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GEOCHEMISTRY

Sc-Bearing Coals from Yakhlinsk Deposit, Western Siberia

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The average Sc content in coals of the world is estimated at 2–4 g/t [1–5]. Occasionally, the Sc concentration can reach 10–15 g/t of coal and 100–200 g/t of ash [1–5]. The latter concentrations are comparable with those in wastes of tungsten, titanium, uranium, and other metallurgical works, which currently serve as the main source of this expensive metal (US$ 10 000–20 000/kg). For a long time, the Sc-rich coals have attracted attention as a potential source of Sc [6–8]. Technology of hydrometallurgical Sc recovery from coal ash was elaborated still in the late 1960s [7, 8]. When developing this technology, the experiments on acid leaching of Sc were performed with coal ashes containing 60–120 g/t Sc.

In this communication, we present the first information on coals with the Sc content of as much as 1 kg/t in ash. Such anomalous Sc concentrations in wastes of solid fuel burning were not reported previously. This finding makes the ideas of utilization of coals for recovery of scandium from the combustion wastes of power plants much more realistic.

The Sc-bearing coal was found in the course of sampling of Well 10671 drilled at the Yakhlinsk oil field of the Shaimsk petroliferous region, Western Siberia (Fig. 1). This well recovered the Jurassic coal-bearing rocks of the Tyumen Formation at a depth of 2295–2410.8 m. This formation is one of the main petroliferous rock complexes of the region. The high percentage of core recovery within this interval (almost 100%) made it possible to carry out the sampling of all penetrated coal seams and beds from 0.1 to 7.0 m thick.

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Coal seams in the lower part of the Tyumen Formation (samples Ya-28, Ya-29, and Ya-34) are hosted in the sediments of small lakes with stagnant and low-flow waters. Fluvial sediments of floodplains (samples Ya-9 and Ya-23) and coastal shallows of intracontinental fresh-water basins (samples Ya-6 and Ya-8) were found in the middle and upper parts of the coaliferous section (mainly, at the roof of coal beds and seams). The sedi-

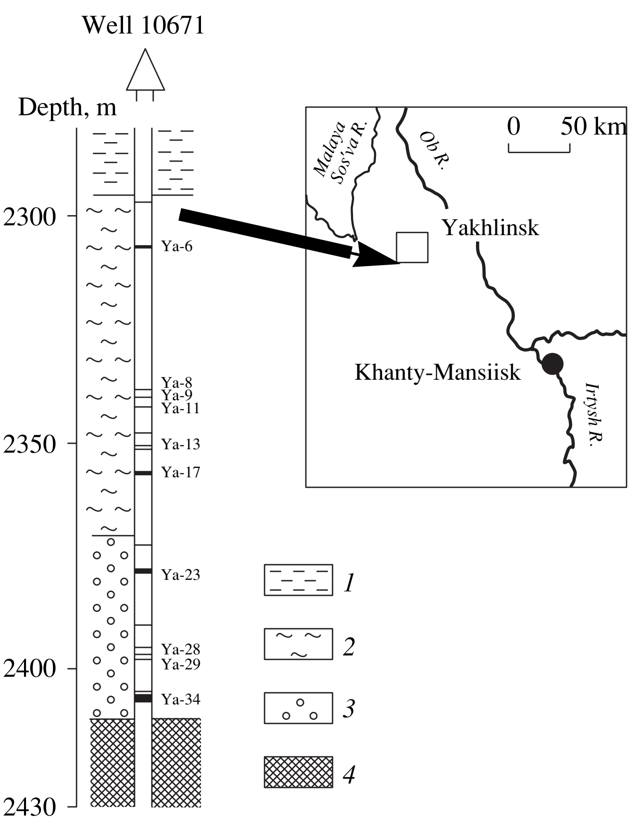

Fig. 1. Location of the Yakhlinsk oil field and generalized section of Well 10671 (lower part) that recovered the Sc-bearing coal. (*1*) Upper Triassic basement rocks; (*2, 3*) continental coal-bearing sedimentary rocks of the Middle–Upper Jurassic Tyumen Formation: (*2*) coastal–basinal, (*3*) lacustrine–fluvial; (*4*) Upper Jurassic marine sedimentary rocks.

