

Trace elements in the Goze Delchev coal deposit, Bulgaria

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Abstract

The geochemistry of trace elements in the underground and open-pit mine of the Goze Delchev subbituminous coal deposit have been studied. The coals in both mines are highly enriched in W, Ge and Be, and at less extent in As, Mn and Y as compared with the world-wide Clarkes for subbituminous coals. Ni and Ti are also enhanced in the underground coals, and Zr, Cr and Mo in the open-pit mine coals.

Characteristic for the trace element contents in the deposit is a regular variation with depth. The following patterns were distinguished for profile I: a — the element content decreases from the bottom to the top of the bed paralleling ash distribution (Fe, Co, As, Sb, V, Y, Mo, Cs, REE, Hf, Ta, Th, P and Au); b — Ge and W are enriched in the near-bottom and near-top coals; c — in the middle part of the bed the content of K and Rb is maximal, while that of U is slightly enriched; d — Ba content decreases from the top to the bottom of the bed. In profile II, W and Be contents decrease from the bottom to the top. The near-bottom, and especially the near-roof samples of profile IV are highly enriched in Ge, while for W the highest is the content of the near-bottom sample.

Ge, Be, As, Mn, Cl and Br are mainly organically associated. The organic affiliation is still strong for Co, B, Sr, Ba, Sb, U, Th, Mo, La, Ce, Sm, Tb and Yb in the underground coals, and Fe, Co, Na, W, Sr, Y and Ag in the coals from the open-pit mine. K, Rb, Ti, Zr, Hf and Ta are of dominant inorganic affinity. The chalcophile and siderophile elements correlate positively with Fe and each other and may be bound partly with pyrite or other sulphides and iron containing minerals.

Compared statistically by the *t*-criteria, the elements Na, Li, Cu, Zn, Pb, Cr, Ni, Co, Mo, Fe and Be are of higher content in the open-pit mine. Tungsten is the only element of higher concentration in the underground mine. The contents of Ge, As, Sr, V, Mn, Y, Zr and P are not statistically different in both mines.

It was supposed that there were multiple sources of the trace elements in the deposit. The source of the highly enriched elements (W, Ge, Be, and As) most probably were the thermal waters in the source area. The contemporary mineral springs are of high content of these elements. Another source were the hosting Mesta volcanic rocks, which are enriched in Sb, Mo, Hf, U, Th, As, Li and Rb. Some of the volcanics were hydrothermally altered and enriched or depleted of many elements. Thus, the hydrothermal solutions were also suppliers of elements for the coals. It is obvious that the contents, distribution and paragenesis, of the trace elements in both Goze Delchev coals reflect the geochemical specialization of the source area, including rocks, paleo- and contemporary thermal waters.

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1. Introduction

The subbituminous Pliocene–Late Miocene Goze Delchev coal deposit is located in southwest Bulgaria (Fig. 1) (Siskov et al., 1986). The basement rocks of the Goze Delchev deposit consist of volcanic and metamorphic rocks. The hydrological conditions are very complicated. The coal-bearing strata are crossed by the Mesta river and its numerous tributaries. There are many hot mineral streams coming from cracks in the gneisses along the east margin of the deposit. There are 16 coal beds in the coal-bearing suite. Two of them are mined, the one being an open-pit mine. The beds' thicknesses are up to 3.2 m in the underground and 8.0 m in the open-pit mine. The resources of the underground mine are about 7 Mt, and that of the open-pit mine are about 1.7 Mt. The coals are used in the Bobovdol power plant and for home-heating. The commercial significance of the deposit is limited (although its geochemistry is of interest). The main characteristics of the coal in the underground mine and the open-pit mine respectively are: R_b , % — 0.41 and 0.27; V^{daf} , % — 49.1 and 56.5; A^{daf} , % — 10.4 to 49.1 and 9.6 to 49.6. The main lithotype in both beds is clarain. Vitrain and xylain are presented in subordinate quantities. The under- and over-lying sediments are clays, containing small quantities of pyrite.

Data on trace elements in the coals from the underground mine were presented along with other Bulgarian deposits (Eskenazy, 1996). This study focuses on the content, vertical distribution, mode of occurrence and genesis of the trace elements in both mines and the differences between them.

2. Materials and methods

The coals studied comprise 89 individual samples (coals, coaly shales and partings) collected along four profiles (Fig. 1). The samples were ashed in an open muffle furnace, the temperature being gradually raised to 500 °C. The ash was dissolved in $HClO_4$ and HF, evaporated to dryness and the residue dissolved in hydrochloric acid. In the solution, the elements K, Na, Li, Rb, Cu, Zn, Pb, Ti, Cr, Mn, Co, Ni and P as well W and Ge in some samples were determined by different wet chemical methods and atomic absorption spectrometry. The elements Be, B, Sc, Ag, Sr, Zr, V, Mo, W and Ge were determined by a number of atomic emission spectroscopy methods. Neutron activation analysis (INAA) was used for Rb, Cs, Ba, As, Sb, Sc, Cr, Co, Ni, REE, Hf, Ta, Th and U. Cl and Br in the open-pit mine coals were determined by X-ray fluorescence. The

results obtained by different methods were compared and checked by parallel measurements of standard geological samples (BCR-1, G-2, clayey shale Tb, and coal ash BS-1). The data have been calculated to a coal basis for every sample.

