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Distribution of Trace Elements in Brown Coals from the Amur River Region and in Their Submicron Fractions

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Abstract—It was established experimentally that the trace elements that are present in brown coal samples in low and ultra-low concentrations are concentrated in the finest fraction of the samples whose particle size is smaller than 1 μm (in a submicron fraction), which was separated using special nanotechnological techniques. A comparative analysis of the concentrations of chemical elements in the gross samples of coal and in the submicron fractions showed the special features of the distribution of trace elements in a coal matrix and prospects for the extraction of potentially valuable elements from coals.

Keywords: brown coal, submicron fraction, trace elements, mass spectrometry

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It is well known that coals are a promising source of rare, scattered, noble, and nonferrous metals and radioactive elements [1–4]. In recent years, the presence of other valuable and strategically important elements, not only Ge and U but also V, Se, and Mg [5, 6], is also of interest. In Russia, germanium-bearing coal is mined at the Pavlovskoe deposit in Primorye (the Spetsugli site), and this coal is burned at Novoshakhtinskaya heat and power plant with the production of germanium concentrate in fly ash. For example, the studied concentration levels of trace elements and their distributions in coals [1–4] showed that both individual coal deposits and beds or individual sections of deposits or layers in which the concentrations of so-called potentially valuable trace elements [2] are higher by factors of tens and hundreds than their concentrations in sedimentary rocks can be metal-bearing. Such coals are of undoubted interest as a raw material for the production of a number of the compounds of potentially valuable trace elements.

In this work, brown coals of the Far Eastern Federal District were test materials considered in terms of the concentrations of trace elements, including potentially valuable trace elements, in them. Coals from the

Table 1. Main quality characteristics of coals from the test deposits, %

Yerkovetsk	Ushumunsk	Mukhenskoe	Khurmulinskoe
W_t^r = 35.6–36.4	W_t^r = 30–35	W_t^r = 33–35	W_t^r = 40.2–46.8
A^d = 14.2–28.4	A^d = 12–32	A^d = 15–30	A^d = 20.0–37.7
S_t^d = 0.28-0.55	S_t^d = 0.4	S_t^d = 0.55	S_t^d = 0.6
V^{daf} = 43.9–61.5	V^{daf} = 57.3	V^{daf} = 50.9	Qi^r = 11.6 MJ/kg
C^{daf} = 66.8–70.5	C^{daf} = 67.5	C^{daf} = 67.8	
H^{daf}= 4.3–6.0	H^{daf}= 5.9–6.5	H^{daf}= 5.3	
Q_i^r = 8.23–13.4 MJ/kg	Q_i^r = 12.2–14.8 MJ/kg	Q_i^r = 12.0–14.0 MJ/kg	

Table 2. Samples of coals and carbonaceous rock selected for the extraction and analysis of submicron fractions

Entry	Sample	Deposit	Sampling site	Ash content, %
1	3727-53	Yerkovetsk	Well 3727, depth of 53 m	13.5
2	3727-59	Yerkovetsk	Well 3727, depth of 58.6 m	10.8
3	3255k-49	Yerkovetsk	Well 3255k, depth of 48.9 m	32.9
4	U-30	Ushumunsk	Well 1138, range of 80.1-80.25	68.5
5	U-56	Ushumunsk	Well 1138, range of 80.95-81.55	11.1
6	M-2	Mukhenskoe	Outcrop no. 1, west side of the field	1.64
7	M-4	Mukhenskoe	The same	4.36
8	Kh-6	Khurmulinskoe	West side of the field, topographic reference 51.04.051 136.49.250	44.7
9	Kh-11	Khurmulinskoe	The same	38.7

Entry no. 4 is a carbonaceous rock sample.

following four deposits were taken for the experiments: the Yerkovetsk deposit in the Western section (Amur oblast), the Ushumunsk deposit (Jewish autonomous oblast), and the Khurmulinskoe and Mukhenskoe deposits (Khabarovsk krai). According to preliminary data [7], these coals can have elevated concentrations of trace elements. These coal-bearing deposits are Cenozoic (P_{1-3}–N_1) in age with grade B coals, group 1B–2B. Table 1 summarizes the main quality characteristics of the test coals.

Relatively recently, a method was developed for extracting and analyzing the nano fractions of various rocks and soils [8]. The invention is based on the fact that a number of chemical elements, including those that do not form their own mineral phases and occur in the sample in a scattered form, are naturally concentrated in an ultrafine fraction, the particle sizes of which lie in a nanometer (more precisely, in a submicron) range from 0.1 to 1000 nm.

The analysis of nano fractions makes it possible not only to dramatically increase the sensitivity (the limit) of determination for rare and scattered elements, thereby considerably expanding the range of chemical elements to be determined, but also to obtain reliable information at ultralow levels of their concentrations. This opens up prospects for the wide use of the invention in various priority areas. One of these areas is the development of new technologies for the extraction of rare and scattered elements from unconventional sources of mineral raw materials, which include coals.

