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Scandium (Sc) geochemistry in coals (Siberia, Russian Far East, Mongolia, Kazakhstan, and Iran)

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ABSTRACT

This research discusses new original data on the geochemistry of scandium (Sc) in the coals of the Asian region of Russia, Mongolia, Kazakhstan, and Iran. In general, the studied coals are enriched in Sc compared with the mean value for coals throughout the world. In different regions of the studied territory, coal deposits with anomalous Sc concentrations (up to commercially important concentrations) were found and the factors that control the Sc contents in those coals were revealed. The composition of the rock types that surround the coal-forming basins and the hydro-geochemical conditions of these basins and deposits determine the levels of Sc accumulation in the coals. It was found that Sc was redistributed and partially lost from the seams during coal metamorphism. Studies of the modes of Sc occurrence in the coals showed the predominance of an organic mode. In addition, the peculiarities of the Sc distribution in the deposits and coal seams indicate a predominantly hydrogenous mechanism for the accumulation of anomalous Sc concentrations in coal and peat. Scandium in coal and peat accumulates by leaching from coal-bearing strata and re-deposition in coal (peat) beds with the participation of soil and ground water enriched with organic acids. Specific conditions for the formation of coal containing Sc-enriched rocks and for the Sc leaching and transportation into coal seams are necessary for the accumulation of high Sc concentrations in the coals. Such conditions that occur in the contemporary mire ecosystems of Western Siberia could also have occurred in ancient basins of peat (coal) accumulation.

1. Introduction

Over the last several decades, trace element research in coal deposits and basins on all continents has shown that coals are the concentrators of many valuable metals, including rare and scattered elements such as Ge, rare earth elements (REEs), Ga, Sc, Zr, Nb, Au, and others (Arbuzov et al., 2006: Baruah et al., 1998; Bouška and Pešek, 1999; Dai et al., 2010, 2012a, 2012b, 2013; Du et al., 2009; Hower et al., 1999, 2002; Mastalerz and Drobniak, 2012; Papanicolaou et al., 2004; Qi et al., 2007; Seredin and Finkelman, 2008; Seredin and Dai, 2012, 2013; Seredin et al., 2013; Sorokin et al., 2013; Suárez-Ruiz et al., 2006; Swaine, 1990; Ward et al., 1999; Yazdi and Esmaeilnia, 2003, 2004; Zhuang et al., 2006). Among them, Sc has drawn particular interest because it is generally not found in its own commercial deposits and is usually produced from ores explored for other metals. However, Sc often forms anomalies in coal ash, up to commercially significant concentrations (Arbuzov and Ershov, 2007; Arbuzov et al., 2003b; Kashirtsev et al., 1999; Seredin and Finkelman, 2008; Seredin et al., 2006; Valiev et al., 1993; Yudovich and Ketris, 2006).

Despite a large amount of information on the concentration of Sc in coals, the geochemistry of Sc has been insufficiently studied. Few studies have been directly devoted to Sc in coals (Arbuzov and Ershov, 2007; Arbuzov et al., 1996, 1997, 2000, 2003a; Borisova et al., 1974; Eskenazy, 1996; Gordon et al., 1968; Guren et al., 1968; Kryukova et al., 2001; Menkovskiy et al., 1968; Seredin et al., 2006; Swaine, 1964; Yudovich and Ketris, 2002, 2006; Yurovskiy, 1968), and existing studies address only certain issues regarding its geochemistry.

Currently, there is no clear concept of the reasons for and conditions of the accumulation of high concentrations of Sc in coals, the modes of Sc occurrence in coals, and the ratios of mineral forms and organic compounds. The relationships between Sc accumulation levels and the conditions of coal accumulation and the petrographic composition of coals are uncertain, due to a lack of commercial interest in coals as a source of Sc. As a consequence, search criteria for Sc-bearing coals have not been developed. The low demand for this element, which is generally due to its notably high price, is completely met by current facilities. Therefore, this situation has not stimulated the study of other sources of Sc. However, the ash of selected coals can compete well with traditional sources of Sc due to the availability of coal and its high concentration in coal.

2. Characteristics of the research objects

The current study on Sc geochemistry was carried out in the Asian region of Russia, Mongolia, Kazakhstan, and Iran (Fig. 1). The research

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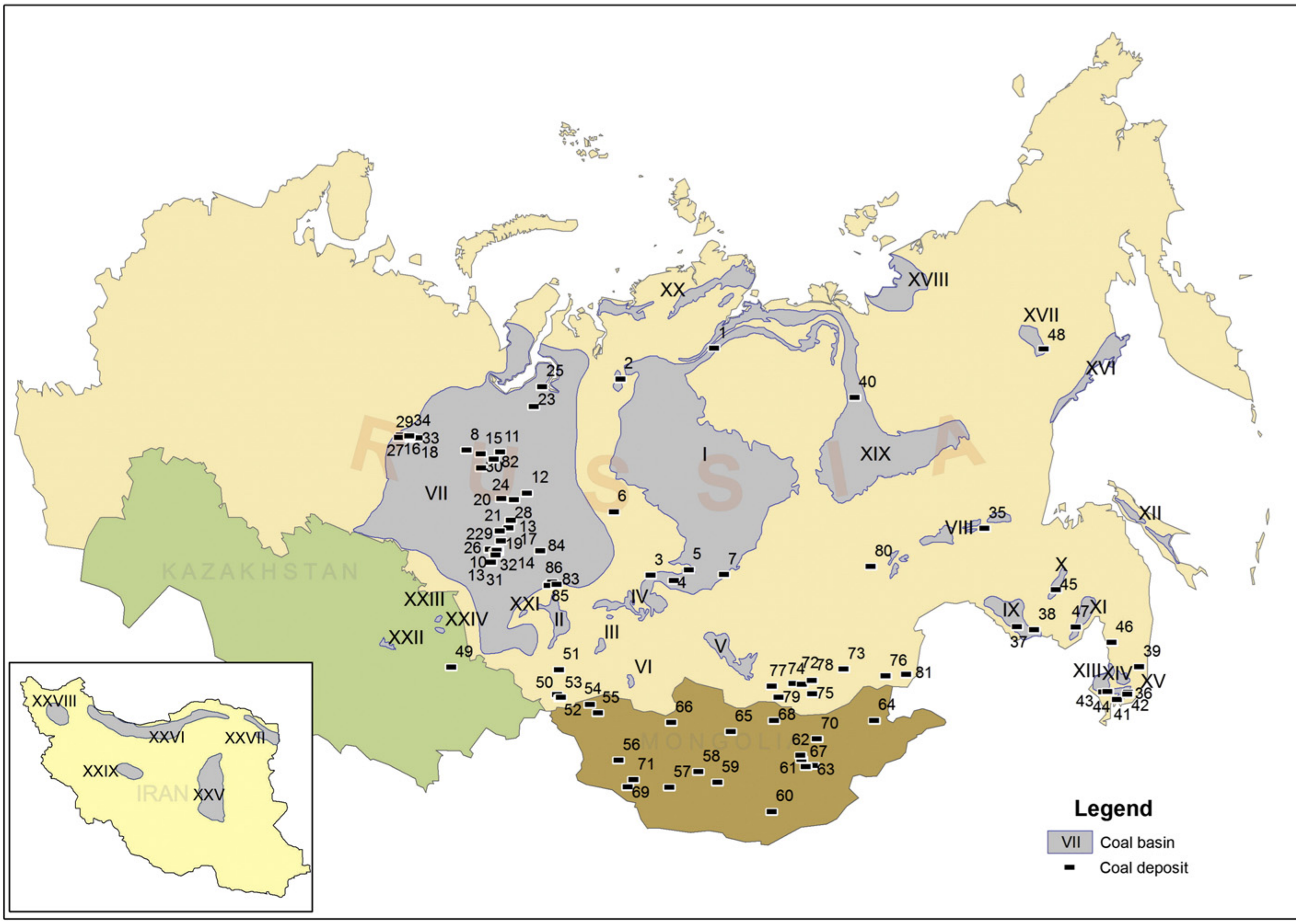

