

Occurrence and distribution of the siderophile elements in some Bulgarian coals

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Й. Кортенски, А. Сотиров — Присутствие и распределение сидерофильных элементов в некоторых углях Болгарии. Пробы собраны из четырнадцати каменноугольных бассейнов и месторождений на территории Болгарии. В них исследовалось содержание и распределение сидерофильных элементов: Fe, Ni, Co, Mn, Cr, V и Ti. Угли различаются по степени углфикации (рангу) и по возрасту. Образцы лигнитных углей взяты из неогеновых бассейнов: Марица-Запад, Станянци, Белибег, Чукурово, а также — из Софийского, Карловского, Самоковского, Кюстендильского, Орановского, Габровницкого бассейнов и из бассейнов Краиштенского района. Суббитуминозные угли взяты из палеогенового Перникского бассейна, а битуминозные — из эоценового Сухострельского бассейна и из сеномановых бассейнов Балкана. Исследован также антрацит пенсильванского возраста из Свогенского бассейна. Большинство из образцов содержат значительные количества сидерофильных элементов. Fe, Ni и Co находятся в негативной корреляции с угольным пеплом каждого из бассейнов, за исключением Белибрежских и Сухострельских углей. Позитивная корреляция Ti и соответствующего угольного пепла выявляется часто. Для Mn, Cr и V корреляция имеет преимущественно негативный характер. В распределении сидерофильных элементов выявлены следующие тенденции: концентрации Ni и Co имеют сходные распределения в углях всех бассейнов. Fe показывает аффинитет к органическому веществу во всех бассейнах за исключением Белибрежского и Сухострельского. Такой же аффинитет характерен для распределения Ni и Co. Аффинитет Mn к органическому веществу установлен в углях Белибрежского, Чукуровского, Карловского, Самоковского и Кюстендильского месторождений. Аффинитет Cr к органическому веществу не устанавливается только в нескольких бассейнах, а именно: в Белибрежском, Чукуровском, Габровницком, Кюстендильском, Орановском, а также — в углях Краиштенского района. Аффинитет V к органическому веществу характерен для углей из бассейнов Марица-Запад, Чукурово, Карлово, а также — для углей из Самоковского, Софийского, Орановского, Габровницкого бассейнов и для Перникских углей. Органический аффинитет Ti установ-

Abstract. Coals from fourteen Bulgarian basins and deposits were sampled. The siderophile elements Fe, Ni, Co, Mn, Cr, V, Ti and their distribution were studied in these samples. The coals have different rank and age. The studied lignite was taken from the Neogene Maritsa-West, Stanyantsi, Belibreg, Chukurovo, Sofia, Karlovo, Samokov, Kyustendil, Oranovo, Gabrovitsa, and Katrishte basins. Subbituminous coal was taken from the Paleogene Pernik Basin, bituminous coal was from the Eocene Suhostrel and Cenomanian Balkan Basins, and the Svoqe Pensilvanian anthracite was also investigated. Most of the studied coals were rich in siderophile elements. Iron, Ni and Co have negative correlation with the coal ash in all coals with exception of Belibreg and Suhostrel coal. Titanium often has positive correlation with the coal ash, and Mn, Cr and V show mainly negative correlation with the ash. The following tendencies of the concentration and distribution of the siderophile elements in the studied coal were established: The concentrations of Ni and Co have similar distribution in the coal from all studied basins. The Fe has organic affinity in all studied coals and Ni and Co have organic affinity in all coals with an exception of Belibreg and Suhostrel coal. The Mn has organic affinity with an exception in the Belibreg, Chukurovo, Karlovo, Samokov, and Kyustendil coal. Cr has organic affinity with an exception of Belibreg, Chukurovo, Gabrovitsa, Kyustendil, Oranovo, and Katrishte coal. Vanadium has organic affinity in the Maritsa-West, Chukurovo, Karlovo, Sofia, Samokov, Gabrovitsa, Oranovo, and Pernik coal. Titanium has organic affinity in the Belibreg, Sofia, Karlovo, Kyustendil, and Svoqe coal. The main factors for the accumulation of the siderophile elements in coals were: 1) location of the basins closely to metallogenic provinces or rocks around the basin with high concentrations of the elements; 2) good conditions for forming of organic and inorganic complexes in the ancient peat bog; 3) fracture and cleat of the coal seams in combination with the presence of infiltration solutions, which contained siderophile elements.

лен в углях Белибрег, в Софийском, Карловском, Кюстендильском бассейнах и в Свогенских углях. Основными факторами накопления сидерофильных элементов в углях являются: 1) пространственная близость бассейнов и металлогенических провинций или размещение бассейнов в близости с породами, содержащими эти элементы; 2) подходящие условия для образования органических и неорганических комплексов в древних болотах 3) трещиноватость и чередование угольных пластов с другими породами в сочетании с присутствием инфильтрационных растворов, содержащих сидерофильные элементы.

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Key words: geochemistry, siderophile elements, element affinity, accumulation factors, and Bulgarian coals.

Introduction

Coals from fourteen Bulgarian basins and deposits were sampled (Fig. 1). The content of the siderophile elements Fe, Ni, Co, Mn, Cr, V, and Ti and their distribution were studied in the samples. The coals have different rank and age. Lignite was sampled from the Neogene Maritsa-West, Stanyantsi, Belibreg, Sofia, Karlovo, Samokov, Kyustendil and Oranovo basins and the Gabrovitsa and Katrishte deposits (Fig. 1). The subbituminous coal was taken from the Paleogene Pernik Basin, the bituminous coal was from Eocene Suhostrel and Cenomanian Balkan Basins, and the anthracite coal was sampled from the Svoге Carboniferous basin.



Fig. 1. Location of the studied coal basins.

1 — Maritsa-West; 2 — Belibreg; 3 — Chukuruvo; 4 — Gabrovitsa; 5 — Karlovo; 6 — Samokov; 7 — Sofia; 8 — Stanyantsi; 9 — Katrishte; 10 — Kyustendil; 11 — Oranovo; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoге. I — lignite; II — sub-bituminous coal; III — bituminous coal; IV — anthracite

Ескенази (1972, 1993) and Eskenazy and Mincheva (1992) published data on the distribution of Mn, Ti, Ni, Co, V and Cr in the coal from other Bulgarian basins.

Geological setting

The studied coal basins are situated in several coal provinces, as divided by Siskov (1997).

The sampled Maritsa-West basin is a part of the Trakia coal province (Southeast). The coal-bearing Neogene sediments are only represented by the Maritsa Formation (Table 1), which contains two coal-bearing levels. This formation is composed of clay, sand, and sandstone. The coal seams from the Brodsko level (low level) are without economic significance. The Kiprenski seam from the Kiprensko level was sampled. The coal-bearing sediments are weakly folded. Two shallow synclines and one anticline have been established. Single faults with low amplitude were noted, too.

The Sofia coal province (Southwest) includes several basins of Miocene-Pliocene and Pliocene age (Table 1).

The coal-bearing Lozenets Formation from the Belibreg basin is of Dacian age. The formation is composed of gravel, sandy clay, clay, and carbonate clay, with five coal seams (Table 1), only one of them with economic significance. The boards of the ancient peat bog were composed of Triassic and Jurassic limestone, dolomite, and silt. The Pliocene sediments fill a graben-syncline with orientation NW-SE. The principal faults are located in the zone with prevailing orientation 110°-125°.

Table 1
Age and rank of the coal from studied Bulgarian basins

Coal province	Basins	Coal-bearing formations	Age	Number of seams	Number of economic seams	Rank of coal
Trakiyska	Maritsa-West	Marishka	Middle Miocene	2	2	L
Sofiyska	Belibreg	Lozenetska	Early Dacian	5	1	L
	Chukurovo	Suite of the clay sandstones and clay	Helvetian	12-16	12	L
	Gabrovitsa	Gabrovishka	Pontian	1	—	L
	Karlovo	Iganovska	Miocene-Pliocene	3	3	L
	Samokov	Alinska	Pontian-Dacian	1	1	L
	Sofia	Gnilyanska	Pontian	1-2	1-2	L
	Stanyantzi	Belozemska	Late Sarmatian	1	1	L
Strumsko-Mestenska	Katrishte	Skrinyanska	Badenian- Sarmatian	1	1	L
	Kyustendil	Skrinyanska	Sarmatian-Meotian	1	1	L
	Oranovo	Oranovska	Badenian	4	1	L
Pernishka	Pernik	Pernishka	Late Oligocene	5	3	SB
	Suhostrel	Suhostrelska	Middle Eocene	3	—	B
Balkanska	Balkan	Coal-bearing	Cenomanian	3-8	3-8	B
Svogenska	Svoqe	Carichinska	Namurian A, B	7-17	7-17	A
		Drenovska	Namurian C- Westphalian B			
		Chibaovska	Westphalian			

L — lignite; SB — subbituminous coal; B — bituminous coal; A — anthracite.