We note that, at present, there are no strict boundaries of the nanosize. Some researchers believe that it is limited to 0.1–10 nm, but others consider an upper limit of 300–400 nm or extend it to 1 μm. Because we did not study in detail the exact sizes of particles in this work, we will refer to the fraction obtained as a submicron fraction (SMF), that is, smaller than 1 μm, bearing in mind that it includes particles of different sizes from 0.1 nm to 1 μm.

It is known that many chemical elements are present in coals in trace amounts, and the concentrations of noble metals are often below the limits of their determination. Therefore, we assumed that an experiment on studying the submicron fractions of coals will provide additional information on the concentrations of trace elements in them.

A comparative analysis of the total content and the concentrations of chemical elements in the SMFs (or nano fractions) can show the degree of their mobility in a coal matrix and outline the prospect of extracting trace elements from coal using nanotechnological methods.

For this study, we selected eight samples of coal and a carbonaceous rock sample. Table 2 summarizes the sampling sites and the ash contents of the samples.

All of the samples were analyzed to determine the total trace element content; the analyses were performed in the Central Laboratory of the Karpinskii All-Russia Research Institute of Geology (VSEGEI).

The following sample decomposition methods were used depending on the elements to be determined [9]: the complete acid digestion of coals (ICP MS analysis) for the determination of Li, Sc, Co, Ni, Cu, Zn, Ge, Ag, Cd, Sb, Re, and Pb and the fusion of coal ash with lithium metaborate and melt dissolution (ICP MS analysis) for the determination of rare earth elements (14 elements) and Be, V, Cr, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cs, Hf, Ta, W, U, Th, Ba, and Sn. Noble metals were analyzed using an individual procedure: after the complete decomposition of a sample, Au, Pt, and Pd were determined by atomic absorption spectrometry. Table 3, which summarizes the results of the analysis, indicates that coals from different deposits differ significantly from each other in the concentrations of a number of elements.

Table 3. Bulk analysis of coal samples for a number of trace elements (the results in g/t are given on a coal basis)

Sample	**Li**	**Be**	**Sc**	**V**	**Cr**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**Rb**
3727-53	3.39	10.91	7.39	26.98	27.26	7.78	4.76	6.37	41.13	6.30	4.01	1.73
3727-59	1.32	7.37	3.99	13.84	14.63	17.25	20.68	4.22	34.39	5.24	2.76	0.69
3255k-49	17.50	19.72	10.10	135.06	53.70	35.54	45.97	30.01	348.24	14.14	2.69	49.94
U-30	47.15	4.33	12.80	70.58	63.77	4.65	19.54	12.90	33.79	25.34	3.78	86.06
U-56	3.65	2.48	4.00	27.08	14.11	8.76	11.56	14.85	5.30	3.87	0.60	9.28
M-2	0.31	0.07	0.75	5.27	1.76	1.41	4.25	5.74	5.59	0.83	0.08	0.89
M-4	1.10	0.29	1.71	34.19	8.96	2.03	8.91	9.42	5.88	3.06	0.39	3.19
Kh-6	22.38	7.28	12.59	104.24	50.74	46.18	156.87	26.72	58.06	19.63	3.27	72.27
Kh-11	17.05	6.83	12.18	98.41	44.06	94.33	249.35	28.83	81.24	16.59	3.23	58.36

Sample	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Cd**	**Sn**	**Sb**	**Cs**	**Ba**	**La**	**Ce**
3727-53	205.96	125.00	68.24	3.17	1.30	0.04	0.37	0.60	0.17	507.71	136.51	318.85
3727-59	172.25	89.51	37.69	0.96	4.73	0.06	0.15	0.38	0.07	390.24	92.63	211.94
3255k-49	87.15	84.35	75.51	6.63	12.77	1.85	1.07	2.08	8.06	116.12	15.55	30.41
U-30	89.02	28.08	173.64	13.95	1.70	0.23	2.81	3.73	25.88	349.21	53.78	109.56
U-56	504.26	16.03	17.53	3.49	2.35	0.04	0.28	2.48	1.32	934.64	29.29	65.31
M-2	13.36	1.10	2.89	0.89	0.75	0.00	0.01	0.12	0.16	25.61	0.42	1.15
M-4	33.07	3.19	16.31	4.35	1.06	0.03	0.04	1.77	0.44	49.95	1.94	5.76
Kh-6	317.93	167.76	101.75	9.04	6.35	0.25	1.16	3.24	7.28	926.13	172.32	249.64
Kh-11	330.01	168.89	89.93	6.87	7.41	0.38	0.93	3.99	6.64	946.68	178.81	259.26

Sample	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
3727-53	47.92	192.88	41.58	8.22	35.60	4.82	26.93	5.32	14.29	2.01	11.77	1.70
3727-59	31.55	130.05	26.36	4.99	22.46	3.07	16.29	3.55	10.16	1.48	9.52	1.43
3255k-49	3.58	15.35	4.05	1.19	5.83	1.18	10.01	2.69	9.01	1.43	9.71	1.67
U-30	11.98	43.23	7.87	1.52	7.35	0.99	5.54	1.02	2.92	0.38	2.73	0.40
U-56	7.98	30.49	5.19	1.10	4.92	0.65	3.18	0.58	1.43	0.19	1.15	0.20
M-2	0.13	0.57	0.15	0.04	0.13	0.02	0.17	0.04	0.13	0.02	0.17	0.03
M-4	0.64	2.82	0.63	0.15	0.61	0.10	0.59	0.12	0.34	0.05	0.30	0.05
Kh-6	33.53	132.06	22.62	5.14	26.82	3.80	22.74	4.61	11.90	1.53	8.17	1.28
Kh-11	33.81	129.53	22.41	5.13	26.77	3.76	22.15	4.44	11.53	1.42	8.33	1.22