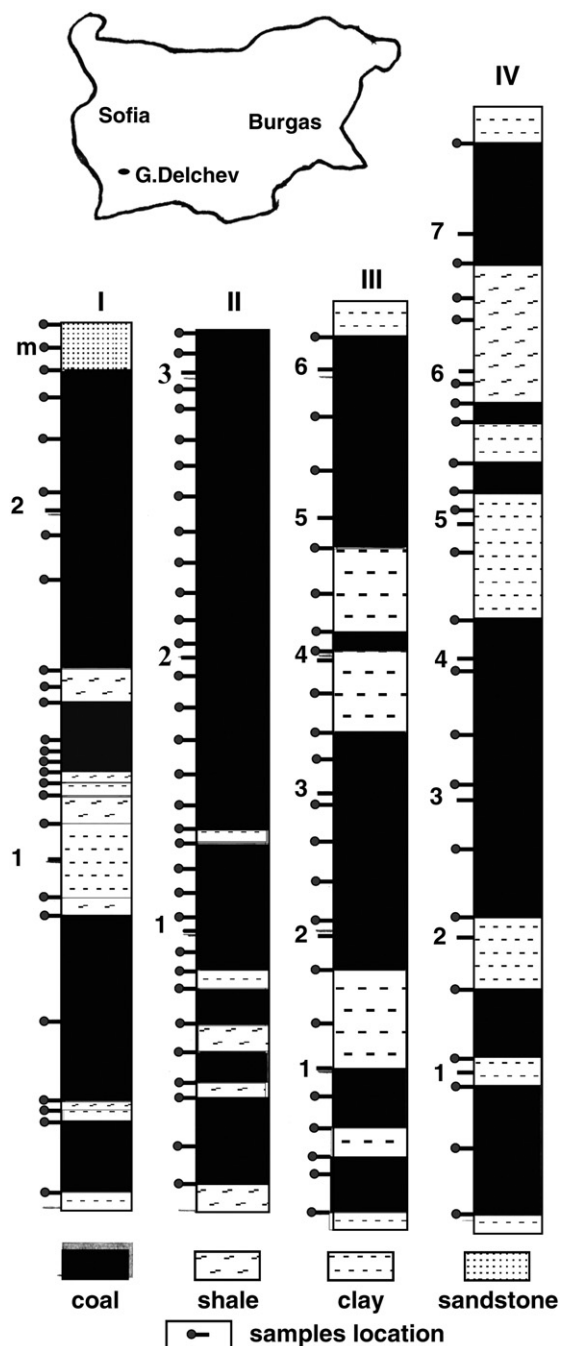


Fig. 1. Location of the deposit and lithological columns: underground mine — profiles I and II; open-pit mine — profiles III and IV.

Table 1

Mean ash and elements content in the coals, coaly shales and partings of the underground mine, ppm

Element	Coals	Coaly shales	Partings	Clarkes for Subbituminous coals	Shales ^a
K, %	0.15±0.09	0.82±0.80	2.0±0.36		2.7
Na, %	0.10±0.04	0.63±0.59	0.99±0.15		0.98
Li	9.3±2.3	28±10	40±12		66
Rb	9.4±5.8	47±28	152±48	10±9 ^b	140
Cs	1.6±1.1	7.7	6.1		5
Be	3.8±2.0	2.1±0.4	6.4	1.2±1 ^b	3
Sr	61±13	81±20	126±53	130±24 ^c	300
Ba	126±85	118	250	120±18 ^c	580
B	19±4.0	34±4.5	57±14	56±3 ^b	100
Cu	16±4.3	53±14	168±98	14±1 ^b	45
Zn	24±6.7	115±49	202±77	18±1 ^b	95
Pb	5.8±1.9	25±13	50±11	6.7±4 ^b	20
As	22±21	30	24	7.4±1.4 ^b	13
Sb	1.0±0.7	1.0±0.2	1.1±0.4	4.4±0.4 ^b	1.5
Ge	4.6±4.4	0.8±0.2	0.5±0.2	1.5±0.3 ^c	1.6
Sc	2.6±0.8	11±1.1	8.2±3.6	2.0±0.4 ^c	13
Ti	806±338	3387±496	4729±508	500±30 ^c	3800
V	17±7.9	111±60	78±16	22±2 ^b	130
Cr	26±14	156±39	121±29	15±1 ^b	90
Mn	315±54	364±128	383±36	100±5 ^b	800
Fe, %	0.9±0.3	3.7±2.1	3.1±1.7		4.8
Co	5.3±1.5	14±5.2	17±3.1	4.2±0.3 ^b	19
Ni	47±19	175±58	196±48	9±0.9 ^b	68
La	12±5.1	34	29	11.6 ^d	92
Ce	14±5.3	67	53±20	19.7 ^d	59
Sm	3.1±0.9	5.2	5.2	2.1 ^d	6.4
Eu	0.5±0.2	0.8	0.7±0.3	0.59 ^d	1
Tb	0.8±0.4	1	1.1±0.4	0.43 ^d	1
Yb	1.1±0.5	1.9	1.5	1.32 ^d	2.6
Lu	0.3±0.2	0.3	0.5	0.31 ^d	0.7
Y	15±7.4	50±30	25±7.5	7.0±1.0 ^b	26
Zr	17±7.5	75±32	89±27	30±3 ^c	160
Hf	0.21±0.13	0.8±0.6	2.9±1.7	1.6 ^d	2.8
Ta	0.15±0.08	0.87	1.3±0.3	0.32 ^d	0.8
W	118±68	100±69	14±4.3	3.5 ^c	1.8
Mo	1.7±0.7	1.5±2.0	2.2±2.5	2.1±0.2 ^b	2.6
Th	8.8±5.2	24±8.4	16±10	3.8±0.2 ^b	12
U	3.4±2.5	7.2±5.3	6.5	2.7±0.3 ^b	
P	89±35	316±184	414±99	220±30 ^b	700
Ag	0.36±0.1	0.12±0.09	0.19±0.07	0.3±0.1 ^c	
Au, ppb	1.9	3	5	1–3 ^a	
Ash, wt. %	18.1±3.4	57.5±9.8	89.4±3.7		

^a Beus and Grigorian (1975).

^b Yudovich and Ketris (2005a,b).

^c Yudovich and Ketris (2002).

^d Arbuzov et al. (2000).

A coal sample from profile I was separated in two specific gravity fractions in a mixture of tetrachloromethane and ethyl alcohol. In the fractions several elements were determined.