Table 1. Sc content in coal and ash from various seams of the Yakhlinsk oil field

Sample	Analytical method					
	A^d, %	INAA		A^d, %	ICP MS	
		Sc, g/t of coal	Sc*, g/t of ash		Sc, g/t of coal	Sc, g/t of ash
Ya-6	16	20.2	126.2	–	–	–
Ya-8	9.7	23.8	245.4	9.3	10.8*	115.7
Ya-9	6.2	30.6	493.5	7.3	23.9*	328.1
Ya-11	4.7	43.4	923.4	4.6	27.4*	596.1
Ya-13	1.0	10.2	1051.5	1.3	11.2	864.1*
Ya-17	0.8	10.3	1320.5	1.0	8.5*	847.5
Ya-23	1.4	15.9	1135.7	1.8	12.5*	715.6
Ya-28	9.8	23.6	240.8	–	–	–
Ya-29	3.8	17.3	455.3	–	–	–
Ya-34	3.9	4.8	123.1	–	–	–

Note: (A^d) ash content; (*) calculated data; (–) not analyzed.

ments of low-flow boggy lakes occur at the base of these beds and coal beds in the lower part of the section. Only coal seam Ya-11 overlies the sediments of a coastal shallow. The fine-grained sediments (mudstone and siltstone) dominate among host rocks. The base of coal beds is usually composed of mudstones, while intercalating mudstones and siltstones are abundant at their roofs, particularly in the upper portion of the section. The data presented above indicate that coals in the lower part of the Tyumen Formation were deposited almost entirely in the lacustrine–alluvial setting. The coastal–basinal type of peat accumulation is inherent to the upper portion of the section [9].

Most of coals recovered by the well mainly consist of vitrinite (R_0 = 0.50–0.59) and pertain to high-volatile B and A ranks (“long-flame” and “long-flame gas” ranks, according to the Russian classification of coals). The ash content varies from 1 to 42.1% [10].

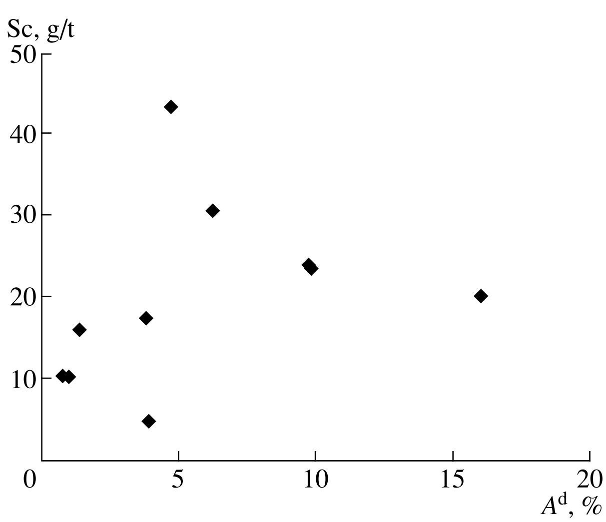

Fig. 2. Sc vs. ash relationship in coals (INAA data).

Sc and other trace elements were determined in 10 of 17 beds and seams with the INAA method at the Nuclear Geochemical Laboratory of the Tomsk Polytechnical University (A.F. Sudyko, analyst). The samples from six seams were additionally analyzed with the ICP-MS method at the Institute of Microelectronic Technology and Ultrahigh-Purity Materials, Russian Academy of Sciences (V.K. Karandashev, analyst). In five samples studied with the ICP-MS method, the Sc content was determined in the ash obtained at 550°C. In sample Ya-13, the element was determined after autoclave decomposition of coal in NHO_3 in the presence of H_2O_2.

The parallel analyses have shown that high Sc contents in coal are recorded by both INAA and ICP-MS methods (Table 1). In six samples, the average Sc content is 22.5 g/t of coal and 773 g/t of ash (INAA data) and 15.7 g/t of coal and 577.8 g/t of ash (ICP-MS) data. In general, in all of ten coal beds sampled with the INAA method, the Sc content varies from 4.8 to 43.4 g/t (average 20 g/t) in coal and from 123.1 to 1320.5 g/t (average 612 g/t) in ash. Such Sc concentrations in ashes exceed its average contents not only in wastes of metallurgical works but also in rare scandium deposits known in carbonate and albite–carbonate metasomatic rocks [11].

Such high concentration of Sc in ash is apparently caused by two factors: (1) anomalous (one order of magnitude or higher) accumulation of this metal in coals and (2) low ash content in the majority of studied coal beds. However, no correlation between Sc content and ash content is established (Fig. 2). This may indicate that the enriched coal was characterized by the initial organic form of Sc accumulation and this metal was delivered to coals in the dissolved form.