Fig. 1. Locations of the studied coal basins and deposits in Northern Asia. *Basins*: I—Tungusskiy, II—Kuznetskiy, III—Minusinskiy, IV—Kansko-Achinskiy, V—Irkutskiy, VI—Ulugchemskiy, VII—Zapadno-Sibirskiy, VIII—Yuzhno-Yakutskiy, IX—Nizhnezeyskiy, X—Bureinskiy, XI—Sredne-Amurskiy Khankaiskiy, XII—Sakhalinskiy, XIII—Razdolnenskiy, XIV—Bikino-Ussuriyskiy, XV—Partizanskiy, XVI—Okhotskiy, XVII—Arkagalinskiy, XVIII—Yano-Omoloyskiy, XIX—Lenskiy, XX—Taimyrskiy, XXI—Gorlovskiy, XXII—Karagandinskiy, XXIII—Ekibastuzskiy, XXIV—Maikubenskiy, XXV—Tabas, XXVI—Alborz. *Coal-bearing regions*: XXVII—North-Khurasan, XXVIII—Maragheh, XXIX—Kashan-Esfahan. *Deposits*: 1—Kayakskoe, 2—Kayerkanskoe, 3—Kokuyskoe, 4—Gavrilovskoe, 5—Kodinskoe, 6—Podkamenno-Tungusskoe, 7—Zheronskoe; 8—Ai-Pimskoe, 9—Archinskoe, 10—Verkhtarskoe, 11—V-Trom'eganskoe, 12—Vostochno-Permyakovskoe, 13—Gerasimovskoe, 14—Grigorievskoe, 15—Konitlorskoe, 16—Lazarevskoe, 17—Letnee, 18—Lovinskoe, 19—Luginetskoe, 20—Malorechenskoe; 21—Myldzhinskoe, 22—Nizhne—Tabaganskoe, 23—Novo-Urengoyskoe, 24—Prigranichnoe, 25—SG-7-397, 26—Severo-Kalinovoe, 27—Talnikovoe, 28—Trassovoe, 29—Umytinskoe, 30—Fedorovskoe, 31—Shirotnoe, 32—Yuzhno-Tabaganskoe, 33—Yakhlinskoe, 34—Symoriakhskoe, 35—Elginskoe, 36—Sergeevskoe, 37—Erkovetskoe, 38—Raichichkinskoe, 39—Voznovskoe, 40—Zhiganskoe, 41—Shkotovskoe, 42—Avangard, 43—Lipovetskoe, 44—Pavlovskoe, 45—Urgalskoe, 46—Bikinskoe, 47—Ushumunskoe, 48—Arkagalinskoe, 49—Karazhira, 50—Kuraiskoe, 51—Pyzhinskoe, 52—Taldu-Dyurgunskoe, 53—Balkhash, 54—Nuurs-khotgor, 55—Hartarvagatai, 56—Ho'ndlon, 57—Zeegt, 58—Uvurchuluut, 59—Bayanteeg, 60—Tavantolgoi, 61—Baganuur, 62—Tugriknuurskoe, 63—Alagtogoo, 64—Aduunchuluun, 65—Saykhan-Ovoo, 66—Mogoingol, 67—Shivee-Ovoo, 68—Shariingol, 69—Maanit, 70—Chandgan Tal, 71—Khurengol; 72—Olon-Shibirskoe, 73—Tataurovskoe, 74—Tarbagataiskoe, 75—Zashulanskoe, 76—Chkaranorskoe, 77—Zagustaiskoe, 78—Burtuiskoe, 79—Okino-Klyuchevskoe, 80—Apsatskoe; 81—Urtuiskoe, 82—Kavrinskoe; 83—Tuganskoe; 84—Kolpashevskoe; 85—Lagernosadskoe; 86—Talovskoe.

issues determined the choice of the study sites and included the estimated Sc content in coals, the mechanisms of accumulation of anomalous concentrations of metals, the effects of various factors of the geological environment on the levels of Sc accumulation in coals and coal ash, the conditions of Sc concentration, and the modes of Sc occurrence in coals with different degrees of metamorphism.

The studied coal deposits of Siberia include nine coal basins and 14 separate deposits. Detailed geological–geochemical research was conducted on four basins: Kuznetskiy, Minusinskiy, Irkutskiy, and Kansko-Achinskiy. The Gorlovskiy, Tungusskiy, Zapadno-Sibirskiy, Ulugchemskiy, and Taimyrskiy basins are less studied but contain rather representative data. The total number of studied samples from the Siberian region is 5212, including 3285 coals and 1927 peats.

The Siberian region contains coals of all ranks (from lignites to anthracites) and with ages ranging from the Devonian to the Palaeogene. Contact metamorphic graphic rocks, developed in the coals, also occur in this area.

The Russian Far East has been less intensely studied. The coals in this region are younger than those in the Siberian region and include Late Jurassic, Cretaceous, Paleogene, and Neogene coals. These coals have a lower rank than those in Siberia, and volcanism played an essential role in the formation of these coal-bearing deposits (Coal base of Russia, 2004). Most of the data were collected from research on coal collections carried out by V.V. Ivanov, A.A. Kumar'kov, M.A. Klimin, V.N. Shvets, and V.A. Melkiy. A total of 291 samples were collected from 13 deposits of this region. However, the numerous deposits and basins of the Russian Far East have been insufficiently studied, and the current information is preliminary.

In this work, representative geochemical research in Mongolia was carried out for the first time. A total of 337 coal samples were collected from 18 deposits of Carboniferous, Permian, Jurassic, and Cretaceous age. Characteristics of the coal deposits of Mongolia include a wide age range of coal formation conditions and an evident zoning in ages directed from east to west. The region's peculiar mineragenY and geochemistry, magmatic and volcanic activities, widespread granitoid formations, and contemporary arid and semi-arid climate have all impacted the geochemical features of the coal deposits of Mongolia.