3. Results and discussion

3.1. Elements contents and mineralogy

Mean element content for coals, coaly shales and partings as well as world-wide Clarke values for subbituminous coals and shales are shown on [Tables 1 and 2](#). W, Ge, Be and to a lesser extent As, Mn and Y are highly enriched in both mines when compared to Clarke values. Ni and Th are also enhanced in the underground coals and Zr, Cr, Mo in the surface mine coals. The contents of all other elements are similar to, or are slightly lower/higher than the Clarke values. For Ge in both mines, and As, W, Th, U in the underground mine the confidence intervals of the means are wide, indicating uneven distribution of the elements. The content of most elements from both mines increases more or less from the coals to the partings. Germanium in both mines, and Mn in the open-pit mine are the only elements whose content decreases towards the partings, indicating that the affinity to the organic matter (OM) is a main factor controlling their distribution.

Table 2

Elements content in the coals, coaly shales and partings of the open-pit mine, ppm

Element	Coals	Coaly shales	Partings
K, %	0.22±0.06	0.36±0.26	nd
Na, %	0.27±0.08	0.43±0.29	nd
Li	24±6.0	65±11	100
Rb	15±3.4	40±8.8	49
Be	9.4±5.2	8.7±2.1	8.3
Sr	62±11	94±38	82
Cu	33±8.5	57±7.3	79
Zn	77±20	140±42	240
Pb	18±3.4	29±4.1	61
As	12±6.8	nd	16
Ge	10±9.6	8.1±6.4	4.8
Ti	1281±247	2611±360	4824
V	19±5.9	46±12	62
Cr	217±54	355±36	844
Mn	307±59	208±29	103
Fe, %	1.5±0.5	2.0±0.3	2.6
Co	10±2.5	12±3.6	18
Ni	169±37	244±29	351
Y	17±6.6	129±42	73
Zr	23±7.0	76±28	62
W	22±4.7	43±32	29
Mo	5.2±3.1	5.4±1.7	2.8
P	88±21	43±32	393
Cl	80±50	30±5.0	nd
Br	8.7±3.4	7.7±2.1	nd
Ag	0.22±0.06	0.25±0.03	0.45
Ash, %	25.2±3.5	49.5±4.9	83.3

nd — not determined.

The coaly shales of the underground mine have the highest contents of As, Sc, V, Cr, Fe, Ce, Yb, W, and Th, while for the open-pit mine this is true for W and Sr only. The partings of both mines are enriched in W, Be, Cu, Zn, Pb, Ni, and Cr relative to the Clarkes for shales (Table 1). The open-pit mine partings are also enriched in Ge and Y, and that of the underground mine in As. It should be pointed out that W and Be are the elements of elevated contents in all lithotypes (Tables 1–3).

Table 3

Elements content in lithotypes selected from a 10 cm layer, profile I

Element	Vitrain		Clarain		Coaly shale	
	In ash	In coal	In ash	In coal	In ash	In coal
Ash, wt. %	8.3		24.4		81.2	
K, %	1.6	0.13	1.8	0.44	2.4	1.9
Na, %	0.89	0.07	0.94	0.23	1.5	1.2
Li	57	4.7	44	11	47	38
Rb	7	0.6	187	46	177	144
Cs	4.4	0.37	nd		13	11
Be	97	8	74	18	2	1.6
Sr	530	44	300	73	180	146
Ba	350	29	828	202	510	414
B	190	16	105	26	74	31
Cu	61	5.1	62	15	62	50
Zn	145	12	84	20	365	296
Pb	19	1.6	65	16	65	53
As	133	11	nd		30	24
Sb	7.3	0.6	nd		1.2	1
Ge	11	0.9	7.1	1.7	0.5	0.4
Sc	20	1.6	12	2.9	6.5	5.3
Ti	2207	183	4260	1039	4913	3989
V	84	7.1	240	59	33	27
Cr	96	8	222	54	171	139
Fe, %	5.7	0.5	4.2	1	6	4.9
Mn	3785	314	802	196	483	392
Co	37	3.1	19	4.6	20	16
Ni	480	40	136	33	137	111
La	75	6.2	nd		61	50
Ce	128	11	nd		94	76
Sm	30	2.5	nd		11	9
Eu	3.9	0.3	nd		1.1	0.9
Tb	8.8	0.7	nd		2.1	1.7
Yb	18	1.5	nd		3.2	2.6
Lu	4.6	0.4	nd		1.1	0.9
Y	320	27	190	46	40	32
Zr	60	4.9	70	17	100	81
Hf	0.5	0.04	nd		4	3.2
Ta	0.5	0.04	nd		1.9	1.5
W	38	3.2	nd		23	19
Mo	16	1	14	3	2	1.6
Th	31	2.6	nd		33	27
U	51	4.2	nd		14	12
P	514	43	457	112	479	389
Ag	0.05	0.004	0.2	0.05	0.3	0.24
Au, ppb			6	2	6	5

nd — not determined.

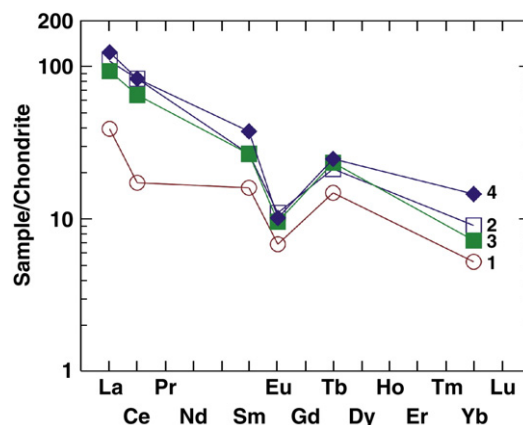


Fig. 2. Chondrite-normalized patterns of REE: 1 — coals; 2 — shales; 3 — partings; 4 — Mesta volcanic rocks.