Virtually all coal beds of the Yakhlinsk field (except the uppermost one) are enriched in Co and Ni along with Sc. The maximum Co and Ni contents in ash samples Ya-17 and Ya-23 reach 1 wt % (Table 2). Anomalous Cr and V contents were revealed in samples Ya-8, Ya-9, Ya-11, and particularly Ya-8. The latter sample is anomalously enriched in not only siderophile, but also lithophile elements (Zr, Hf, and Nb). The Yakhlinsk field is also characterized by high concentrations of Be and Sb (nearly all beds are more enriched in these trace elements relative to World coal).

Despite a wide range of trace elements contained in the Yakhlinsk coal, none of them are correlated with Sc. Some correlation is only established between Sc and HREE (Fig. 3). The REE patterns of Sc-bearing coal beds are close in shape. In comparison with coals from the United States, where the REE patterns are close to the NASC pattern, the Yakhlinsk coal is depleted in LREE, enriched in HREE, and characterized by distinct Y maximum (Fig. 4). A similar shape of NASC-nor-

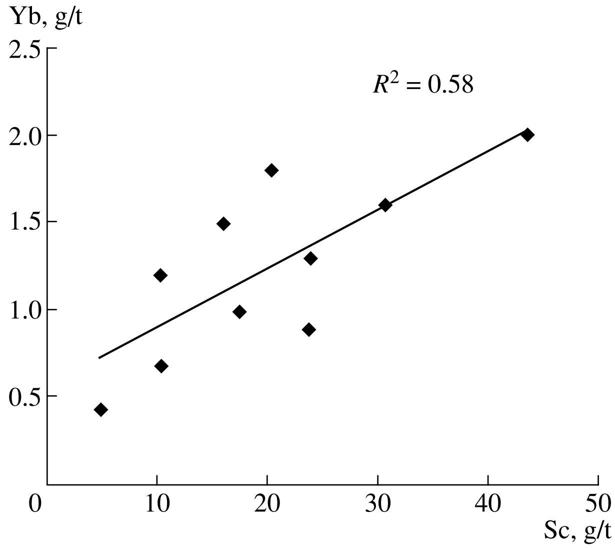

Fig. 3. Sc vs. Yb relationship in coals (INAA data). Reliability of approximation is shown.

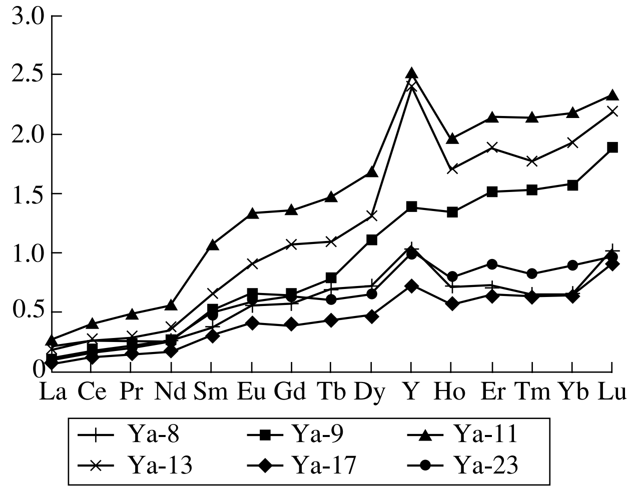

Fig. 4. USA coal [5]-normalized REE patterns of Sc-bearing coals (ICP-MS data).

malized REE patterns is observed in carbonated groundwaters with high F and gaseous CO_2 concentrations [12] and in some metasomatites, including Sc-bearing varieties [11]. It is noteworthy that the metasomatites are enriched not only in Sc, but also in Y and HREE. A similar situation is observed in ashes of four coal samples (Ya-11, Ya-13, Ya-17, and Ya-23). The REE contents range here from 0.11 to 0.36 wt %, and the Y content accounts for 30–50% of the total REEE. The REE concentration and distribution in ashes of these samples are comparable with those in the HREE- and Y-bearing weathered clayey rocks mined in China. Thus, a principal possibility exists to mine this coal and to recover Sc, HREE, and Y from burning wastes.