The Stanyantsi basin is situated into a region composed of Triassic (conglomerate, sandstone, siltstone, limestone, and dolomite), Jurassic (sandstone, siltstone, and limestone), and Upper Cretaceous (marl and limestone) rocks. Бацев (1999) reports four formations: the Dvechkenska Formation, the Belozemska Coal-bearing Argillite Formation, the Zainishka Sandstone-Argillite Formation, and the Stanyanska Conglomerate-Sandstone Formation. The Belozemska Formation includes lake-type silt and sand-argillite clay, black clay, carbonate clay, marl, limestone and a coal seam at its base. The coal seam is 20 m thick. The thickness of the formation is 30-60 m. The formation age is Upper Sarmatian. The lignite-bearing sediments fill a block-graben structure with NW-SE direction. The coal is lignite.

The Sofia basin is located in the Sofia field (Fig. 1). The bottom and the boards of the basin are composed of Paleozoic, Triassic, Jurassic and Cretaceous sediments; Cretaceous andesites; and Paleogene rocks. Каменов, Коюмджиева (1983) divided the Neogene sediments of the colored clastic formation and the Sofia group, which consists of three formations: Gnilyane, Novoiskar and Lozenets formations. The Gnilyane Formation is coal-bearing. It is composed of gravel, conglomerate, sand, sandstone, silt and clay. One coal seam, known as

Balsha Coal-bearing Member, is found in the upper part of the Gnilyane Formation. It has an average thickness of 30 m, but sometimes it is tectonically 70-90 m thick. Its composition is complicated — with many thin layers of coal clay and clay. Sometimes the high-ash (Kremikovski) lignite seam appears under the main seam. The thickness of the Pontian Gnilyane Formation is 100-150 m. The basin is a graben-syncline (Sofia syncline), with a NW-SE direction. The layers are inclined from 10° to 15°. There are known faults with NW-SE direction and SW-NE direction and amplitude up to 100 m.

The Chukurovo basin is located 40 km southeast of the city of Sofia (Fig. 1). The lignite-bearing sediments are of Helvetian age. They are determined from Kamenov (1956) as Formation of the clay sandstone and clay with the Chukurovo coal seam (Кацков, Илиев, 1983). They consist of clay, sandy clay, sandstone, and coal seams with a thickness of 12-18 m. In the southern part, the coal seams compose one complicated coal complex with thickness up to 40 m. The coal-bearing sediments fill the Chukurovo graben, a weakly folded syncline, which has NW-SE orientation. The board of the basin is composed of Formation of the phyllitoid schist and phyllite (Silurian-Devonian), Pancharevo Formation (Middle Triassic) and Gintsi Formation (Middle-Upper Jurassic).

The Samokov basin is located in the Palakariya graben. The Neogene sediments were divided by Анимова, Коюмджиева (1991) who distinguished the lower conglomerate-sandstone formation, Alino and Reliovska Formations. The Alino Formation is coal-bearing and has a Pontian-Dacian age. It contains one lignite seam with thickness 2-9.5 m. The board of the basin is composed of the rocks of the Plana Pluton (diorite, quartz-diorite, granite) and Proterozoic biotite and mica gneisses.

The coal-bearing sediments of the Karlovo basin are represented by the Iganovo Formation, composed of clay, sandstone and silt. Three lignite seams are referred to a Moskovets Member with Miocene-Pliocene age. The coal-bearing sediments fill one NW-SE graben.

The Gabrovitsa basin is located in a graben about 80 km south of Sofia (Fig. 1). The basement and the board are composed of metamorphic rocks with Proterozoic age, granite, and sandy-clay Oligocene sediments. Вацев, Йорданов (1995) introduced four formations, and namely, the Belidolska, Gabrovishka, Dolnopolska, and Drandarishka Formation. The Pontian Gabrovishka Formation contains one lignite seam with thickness up to 2.4 m, with alternation of sandstone, clay sandstone, clay, coal clay and thin coal layers (Table 2).

The coal-bearing sediments of the Kyustendil basin were subdivided into three formations by Вацев, Бонев (1994), and namely: Spasovishka Argillite-Conglomerate-Sand Formation, Skrinianska Sandy-Argillite Formation and Koilishka Conglomerate Formation. The Skrinianska Sandy-Argillite Formation is coal-bearing. The Nikolichevski coal seam with an average thickness of 5 m is situated at the base of the formation. The coal seam is covered by clay, sandy-silt clay with diatomite, carbonate clay, marl, sandstone, and sand. The age of the Skrinianska Formation is Sarmatian-Meotian and Pontian (Upper Miocene). The coal-bearing sediments fill a graben structure, named Kyustendil graben. The seam dips at angles of 5-10°. The coal exhibits a transition from lignite to subbituminous.

The bottom and the boards of the Oranovo-Simitli basin are composed of amphibolite, schist, gneiss, marble, and Paleogene sediments. The Neogene of the Simitli graben is subdivided (Вацев, 1991) into five formations: Drachevishka Conglomerate Formation, Oranovo Coal-bearing Formation, Duarska Sandy Conglomerate Formation, Gradevska Conglomerate Formation and Revalska Conglomerate-Sandy Formation. The Badenian Oranovo Formation is represented by an alternation of sandstone and silt, also sandy clay, bi-

Table 2
Number of samples from coal seams

Basins	Rank	Number of economic seams	Sampled seam	Thickness, m	Number of samples	
					Core	Channel
Maritsa-West	L	2	Kiprenski	2.8		38
Belibreg	L	1	II	20		39
Chukurovo		12	Coal complex	40		40
Gabrovitsa		—	I	1.8	35	5
Karlovo		3	I	1.9	13	
			II	1.4	10	
Samokov		1		8	31	
Sofia		1-2	Balshenski	25	54	5
Stanyantzi		1		22		38
Katrishte	L	1		15		22
Kyustendil		1	Nikolichevski	9.5		39
Oranovo		1	IIa	28		61
Pernik	SB	3	B	1.5		15
			D	3.8		20
Suhostrel	B	—	II	1		17
Balkan	B	3-8	VI	1.2-6.8		26
Svoqe	A	7-17	I	1.5	32	
			II	1.3	29	
			III	1.2	29	

L — lignite; SB — subbituminous coal; B — bituminous coal; A — anthracite.

tumen-rich clay, coal clay, and coal seams. The lignite coal seams have thickness from 1 to 8 m with local thick parts (up to 30 m). The Oranovo-Simitli coal basin is a graben-syncline (the Simitli graben) broken by the Krupnik fault, Gradevski fault and the Struma deep fault.

The Skrinyanska Sandy-Argillite Formation of the Katrishte basin is coal-bearing. It is composed of clay, sandy-silt clay with diatomite, carbonate clay, marl, sandstone, and sand. The age of the formation is Badenian-Sarmatian. One coal seam with thickness up to 15 m is known (Table 2). The coal-bearing sediments fill a graben structure. The coal is lignite to subbituminous.

The Pernik basin is located about 30 km southwest of Sofia (Fig. 1). Paleozoic (conglomerate, sandstone and siltstone), Lower Triassic (conglomerate, sandstone and siltstone), Middle and Upper Triassic (argillite, limestone and dolomite), Jurassic (siltstone and argillite), and Upper Cretaceous (andesite of the Lyulin Pluton, sienite and diorite of the Vitosha Pluton) rocks build the bottom and the boards of the basin. The coal-bearing Paleogene sediments have been subdivided by R. Bergeov and B. Kamenov (s. Зарочев et al., 1994) into five formations: conglomerate-sandstone formation, bitumolite formation, varicolored sub-coal formation, coal-bearing formation, and formation of the thin layered argillite. The coal-bearing formation is represented by sandstone, sandy clay, thin-layered silt, argillite, and coal seams. In the central part of the basin, there are five coal seams with thickness up to 20 m. In the northwestern part of the basin, the coal seams are combined into one coal complex with thickness up to 30 m. The age of the coal is Upper Oligocene. The sediments accumulated in the Pernik graben are folded in one large syncline — the Pernik syncline. There are many known faults with amplitudes from 2 to 15 m to 100-150 m. The coal is subbituminous B.

The coal-bearing sediments of the Suhostrel basin are in from the Upper Eocene Suhostrel Formation (Маринова, 1993). A Piliovo Member contains coal seams of bituminous coal. The coal seams alternate with sandstone, siltstone, argillite, and coal argillite. The bottom and the boards are composed of Proterozoic schist and Paleozoic breccia-conglomerate, sandstone, siltstone, and argillite. The coal-bearing sediments of the Suhostrel and South-Suhostrel synclines are weakly folded.

The bottom and the boards of the Balkan basin are composed of sediments with different age: Paleozoic granodiorite of the Tvarditsa Pluton, Lower Triassic, and Jurassic and Lower Cretaceous sandstone, argillite, marl, and dolomite. Кънчев и др. (1995) divided 3 formations in the Cenomanian sediments: the principal clastic formation, the coal-bearing formation, and the supra-coal marl formation. The basin is a complicated folded system with anticlines, synclines and folds. The sediments are fractured along many faults with amplitude up to 600-700 m. The coal is bituminous.