Chondrite-normalized patterns of the REE in the coals, shales and partings are shown in Fig. 2. They are similar to each other and to the REE patterns of the Mesta volcanic rocks (Eskenazy et al., 1984a) from the source area.

Mineralogy of samples was determined using X-ray diffraction (XRD) on coal and coaly shales. The following minerals were detected in the open-pit mine coals and coaly shales: quartz, kaolinite, montmorillonite (main minerals); illite, pyrite, chlorite, feldspar, marcasite, calcite and dolomite (secondary minerals). Quartz (main mineral) and feldspar, chlorite and mica (secondary minerals) were detected in the coal from the underground mine.

3.2. Distribution across the vertical section of the bed

Vertical distribution and marginal enrichment of different elements, in particular Ge, have been studied for many coals. Uneven distribution or distribution following a distinct pattern were established for different elements (Zilbermint et al., 1936; Kear and Ross 1961; Inagaki, 1967; Yung-Chin, 1969; Yudovich, 1978; Imai et al., 1984; Pareek and Bardhan, 1985; Hill, 1990; Seredin, 2005; Lin et al., 2001; Arbuzov et al., 2000, 2003; Hower et al., 2002, 2005; Zhuang et al., 2006).

Characteristic for most elements in profile I is a regular variation with depth. Examples are presented on Fig. 3. Several distribution patterns could be distinguished:

- The element content decreases from the bottom to the top of the bed, paralleling ash distribution. Most elements displayed this trend (As, V, Fe, Co, Y, Mo, Cs, REE, Hf, Ta, Sb, Th, P and Au). Although not following strictly this pattern, the content of Sr, Zr, Ti, Sc, Pb, Zn, Cr, Mn and Cu is highest in the lower bench as well. This trend may be explained by more

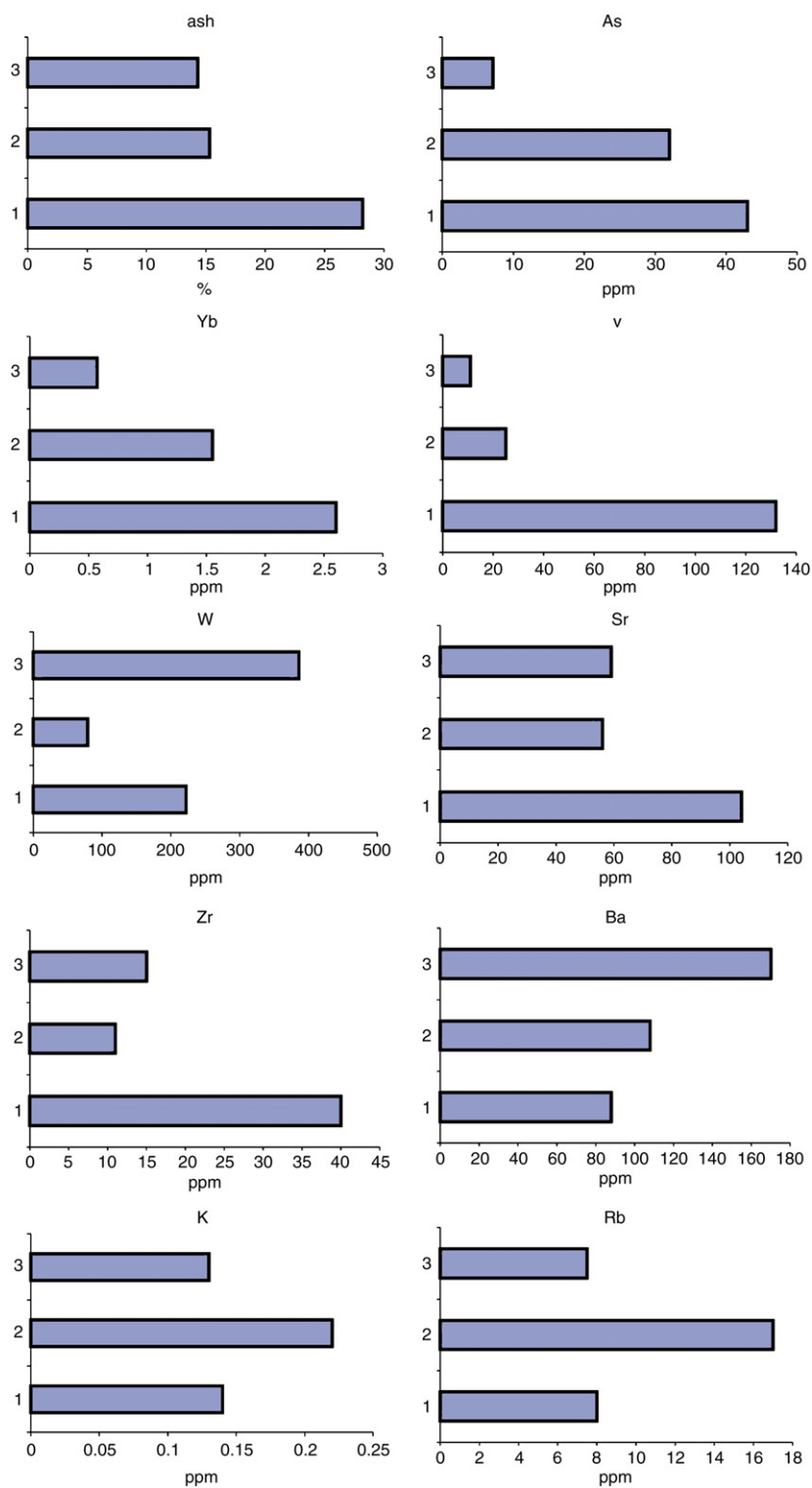


Fig. 3. Vertical distribution of elements in profile I, underground mine: 1 — near-bottom bench; 2 — middle bench; 3 — near-roof bench.