The nature of Sc concentration in coals of the Yakhlinsk field remains ambiguous. The following models seem to be the most plausible:

(1) Scandium was delivered to peat bogs by the Sc-rich surface water as a result of the weathering of the surrounding mafic rocks enriched in the metal (up to 35 g/t). Such a model is supported by the following data: (i) anomalous Ni and Co concentrations are recorded in most coal seams; (ii) the presence of peat with high Sc concentration (up to 340 g/t in ash) in present-day West Siberian peat bogs surrounded by basalts and basic intrusions (S.I. Arbuzov, unpublished data). However, this model is inconsistent with Sc concentration in the uppermost coalbed (sample Ya-6), where anomalous concentrations of Ni and Co are absent.

(2) Sc was delivered at the stage of diagenesis and early epigenesis of organic matter by hydrothermal solutions that leached this metal from basement rocks composed of the Late Triassic basalts and rhyolitic extrusions. This possibility is indicated, for example, by the wide development of quartz–carbonate–kaolinite–dickite argillic alteration in the Jurassic coaliferous sediments, testifying to the outburst of hydrothermal activity in the Shaimsk district in the Late Jurassic–Early Cretaceous [13]. Anomalous Sb concentrations in the Sc-bearing coal is another argument in favor of hydrothermal mechanism.

(3) Sc entered into the coal seams at the stage of catagenesis of organic matter owing to its selective removal from host rocks by aggressive groundwaters released in the course of subsidence and dehydration of clayey sediments under the load of an overlying sequence [14]. This model is consistent with the following observations: (i) occurrence of Sc-bearing coal beds at depths favorable for development of elision processes; (ii) elevated Sc contents in many Mesozoic coal fields of the West Siberian basin, including those located far from basic rock fields. Based on the analysis of 49 coal samples, the average Sc content in these fields is 16 g/t of coal [15], which is several times higher than the background value for coals. The maximum Sc content reaches 230 g/t of coal (Arbuzov, unpublished data).

All the models considered above provide for Sc transport in dissolved form and its absorption by organic matter of peat or coal. Further investigations of Sc-bearing coals of West Siberia at the Tomsk Polytechnic University will show which model is true. One cannot rule out that anomalous accumulations of scandium are related to polygenetic processes.

Thus, the data discussed above demonstrate a possibility to find coal seams with the Sc concentration exceeding the background value by an order of magnitude or more. If sufficiently thick and low-ash coal beds with such a high Sc concentration are to be found at a depth accessible for mining, their burning wastes may be considered a promising source of scandium. The