The Svoge basin is located, about 30 km north of the city of Sofia (Fig. 1). Тенчов (1966) and Русанов, Попов (1987) subdivided the carboniferous sediments into four formations. The Tsarichina Formation (Namurian A, B) is composed of conglomerate, sandstone, silt, argillite, and thin coal seams with a total thickness of 150-200 m. Sandstone, silt, and argillite comprise the Dramsha Formation (Namurian C). The Drenovska Formation (Namurian C-Westphalian B) is composed of conglomerate, sandstone, silt, argillite, coal argillite, and coal seams. Chibaovo Formation (undetermined Westphalian) includes conglomerate, sandstone, silt, argillite, and coal seams. The underlying rocks are sediments with Ordovician, Silurian, Devonian, and Lower Carboniferous age. The Upper Carboniferous sediments are covered by Triassic and Quaternary rocks. The Svoge basin is settled into the frame of the EW Svoge syncline. The carboniferous sediments are highly fractured in two systems: NE-SW and NW-SE. The coal rank is from semi-anthracite to meta-anthracite.

Methods

Coal seams from 14 coal basins were sampled. The samples were channel and/or core (Table 2). Five-hundred-ninety-eight coal and coal shale samples were ground in an agate mortar to <25 mm particle size. Five grams of each sample were combusted at the temperature of 800°C (high temperature ashing) in an oven. The ash was analyzed by Instrumental Neutron Activation Analysis (INAA), Atomic Adsorption Analysis and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The results were processed statistically and the coefficients of correlation between the elements and the ash content (A^d — dry ash) were determined. The Clarke value of Юдович и др. (1985) for the coal ash is used. The latter au-

thors to sum up results from about 10 000 samples from different rank coal from the former Soviet Union, USA, England, Germany, Australia, India, Austria, Canada, Denmark, Portugal, Rumania, Bulgaria, Hungary, France, South Africa, the former Czechoslovakia and other countries.

Results and Discussion

Many authors studied the factors, which influence on the distribution and presence of the elements in coal; for example Yudovich (1978), Войткевич et al. (1983), Swaine (1990), Finkelmann (1995), Eskenazy (1996), and Коптенски (1998).

The main factors which influence the distribution of the siderophile elements in the coals taken into consideration in the present study were: 1) the concentration of elements Fe, Ni, Co, Mn, Cr, V, Ti in the peat-forming plants; 2) the concentration of the Fe, Ni, Co, Mn, Cr, V, Ti in the rocks around the ancient peat bogs; 3) the type and the directions of supplying of the peat bogs with elements or minerals (surface or ground water supplying); 4) the parameters of the environment (pH, Eh) of the ancient peat bogs; 5) cleat and fracture of the

coal seam; 6) the presence and type of the mineralized water in the coal seam.

Iron

The ash of the lignite from the Katrishte deposit contains the highest concentration of iron, with comparison to the Fe content in the coal ash from the other studied basins (Table 3). The ash of the lignite from the Maritsa-West, Chukurovo, Sofia and Stanyantsi basins and Gabrovitsa deposit contains more than 10% Fe. The average Fe concentration in the ash of the sub-bituminous coal from the Pernik basin is 18.23%. The lowest iron content is found in the ash of the Karlovo lignite and the Svoqe anthracite. The iron content in the coal ashes from the Maritsa-West, Chukurovo, Sofia, Pernik, Stanyantsi basins and the Gabrovitsa and Katrishte deposits is higher than the data for the other world basins (with an exception of the Teruel coal ash) (Table 4). Coal ashes from the Karlovo lignite and the Svoqe anthracite have lowest concentrations of Fe in comparison with other basins from Table 4.

Iron has a negative coefficient of correlation with the ash content in the studied coal, especially in the coal from the Pernik, Maritsa-

Table 3

Average content of the siderophile elements in coal ash from studied Bulgarian basins

Coal province	Basins	Rank	Number of samples	Fe, %	Ni, ppm	Co, ppm	Mn, ppm	Cr, ppm	V, ppm	Ti, ppm
Trakiyska	Maritsa-West	L	38	12.1	57.7	19.8	1660	50.1	61.7	ND
Sofiyska	Belibreg	L	39	6.9	4.2	2.1	1150	49.9	18.8	300
	Chukurovo		40	14.6	90.5	73.6	344	21.3	33.6	1140
	Gabrovitsa		40	11.2	26.6	6.8	604	75.0	96.6	611
	Karlovo		23	4.3	16.2	9.1	114	144.7	147.4	4320
	Samokov		31	7.7	136.2	29.2	1314	120.7	149.0	2430
	Sofia		59	11.8	107.1	36.2	790	130.0	170.0	6900
	Stanyantzi		38	10.9	62.7	6.8	150	ND	130.0	1860
Strumsko-Mestenska	Katrishte	L	22	29.6	109.8	30.5	588	7.5	26.4	2880
	Kyustendil		39	13.8	11.6	3.1	426	200.4	83.4	2094
	Oranovo		61	6.5	51.9	19.7	800	17.7	25.3	2600
Pernishka	Pernik	SB	35	18.2	331.2	150.2	755	106.0	250.0	4785
	Suhostrel	B	17	6.2	10.1	9.2	370	277.0	277.0	1000
Balkanska	Balkan	B	26	7.4	18.4	14.6	144	85.4	142.4	2600
Svogenska	Svoqe	A	90	5.8	106.5	59.9	1067	218.6	176.4	12575
	Clarke for lignite and sub-bituminous coal ¹			ND	51.0	20.0	510	70.0	120	2600
	Clarke for bituminous coal and anthracite ¹			ND	90.0	34.0	460	86.0	180	4600

¹ — по Юдович и др. (1985); L — lignite; SB — subbituminous coal; B — bituminous coal; A — anthracite; ND — no data.

Table 4

Average content of studied elements in coal ash from different world coal basins

Country, Basin	Rank	Fe, %	Ni, ppm	Co, ppm	Mn, ppm	Cr, ppm	V, ppm	Ti, ppm	References
Austria	L	ND	250	80	500	155	300	5000	1
Hungary, Northeast basin	L	9.5	80	12	100-150	30-60	80-110	1613	2
Belarus	SB	ND	16	ND	90	22	110	ND	3
Serbia, Kosovo	L	ND	59-228	4-26	ND	8-375	8-160	486-4597	4
Canada, Saskatchewan	SB	3.61	27.3	12.1	140.6	97.2	25.0	3900	5
India, East Bokaro	B	ND	77-150	26-80	200	95	92	ND	6
Bulgaria, Elhovo	L	ND	113	45	854	60	941	7605	7
England, Eggbourg	B	9.45	140	ND	750	200	348	5600	8
England, Barnsley	B	3.69	52	ND	200	107	173	5800	9
Bulgaria, Burgas	SB	9.4	12	12	572	20	123	3653	10
Greece, Drama	L	ND	56-93	79-366	ND	91-213	110-188	ND	11
Spain, Teruel	L	11.61	88	29	ND	134	208	5080	12

1 — Brandenstein et al. (1960); 2 — Veto (1973); 3 — Бордон (1973); 4 — Rupert et al. (1996); 5 — Beaton et al. (1991); 6 — Parrek and Bardhan (1985); 7 — Eskenazy (1996); 8 — Spears and Martinez-Tarazona (1993); 9 — Spears and Amin (1981); 10 — Eskenazy, Mincheva (1983); 11 — Filippidis et al. (1996); 12 — Querol et al. (1997a); ND — no data. L — lignite; SB — sub-bituminous coal; B — bituminous coal; A — anthracite.

Table 5

Correlation coefficients between various elements and ash content

Coal province	Basin	Rank	Statistical mean values	Fe-Ash	Ni-Ash	Co-Ash	Mn-Ash	Cr-Ash	V-Ash	Ti-Ash
Trakiyska	Maritsa West	L	± 0.28	-0.69	-0.72	-0.61	-0.48	-0.29	-0.49	-
Sofiyska	Belibreg	L	± 0.20	-0.57	+0.37	+0.35	+0.37	+0.20	+0.02	-0.32
	Chukurovo	L	± 0.21	-0.50	-0.68	-0.61	+0.33	+0.05	+0.21	+0.64
	Gabrovitsa	L	± 0.25	-0.36	-0.35	-0.26	-0.56	+0.08	-0.04	+0.03
	Karlovo	L	± 0.41	-0.51	-0.50	-0.45	+0.05	-0.68	-0.72	-0.03
	Samokov	L	± 0.35	-0.11	-0.09	-0.05	+0.04	-0.39	-0.02	+0.39
	Sofia	L	± 0.22	-0.42	-0.42	-0.23	-0.08	-0.36	-0.39	-0.31
	Stanyantzi	L	± 0.32	-0.01	-0.04	-0.13	-0.53	-	+0.43	+0.68
Strumsko-Mestenska	Katrishte	L	± 0.40	-0.81	-0.71	-0.43	-0.41	+0.56	+0.49	+0.02
	Kyustendil	L	± 0.32	-0.45	-0.74	-0.65	+0.09	+0.05	+0.39	-0.48
	Oranovo	L	± 0.25	-0.67	-0.44	-0.37	-0.38	+0.40	-0.41	+0.12
Pernishka	Pernik	SB	± 0.33	-0.60	-0.67	-0.53	-0.34	-0.45	-0.45	+0.41
	Suhostrel	B	± 0.29	-0.41	+0.55	+0.35	-0.29	-0.30	+0.19	+0.01
Balkanska	Balkan	B	± 0.36	-0.57	-0.05	-0.52	-0.47	-0.37	+0.03	+0.24
Svogenska	Svoqe	A	± 0.21	-0.11	-0.35	-0.25	-0.45	-0.42	+0.09	-0.36

L — lignite; SB — subbituminous coal; B — bituminous coal; A — anthracite; ND - no data.