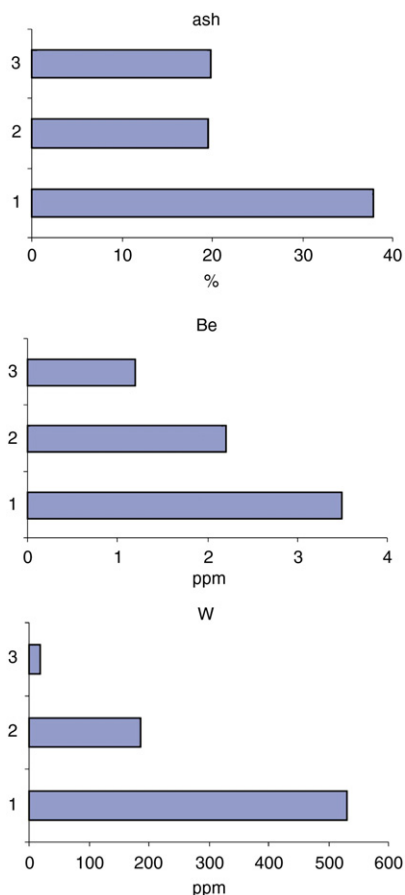


Fig. 4. Vertical distribution of ash, Be and W in profile II: 1 — near-bottom bench; 2 — middle bench; 3 — near-roof bench.

intensive influx of mineralized solutions and/or detrital material. The ash yield of the lowest bench is twice that of the middle and upper benches. One more factor could be the small thickness of the near-

bottom coal bench — 20 cm, while the near-roof bench thickness is 1 m.

- b The variation of Ge and W is specific (Fig. 3). Both elements are enriched in the coals from the bottom and the top of the bed. It should be pointed out that the single near-roof and near-bottom samples are three to 10 times higher in Ge and W content as compared with the other samples. This phenomenon of highly marginal enrichment of elements, especially of Ge was discussed broadly through the years and summarized later by Yudovich (1978, 2003).
- c Only three elements have maximum contents in the middle part of the bed — Na, K, and Rb, indicating the association of Rb with K and Na. Uranium is also slightly enriched in the middle part of the bed.
- d Ba is the only element whose content decreases from the top to the bottom of the bed.

In profile II, W and Be contents decrease from the bottom to the top (Fig. 4). In the background of this similar trend there is a difference — the W content of the bottom is 30× that of the top part, while for Be the difference is 2.9×, and that of the ash is 1.9×. It may be supposed that it was not only because of a more intensive influx of W — perhaps the element was more strongly trapped there by the organic matter.

In profile IV, the lower and, especially, the upper samples are highly enriched in Ge (Fig. 5). It should be emphasized that the mean Ge content for the partings is very high as well, and parallels that of Ge in the coals: 13 ppm at the top and 5.6 at the bottom of the bed. There is no a distinct trend for W in the same profile (Fig. 5). The thinnest coal layer (0.4 cm) has an enhanced content of both, Ge (43 ppm) and W (44 ppm).

There are no distinct vertical trends for most elements in the open-pit mine.

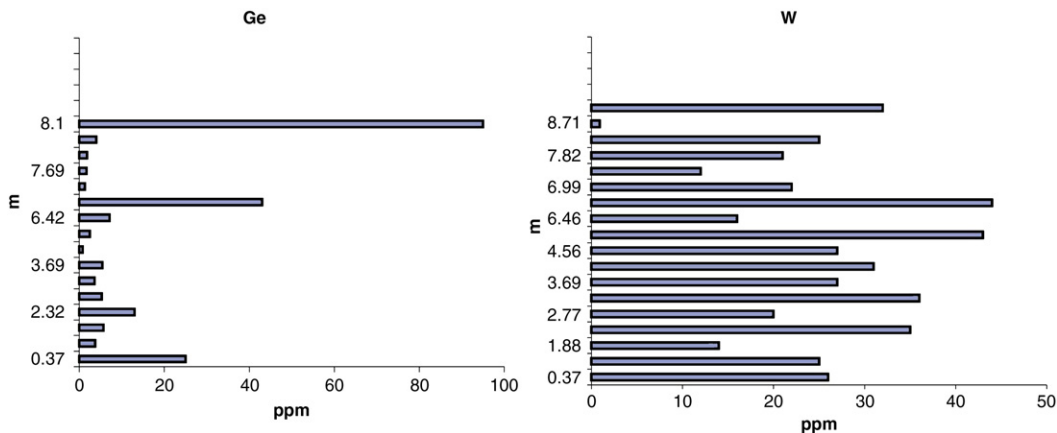


Fig. 5. Vertical distribution of Ge and W in profile IV, open-pit mine.

