trace elements in the coals were noted by Minchev and Eskenazy (1966), Eskenazy (1994), Vassilev et al. (1995), Seredin and Danilcheva (2001), Gouin et al. 2007). These factors are: (1) optimal combination of the pH and Eh values; (2) circulating water/hydrothermal solutions; (3) volcanic activity; (4) tectonic specificity; (5) petrographic composition; (6) the host rocks characteristics; (7) high specific surface of the vitrain; (8) the ability of Ge to form stable organic complexes.

The specific affinity to Ge of the different species plants could be noted also.

The role of Fe and S as factors that influenced the trace-element concentrations should be considered hypothetically. (1) Both elements are adsorbed or bonded in the vitrain. There is a possibility for Fe to form compounds with the organic acids. (2) Both elements form the dominating epigenetic mineralization that in the Pchelarovo (Fig. 1) coal deposits is Fe-sulphide (Yossifova et al. 2007) and in Vulche Pole coal deposits is Fe-sulphate. Pchelarovo is a small coal deposit in the same region of Bulgaria, characterized by high contents of rare elements (Yossifova et al. 2007). Most of the trace element concentrations associated with the above mineralization. It should be considered the possibility for the existence of a single? source for both the infiltrating solutions and the subsequent hydrothermal solutions in the basin. The possibility for remobilization of some elements from the coal matter and host rocks cannot be also excluded. The Ca concentrations have low values (lower than the detection limit of the equipment) both in the Pchelarovo (Yossifova et al. 2007) and the Vulche Pole coal deposits. The Ca sulphates and Ca carbonates have trace occurrence or they are absent in these deposits. However, it can be stated that probably Ca do not have active role in formation of the metal organic complexes.

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References

ANCEY M., BASTENAIRE F. and TIXIER R., 1978. Applications des méthodes statistique en microanalyse. In: MAURICE F., MENY L. and TIXIER R. (Editors). Microanalyse et microscopie électronique à balayage. Les éditions de physique, Les Ulis., 7, pp. 323-339.

BEUS A. and GRIGORIAN C., 1975. Geochemical methods of prospecting and exploration of solid mineral resource deposits. Nedra, Moskow, 279 pp. (in Russian).

ESKENAZY G., 1994. Geochemistry of germanium in Bulgarian coal deposits. Ann. Univ. Sofia, Livre 1-Geol., 86, pp. 175-195 (in Bulgarian, with English and Russian Abstr.).

GOUIN J., LEROUGE C., DESCHAPMS Y., LAGGOUN-DEFARGE F., YOSSIFOVA M. and YANEV Y., 2007. Petrological and geochemical characterization of Ge-bearning coals from eastrn Rhodopes, Bulgaria. Digging Deeper. 9th Biennial SGA Meeting, August 20–23, 2007, Dublin, Ireland, II, pp. 1521-1524.

JIMÉNEZ A., IGLESIAS MJ., LAGGOUN-DÉFARGE F. and SUÁREZ-RUIZ I., 1998. Study of physical and chemical properties of vitrinites. Inferences on depositional and coalification control. Chem.Geol., 150, 197-221.

KOJUHAROV D., BOIANOV I., KOJUHAROVA E., GORANOV A., SAVOV S. and SHILIAFOV G., 1995. Descriptions to the geological map of Bulgaria, M 1:100 000, Svilengrad area, Sofia, 65 pp. (in Bulgarian).

MINCHEV D. and ESKENAZY G., 1966. Trace-elements in the coals of Bulgaria. Germanium and other trace elements in the coals of the Vulche Pole deposit – East Rhodope mountain. Ann. Univ. Sofia, Livre 1-Geol., 59, pp. 357-372 (in Bulgarian with English Abstr.).

SEREDIN V. and DANILCHEVA J., 2001. Mineral Deposits at the Beginning of the 21st Century. In: PIESTRZYŃSKI et al. (Editors), Swet & Zeitlinger Publishers Lisee, pp. 89-92.

ŠIŠKOV G., VALĆEVA S. and KORTENSKI K., 1988. Influence of increasing thermal flux on organic matter in the Rhodope Paleogene sediments. Comp. Rendus de l'Academie Bulg. Sci., 41, 10, pp. 85-88.

SOLODOV N., SEMENOV E. and BURKOV V., 1987. Geological handbook on heavy lithophilic trace metals. Nedra, Moscow, 438 pp. (in Russian).

VASSILEV S., ESKENAZY G., TARASSOV M. and DIMOV V., 1995. Mineralogy and geochemistry of a vitrain lens with unique trace element content from the Vulche Pole coal deposit, Bulgaria. Geol. Balc., 25, 3-4, 111-124.

VINOGRADOV A., 1962. Average element contents of major types magmatic rocks in earth crust. Geochimia 7, 555-572 (in Russian).

YOSSIFOVA M., DESCHAMPS Y. and LEROUGE C., 2007. Trace elements in Phelarovo coal, Bulgaria. CD of 2007 ICCS&T, August 28-31, 2007, Nottingham, UK, vol. (session) 6B4, pp. 1-11.

YUDOVICH Ya.E. and KETRIS M.P., 2005. Toxic trace elements in coal. Institute of Geology, Ekaterinburg, 655 pp. (in Russian)

YUDOVICH Y., KETRIS M. and MERTC A., 1985. Trace Elements in Coal. Nauka, Leningrad, 239 pp. (in Russian).