West and Oranovo basins and the deposit of Katrishte (Table 5). The coefficients of correlation between the Fe content and the ash content in this coal vary from -0.6 to -0.81. The average Fe concentration in the studied coals decreases, when the ash content increases. That negative relationship is well established for the Maritsa-West and Oranovo coal (Fig. 2). The average concentration of the Fe in

the Svoqe anthracite and Stanyantsi lignite does not change significantly with ash content increasing (Fig. 2). The coefficients of correlation of Fe with the ash contents in these coals and Samokov lignite also are under statistical mean values (Table 5). Pyrite is present in all studied coals and siderite and chalcopyrite are frequently observed minerals. Iron is present as a trace element in calcite and dolomite, its

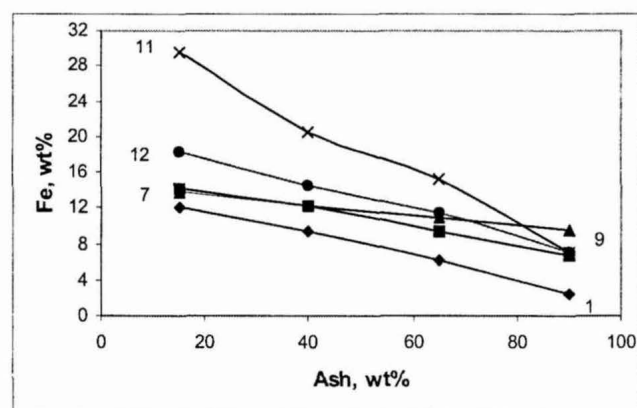
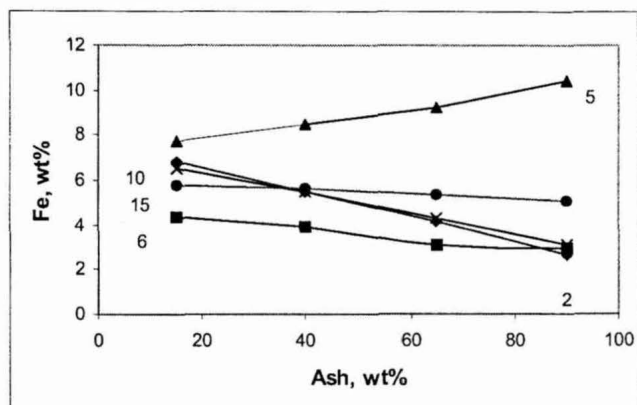
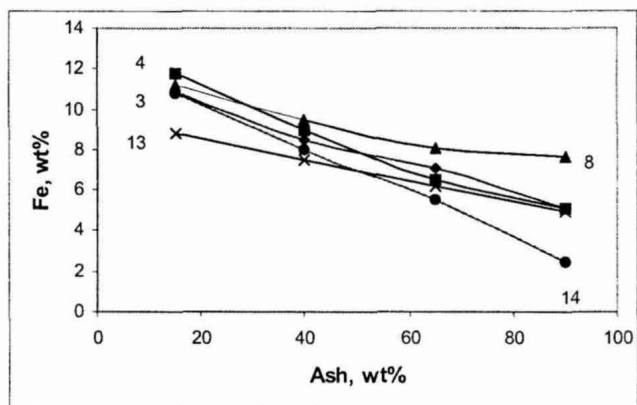


Fig. 2. Plot of the distribution of the average Fe concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%.

1 — Maritsa-West; 2 — Stanyantsi; 3 — Beli breg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoqe

content varying from 1 to 5% (Kortenski, 1992).

The reference data for the prevailing affinity of Fe is shown in Table 6. Манская, Дроздова (1964) established the optional environment for deposition of the element as a metal-organic combination — pH ranges of 3-6. Ward (1992) also suggested that, when Fe is not in the siderite (formed iron acid phase environ-

ment), it can form metal-organic combinations.

The high concentration of Fe in the studied coal is a result of all of the above-mentioned factors. Iron is present in plant tissues (average about 0.014%, according to Bowen, 1966). The biogenetic contribution of Fe is possible, but the role of that factor is not strong, because there is a large difference between Fe contents in the coals of similar taxonomy within one province — for an example the Sofia province (Table 3). The concentration of Fe in Bulgarian coal depends on its concentration in the rocks around the peat bogs (especially, when the basin is situated near metalogenic provinces). Probably, the Fe content in the coal from the Sofia (11.8%) and Chukurovo (14.6%) basins is comparatively high because these basins are situated near the Kremikovtsi iron ore deposit. That ore deposit is probably the source of the iron for the ancient peat bog.

The cleat and fracture of the coal of the coal seams is high for the Oranovo, Pernik, Balkan and Svoqe basins. Mineral solutions, which penetrated the coal seams at the time of diagenesis, catagenesis or metagenesis probably were poor in Fe, because the concentration of the element in these coals is not high, with the exception of the Pernik coal.

Nickel

The concentration of Ni is more than two times the Clarke number in the coal ash from the Pernik, Sofia, Samokov, Chukurovo and the Katrishte basins. The Ni content in the coal ashes from the Maritsa-West, Stanyantsi, Oranovo and Svoqe is approximately identical with the Clarke number. The Ni content in the coal ash is lower than the Clarke number in the other Bulgarian basins. The Ni concentration in the studied Bulgarian coals is lower than that some Austrian and British coals (Table 4).

For Bulgaria, the Ni concentration is highest in the subbituminous coal and some lignite and it is very low in the bituminous coal (Table 3). This data is opposite from the suggestion of Юдович и др. (1985), that the concentration of Ni increases with an increase of coal rank.

Zubovic (1966) reported data for an organic affinity of Ni (59%) for some American coals. The presence of Ni with organic affinity is a result of reaction of these elements with the organic matter (Szalay, Szalagyi, 1969). Many authors have reported data for various affinities of Ni (Table 6).

The negative coefficient of correlation between the Ni and ash content is established in

Table 6
Reference data of the siderophile element affinities

Elements	Reference data of the element affinities		
	Organic	Intermediate	Inorganic
Fe	Newman et al. (1997)	Beaton et al. (1991); Querol et al. (1997c)	Gluskoter et al. (1977) and Querol et al. (1997b)
Ni	Otte (1953); Nichols and Loring (1962); Oelschlegel (1964); Юдович, Шасткевич (1966); Ward (1980); Finkelman (1995); Warwick et al. (1997)	Zubovic et al. (1966); Смирнов (1969); Pareek and Bardhan (1985); Eskenazy et al. (1986); Kojima and Furusawa (1986); Gluskoter et al. (1977); Swaine (1990); Ескенази, Минчева (1992)	Хризман (1960); Юровский (1968); Beaton et al. (1991); Filipidis et al. (1996); Querol et al. (1992, 1997a,b); Crowley et al. (1997)
Co	Nichols and Loring (1962); Oelschlegel (1964); Ward (1980); Finkelman (1995); Filipidis et al. (1996)	Otte (1953); Zubovic et al. (1966); Смирнов (1969); Gluskoter et al. (1977); Eskenazy et al. (1986); Kojima and Furusawa, (1986); Swaine (1990); Beaton et al. (1991); Ескенази, Минчева (1992); Crowley et al. (1997)	Хризман (1960); Юровский (1968); Parrek and Barhan (1985); Querol et al. (1992, 1997a,b)
Mn	Минчев, Ескенази (1961); Beaton et al. (1991); Eskenazi (1996); Pipiringos (1966); Querol et al. (1997,b,c); Crowley et al. (1997)	Идзиковски, Трзебятowski (1960); Spears and Tarazona (1993)	Otte (1953); Lentwein and Rosler (1956); Ломашов, Лосев (1962); Минчев, Ескенази (1972); Gluskoter et al. (1977); Kojima and Furusawa (1986)
Cr	Otte (1953); Gluskoter et al. (1977); Ескенази, Минчева (1992); Eskenazi (1996)	Смирнов (1969), Kojima and Kurusawa (1986)	Ward (1980); Parrek and Bardham (1985); Beaton et al. (1991); Querol et al. (1992); Griene and Goodarzy (1993); Fillipidis et al. (1996); Crowley et al., 1997)
V	Otte (1953); Ward (1980); Parrek and Bardham (1985); Kojima and Kurusawa (1986); Spears and Martinez-Tarazona (1993)	Zubovic et al. (1961); Смирнов (1966); Узунов (1973); Querol et al. (1997c)	Beaton et al. (1991); Querol et al. (1997b)
Ti	Otte (1953); Щербина (1980); Kojima and Kurusawa (1986)	Crowley et al. (1997); Warwick et al. (1997)	Смирнов (1969); Beaton et al. (1991); Querol et al. (1997b,c)