Minor data were collected for the coal-bearing deposits of Kazakhstan, including coals of Carboniferous age from the Ekibastuz and Karagandinskiy basins and coals of Jurassic age from the Maikubenskiy basin and the Karazhira deposit. S.Yu. Kalinina, A.Ya. Pshenichkin, and S.V. Azarova aided in the collection of samples from the Kazakhstan deposits.

Additionally, a large-scale specialised geochemical sampling of the Iranian coal deposits available for study was carried out for the first time. A feature of these materials is the predominance of coals with a high degree of metamorphism. Two coal basins (Tabas and Alborz) and three separate coal-bearing regions occur in Iran. A total of 610 samples of coal and coal-containing rocks were collected from 34 deposits. The Iranian coals generally formed in the Triassic–Jurassic period, and coal deposits of Carboniferous age do not have commercial significance. A feature of the coal-forming processes in Iran is an unstable tectonic environment, which caused the formation of numerous thin coal seams with high ash yields. The source rock area of the coal basins includes complexes of primarily mafic-andesite composition.

The collection of studied samples from Siberia, the Russian Far East, Kazakhstan, Mongolia, and Iran encompasses the general types of coals formed under various geotectonic conditions and in a variety of depositional environments. Their rank ranges from immature brown coals to anthracites, and their ages range from Devonian to Neogene. The modern peat deposits of Western Siberia were also studied.

3. Methods

This study is based on the results of a qualitative analysis of Sc in 6155 samples of coal and peat and more than 2000 samples of coal-containing rocks from different deposits. The coal seams were sampled using the channel method, with differentiated sampling at coal-mining facilities in open casts and mines, in natural outcrops, and also in drill cores. The length of the sampling intervals was dependent on the thickness and structural complexity of the seam, and ranged from 0.15 to 2 m on average. Thin coal layers separated by rock interbeds, the rock interbeds themselves, clastic dikes, sulfide inclusions, carbonate concretions, and other mineral formations were studied separately. The separate sections were sampled in detail using intervals ranging from 0.5 cm to 10 cm. The lateral variability of Sc was estimated in some sections of a coal seam in the direction of its strike.

The Sc concentration in the majority of samples was directly examined via instrumental neutron-activation analysis (INAA) of the coal without preliminary ashing to avoid metal losses. Laboratory analyses for coal, coal ash, and rocks were carried out at the Nuclear Geochemical Laboratory of the Department of Geoecology and Geochemistry of Tomsk Polytechnic University in Russia (NGL of TPU) (analyst: A.F. Sudyko). The samples were exposed to radiation treatment in the IRT-T research nuclear reactor. The weight of each INAA sample ranged from 100 mg to 200 mg, and the detection limit for Sc in coal was 0.02 ppm. A portion of the samples was examined using mass spectrometry with inductively coupled plasma mass spectrometry at the Institute of Problems of Microelectronics and Particularly Clean Materials at the Russian Academy of Sciences in Chernogolovka, Russia (executor: V.K. Karandashev) and at the Analytical Center of Geochemistry of Natural Systems of Tomsk State University in Russia (analyst: Yu.V. Anoshkina). The convergence of the results from the different methods was satisfactory. As a control, Sc was determined in coal and coal ash with conversion of the concentrations from the ash to coal and vice versa. The quality of INAA analysis was controlled according to the different standards for coal ash and rocks (Table 1).

Table 1
Scandium in standard samples.

Standard sample	Passport data, ppm	NGL of TPU
Rhyolite JR-1	5.07 ± 0.54	5.4 ± 0.1
Rhyolite JR-2	5.59 ± 1.22	5.5 ± 0.1
GraniteJG-2	2.42 ± 0.42	2.4 ± 0.04
Granodiorite JG-3	8.76 ± 0.55	8.7 ± 0.12
ZUK-1 GSO7125-94	11.0 ± 1.0	11.1 ± 0.3
Garnet-biotiteplagiogneiss GBP-1	14.3 ± 2.2	14.5 ± 0.2
Dark shale GSL-1	20.0 ± 3.0	21.0 ± 0.5

The mean Sc content in the coals was estimated using consecutive data averaging. The mean Sc contents were calculated in terms of the weighted means for the thickness of the sampling intervals in the coal seams, for the seam thickness in the deposits, and for the coal mass (resources) in the deposits (Arbuzov and Ershov, 2007).

The calculations made for the mean Sc contents of samples from the Russian Far East and Kazakhstan are less reliable, due to less intensive sampling of the basins and deposits. Therefore, the obtained data are preliminary.

The peat and brown coal samples were separated into different geochemical fractions for analysis of the modes of Sc occurrence (analyst S.G. Maslov). The following fractions were extracted from the peat according to Instorf's method (Lishtvan and Korol, 1975): bitumen (by extraction with benzene), water-soluble and easily hydrolysable substances (by treatment with 4% HCl), humic and fulvic acids (by treatment with NaOH), and residual coal. Humic acids were extracted from the brown coals according to the Russian standard GOST 9517–94 and from the bitumens according to GOST 10969–87. All fractions were analysed via INAA for Sc determination. The mineral modes of Sc occurrence were studied under a Hitachi 3400S scanning electronic microscope (analyst: S.S. Ilenok).

The selected combination of analytical methods allowed for the estimation of the contents, distribution regularities, and conditions of the Sc concentration in coals.

4. Results and discussions

4.1. Scandium content in coal

The mean content of Sc in the studied coals of Siberia, the Russian Far East, Kazakhstan, Mongolia, and Iran is 4.3 ppm, with an average ash yield of 13.1% (Table 2). The mean value was calculated in terms of the weighted mean for the coal resources. These calculations did not include those made for the Zapadno-Sibirskiy basin because, according to a preliminary estimation, the resources of this basin considerably exceed the official estimated world coal resources and also contain anomalous Sc concentrations of up to 0.23% in the coal ash. The estimated mean content of Sc from the 67 deposits and basins is 4.6 ppm, and the median is 4.2 ppm. These data correspond well with the estimated geometric mean of Sc in the coals of China (Dai et al., 2012c; Ren et al., 1999) and are similar to the mean Sc content in the coals of the USA (Finkelman, 1993). However, these values are slightly higher than the estimated mean content for the coals of the world (3.9 ppm) reported by Ketris and Yudovich (2009).

The mean content of Sc in coals from individual deposits ranges from 0.85 ppm (the Urtuiskoe deposit in Transbaikalia) to 16.0 ppm (the Zapadno-Sibirskiy basin, Mesozoic coals). In individual samples of the Pereyaslovskoe deposit of the Kansko-Achinskiy basin, the Sc concentration can reach up to 230 ppm (Arbuzov et al., 2008).

In the coal ash, the mean Sc content ranges from 7.3 ppm (the Aduunchuluun deposit, Mongolia) to 150 ppm (the Zapadno-Sibirskiy basin, Mesozoic coals).

Coals of different ages differ in Sc concentration, even within the same region. Coals of Devonian age display rather constant and high

Table 2
Content of scandium in coal and coal ash (Siberia, Russian Far East, Mongolia, Kazakhstan and Iran).