Sample	**Hf**	**Ta**	**W**	**Re**	**Pb**	**Th**	**U**	**Ag**	**Au**	**Pd**	**Pt**	
3727-53	2.30	0.27	0.71	0.008	3.75	5.32	1.38	0.012	<0.002	<0.03	<0.04	
3727-59	1.26	0.10	1.50	0.005	1.76	2.84	0.79	0.001	<0.002	<0.03	<0.04	
3255k-49	2.16	0.51	5.08	0.014	24.71	8.28	2.96	0.139	<0.002	<0.03	<0.04	
U-30	4.64	1.03	26.82	0.007	34.96	15.31	3.77	0.095	<0.002	<0.03	<0.04	
U-56	0.51	0.15	3.77	0.005	7.80	3.77	1.05	0.030	<0.002	<0.03	<0.04	
M-2	0.08	0.01	0.71	0.001	0.73	0.21	0.15	0.001	<0.002	<0.03	<0.04	
M-4	0.43	0.05	1.22	0.005	1.50	0.68	0.19	0.001	<0.002	<0.03	<0.04	
Kh-6	3.18	0.72	2.78	0.012	27.41	11.58	2.76	0.082	<0.002	<0.03	<0.04	
Kh-11	2.89	0.55	2.06	0.008	27.67	10.74	2.78	0.122	<0.002	<0.03	<0.04	

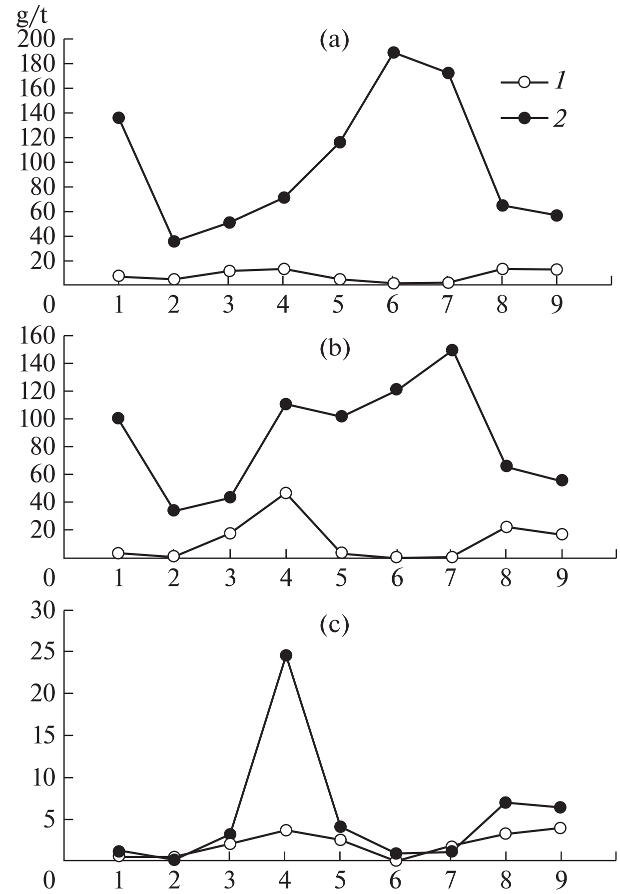

Fig. 1. Concentrations of (a) Sc, (b) Li, and (c) Sb (*1*) in the sample as a whole (bulk analysis) and (*2*) in the submicron fraction of coal. The abscissa axis refers to entry numbers in Table 2: (*1–3*) the Yerkovetsk deposit, (*4*, *5*) Ushumunsk deposit, (*6*, *7*) Mukhenskoe deposit, and (*8*, *9*) Khurmulinskoe deposit.