most of the investigated coals (Table 5). This negative coefficient varies from -0.5 to -0.74 in the lignite from Maritsa-West, Chukurovo, Kyustendil, Katrishte, Karlovo and subbituminous coal from Pernik (Table 5). The concentration of Ni decreases, when the ash content increases (Fig. 3). The lignite from Stanyantsi, Samokov and the bituminous coal from Balkan basin have coefficients of correlation between Ni concentration and ash content under the statistical mean value (Table 5). The Ni content in the Stanyantsi and Samokov, and Balkan coals is almost constant when the coal ash increases (Fig. 3). Only the Belibreg and Suhostrel coal have positive coefficients of correlation between ash Ni content and the concentration of Ni increases with the increasing of the ash content (Fig. 3).

The plants were an important factor for the supplying of the peat bog with Ni. Юдович et al. (1985) reported a biogenetic presence of

this element. The biogenetic factor is not so important, because the Ni concentration in plants is low — up to 3 ppm (Bowen, 1966). The high content of Ni probably relates with its transportation from the adjacent source rocks into the peat bog. The element is not present in the infilling cracks and cavity-infiltration pyrite observed in the Bulgarian coals (Kortenski, Kostova, 1996). A direct ratio between Fe and Ni was not established (Fig. 9). Probably, the high cleat and fracture of the coal seams of Pernik, Balkan and Svoге basins and respectively the presence of the infilling infiltrational pyrite mineralization have not been very important for the concentration of Ni.

Cobalt

The coal ashes from Samokov, Chukurovo, Sofia, Pernik, Svoге, and Katrishte basins have concentrations of Co higher than the Clarke

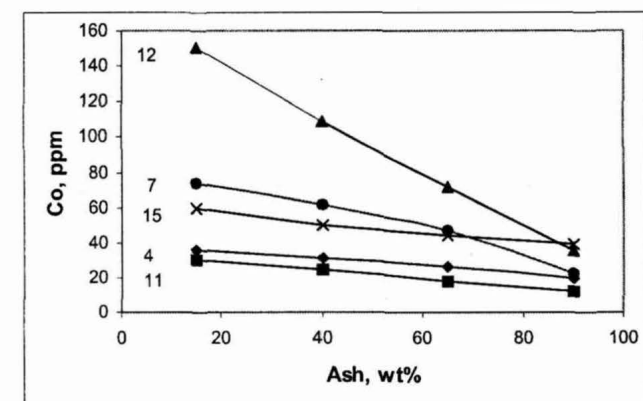
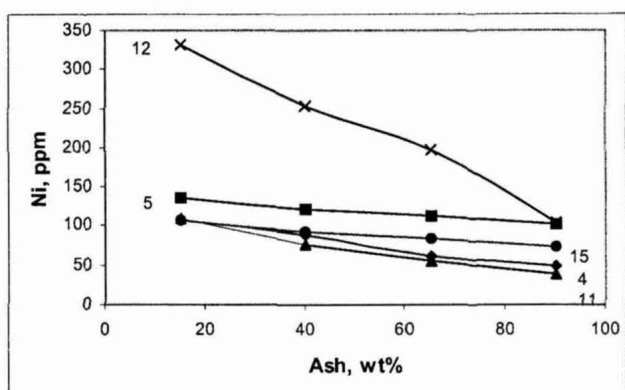
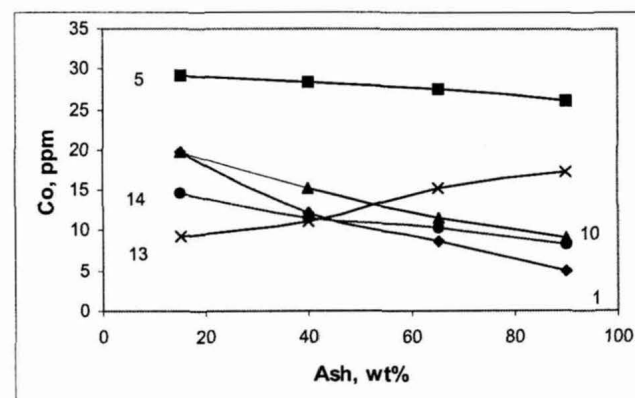
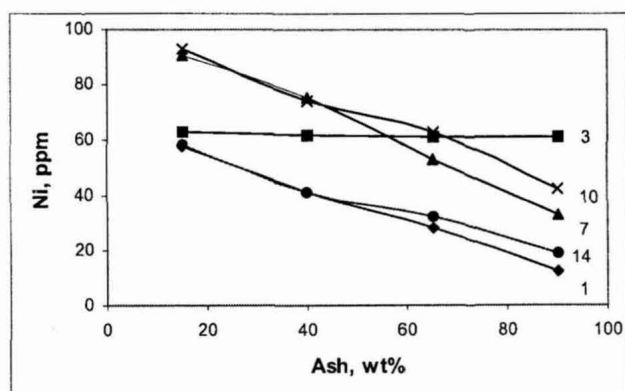
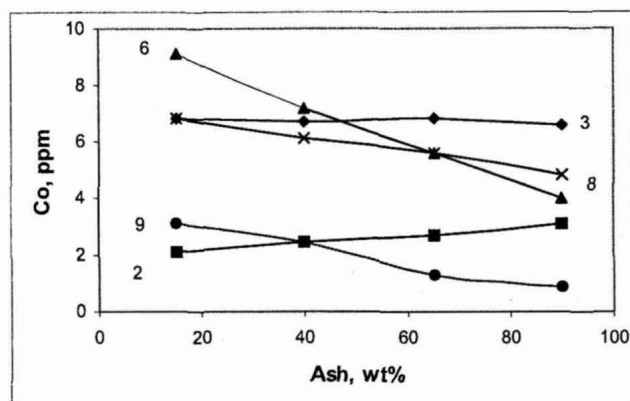
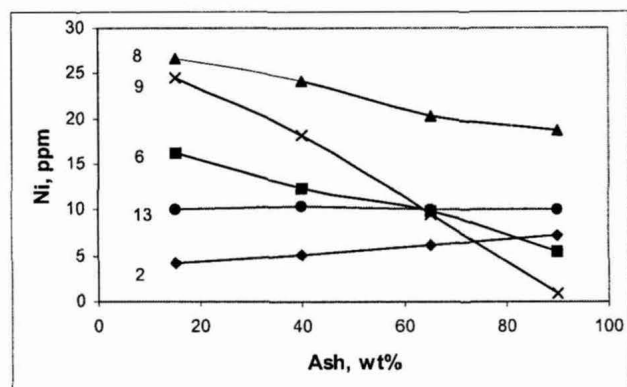


Fig. 3. Plot of the distribution of the average Ni concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%.

1 — Maritsa-West; 2 — Stanyantsi; 3 — Belibreg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoje

Fig. 4. Plot of the distribution of the average Co concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%.

1 — Maritsa-West; 2 — Stanyantsi; 3 — Belibreg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoje

value (Table 3). The Co concentration is approximately the same as the Clark values in the coal ashes from the Maritsa-West and Oranovo basins. The Co content in the coal ash less than the Clarke value in all other basins (Table 3). The concentration of Co in the coal ash from the Pernik basin is significantly higher than the data from the other basins in Table 4.

Most of the studied coals have negative coefficients of correlation between the concentration of Co and their ash content (Table 5). Figure 1 shows that the concentration of Co decreases with increasing ash content. The negative coefficient of correlation is most significant (from -0.52 to -0.65) (Table 5) for coal from Maritsa-West, Chukurovo, Kyustendil, Pernik, and Balkan basins. The corre-

lation coefficients between Co and the ash content of the coal from Stanyantsi and Samokov is below the statistical mean values and the concentration of Co does not change with variations in the ash content (Fig. 4). The Belibreg and Suhostrel coals have a positive correlation and the Co concentration these coal increases with increasing ash content (Table 5).

Many authors published data for Co affinity (Table 6). Zubovic (1966) noted an organic affinity of Co (53%) for some American coals. The presence of Co with organic affinity is a result of reaction of the element with the organic matter (Szalay and Szalegui, 1969). Swaine (1990) noted an association of Co with pyrite.

The factors which influence on the distribution of the Co concentration are similar to that of Ni.