Coal basin, deposit	Number of samples	Rank	A^d, %	Content of scandium, ppm			
				Coal			Coal ash*
				Average	Min	Max	
Siberian region							
Devonian coals							
Barzasskoe	14	SB	32.5	6.4 ± 0.7	2.5	11.3	19.7
Ubrusskoe	6	B	49.2	8.7 ± 1.3	5.7	14.3	17.7
Mean	20		35.3	6.8 ± 0.8			19.2
Carboniferous–Permian coals							
Gorlovskiy	24	A	7.0	2.9 ± 0.5	0.33	10.3	41.4
Kuznetskiy	1394	SB-A	13.5	3.9 ± 0.1	0.35	20.2	28.9
Minusinskiy	490	SB-B	16.9	8.2 ± 0.6	1.3	30.4	48.5
Tungusskiy	67	SB-A	14.1	4.6 ± 1.4	0.5	29.3	32.6
Taimyrskiy	51	SB-SA	24.4	7.4 ± 0.6	1.3	17.8	30.5
Kuraiskoe	12	B	25.2	6.9 ± 0.9	1.7	12.3	27.4
Mean	2038		13.5	4.5 ± 0.8			33.2
Mesozoic coals							
Pyzhinskoe	6	B	6.5	2.9 ± 1.4	2.1	10.9	44.6
Kansko-Achinskiy	524	SB-B	9.8	2.9 ± 0.5	0.23	233	29.6
Irkutskiy	129	SB-B	14.3	6.7 ± 0.9	0.21	43.1	46.9
Ulugkhemskiy	45	B	9.3	2.3 ± 0.5	0.1	14.6	44.6
Zapadno-Sibirskiy	172	SB-B	10.6	16.0 ± 2.1	0.2	107	150
Tungusskiy	30	SB	12.6	3.9 ± 0.6	1.2	30.4	23.8
Kuznetskiy	3	SB	17.3	6.4 ± 1.4	3.6	8.2	37.0
Olon-Shibirskoe	40	SB	15.3	4.6 ± 0.5	1.6	12.0	32.8
Tataurovskoe	31	SB	13.3	1.3 ± 0.4	0.3	10.3	9.8
Tarbagataiskoe	34	SB	10.9	1.5 ± 0.5	0.5	14.1	13.8
Zashulanskoe	18	B	7.3	1.2 ± 0.4	0.6	6.7	16.4
Chkaranorskoe	41	SB	10.0	1.2 ± 0.2	0.4	6.9	12.0
Zagustaiskoe	13	SB	18.2	4.0 ± 1.1	0.5	9.0	22.0
Burtuiskoe	18	SB	9.5	2.8 ± 0.4	0.7	8.6	29.5
Okino-Klyuchevskoe	8	SB	19.2	4.7 ± 1.3	2.2	8.0	24.5
Urtuiskoe	8	SB	7.9	0.85 ± 0.13	0.5	1.4	10.8
Apsatskoe	5	B	12.3	2.7 ± 0.3	1.8	3.5	22.0
Mean	1125		12.0	3.9 ± 0.9			32.5
Paleogene coals							
Zapadno-Sibirskiy	73	L	30.7	13.3 ± 0.6	5.9	23.2	43.3
Taldu-Dyurgunskoe	29	L	19.8	9.1 ± 0.8	3.6	18.4	46.0
Mean	102		30.7	13.3 ± 0.6			43.3
Peat							
Zapadno-Sibirskiy	1927		7.3	0.88 ± 0.17	0.1	10.4	12.2
Russian Far East region							
Late Jurassic–Lower Cretaceous coals							
Erkovetskoe	23	SB	14.2	2.0 ± 0.7	0.7	13.7	14.1
Raichichkinskoe	19	SB	13.6	3.5 ± 0.8	0.5	12.4	25.7
Elginskoe	47	B	16.1	2.1 ± 0.7	0.6	31.4	13.0
Urgalskoe	58	B	25.7	5.1 ± 0.3	2.4	13.1	19.8
Lipovetskoe	4	SB	32.7	4.2 ± 0.5	3.2	5.7	12.8
Mean	151		17.9	2.8 ± 0.6			15.4
Paleogene–Neogene coals							
Shkotovskoe	7	SB	16.2	6.4 ± 1.3	1.9	12.3	39.5
Pavlovskoe	40	SB	14.2	4.6 ± 0.6	0.4	17.6	32.4
Bikinskoe	16	SB	17.4	10.5 ± 2.5	3.2	36.4	60.3
Ushumunskoe	9	SB	10.1	2.9 ± 0.6	1.0	6.7	28.7
Yano-Omoloyskiy	16	B	33.0	4.6 ± 1.0	0.6	16.6	13.9
Sakhalin	39	SB-B	16.2	9.1 ± 0.7	1.5	20.6	56.2
Voznovskoe	6	SB	21.1	2.3 ± 0.8	0.9	5.1	10.9
Sergeevskoe	7	L	15.8	3.0 ± 0.4	2.0	5.3	19.0
Mean	140		23.5	6.8 ± 0.9			28.9
Kazakhstan							
Carboniferous coals							
Karagandinskiy	5	B	13.5	8.0 ± 1.7	4.3	13.5	59.3
Ekibastuz	41	B	36.1	8.3 ± 0.4	4.1	15.2	23.0
Mean	46		24.8	8.1 ± 0.5			32.7
Jurassic coals							
Karazhira	7	SB	11.2	8.9 ± 0.9	6.0	12.7	79.7
Maikubenskiy	10	SB	25.5	8.1 ± 1.6	3.2	13.0	31.8
Mean	17		18.4	8.5 ± 1.3			46.3
Mongolia							
Carboniferous coals							
Nuurst-khotgor	122	B	18.2	3.4 ± 0.3	0.7	21.8	18.7
Khartarvagatai	10	B	18.7	2.7 ± 0.2	2.0	3.4	14.4

(continued on next page)

Table 2 (*continued*)