Table 2. Trace element contents in coal and ash of the Yakhlinsk oil field

Element	Sample									
	Ya-6*		Ya-8		Ya-9		Ya-11		Ya-13	
H, m	0.6		0.1		0.1		0.1		0.15	
A^d, %*	16		9.5		6.8		4.7		1.1	
Material	C	A	C	A	C	A	C	A	C	A
Li [14.8]	–	–	12	125.6	9.2	136.1	6.4	138.3	1.9	169
Be [2.1]	–	–	6.4	67.7	6.7	99.8	12.7	273	5.9	523.7
Na, %	0.077	0.48	0.081	0.87	0.045	0.62	0.021	0.45	0.019	1.76
Mg, %	–	–	0.064	0.69	0.23	0.31	0.01	0.24	–	–
Al, %	–	–	1.1	11.85	0.69	9.4	0.47	10.25	–	–
K, %	–	–	0.19	2.0	0.98	1.34	0.02	0.42	–	–
Ca, %	0.34	2.1	0.02	0.2	0.025	0.34	0.027	0.58	–	–
Sc** [2.7]	20.2	126.3	17.3	181.8	27.3	404.1	35.4	761.5	10.7	944.2
Ti, %	–	–	0.11	1.1	0.065	0.89	0.096	2.08	–	–
V [24.2]	–	–	394.6	4146.1	42.6	631.8	71.5	1537.6	1.9	170.1
Cr [14.2]	34.2	214	109.2	1147.4	31.9	473	45.4	975.8	4.3	377.9
Mn	–	–	8	87	5	63	2	44	–	–
Fe, %	0.86	5.4	0.11	1.2	0.064	0.87	0.035	0.75	0.032	2.9
Co** [4.5]	3.6	22.5	6.5	67.8	16.6	246.3	19.2	413.5	15.6	1375.4
Ni [10.2]	–	–	95.6	1004.8	87.1	1291	39	838.7	13.9	1223.5
Cu [11.8]	–	–	25.2	264.8	6.7	98.9	26.1	561.9	3.2	281.5
Zn [27.8]	–	–	12.1	127.2	8.9	131.8	8.1	173.8	32.7	2879.2
Ga [6.5]	–	–	5.2	54.5	16.9	250	6.9	148.8	2.6	226.8
Rb [15]	–	–	12.1	126.8	4.1	60.9	0.8	16.7	0.2	15.3
Sr [103]	–	–	19.1	200.8	25	370.6	24.7	530.3	12.2	1074.4
Y [7.5]	–	–	7.9	82.9	10.4	154.4	18.9	406.5	18	1585.9
Zr [37]	–	–	1287.3	13527.1	489.6	7252.8	263.2	5659.3	–	–
Nb [2.2]	–	–	20.2	211.8	9.8	145.3	3.4	73.5	–	–
Mo [2.4]	–	–	0.2	2.1	0.2	2.3	0.2	3.8	–	–
Sb** [1.2]	1.9	11.9	25.9	272	13.8	205.1	5.9	127.3	1.4	123.3
Cs [1.2]	–	–	1.2	12.1	0.4	6.3	0.1	1.2	0.01	1.2
Ba [129.8]	416	2600	213.4	2242.5	231.8	3433.5	195.3	4200.3	71.7	6318
Hf [1.2]	3.2	20	12.9	135.6	5.4	80.4	4.8	104.1	0.3	25.6
Ta [0.3]	0.4	2.5	0.2	2	0.1	1.6	0.1	2.8	–	–
Pb [12.8]	–	–	9	94.1	5.5	81.5	3.6	77.3	6.7	590
Th** [3.8]	3.4	21.3	2.2	23.5	1.6	23.8	3.1	67.1	0.2	15.6
U** [2.2]	2.1	13.1	1.4	14.3	1.1	16	2	43.7	1.8	158.1
La [12]	7.4	46.3	2.5	26.8	1.5	22.3	3.4	73.6	2.2	197.9
Ce [21]	12.7	79.4	5	52.9	3.9	57.1	8.6	184	5.6	491.7
Pr [2.4]	–	–	0.6	6.2	0.6	8.2	1.2	25.3	0.7	61.7
Nd [9.5]	–	–	2.5	26.4	2.4	36.1	5.4	116.4	3.5	304.5
Sm [1.7]	1.7	10.6	0.6	6.7	0.9	12.9	1.8	39	1.1	98.2
Eu [0.4]	0.6	3.8	0.2	2.3	0.3	3.9	0.5	11.5	0.4	31.8
Gd [1.8]	–	–	1	10.9	1.2	17.3	2.4	52.2	1.9	168.6
Tb [0.3]	0.4	2.5	0.2	2.2	0.2	3.5	0.4	9.5	0.3	28.9
Dy [1.9]	–	–	1.4	14.3	2.1	31.1	3.2	68.6	2.5	218.2
Ho [0.4]	–	–	0.3	2.7	0.5	7	0.7	14.7	0.6	52.5
Er [1]	–	–	0.7	7.7	1.5	22.3	2.2	46.3	1.9	166.3
Tm [0.15]	–	–	0.1	1	0.2	3.4	0.3	6.9	0.3	23.4
Yb [0.95]	1.8	11.3	0.6	6.7	1.5	22	2.1	44.5	1.8	160.9
Lu [0.14]	0.5	2.8	0.1	1.5	0.3	3.9	0.3	7	0.3	26.9

Table 2. (Contd.)