Manganese

The Mn content in the coal ash from most of the investigated basins is higher than the Clarke value for Mn concentration in coal (Table 3). The Mn concentration in the coal ash from Kyustendil, Stanyantsi, Chukurovo, Karlovo and Balkan basins are less than the Clarke value. The Mn concentration in the ash of the studied basins (with the exception of Stanyantsi, Karlovo, and Balkan basins) is higher than Mn concentrations from selected world basins (Tables 3, 4).

The coefficients of correlation of Mn concentrations with the ash content are negative for most of the studied coals, varying between -0.08 and -0.56 (Table 5). The concentrations of manganese in coals with a negative correlation to ash content decrease with increasing ash content (Fig. 5). The Mn concentration has values of the coefficients of correlation under the statistical mean for the coal from Sofia, Chukurovo, Karlovo, Samokov and Kyustendil (Table 5). The Mn content does not appear to change with changes in ash content (Fig. 5). A high positive coefficient of correlation is illustrated only for the lignite from Belibreg basin (Table 5). Here the concentration of Mn increases, when the ash content increases (Fig. 5).

Many authors determined affinities of Mn (Table 6). The organic presence of Mn is mainly probably related to biogenetic activities. Юдович et al. (1985) and Ескенази (1993) suggested that when the pH is between 5 and 7, Mn is present not only in the carbonates, but it may also be present in organic complexes.

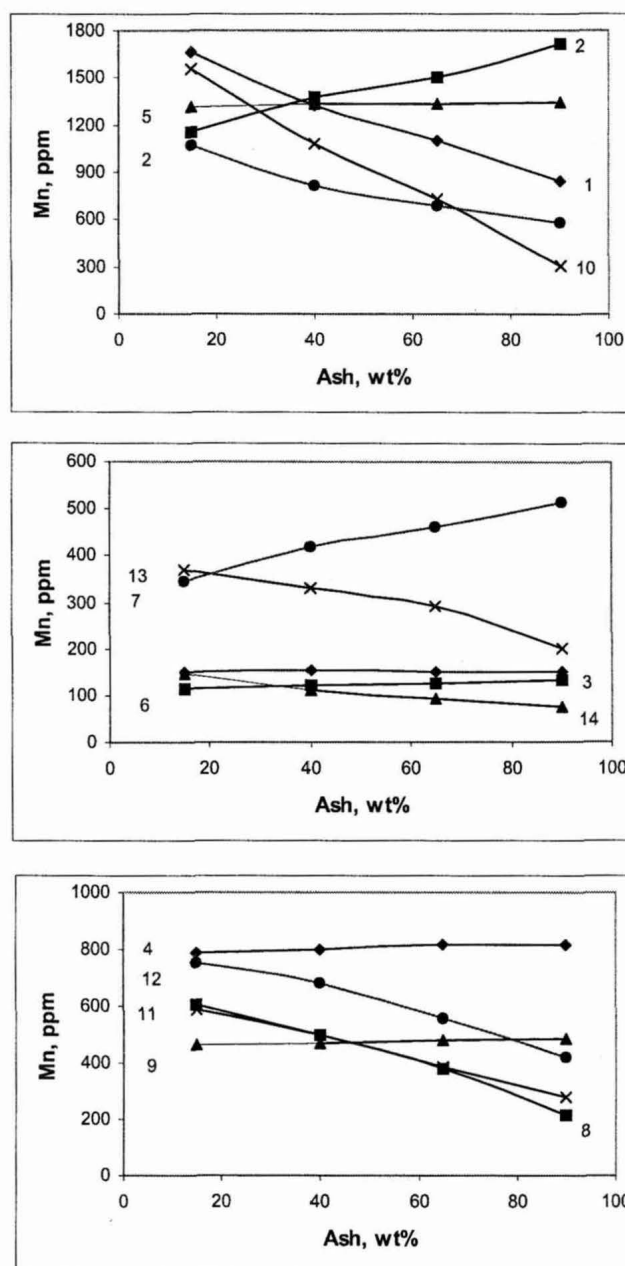


Fig. 5. Plot of the distribution of the average Mn concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%. 1 — Maritsa-West; 2 — Stanyantsi; 3 — Belibreg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoge

An important factor that influences concentration of Mn in coal is the presence of the element in the source rocks around the ancient peat bogs. This appears to be the main reason for the high content of Mn in the Belibreg lignite, where the source rocks adjacent to the basin are Triassic and Jurassic limestone. The presence and active infiltration of carbonate mineralization are important factors for the high Mn concentration (Pernik, Oranovo and

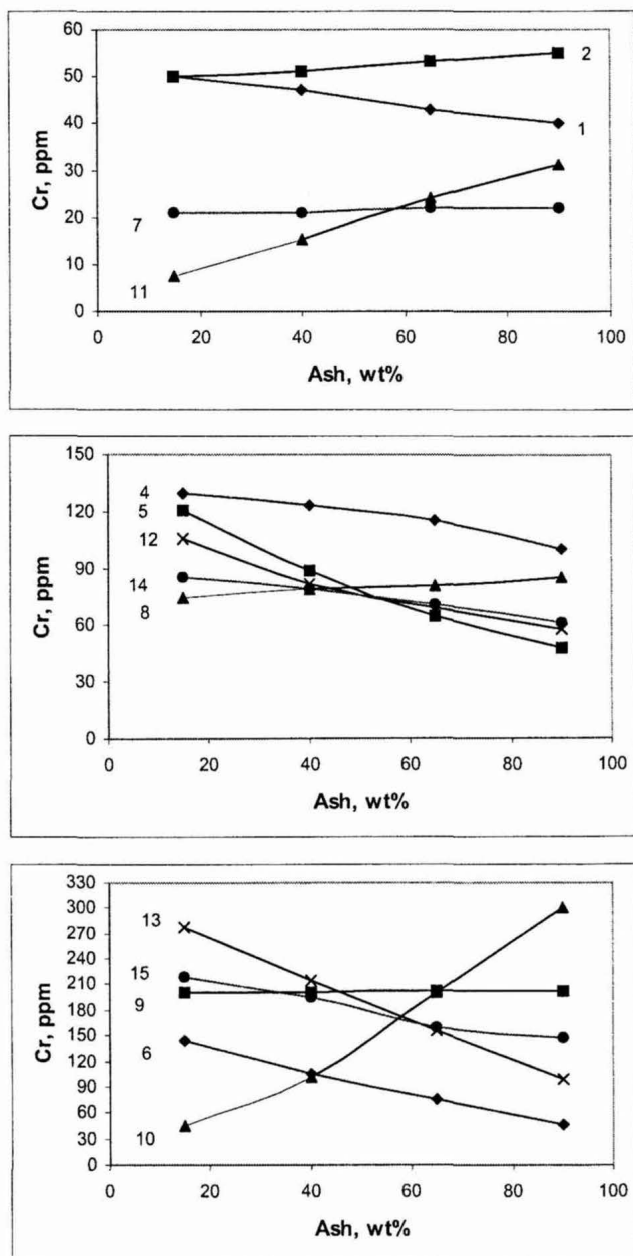


Fig. 6. Plot of the distribution of the average Cr concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%.

1 — Maritsa-West; 2 — Stanyantsi; 3 — Belibreg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoje

especially Svoje coal). The Mn content is up to 1% in the infiltration carbonates from the Svoje basin (Kortenski, 1992).

Chromium

The chromium distribution in the different coal ashes is not uniform. It varies from 1.5-3.1 times the Clarke value for the Sofia,

Karlovo, Samokov, Kyustendil, Pernik, Svoje, and Suhostrel basins (Table 3); to 3.3-9.3 times less than the Clarke values for coal ashes (Chukurovo, Oranovo and Quartette) (Table 3). The Cr concentration in the coal ash from the Katrishte deposit is very low, but the coal ashes from the Suhostrel and Svoje basins contain highest concentration of this element in comparison with coals from other basins (Tables 3, 4).

In the present study the bituminous and anthracite coals have higher Cr concentration (with the exception of the Balkan basin 85.4 ppm) than the lignite and subbituminous coals (Table 3). Possibly the depositional environments and the rank of the coal are important for the concentration of the element.

Various reference data for the affinity of Cr is reported in Table 6. Zubovic et al. (1961) are suggested that Cr^{3+} frequently and easily reacts with organic acids. Querol et al. (1997b, c) found that Cr has very high positive coefficient of correlation with the aluminum-silicate content of the coal.

Most of the studied Bulgarian coals have a negative coefficient of correlation between the concentration of Cr and the ash content. This negative coefficient is highest (-0.68) in the lignite from Karlovo (Table 5). The Cr concentration in this coal decreases, when the ash content increases (Fig. 6). The coals from Oranovo and Katrishte basins have positive coefficients of correlation between the Cr and the ash content (Table 5), the Cr concentration increasing with increasing ash content (Fig. 6). The Chukurovo, Kyustendil and Gabrovitsa lignite have positive coefficients of correlation of the Cr with the ash content, but the value is lower from the statistical mean values (Table 5). The Cr concentration does not vary greatly with changes in ash content (Fig. 6).