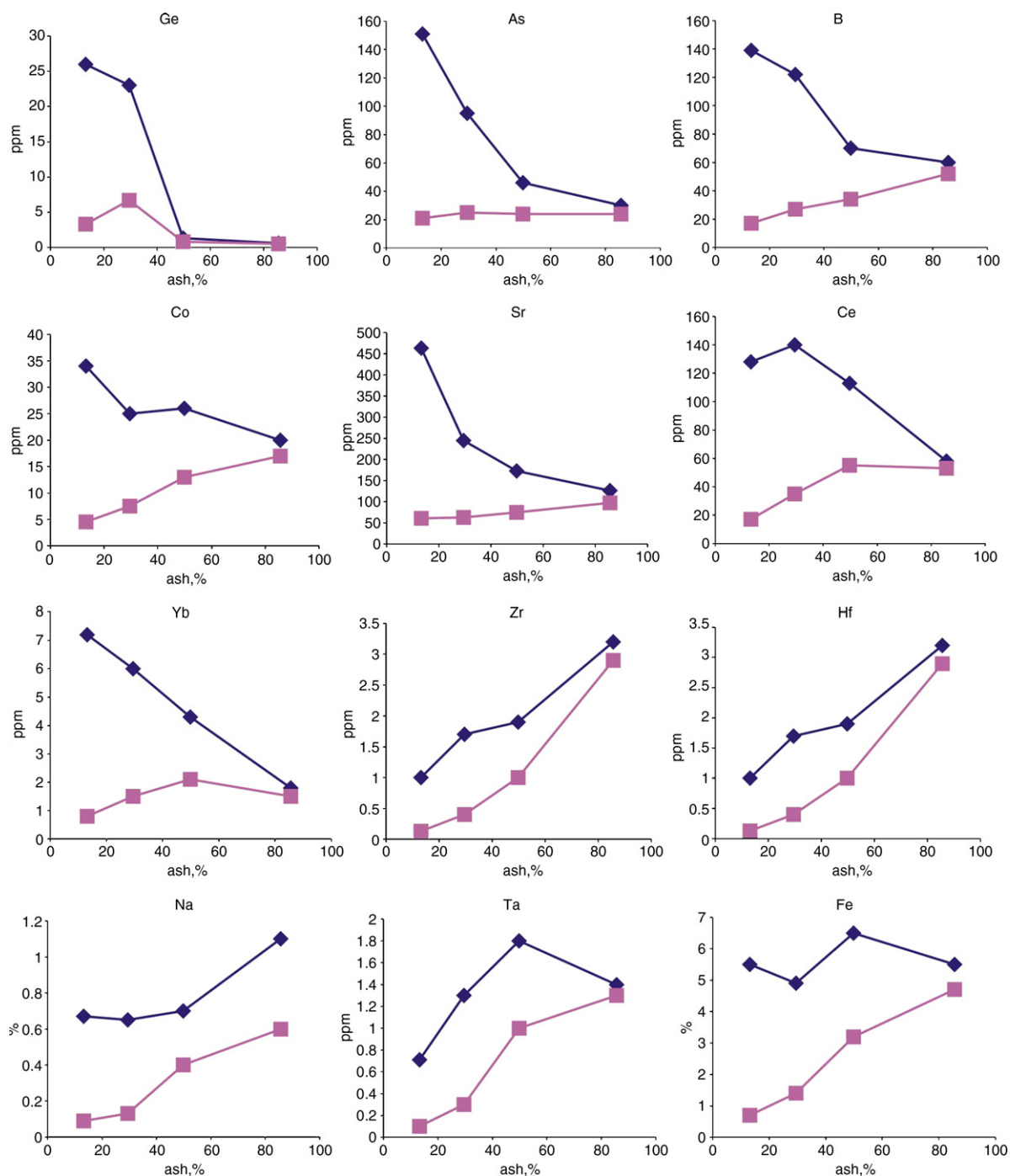


Fig. 6. Element content vs ash content in the underground mine.

3.3. Mode of occurrence of the elements

Major, minor and trace elements occur in coal as inorganic phases or are organically associated. Most elements in every deposit are usually present in both forms. The ratio of the two modes of occurrences varies.

In low-rank coals, the organically bound part of the elements is higher. Huggins and Huffman (2004) stated “the loss of carboxyl and other oxygen functionality as coals of increasing rank evolve results in the mineralization of many elements”. Distinguishing the mode of occurrence for every single element in each deposit may

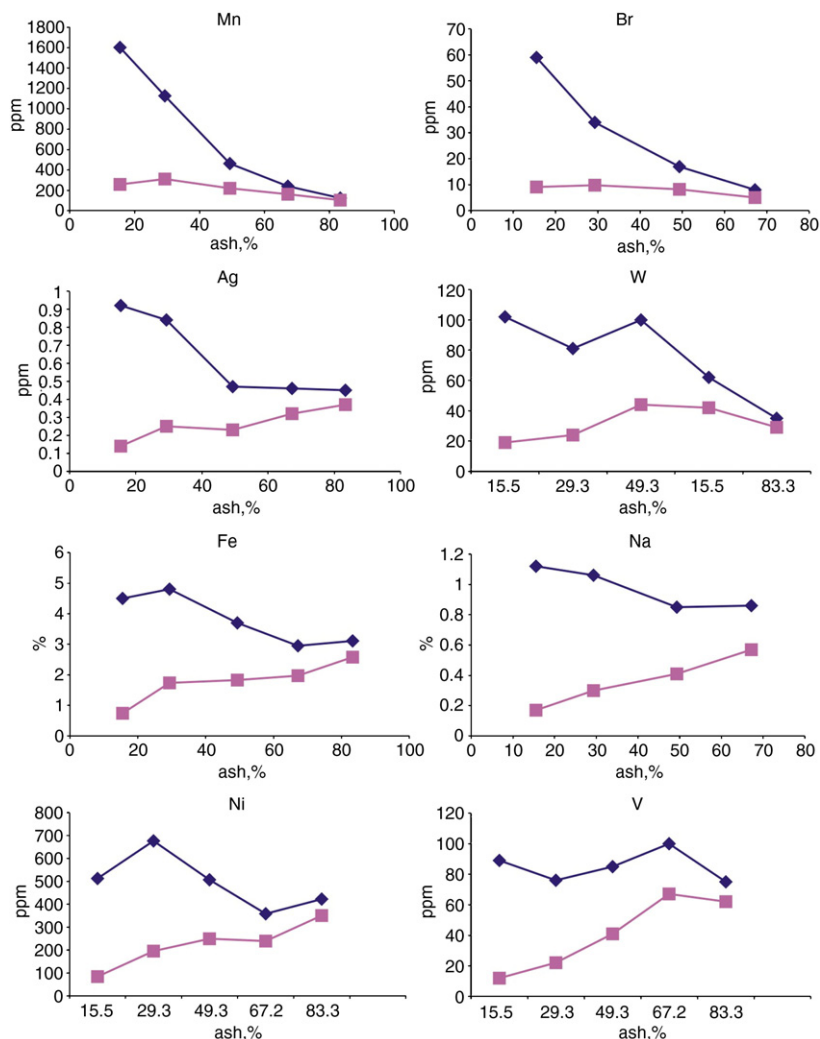


Fig. 7. Element content vs ash content in the open-pit mine.