Element	Sample									
	Ya-17		Ya-23		Ya-28*		Ya-29*		Ya-34*	
H, m	0.3		1		0.1		0.1		1.7	
A^d, %*	0.9		1.6		9.8		3.8		3.9	
Material	C	A	C	A	C	A	C	A	C	A
Li [14.8]	2.1	235.4	2.9	186.8	–	–	–	–	–	–
Be [2.1]	7.4	832.3	7.3	466	–	–	–	–	–	–
Na, %	0.022	2.24	0.024	1.34	0.17	1.7	0.04	1.05	0.02	0.51
Mg, %	0.004	0.35	0.006	0.31	–	–	–	–	–	–
Al, %	0.09	9.33	0.17	9.9	–	–	–	–	–	–
K, %	0.002	0.24	0.006	0.32	–	–	–	–	–	–
Ca, %	0.01	1.11	0.016	0.93	–	–	–	–	–	–
Sc** [2.7]	9.4	1054.8	14.2	902.3	23.6	240.8	17.3	455.3	4.8	123.1
Ti, %	0.007	0.69	0.031	1.76	–	–	–	–	–	–
V [24.2]	1.7	196.1	4.1	261.3	–	–	–	–	–	–
Cr [14.2]	3.9	436.8	20.6	1304.9	53.3	544	19.5	514	7.5	192
Mn	3	268	3	181	–	–	–	–	–	–
Fe, %	0.022	2.23	0.037	2.13	0.14	1.4	0.042	1.1	0.039	1.0
Co** [4.5]	14.4	1613.9	71.9	4565	12	122.4	11.1	292.1	23.2	594.9
Ni [10.2]	68.7	7723.2	106	6732.1	–	–	–	–	–	–
Cu [11.8]	2.8	309.8	6.1	388.3	–	–	–	–	–	–
Zn [27.8]	6.5	727.4	5	316.2	–	–	–	–	–	–
Ga [6.5]	7.3	819.1	8.4	531.1	–	–	–	–	–	–
Rb [15]	0.2	17	0.3	19	–	–	–	–	–	–
Sr [103]	6.5	727.8	9.6	608.6	–	–	–	–	628.7	16 120
Y [7.5]	5.4	604.3	13.8	876.6	–	–	–	–	–	–
Zr [37]	5.2	579.1	20.5	1304.7	–	–	–	–	–	–
Nb [2.2]	0.3	28.4	0.5	30.5	–	–	–	–	–	–
Mo [2.4]	0.1	12.1	0.3	18.9	–	–	–	–	–	–
Sb** [1.2]	9.6	1080.2	2.8	179	11.6	118.4	5.6	147.4	–	–
Cs [1.2]	0.01	1.4	0.02	1	1.9	19.4	–	–	–	–
Ba [129.8]	34.4	3868.4	31.8	2018.2	320	3265.3	190	5000	283.1	7260
Hf [1.2]	0.2	24.5	0.2	11	4.3	43.9	2	52.6	0.6	15.6
Ta [0.3]	0.01	1.4	0.04	2.8	–	–	–	–	–	–
Pb [12.8]	3.1	350.8	4.3	272.3	–	–	–	–	–	–
Th** [3.8]	0.4	43.8	0.3	16.3	2.9	29.6	1.5	39.5	0.2	3.8
U** [2.2]	0.9	96.1	1	63.1	2.6	26.5	1.9	50	0.8	10.2
La [12]	0.9	102.3	1.3	80.3	4.9	50	1.4	36.8	3.3	84.6
Ce [21]	2.6	293.2	3.4	217.4	9.5	96.9	2.9	76.3	13.9	356.4
Pr [2.4]	0.4	41.7	0.5	30.5	–	–	–	–	–	–
Nd [9.5]	1.7	187.2	2.5	158.6	–	–	–	–	–	–
Sm [1.7]	0.5	60.3	0.8	52.8	1.2	12.2	0.6	15.5	1.8	46.2
Eu [0.4]	0.2	18.4	0.2	14.9	0.3	2.6	0.3	6.6	0.4	11
Gd [1.8]	0.7	80.6	1.2	73.1	–	–	–	–	–	–
Tb [0.3]	0.1	14.6	0.2	11.5	0.4	4.4	0.4	10.8	0.2	6.2
Dy [1.9]	0.9	100.6	1.3	79.8	–	–	–	–	–	–
Ho [0.4]	0.2	22.4	0.3	17.7	–	–	–	–	–	–
Er [1]	0.6	72.3	0.9	57.6	–	–	–	–	–	–
Tm [0.15]	0.1	10.7	0.1	7.9	–	–	–	–	–	–
Yb [0.95]	0.6	69.7	0.9	54.1	0.9	9.1	1	26.1	0.4	11
Lu [0.14]	0.1	14.5	0.1	8.7	0.2	2.1	0.3	6.6	0.1	1.5

Note: Na, Mg, Al, K, Ca, Ti, and Fe contents are given in wt %; contents of other elements, in g/t; (C) coal: (A) ash; (*) samples analyzed only with the INAA; (**) average values of the results obtained at different laboratories; (–) not analyzed. The background trace element contents in coals [3] are given in brackets.

complex development of such coals with recovery of Sc as a by-product will lead to appreciable depreciation of this valuable metal and thus will foster its industrial application.

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