The average Cr content in plants is low — 0.23 ppm (Bowen, 1966). In the studied Bulgarian coals, the main reasons for the high concentration of Cr are: 1) the presence of Cr in the rocks around the basins and 2) good conditions for accumulation of Cr in the peat bogs. The relationship between the Cr concentration in the Sofia lignite and the Cr concentration from the adjacent Vitosha Pluton has been established. The Cr content in the andesites from Vitosha pluton is 270 ppm (Кортенски, 1986). Probably, the clay minerals derived from the pluton because the main Cr source in the peat bog. Epigenetic mineralization appears not to have influenced the Cr content in the coal, because the Cr concentra-

tion in the infiltrational calcite and dolomite from the Svoje anthracites is very low — from 0 to 100 ppm (Kortenski, 1992).

Vanadium

The concentration of V in the coal ash from the Sofia, Karlovo, Samokov, Pernik basins and Suhostrel deposit is greater (1.2-2.1 times) than the Clarke values (Table 3). The V concentration in the ash from Stanyantsi and Svoje is approximately equal to the Clarke value. The coal ashes from all other basins contain V in concentrations less than the Clarke value. The ash from the Belibreg lignite has the lowest concentration of V and Oranovo and Katrishte coal ashes have nearly the same amount as some Canadian coals (Table 4). The V content in the other studied coal is identical of the data for selected world basins (Table 4; with the exception of some Canadian coals).

The V concentration in the Bulgarian bituminous coal and anthracite is higher, than in the lignite and subbituminous coal (Tables 3, 4).

The coefficient of correlation between V concentration and the ash content is negative (ranging from -0.39 to -0.72) for the coal from Karlovo, Maritsa-West, Sofia, Oranovo and Pernik (Table 5). The concentration of the element in these coals decreases, when the ash content increases (Fig. 7). Positive correlation coefficients (from $+0.21$ to $+0.49$) are established for the lignite from Chukurovo, Stanyantsi, Katrishte and Kyustendil (Table 5). The V concentration increases with the increasing of the ash content (Fig. 7). The coefficient of correlation between the element and the ash content is positive or negative, but it has absolute value below the statistical important value for the coal from Belibreg, Samokov, Gabrovitsa, Suhostrel, Balkan and Svoje (Table 5). The V content changes insignificantly, when the ash content changes (Fig. 7).

Many authors have published data suggests a prevailing V affinity (Table 6). Войткевич et al. (1983) suggested that, in the presence of organic matter, VO_3^- reduces to VO_2^+ , which can react with humic acids.

The V content in plants is low — only 1.6 ppm (Bowen, 1966). V may have been transported together with clastic minerals into the ancient peat bog. The V concentration in Sofia lignite is 170 ppm and the V content in the Vitoshka pluton (the Southern side of the basin) is 130 ppm (Кортенски, 1986). The Vitoshka pluton andesites are probably the source of the

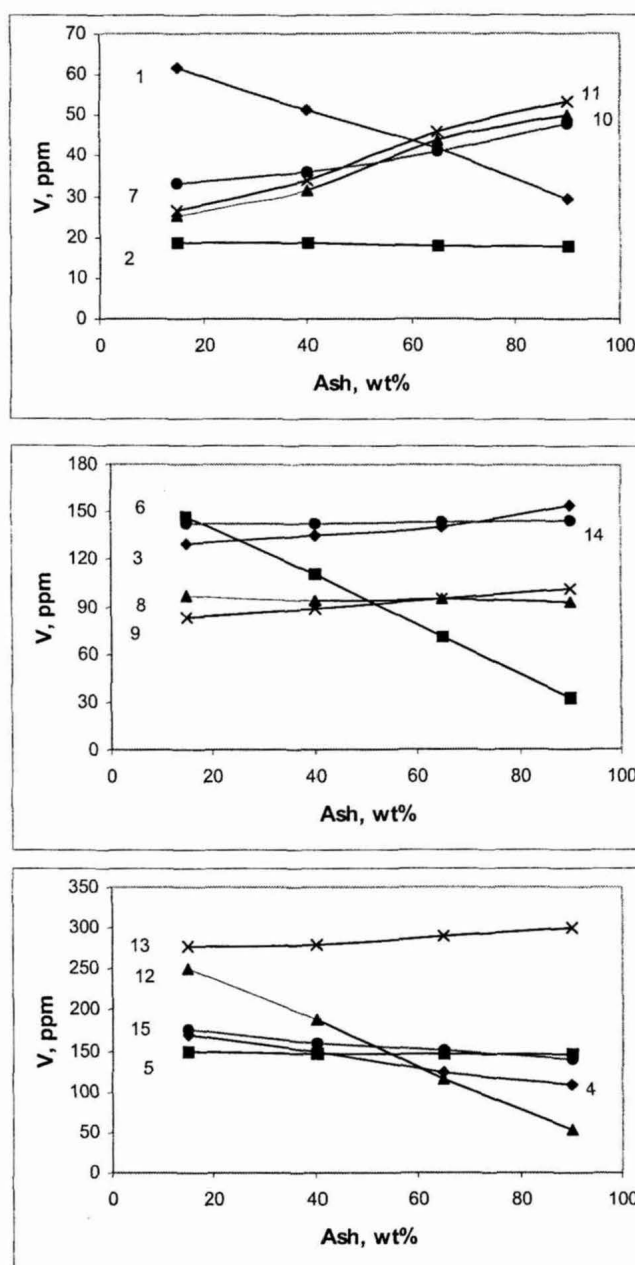


Fig. 7. Plot of the distribution of the average V concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%.

1 — Maritsa-West; 2 — Stanyantsi; 3 — Belibreg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoje

V in the Sofia ancient peat bog. Vanadium might have accumulated in the clay minerals or in the organic matter. The epigenetic mineralization appears not to have influenced on the V concentration in the studied coal, with the exception of the infiltrational of siderite into the Svoje anthracites. Its content is from 300 to 1000 ppm (Kortenski, 1992).

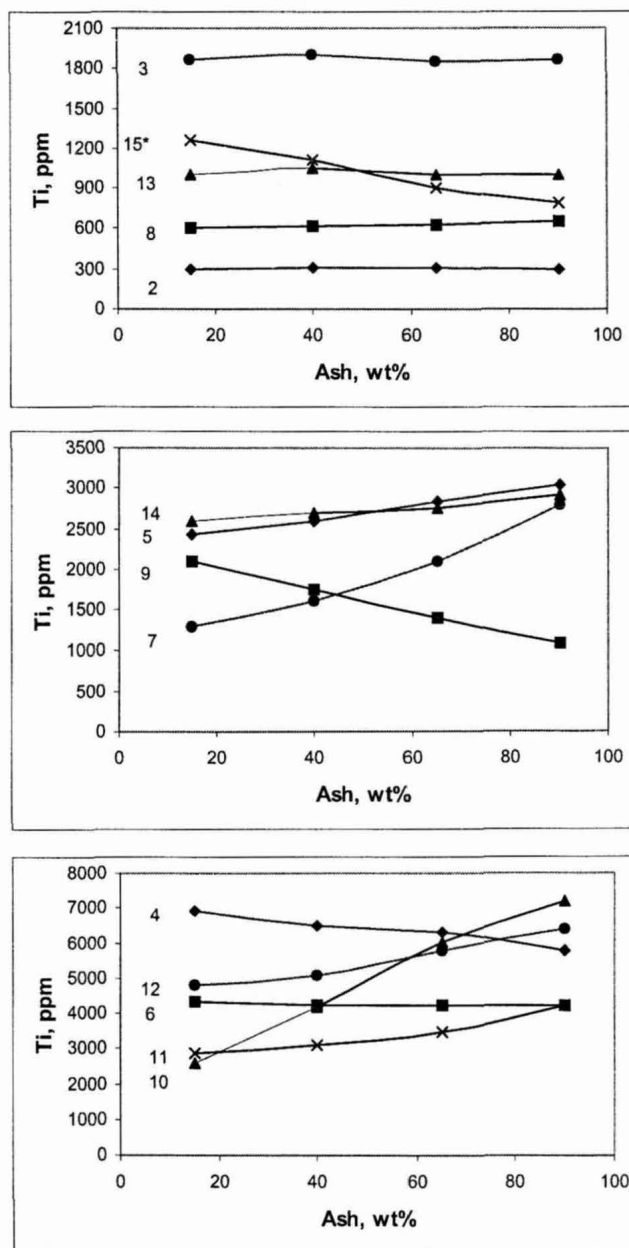


Fig. 8. Plot of the distribution of the average Ti concentration versus ash content. The average concentrations were determined in the following intervals of the ash content: 0-30%; 30-50%; 50-80% and >80%.