be achieved by indirect and direct methods. The mode of occurrence of the elements in the Goze Delchev deposit is discussed based on indirect evidences — the relationship between element content vs ash yield and the correlation coefficients between the elements, which were calculated separately for coals and coaly shales. In Figs. 6 and 7, the distribution patterns for some of the elements vs ash yield are presented. The following patterns of distribution have been distinguished:

a The content of Ge, As, Be, Mn, Cl, and Br in both mines decreases both in ash and coal with increasing ash content, which indicates a dominant association with the organic matter. Most elements of this group are in many deposits organically associated, while As occurs largely in Fe-sulphides (Finkelman, 1995;

Diehl et al., 2004; Shaver et al., 2006; Ruppert et al., 2005; Hower et al., 2007). However, in some deposits presence of As_{org} has been suggested (Filby et al., 1977; Clark et al., 1980; Goodarzi, 1987; Yudovich and Ketris, 2005b). By X-ray absorption fine structure (XAFS) spectroscopy the presence of organically bound As was proved directly (Huggins et al., 1996; Huggins and Huffman, 2006).

b The following elements decrease in ash and increase, more or less, in the coal: B, Co, Sr, Ba, Sb, U, Th, and Mo in the coals from the underground mine, and Fe, Na, Co, W, Sr, and Y, and Ag in the coals from the open-pit mine. For this group of elements, the organic affinity is still strong. The REE, excluding Eu, belongs to this group. The trend is more distinct for the HREE (Tb, Yb, and Lu), in agreement with

Table 4

Correlation coefficients among sulphophile and siderophile elements for the coals of the underground mine (above) and the open-pit mine (below)

	Fe	Co	Ni	Cr	Cu	Zn	Pb	As	Mo	Ti
Fe	1	0.79	0.93	0.92	0.86	0.64	0.84	0.36	0.81	0.86
Co	0.44	1	0.92	0.71	0.53	0.57	0.51	0.66	0.93	0.46
Ni	0.77	0.55	1	0.86	0.74	0.69	0.65	0.49	0.87	0.68
Cr	0.48	0.64	0.77	1	0.94	0.59	0.84	0.17	0.75	0.91
Cu	0.24	0.52	0.53	0.5	1	0.45	0.81	0.09	0.54	0.94
Zn	0.38	0.46	0.45	0.5	0.48	1	0.46	0.28	0.72	0.55
Pb	0.28	0.44	0.42	0.5	0.48	0.35	1	−0.05	0.65	0.88
As	0.68	0.26	0.56	0.33	0.05	0.18	0.08	1	0.56	0.07
Mo	0.82	0.27	0.7	0.53	0.3	0.2	0.34	0.75	1	
Ti	0.29	0.42	0.52	0.66	0.75	0.64	0.64	0.01	0.22	1

Bold — statistically significant values at 95% level.

their higher organic affinity as established for other coals (Eskenazy, 1995; Seregin, 1996, 2005; Schatzel and Stewart, 2003). This conclusion is supported by the values of Ce_n/Yb_n , which are 2.3 for the coals, 9.1 for the coaly shales, and 10.5 for the partings in the underground coals.

- c With increasing ash, the element contents increase both on ash and coal basis. Such distribution is antipode to group “a”. The elements are mainly of inorganic affinity — K, Rb, Ti, Na, Pb, Zr, Hf, and Ta from the underground mine and Li, Rb, and Zr in the coals of the open-pit mine.
- d The following elements are distributed more or less uneven in the ash, and their content in coal increases

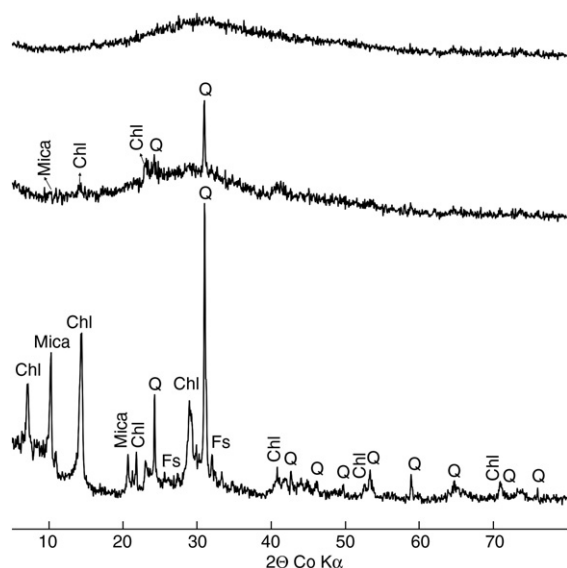


Fig. 8. X-ray diffraction patterns of vitrain, clarain and coaly shale selected from a 10 cm layer, profile I (Table 3).

parallel with ash: Fe, Cu, Zn, Ni, Cr, V, Sc, Au, Y, Cs, and P, from the underground mine, K, Zn, Pb, Cu, Ni, Cr, Ti, V, and P from the open-pit mine. Most of these elements correlate positively with the ash in the coals. Some of them are chalcophile (Cu, Zn, and Pb) or siderophile (Fe, Ti, Ni, Cr, V, and Sc) elements, and may be bound partly with pyrite or other sulphides and iron containing minerals which are unevenly distributed. Positive correlation coefficients among some of these elements support such mode of occurrence (Table 4).

Some elements exhibit stronger correlation with other elements in the coals than in the coaly shales. For instance, Na correlates with K in the coals ($r=0.54$), while in the shales there is no correlation between them. On the other hand, Rb correlates with K both in coals and shales (0.89 and 0.81) respectively. This may be explained by the statement of Ward et al. (1999): “Rb is intimately related to K itself, and not to any particular mineral component”. Just the opposite is the case with Y — in the coals Y correlates strongly with Sr (0.79), while in the shales there is no correlation (−0.30) between them. In the coals, the behaviour of both elements is dominated by their affinity to organic matter and phosphates, while in the shales except with the organic matter they may be bound or sorbed by the minerals present. Ge and W do not correlate each other or with any other element — they are bound to the organic matter but their marginal enrichment is of primary importance as well.