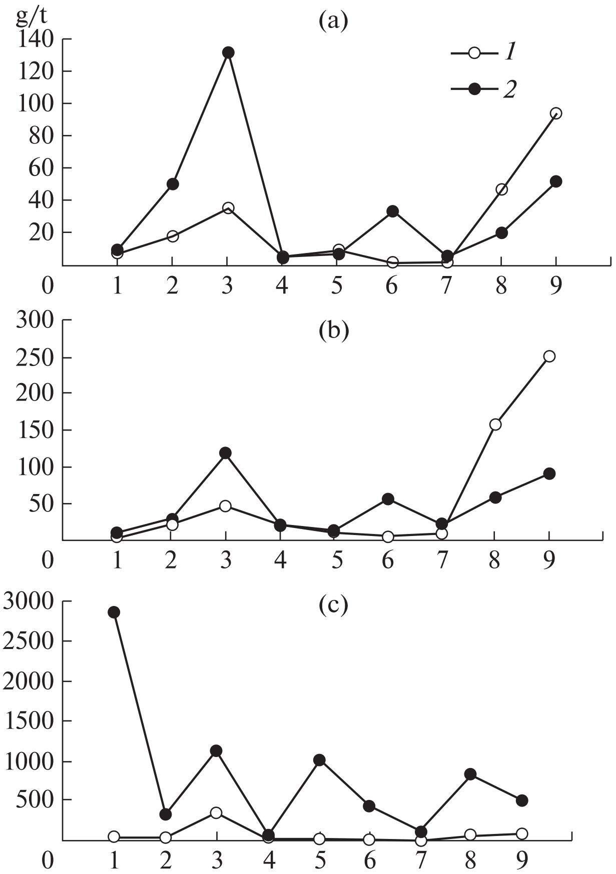

Fig. 2. Concentrations of (a) Co, (b) Ni, and (c) Zn (*1*) in the sample as a whole (bulk analysis) and (*2*) in the submicron fraction of coal. The abscissa axis refers to entry numbers in Table 2: (*1–3*) the Yerkovetsk deposit, (*4*, *5*) Ushumunsk deposit, (*6*, *7*) Mukhenskoe deposit, and (*8*, *9*) Khurmulinskoe deposit.

Thus, in the coals of the Mukhenskoe deposit, the concentrations of less Sr, Cd, Sc, and Cs were smaller by an order of magnitude, the concentrations of Y, Zr, Ni, and Cu were lower by a factor of dozens, and the concentrations of rare-earth elements were lower by two orders of magnitude. It is also important to note that coal samples from the same deposit can significantly, sometimes by orders of magnitude, differ from each other not only in the ash content but also in the concentrations of most trace elements. As for the noble metals Au, Pt, and Pd, their concentrations in all of the test samples were lower than the limits of determination of the method of analysis. Extraction of submicron coal fractions was carried out according to a patented procedure [8]. The samples of coal were crushed and ground to a standard size, 200 mesh or 0.074 mm, for analytical studies. A 30-g sample of coal was placed in a 1-dm^3 glass flask, and 300 mL of hot deionized water (90–100°C) was added; the mixture was thoroughly mixed several times for 4 h. Water extracted all of the water-soluble species (ions, molecules, and ultrasmall particles) from the pore space of coals to a colloid-saline solution or a so-called coal colloid (CC). The solution was settled for 20 h and passed through a membrane filter to cut off random particles larger than 1 μm; the solution was carefully dried at a temperature of 40–50°C. The dry residue after the removal of water can be called a specific submicron fraction (or a nano fraction) of coals.

For use in the subsequent calculations, we determined the SMF concentration in a colloid-saline solution (CC). For this purpose, a 100-mL aliquot portion of the solution was evaporated in a Petri dish at a temperature of 40–50°C to constant weight, and the dry residue was weighed. On the removal of water, various physicochemical processes can occur to distort the composition of CC: the sticking of particles into insoluble conglomerates, including the formation of coarser particles (larger than 1 μm) of insoluble salts, which will not transfer into an aqueous solution once again after drying. Therefore, we initially performed the mass-spectrometric analysis of the primary

Table 4. Concentrations of chemical elements (g / t) in the submicron fractions of coals