Coal basin, deposit	Number of samples	Rank	A^d, %	Content of scandium, ppm			
				Coal			Coal ash*
				Average	Min	Max	
Mongolia							
Carboniferous coals							
Ho'ndlon	8	B	9.4	1.8 ± 0.3	1.0	3.4	19.1
Zeegt	10	B	12.5	1.2 ± 0.2	0.6	2.2	9.6
Mean	150		14.7	2.3 ± 0.5			15.6
Permian coals							
Tavantolgoi	10	B	9.8	1.8 ± 0.2	1.5	2.4	18.4
Maanit	16	B	20.2	4.9 ± 0.5	1.1	7.5	24.3
Uvurchuluut	5	L	17.2	7.9 ± 2.5	3.0	14.5	45.9
Khurengol	28	B	38.9	4.8 ± 0.3	1.9	8.2	12.3
Mean	49		21.2	4.9 ± 1.2			22.5
Jurassic coals							
Saykhan-Ovoo	6	B	9.7	3.9 ± 0.9	2.4	5.8	40.2
Mogoingol	15	SB	14.8	4.2 ± 1.5	0.8	12.8	28.4
Bayanteeg	8	SB	14.8	11.6 ± 1.8	7.4	23.7	78.4
Shariingol	29	L	12.2	6.0 ± 0.5	2.3	11.1	52.7
Mean	58		12.9	6.4 ± 2.5			49.9
Cretaceous coals							
Alagtogoo	10	B	28.6	3.0 ± 0.8	1.4	8.5	10.5
Aduunchuluun	10	L	12.5	0.9 ± 0.1	0.45	1.5	7.3
Baganuur	2	L	8.1	1.1 ± 0.1	1.0	1.2	13.6
To'grognuur	7	L	13.3	2.3 ± 0.3	1.1	3.6	17.3
Shivee-Ovoo	28	L	–	1.3 ± 0.4	0.6	4.2	–
Chandgan Tal	13	L	21.3	11.2 ± 3.5	1.5	31.7	52.6
Mean	70		16.8	3.3 ± 1.6			19.7
Iran							
Trias–Jurassic coals							
Tabas	148	B-A	22.9	8.1 ± 0.4	0.2	26.5	35.4
Alborz	62	B	22.1	10.9 ± 0.8	0.8	23.8	47.8
North-Khurasan region	28	B	23.5	10.2 ± 1.3	2.2	24.4	43.4
Maragheh region	13	B	26.3	16.8 ± 2.5	3.0	30.6	63.9
Kashan-Esfahan region	3	B	36.0	11.9 ± 0.7	10.7	13.0	33.1
Mean	254		24.0	11.6 ± 1.4			48.3
Mean for Asia	6157		13.1 ± 1.1	4.3 ± 0.4			32.8
Clarke for coals**	8400			3.9			23.0

Note: no data; *Calculated for the ash; **According to Ketris and Yudovich, 2009; L—lignite, SB—subbituminous, B—bituminous, SA—semi-anthracite, A—anthracite,

Sc concentrations compared with world average data. The specific coastal-marine conditions of coal formation during this period gave rise to a high mineral matter concentration in the coals (Table 2) and, as a result, the concentration of Sc in the coal ash is rather low (19.2 ppm).

Coals of Carboniferous–Permian age are notable for their considerable variation in Sc concentration. In Siberia, the Sc concentration ranges from 2.9 ppm in the anthracites of the Gorlovskiy basin to 8.2 ppm in the coals of the Minussinsk basin. The coals of Kazakhstan (Karagandinskiy and Ekibastuz basins) have high Sc contents. The Carboniferous coals of Mongolia are primarily lean in Sc, but high Sc concentrations are observed in the Permian coals (Table 2).

Coals of Mesozoic age are abundant in all territories of Northern Asia and Iran, and are notable for their considerable variation of Sc concentration. Anomalous Sc-bearing coals have been found in the Zapadno-Sibirskiy and Irkutskiy basins in Siberia, in the deposits of Bayanteeg, Shariingol, and Chandgan Tal in Mongolia, and in most deposits in Iran. The Jurassic coals of Kazakhstan are also notable for their high Sc contents. Mesozoic coals show anomalously high Sc contents, but also display anomalously low values ranging from 1 to 2 ppm (the deposits of Urtuiskoe, Zashulanskoe, Kharanorskoe, and Tataurovskoe in Transbaikalia).

Coals of Palaeogene–Neogene age are abundant in Siberia and the Russian Far East, and are mainly notable for their high Sc content. However, because of the high ash yield, the Sc concentration in the ash is often lower than the mean value for the studied region. Among the young coals, coals of the Zapadno-Sibirskiy and Sakhalinskiy basins, the Taldu-Dyurgunskoe deposit in Altai and the Bikinskoe deposit in Primorye have high Sc contents. The Sakhalin coals contain 9.1 ppm Sc, and the coal ash contains 56.2 ppm Sc. This anomaly in the coals of this basin was caused by the specific femic composition of the source rock area of the basin.

4.2. Regularities of Sc distribution

4.2.1. Lateral heterogeneity

Considerable variations in the average Sc content of the deposits and basins illustrate the irregular distribution of Sc over space and time. The heterogeneity of the Sc content in the coals of a single age also indicates the considerable lateral variability of the Sc concentration within the study region.

Anomalously high concentrations of Sc have been identified in coals of different ages, but more often, are generally observed in coal deposits of Jurassic age. Maximum Sc contents up to 0.23% have been observed in the coal ash of the Tyumenskaya suite north of the West Siberian Plain. These coals are notable for their low ash yield, which in certain cases does not exceed 1% but commonly ranges from 2% to 10%. The Sc concentration in the coal is also anomalous and reaches as high as 83.6 ppm.

The highest Sc concentration of 230 ppm was observed in the coal of thin seam No. 1.2 of the Beresevskoe deposit in the Kansko-Achinskiy basin. However, because of the high ash yield, the Sc content of the coal ash is 870 ppm. The coals of the Irkutskiy basin are also anomalously Sc-bearing. In certain cases the Sc content exceeds 40 ppm, and the concentration in the coal ash ranges from 300 ppm to 500 ppm. Some researchers (e.g., Kryukova et al., 2001) have indicated high levels of Sc accumulation in the coal ash of the Azeiskoe deposit in this basin. Anomalous Sc-bearing coals of Jurassic age have also been observed in the northern portion of the Lenskiy basin and the northwestern portion