The association of all elements both with the inorganic and organic matter of the coal is confirmed by the data for vitrain, clarain and coaly shale selected from a 10 cm layer (Fig. 8 — profile I, Table 3). For many elements, the contents are maximal in the ash of vitrain: Be, Sr, B, As, Sb, Ge, Sc, Mn, Co, Ni, REE, Y, W, Mo, U, and P. Several elements have highest concentrations in the clarain sample: Rb, Ba, V, and Cr, and those with highest content in the coaly shale are K, Na, Cs, Zn, Pb, Ti, Zr, Hf, Ta, Ag, and Au. The ratio

Table 5

Elements content in specific gravity fractions of sample 2 (29% ash) from profile I, ppm

Density	Ash, %	Ge	W	Mn	Mo	Ni	Co	Cr	Zn	Cu	Pb
1.2–1.4	12.1	54	230	1342	5	685	52	570	65	145	28
1.4–2.0	23.8	2	nd	184	nd	548	50	230	298	120	53

nd — not determined.

Ce_n/Yb_n is 1.9 for the vitrain sample and 7.5 for the coaly shale, indicating once more the relative enrichment of the HREE in the coal-forming process. The comparison of the XRD patterns of the three samples reveals that no minerals were detected in vitrain (at about 5% detection limit) suggesting that the trace elements are mainly organically associated. The clarain sample contains quartz and small amounts of mica and chlorite. In the coaly shale quartz, chlorite, feldspar and mica were detected. These minerals along with the main elements Si, Al, K, Na, Fe, and Mg may be carriers of many trace elements: Mn, Ti, Ba, Sr, Li, Ni, Cr, Co, P, V, Be, and Zn. The equal concentration of iron in vitrain and the coaly shale sample also indicates that the element is both organically and inorganically associated.

In two specific gravity fractions of a sample with 29.8% ash, a number of elements were determined (Table 5). The results confirmed the dominant organic affinity of Ge, W, Mn, Mo and the intermediate affinity of Ni, Co, Cr, Zn, Cu, and Pb. In two more coal samples, the W content was determined in specific gravity fractions: in the lighter fractions (1.2–1.4) the W content was respectively 3.9× and 5.6× higher than in the 1.4–2.0 fractions, suggesting organic association.

4. Conclusions

- The elements determined in both deposits were compared statistically by the *t*-criteria. In the open-pit mine higher are the element contents of Na, Li, Cu, Zn, Pb, Cr, Ni, Co, Mo, Fe, and Be. Most of them are chalcophile or siderophile elements and their enhanced contents may be explained by the presence of pyrite, which was not found in detectable amounts by XRD in the underground coals. Tungsten is the only element of higher concentration in the underground mine. Ge, As, Sr, V, Mn, Y, Zr, and P are of not statistically different contents in both mines.
- Yudovich and Ketris (2002, 2005a) defined the term “coalophile elements” for elements enriched in the coal ash as compared with the host rocks. These elements may be trapped from solutions by the coal organic matter, present as autogenic minerals or included in autogenic minerals. For every single deposit, the coalophile elements may be revealed by the ratio “element content in the coal ash/element content in the hosting sediments”. In the Goze Delchev coals, this coalophile coefficient is between 2 and 5 for the elements Mo, Yb, Y, Sb, Sr, As, Ba, Eu, Tb, Yb, Ce, Sm, Lu and U. Above 5 are the coefficients for Be, Ge, W, and Mn, indicating these elements as characteristic for the coals.
- It is supposed that there were multiple sources of the trace elements in the deposit. The source of the highly enriched elements in both coals (W, Ge and Be) are most probably thermal waters. In the source area of the deposits occur nitrogen-bearing mineral springs, linked with the post-volcanic activity which are of high content (μg/l) of W — 110, Ge — 16, Be — 4.2, and As — 84 (Pentcheva et al., 1997). The thermal waters have an also elevated content of Mo, Sb, Zn, Cr, Mn, Co, V, and Ti, and may be partly the source of these elements in the coals.
- The source area of the deposit comprises the Mesta volcanic rocks. The volcanism was multiphase and synchronous to the Late Eocene–Oligocene sedimentation (Harkovska et al., 1983). They are enriched in Sb, Mo, Hf, U, Th, As, Li, and Rb when compared with the Clarkes for acid igneous rocks, while the REE content is somewhat lower than the respective Clarkes (Eskenazy et al., 1984a,b). Two types of hydrothermal alteration of the volcanics were established (Harkovska et al., 1983): 1 — rock alteration involving a removal of K and Na, accompanied with enhanced content of Cr, As, Co, Mn, Zn, and Sb; 2 — rock alteration involving removal of Na and supply of K with enhanced contents of As, Mo, Sb, U, and Th. On the other hand, part of the hydrothermally altered rocks are depleted in REE, Sc, Cr, Mn, Co, Zn, Hf, Ta, Th, Li, Rb, and Ba. Hence, the hydrothermal solutions should have been the supplier of many elements in which they were initially enriched and some elements extracted from the volcanics.
- The detrital material entering the peat bog is another source of the elements. This is supported by the positive correlation among many elements and ash yield, and as well the similar vertical distribution of many elements and ash (Fig. 3). For some elements the part due to the input of detrital material is dominant (Rb, Zr, and Hf), while for others (Ge and W) it is negligible.
- It is obvious that the contents, paragenesis, and distribution of the trace elements in both Goze Delchev coals reflect the geochemical specialization of the source area, including rocks, paleo- and contemporary thermal waters.

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