Sample	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Ge	As	Se
3727-53	6.81	135.10	57.31	310.50	8.02	8.42	22.25	2852.13	3.66	4.09	127.22	44.64
3727-59	4.35	34.93	20.05	89.57	49.50	28.65	3.01	326.62	2.58	1.33	156.45	21.87
3255k-49	33.37	49.92	470.92	157.13	131.45	118.19	33.49	1111.96	3.61	16.64	2206.97	199.70
U-30	6.23	70.37	105.26	152.22	4.87	21.37	22.52	64.52	22.12	21.88	81.73	17.40
U-56	8.93	115.47	52.99	275.27	7.31	13.74	16.62	991.89	1.76	0.84	283.70	38.95
M-2	15.40	188.88	56.31	469.37	32.92	55.43	32.79	425.75	2.61	1.02	405.56	58.67
M-4	8.15	172.03	58.99	419.22	5.09	21.55	19.00	107.64	4.28	0.69	426.75	60.48
Kh-6	4.98	64.10	52.53	146.48	19.78	57.61	17.90	815.45	8.37	2.58	70.61	20.87
Kh-11	3.50	56.26	46.14	136.79	51.40	89.38	14.43	505.24	6.16	2.45	75.36	19.41
Sample	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**Cs**	**Ba**
3727-53	926.00	26.25	13.91	2.15	2.69	2.13	0.13	1.18	1.20	8.83	1.12	4463.44
3727-59	1304.85	2.19	7.18	0.51	2.15	0.30	0.03	<0.01	0.21	2.09	0.60	391.80
3255k-49	465.19	29.11	27.79	2.62	24.80	1.51	0.04	0.64	3.23	2.93	1.94	313.19
U-30	79.19	15.35	134.37	9.21	41.43	0.28	0.10	2.98	24.53	1.89	19.40	208.79
U-56	136.09	1.42	10.01	1.71	7.16	0.76	0.11	1.05	4.10	6.88	1.22	1188.17
M-2	719.87	1.73	19.18	2.22	<0.01	0.52	0.20	0.90	0.87	8.16	3.35	440.04
M-4	510.76	2.16	14.42	2.18	1.93	0.76	0.11	1.34	1.12	8.68	3.44	279.74
Kh-6	366.48	25.33	28.49	4.07	4.08	0.47	0.06	1.08	6.99	2.58	3.84	1550.00
Kh-11	321.14	20.53	23.70	2.84	4.55	0.33	0.05	0.83	6.42	1.64	2.71	909.32
Sample	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**
3727-53	112.41	19.25	73.48	12.24	3.00	11.16	1.25	7.00	0.91	3.33	0.41	2.06
3727-59	0.77	0.31	0.25	0.11	0.04	0.14	0.03	0.19	0.07	0.19	0.05	0.23
3255k-49	3.19	0.37	2.36	0.58	0.30	1.67	0.33	2.42	0.95	3.53	0.65	5.54
U-30	76.08	7.63	27.65	5.25	0.98	5.12	0.62	3.57	0.73	1.67	0.26	1.57
U-56	3.46	0.39	1.20	0.31	0.19	0.18	0.07	0.16	0.01	0.13	0.09	0.09
M-2	1.71	0.16	0.69	0.16	0.12	0.10	0.09	0.21	0.05	0.18	0.17	0.29
M-4	2.92	0.30	2.12	0.16	0.05	0.21	0.09	0.26	0.04	0.16	0.14	0.16
Kh-6	67.33	7.34	27.33	4.16	0.93	5.77	0.75	3.92	0.76	1.78	0.31	1.39
Kh-11	51.61	5.25	22.02	2.96	0.91	4.67	0.58	3.01	0.56	1.44	0.25	1.18
Sample	**Hf**	**Ta**	**W**	**Re**	**Tl**	**Pb**	**Bi**	**Th**	**U**			
3727-53	0.81	0.36	1.07	0.04	0.16	2.73	0.05	1.54	0.37			
3727-59	0.17	0.09	0.85	0.01	0.44	1.02	0.01	0.07	0.09			
3255k-49	0.95	0.21	7.33	0.19	0.32	3.90	0.06	1.65	1.30			
U-30	2.82	0.81	68.92	0.01	0.30	15.88	0.19	12.16	2.88			
U-56	0.30	0.30	7.18	0.04	0.06	2.43	0.06	0.32	0.09			
M-2	0.41	0.52	0.89	0.03	0.25	1.20	0.04	0.34	0.33			
M-4	0.28	0.40	0.42	0.05	0.05	0.85	0.01	0.75	0.28			
Kh-6	0.69	0.37	1.66	0.10	0.24	10.80	0.19	2.80	0.69			
Kh-11	0.55	0.26	0.81	0.08	0.22	7.54	0.21	1.92	0.60			

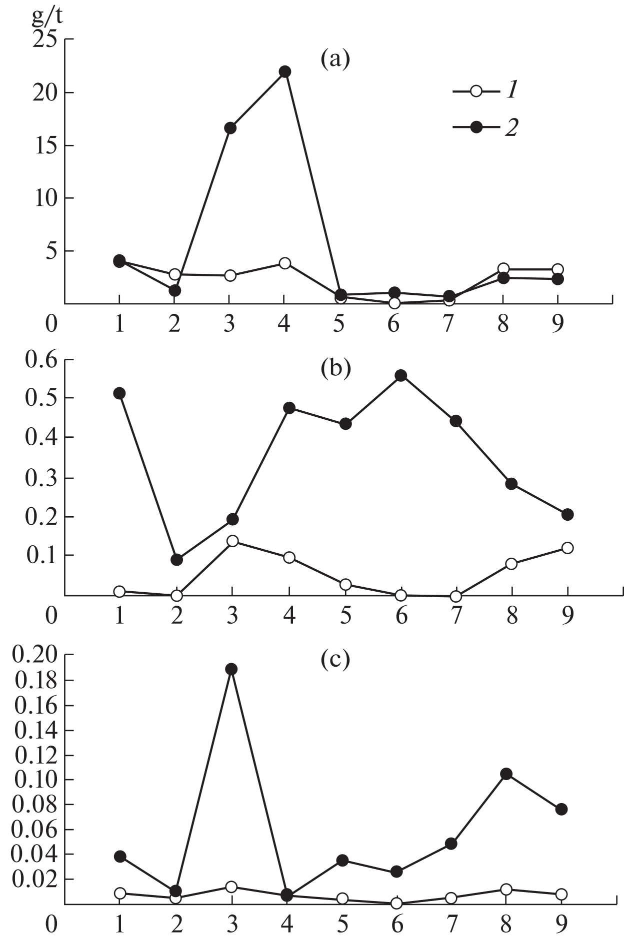

Fig. 3. Concentrations of (a) Ge, (b) Ag, and (c) Re (*1*) in the sample as a whole (bulk analysis) and (*2*) in the submicron fraction of coal. The abscissa axis refers to entry numbers in Table 2: (*1–3*) the Yerkovetsk deposit, (*4*, *5*) Ushumunsk deposit, (*6*, *7*) Mukhenskoe deposit, and (*8*, *9*) Khurmulinskoe deposit.