1 — Maritsa-West; 2 — Stanyantsi; 3 — Belibreg; 4 — Sofia; 5 — Karlovo; 6 — Samokov; 7 — Chukurovo; 8 — Gabrovitsa; 9 — Kyustendil; 10 — Oranovo; 11 — Katrishte; 12 — Pernik; 13 — Suhostrel; 14 — Balkan; 15 — Svoge

Titanium

Compared to the results of other studied basins, the Ti concentration is greatest in the Svoge anthracite and the Sofia lignite (Table 3). The Ti content in the coal ashes from the Karlovo, Katrishte and Pernik is 1.1-1.8 times higher than the Clarke values (Table 3). The Ti

in the coal ashes from all other basins have Ti below the Clarke value. In comparison with results from selected coal basins (Table 4), the concentration of Ti is lower in the studied coal from Bulgaria, with an exception of the Svoge anthracite and Sofia lignite (Tables 3, 4).

The coefficients of correlation between the Ti concentration and the ash content are negative (-0.31 to -0.48) in the coal from the Belibreg, Sofia, Kyustendil, and Svoge basins (Table 5). In these coals the Ti concentration decreases, when the ash content increases (Fig. 8). Positive correlation between the Ti and ash was established only for the coals from Chukurovo, Stanyantsi, Samokov, Pernik and Balkan basins ($+0.21$ to $+0.68$) (Table 5). The Ti concentration in these coals increases, when the ash content increases (Fig. 8). The coals from Karlovo, Oranovo, Gabrovitsa, Katrishte, and Suhostrel basins have correlation coefficients below the statistical mean (Table 5), but the Ti concentration does not change when the ash content changes (Fig. 8).

Ti has different affinities according to the data presented in Table 6. Querol et al. (1997 b, c) established a relationship between Ti concentrations and the aluminum-silicate part of the mineral matter in the coal. Юдович и др. (1985) noted that the organic complexes of Ti are unstable and they can become oxides.

The source of Ti in coals is not from the plants, because the element content is usually 1 ppm (Bowen, 1966). Probably, in the studied Bulgarian coals, the main source of the concentration of Ti is the rocks adjacent to the peat bogs. For example, the rocks from the source areas of the Sofia basin contain Ti from 1700 to 2900 ppm (Кортенски, 1986). The mineral forms of Ti are mainly rutile and clay minerals. Moreover, Ti presents as trace amounts in other minerals. Kortenski and Kostova (1996) established the presence of Ti concentrations in various pyrite forms from 0.01 to 1 % and Kortenski (1992) published data for 0.03-1% Ti concentrations in various syngenetic carbonates from the Balkan and Svoge coals.

An important factor appears to be the fractures and cleats in the coal seams and the type of the ground water solutions that moved through the seams. Kortenski and Kostova (1996) reported Ti concentrations about 0.03% in secondary pyrite from Balkan and Svoge basins and the concentration of the element is up to 5% in the infiltrational siderite from Svoge (Kortenski, 1992).

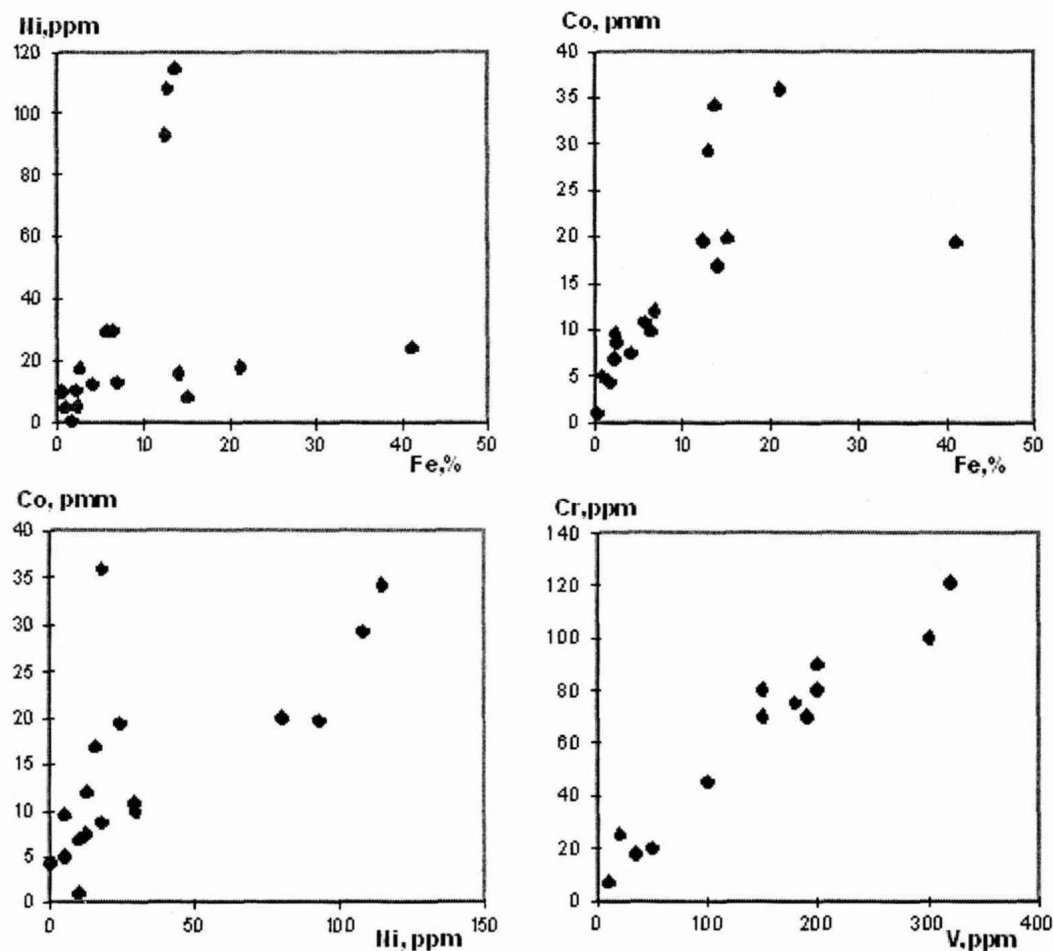


Fig. 9. Relationship between the content of some siderophile elements in coals from different basins

Conclusions

All data presented above suggest that the studied Bulgarian coals have high concentrations of siderophile elements Fe, Ni, Co, Mn, Cr, V, Ti. The concentrations of the elements are not related to coal rank. The following tendencies of the concentrations and distribution of the siderophile elements in the studied coal were established:

The correlation coefficient between Ni and Co is positive and very high (Fig. 9). A similar correlation between Cr and V is observed also (Fig. 9), but their distribution differs from Ni and Co distribution. All other elements have different concentrations in the studied coals, as a result of different local sedimentation or epigenetic conditions.

The elements Ni and Co have similar inorganic or organic affinities in all studied coal samples. The values of their coefficients of correlation with the ash content are very similar (Table 3). Ni has a mixed affinity and Co has an organic affinity only in the Balkan coal. The affinity of the Fe is very interesting, which is

similar to the affinity of Ni and Co. The values of their correlation coefficients with the ash are very similar also (Table 5). The Belibreg and Suhostrel coals are an exception, because the Ni and Co have an inorganic affinity. The environment of the Belibreg ancient peat bog was probably near neutral ($\text{pH}=6.5-7.5$), but the environment of the Suhostrel peat bog was probably acid ($\text{pH}=3-5$) (Kortenski and Kostova, 1996). Probably, Fe, Ni, and Co have an organic affinity when the pH of the environment varies between 5 and 6. Fe and Co have equal correlation coefficients with ash content in the Balkan coal (Table 3). The Cr and V have similar affinity only in the coal from Sofia, Maritsa-West, Karlovo, Pernik, Katrishte and Gabrovitsa.

The affinity of all siderophile elements is absolutely identical only in the Maritsa-West lignite (which has an organic affinity). The environment acidity of the ancient peat bog was probably $\text{pH}=4-6$ (Kortenski, 1992). The siderophile elements have an organic affinity in the coal from Sofia (with the exception of Mn, which has mixed affinity, but it has negative

coefficient of correlation with the ash content), Karlovo (with the exception of the mixed affinity of Mn and Ti, but Ti has negative coefficient of correlation with the ash content), Svoje (with an exception of the mixed affinity of the Fe and V, but the Fe has negative coefficient of correlation with the ash content), and Pernik (with an exception of the inorganic affinity of Ti). The siderophile elements have different affinity in all other studied coals, but some of the elements appear to have identical affinities, with an exception of the Stanyantzi and Suhostrel coal (Table 3).

The major factors for the accumulation of the siderophile elements in the studied Bulgarian coals were: 1) the location of the basins close to metallogenic provinces (Sofia and Samokov basins) or the high concentrations of the elements in the source rocks around the basins (Pernik, Svoje, etc.); 2) optimal environment (pH, Eh) for the formation of organic or inorganic complexes in the ancient peat bogs; 3) the cleat and fracture of the coal seams with combination of presence of solutions, which contains siderophile elements (Pernik, Balkan and Svoje basins).

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