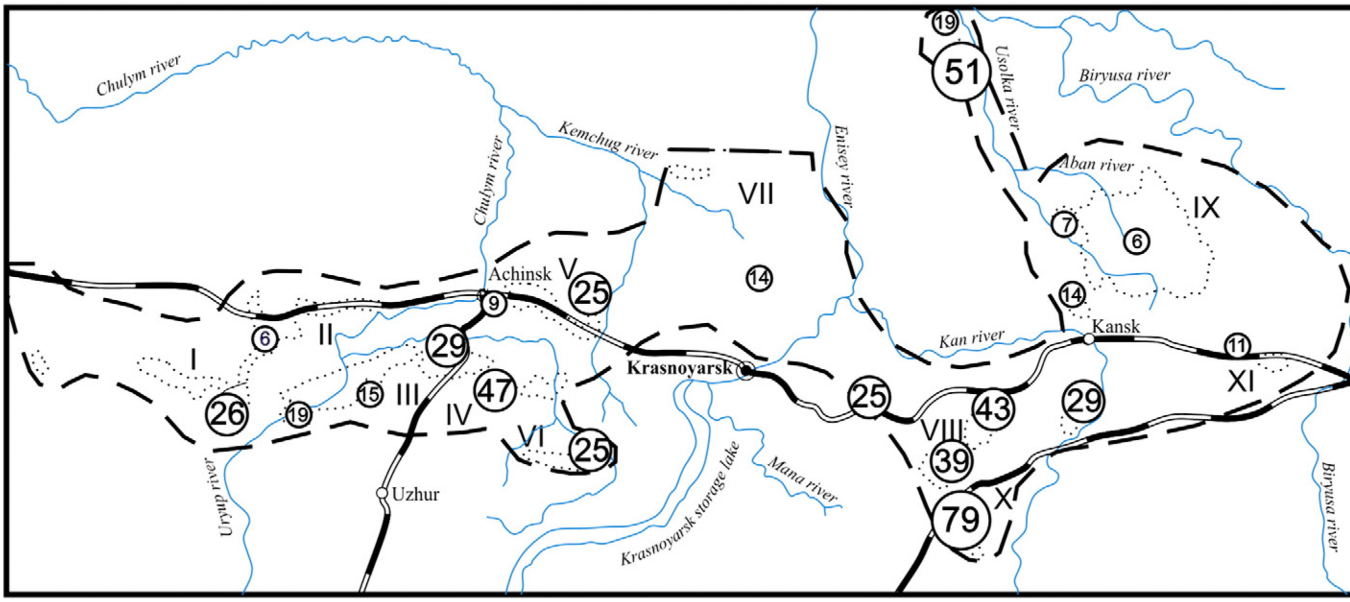

Fig. 2. Scandium (Sc) content in coal ash from the deposits of the Kansko-Achinskiy basin (numbers in circles). Coal-bearing regions: I—Itat-Barandatskiy; II—Bogotolskiy; III—Beresovsko-Nazarovskiy; IV—Glyadensko-Serezhskiy; V—Uluisko-Kemchugskiy; VI—Balakhtinskiy; VII—Prieniseiskiy; VIII—Rybinskiy; IX—Abanskiy; X—Sayano-Partizanskiy; XI—Poiminskiy.

of the vast region of coal accumulation (Kashirtsev et al., 1999). Such coals are also known to occur in the Triassic–Jurassic coal deposits in Iran (Goodarzi et al., 2006; Yazdi and Esmaeilnia, 2004) and are less typical for Mongolia, but individual deposits enriched with Sc have also been found in this area (the Bayanteeg and Shariingol deposits). Scandium-enriched coals have also been found among coal-bearing formations of Palaeogen–Neogene age in the deposits and basins of Siberia and the Russian Far East (the Bikinskoe deposit, Sakhalinskiy basin). In all cases, the high Sc concentrations are related to areas with an abundance of mafic rocks with high Sc concentrations in the sediment-source areas of the coal basins.

Within the coal deposits and basins, the concentration and distribution of Sc also depend on the presence of particular rocks in the sediment-source area. For example, in Kuzbas, Sc-bearing coals are located in the southern portion of the basin, where mafic and ultramafic complexes are abundant in the source area (Mountain Shoria). In the Kansko-Achinskiy basin, the varied composition of the source rock area led to rather heterogeneous Sc contents in the coal deposits (Fig. 2).

In Iran, the Sc distribution in the coals of the Tabasskiy basin shows a distinct zoning pattern. This zoning appears as a decrease in the Sc concentration in the coals (Fig. 3) and coal ash in the direction from the sediment-source rock area of the basin of the continental sedimentation — from west to east.

Within individual seams in different deposits, the lateral distribution of Sc is often irregular (Fig. 4) and Sc shows the same distribution regularities observed within the deposits and basins.

4.2.2. Vertical heterogeneity

The vertical distribution of Sc is also as heterogeneous as the lateral distribution. In a section of a coal-bearing stratum, the Sc content naturally varies from the bottom upwards within the stratigraphical units. Different variants caused by the peculiarities of geological development are possible. However, overall, the bottom and top portions of a section within the stratigraphical units are more heavily enriched in Sc. In Kuzbas, the top portions and the foundation of the Balakhonskaya and Kolchuginskaya series are distinctly enriched in Sc compared with the middle portions (Fig. 5); the same is observed for the coal-bearing section of the Kansko-Achinskiy basin.

The vertical distribution of Sc in an individual coal seam is more highly varied. Like other coal-affinity elements (Ketris and Yudovich, 2009), Sc is primarily concentrated in the near-contact zones of coal seams or close to the top and bottom parts of a seam (Fig. 6).

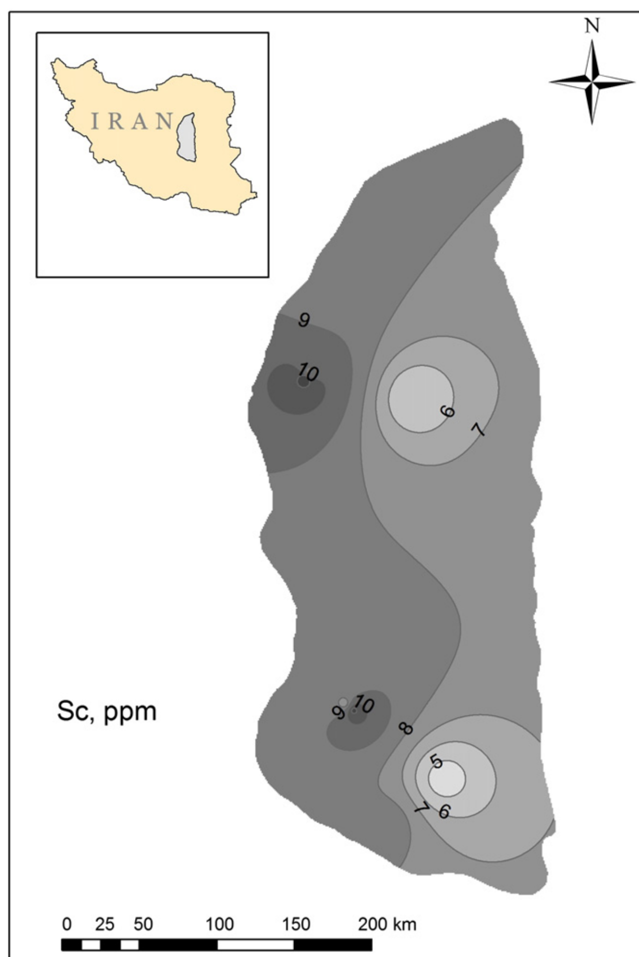

Fig. 3. Lateral distribution of Sc in the coals of the Tabasskiy basin.