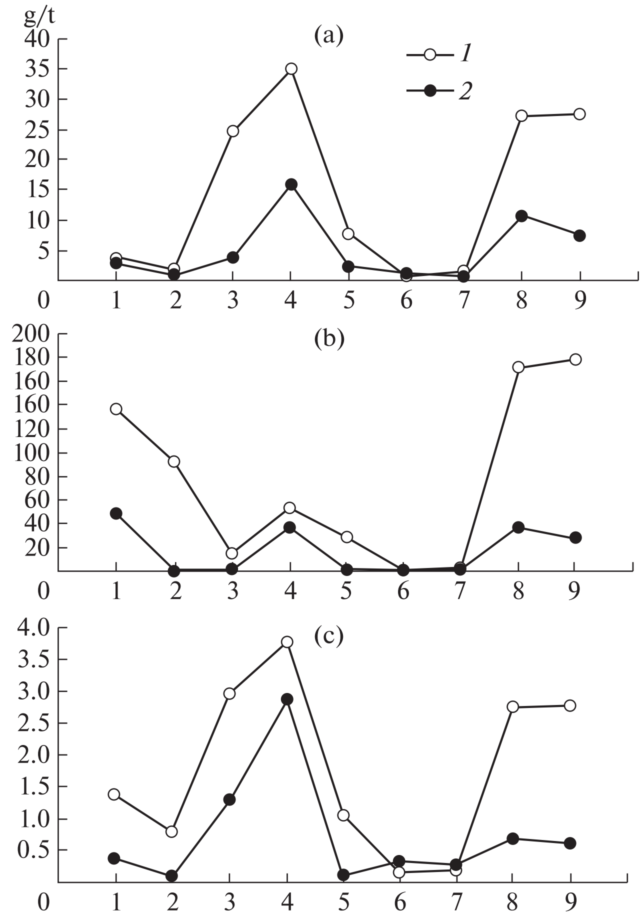

Fig. 4. Concentrations of (a) Pb, (b) La, and (c) U (*1*) in the sample as a whole (bulk analysis) and (*2*) in the submicron fraction of coal. The abscissa axis refers to entry numbers in Table 2: (*1–3*) the Yerkovetsk deposit, (*4*, *5*) Ushumunsk deposit, (*6*, *7*) Mukhenskoe deposit, and (*8*, *9*) Khurmulinskoe deposit.

(native) solutions to determine the concentrations of chemical elements in solution (CC) and then calculated their concentrations on a dry matter basis, that is, on an SMF basis. All of the experiments were performed in the Central Laboratory at the Karpinskii All-Russia Research Institute of Geology (VSEGEI).

Data on the concentrations of chemical elements in the SMFs of coals, which are given in Table 4, indicate that a number of trace elements are actually concentrated in the submicron fraction of coal, as compared with the bulk analysis of coal samples. Figures 1–4 graphically show the concentrations of some chemical elements in the general sample (bulk analysis) and in the SMFs.

Lithium, zinc, chromium, silver, rhenium, and scandium (Figs. 1–3) were concentrated in the SMFs of all samples to various degrees, whereas lead, uranium, and lanthanum did not exhibit this effect in the samples (Fig. 4). The behavior of the majority of trace elements depends on the deposit, although it may vary within a deposit for samples with different ash contents. Thus, the concentration of antimony in a submicron fraction was mostly observed for one of the samples from the Ushumunsk deposit; this effect was not observed in the samples from other deposits (Fig. 1).

In order to quantify the enrichment level of the submicron fraction with trace elements, the enrichment factor K was calculated as a ratio between the element concentration in the SMF and the total concentration of the element. The values of K lower and higher than 1 correspond to the depletion and enrichment of SMF, respectively (Table 5).

In general, the values of $2 > K > 1$ are not of great practical interest; therefore, we consider only the elements for which $K > 2$. Table 5 indicates that, in general, not only K but also the number of elements accumulated in the SMFs increase with decreasing the ash content of coal. Especially high values of K were found

Table 5. Enrichment factors of chemical elements in the submicron fractions of coals from the Far East ($K > 2$ are highlighted)