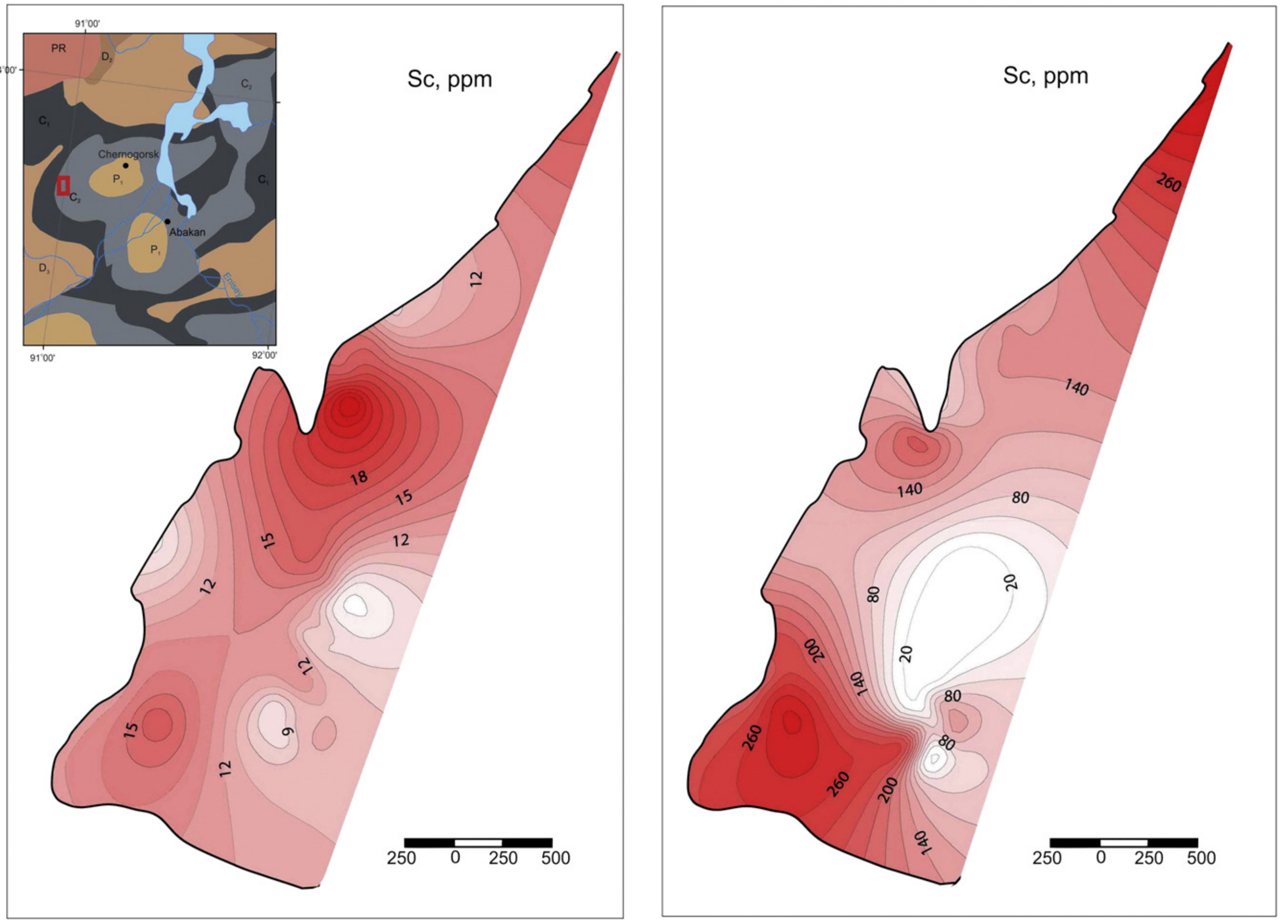

Fig. 4. Scandium (Sc) distribution in the coal (left picture) and coal ash (right picture) of the Dvukharshinny seam of the Chernogorskoe deposit (Minusinskiy basin).

The study of modern peat deposits shows that the formation of near-contact enrichment zones begins as early as the peat formation stage. The absence of a direct connection with coal ash indicates a hydrogenous origin of these near-contact anomalies.

Near-contact enrichment zones were not observed in all of the studied coal sections, but they undoubtedly prevail. The composition of the overlying and subjacent sediments does not influence the presence or absence of these zones, which are equally developed in the presence of the sandstone, siltstone, and argillite components of the coal-containing rocks. The near-contact zones in the modern peat deposits of Western Siberia are rarely developed and less contrasting, but even at the bottom of the peat deposits the Sc content in the peat ash can exceed 100 ppm, whereas the background values range from 5 ppm to 10 ppm. Such enrichment zones were found in both minerotrophic and ombrotrophic peatlands (Fig. 7). In a section of one peat deposit, the near-bottom zones enriched in Sc alternate with zones without Sc enrichment or with low Sc concentrations.

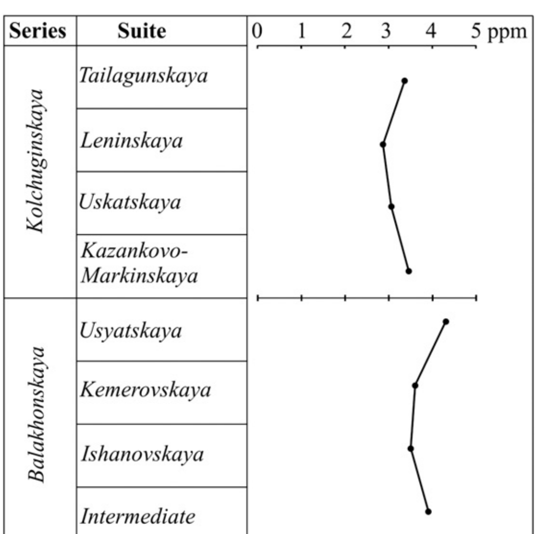

Fig. 5. Distribution of Sc in sections of the coal-bearing deposits in Kuzbas.

The thickness of the near-contact (near-top and near-bottom) zones with high Sc concentrations usually ranges from 10 cm to 15 cm, and does not depend on the thickness of the coal seam. A similar distribution was also observed for germanium, with a higher mean content of metal in the thin seams than in the thick seams (Hower et al., 2002; Lomashev and Losev, 1962; Yudovich, 2003). This observation is explained by the higher proportion of enriched near-contact intervals in the sections of low-thickness seams compared with that of thicker seams. In the seams measuring less than 30 cm in thickness, the near-top and near-bottom enrichment zones often overlap each other and together form an anomalously Sc-enriched seam. In individual cases, the Sc concentration in the coal ash of such seams can reach up to 0.2%. Therefore, under otherwise identical conditions, the thinner a coal seam is, the higher the mean Sc content becomes. The significant negative correlation identified between coal bed thickness and the mean Sc content in coal and coal ash confirms this observation. For the anomalous Sc-bearing coals of the Zapadno-Sibirskiy basin, in particular, the correlation