	Deposit								
	Khurmulinskoe		Ushumunsk		Yerkovetsk (West)			Mukhenskoe	
	Enrichment factor								
	Sample								
	Kh-6	Kh-11	U-30	U-56	3727-53	3727-59	3255k-49	M-2	M-4
Ash content, %	44.7	38.7	68.5	11.1	13.5	10.8	32.9	1.64	4.36
Li	2.95	3.29	2.35	28.00	29.64	26.21	2.49	386.55	136.16
Be	0.68	0.51	1.44	3.60	0.62	0.59	1.69	223.06	28.48
Sc	5.09	4.62	5.50	28.88	18.29	8.76	4.94	253.25	100.63
V	0.50	0.47	1.49	1.96	2.12	1.45	3.49	10.68	1.73
Cr	2.89	3.10	2.39	19.51	11.39	6.12	2.93	267.22	46.78
Co	0.43	0.54	1.05	0.83	1.03	2.87	3.70	23.27	2.51
Ni	0.37	0.36	1.09	1.19	1.77	1.39	2.57	13.05	2.42
Cu	0.67	0.50	1.75	1.12	3.49	0.71	1.12	5.71	2.02
Zn	14.05	6.22	1.91	187.15	69.35	9.50	3.19	76.22	18.32
Ga	0.43	0.37	0.87	0.46	0.58	0.49	0.26	3.15	1.40
Ge	0.79	0.76	5.79	1.40	1.02	0.48	6.19	12.64	1.78
Rb	0.53	0.48	0.78	1.74	9.69	9.81	0.80	51.04	13.64
Sr	1.15	0.97	0.89	0.27	4.50	7.58	5.34	53.87	15.44
Y	0.15	0.12	0.55	0.09	0.21	0.02	0.35	1.57	0.68
Zr	0.28	0.26	0.77	0.57	0.20	0.19	0.37	6.64	0.88
Nb	0.45	0.41	0.66	0.49	0.68	0.53	0.40	2.49	0.50
Mo	0.64	0.61	24.36	3.05	2.07	0.45	1.94	0.97	1.82
Ag	3.47	1.70	5.00	14.50	44.42	944.23	1.40	555.94	441.48
Cd	1.85	0.87	1.21	19.14	49.77	5.16	0.82	106.48	27.73
Sn	0.93	0.89	1.06	3.76	3.21	0.00	0.60	39.00	38.22
Sb	2.16	1.61	6.57	1.65	2.02	0.54	1.56	7.45	0.63
Cs	0.53	0.41	0.75	0.92	6.46	8.80	0.24	21.57	7.74
Ba	1.67	0.96	0.60	1.27	8.79	1.00	2.70	17.19	5.60
La	0.22	0.16	0.69	0.05	0.36	0.00	0.08	2.15	1.15
Ce	0.27	0.20	0.69	0.05	0.35	0.00	0.10	1.48	0.51
Pr	0.22	0.16	0.64	0.05	0.40	0.01	0.10	1.21	0.47
Nd	0.21	0.17	0.64	0.04	0.38	0.00	0.15	1.20	0.75
Sm	0.18	0.13	0.67	0.06	0.29	0.00	0.14	0.21	0.25
Eu	0.18	0.18	0.64	0.17	0.36	0.01	0.25	2.92	0.36
Gd	0.22	0.17	0.70	0.04	0.31	0.01	0.29	0.77	0.34
Tb	0.20	0.16	0.63	0.11	0.26	0.01	0.27	4.90	0.89
Dy	0.17	0.14	0.64	0.05	0.26	0.01	0.24	0.59	0.44
Ho	0.16	0.13	0.71	0.03	0.17	0.02	0.35	0.21	0.32
Er	0.15	0.13	0.57	0.09	0.23	0.02	0.39	1.38	0.49
Tm	0.20	0.18	0.67	0.49	0.20	0.04	0.46	7.13	3.02
Yb	0.17	0.14	0.58	0.08	0.18	0.02	0.57	1.74	0.54
Lu	0.20	0.14	0.64	0.23	0.18	0.03	0.61	0.59	0.79
Hf	0.22	0.19	0.61	0.59	0.35	0.14	0.44	5.10	0.65
Ta	0.51	0.46	0.79	1.97	1.33	0.90	0.41	46.08	7.47
W	0.60	0.39	2.57	1.90	1.50	0.57	1.44	1.26	0.34
Re	8.73	9.32	1.10	7.88	4.62	1.92	13.56	18.11	10.35
Pb	0.39	0.27	0.45	0.31	0.73	0.58	0.16	1.66	0.57
Th	0.24	0.18	0.79	0.08	0.29	0.02	0.20	1.62	1.11
U	0.25	0.22	0.76	0.09	0.27	0.12	0.44	2.23	1.45

Table 6. Concentrations of noble metals in the submicron fractions of coals, g / t

Sample	Ag	Ru	Rh	Pd	Ir	Pt	Au
3727-53	0.512	0.574	0.117	0.312	0.039	0.077	0.289
3727-59	0.092	0.152	0.054	0.135	0.010	0.010	0.016
3255k-49	0.194	0.081	0.058	0.219	0.014	0.030	0.065
U-30	0.475	0.117	0.040	0.614	0.008	0.023	0.109
U-56	0.436	0.160	0.081	<0.001	0.036	<0.001	0.115
M-2	0.556	0.230	0.140	0.377	0.015	0.029	0.165
M-4	0.441	0.515	0.126	0.246	<0.001	0.041	0.327
Kh-6	0.284	0.133	0.059	0.418	0.018	0.027	0.048
Kh-11	0.207	0.189	0.043	0.248	0.020	<0.001	0.036

for low-ash samples from the Mukhenskoe coal field: they were dozens of units for V, Co, Ni, Zn, Ge, Rb, Sr, Cs, Ba, Ta, and Re, 100–300 for Li, Be, Sc, Cr, and Cd and about 500 for Ag. The analysis of the samples for gold and platinum group metals is of particular importance. Table 6 summarizes the results of the analysis of SMFs for these metals.

Although the values of noble metals are below the limits of detection in the bulk analysis (see Table 3 for Au, Pd, and Pt), these values in the submicron fraction are several times or orders of magnitude higher than the detection limits. In this case, of course, it is impossible to calculate the enrichment factor K (for Au, Pd, and Pt). However, it is possible to calculate the correlation coefficients for the pairs of elements: they are 72% for the Ag–Au and Rh–Ru pairs.

Another important point is the recovery of an element in the SMF from the sample of coal. The calculation takes into account the amount of the submicron fraction (its percentage) and the concentration of the element. It turned out that the degree of extraction for most chemical elements is very small. This group includes all rare-earth elements, U, Hf, Zr, Nb, Y, Ga, and Pb—the percentage of their extraction is lower than one; no more than 5% of Co, Ni, V, Ge, Sb, and Ba is extracted with water. Table 7 summarizes the elements whose degree of extraction was higher than 5%.

Note that Table 7 contains only two elements from both of the samples from the Khurmulinskoe deposit: Zn (9.27% for X-6) and Re (5.76–6.43%). The recovery of other elements is different, and it can reach 50% for Sc and Cr (sample M-2), 62% for Zn (sample U-56), 73% for Li (sample M-2), and 100% for Ag (samples 3727-59, M-2, and M-4). The low-ash samples from the Mukhenskoe deposit, especially M-2, exhibited the highest degrees of trace element recov-

Table 7. Recovery of chemical elements into the submicron fraction of coal samples

Sample	Ash content	SMF in coal (rock)	Element recovery into SMF from coal, %					
	%		Li	Be	Sc	Cr	Zn	Rb
3727-53	13.5	0.3	8.89		5.49		20.81	
3727-59	10.8	1.15	30.14		10.07	7.04	10.92	11.28
3255k-49	32.9	0.87						
U-30	68.5	0.75						
U-56	11.1	0.33	9.24		9.53	6.44	61.76	
M-2	1.64	0.19	73.44	42.38	48.12	50.77	14.48	9.70
M-4	4.36	0.21	28.59	5.98	21.13	9.82		
Kh-6	44.7	0.66					9.27	
Kh-11	38.7	0.69						

Sample	Element recovery into SMF from coal, %							
	Sr	Mo	Ag	Cd	Sn	Cs	Ta	Re
3727-53			13.33	14.93				
3727-59	8.71		100.0	5.93		10.12		
3255k-49	5.00							11.80
U-30		18.27						
U-56			5.00	6.32				
M-2	10.23		100.0	20.23	12.96		8.76	5.00
M-4			92.71	5.82	8.03			
Kh-6								5.76
Kh-11								6.43

ery: 73% Li, 42% Be, 48% Sc, 50% Cr, and 100% Ag were recovered into the submicron fraction, and the significant amounts of Zn, Rb, Cd, Ta, Sn, and Sc were also extracted.

Thus, we can draw the following conclusions:

(1) The amounts of a submicron fraction in the test samples from the Yerkovetsk (three samples were analyzed), Ushumunsk (two samples), Khurmulinskoe (two samples), and Mukhenskoe (two samples) deposits ranged from 0.2 to 1.2%.

(2) The elements present in the samples of brown coal in low and ultralow concentrations were concentrated in the finest fraction of the samples, the particle size of which was smaller than 1 μm (in the submicron fraction).

(3) The rare and scattered elements Sc, Ag, Re, Au, Pt, and Pd and the elements that form water-soluble salts (Zn, Li, etc.) were concentrated in the submicron fractions.

(4) The degree of extraction for most chemical elements in the SMF was very small. This group included all rare-earth elements and U, Hf, Zr, Nb, Y, Ga, and Pb—the percentage of their extraction was lower than one; no more than 5% of Co, Ni, V, Ge, Sb, and Ba were extracted with water. However, the degree of extraction of some chemical elements (Ag, Li, Zn, Sc, and Cr) only by this method reached 30–100%. Rb, Cd, Ta, Sn, and Re were extracted in significant or noticeable (> 5%) amounts. Thus, we can hypothesize that the elements Ag, Li, Zn, Sc, and Cr in the low-ash coal samples predominantly occurred in the organic matter (especially Ag), and Rb, Cd, and Ta, to a significant extent.

(4) The degree of extraction of trace elements from coal in the SMF clearly depended on the ash content of the sample (and the distribution of chemical elements in the organomineral matrix): the extraction of trace elements from coal in the SMF did almost not occur from high-ash coals (samples 3255k-49, Kh-6, and Kh-11) and carbonaceous rock (sample U-30). The exception was Mo: the recovery from U-30 in the SMF was 18.27%; the enrichment factor in SMF was 24.36.

Rare earth elements and Hf, W, U, Th, and Ga were almost not extracted into the submicron fraction. The exceptions are Ga, Eu, Tb, Tm, and Hf in an extremely low-ash (A^d = 1.64%) coal sample from the Mukhenskoe deposit.

(5) In view of the above, it is possible to develop technologies for the sequential extraction (and separation) of elements from coal with water with the subsequent ashing and the production of a concentrate of the elements (rare-earth etc.) that cannot be recovered into the submicron fraction. For the extraction of these elements, the rare-earth metal concentrate should be subsequently processed by the methods of acid leaching.

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