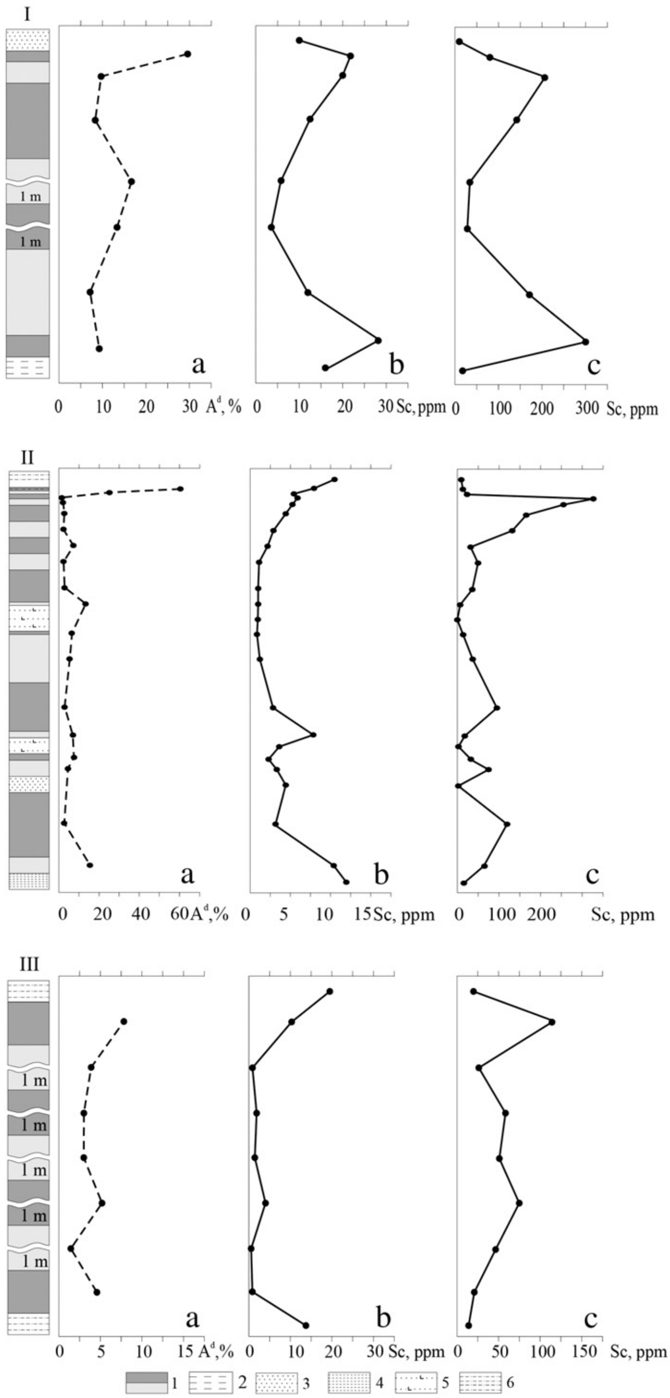

Fig. 6. Distribution of ash yield (a) and Sc in coal (b) and coal ash (c) in vertical sections of coal seams. I—brown coal; Rybinskiy-II seam, Borodinskoe deposit, Kansko-Achinskiy basin. II—bituminous coal; Dvukharshinniy seam, Minussinskiy basin. III—anthracite Glavny-II seam, Urgunskoe deposit, Gorlovskiy basin. *Legend*: 1—coal, 2—argillite, 3—siltstone, 4—sandstone, 5—tonstein.

coefficient between the Sc content and the seam thickness, with 49 seam intersections, is −0.31.

5. Modes of occurrence of Sc in coal

The modes of occurrence of Sc in coal reflect the conditions of its accumulation in the coal seam. In general, the modes of Sc occurrence have not insufficiently been studied. According to the data of Finkelman (1981, 1993), Sc in coals is associated with both organic and mineral matter. By analysing the modes of Sc occurrence in anomalously Sc-bearing coals, Finkelman (1981) observed that the clay matter could not provide for such high concentrations, and he suggested that one of the possible modes of Sc occurrence in such coals was aluminninophosphates. The Sc content in these materials (variscite, crandallite, hamlinite, etc.) can reach up to 1%; among native Sc minerals. Finkelman (1981, 1993) has only identified Sc-containing zircons. As a possible explanation for the formation of organic complexes of Sc, Finkelman (1981) supposed that Sc must have a weak association with organic matter due to the peculiarities of its atomic structure. At the same time, many researchers have noted the important role played by organic matter in Sc accumulation (Filby et al., 1977; Given and Miller, 1987; Gluskoter et al., 1977; Guren et al., 1968; Kryukova et al., 2001; Lyons et al., 1989; Swaine, 1964; Vassilev et al., 1994; Yudovich and Shastakevich, 1966).

The modes of occurrence of Sc may be modified during the coalification process, and therefore, it would be rational to examine their chemistry during different stages of coalification from peat to bituminous coals.

Study of the modes of Sc occurrence in 57 samples of peat and brown coal from different deposits of Siberia, Mongolia, and Kazakhstan has shown that a large amount of Sc is contained in the organic matter, despite the different Sc contents in the coal or peat (Fig. 8).

More than 60% of the Sc in peat is concentrated in the organic matter (bitumen, humic, and fulvic acids), and another 30% is concentrated in mineral matter (insoluble residue). In individual samples, up to 75% of the total metal content may be concentrated in the humic and fulvic acids. The proportion of Sc in the humic acids of minerotrophic peat is higher than that in ombrotrophic peat (69% and 59% correspondently). The humic form of Sc prevails in peat. The fraction of Sc in the fulvic acids was higher than that in the humic acids in only one of the 21 samples. In the bitumen extracts, the Sc content did not exceed 1% of the total Sc content. According to these data, a significant amount of the Sc in peat is connected to the organic matter. In fact, Sc in mineral form, which is concentrated in the insoluble residue, can be largely connected to complicated organic complexes (humins), which are insoluble after alkali treatment. In ombrotrophic peat, the proportion of insoluble residue in the total Sc balance is higher than in minerotrophic peat (32% versus 27% on average in minerotrophic peat with an ash yield ranging from 4% to 10%).

The concentration of Sc in the humic and fulvic acids of brown coals ranges from 10% to 73% of the total Sc in individual samples. Of the total Sc content, 22% to 90% is concentrated in the insoluble residue. Overall, in 36 coal samples, the humic and fulvic acids and bitumens contain 52% of the Sc and the insoluble residue contains 48% (Fig. 6). The significance of the humic acids with respect to the Sc concentration was determined to be greater for high-Sc coals compared with that of ordinary coals. In Sc-bearing coals, the portion of organic matter in the total Sc balance can exceed 90%. Moreover, the role of the humic acids in Sc accumulation was determined to decrease as the degree of coal metamorphism increases (Table 3).

These data agree well with the results of research on brown coals with various degrees of coalification (lignites and sub-bituminous coals) obtained by Irkutsk geologists (Kryukova et al., 2001). The role of the decrease in humic acids in Sc accumulation during coal metamorphism indicates a change in the mode of the occurrence of Sc. The newly formed modes could represent insoluble organic substances, such as humins and authigenic-mineral matter. According to Finkelman et al. (1990), experiments on Sc leaching from various reagents shows that the Sc extracted by hydrochloric acid does not practically depend on the degree of coal metamorphism. This fact indicates either the conservation of complex metal–organic compounds that are insoluble in alkali or the conversion of Sc into mineral forms that are soluble in HCl. The sharp increase in the proportion of humic acids affecting the Sc concentration during coal oxidation points to an organic mode of occurrence. For example, in much of the oxidised coal of the Saykhan-Ovoo deposit in Mongolia, the fraction of regenerated humic and fulvic acids in the metal accumulation exceeds 80% (Table 3).

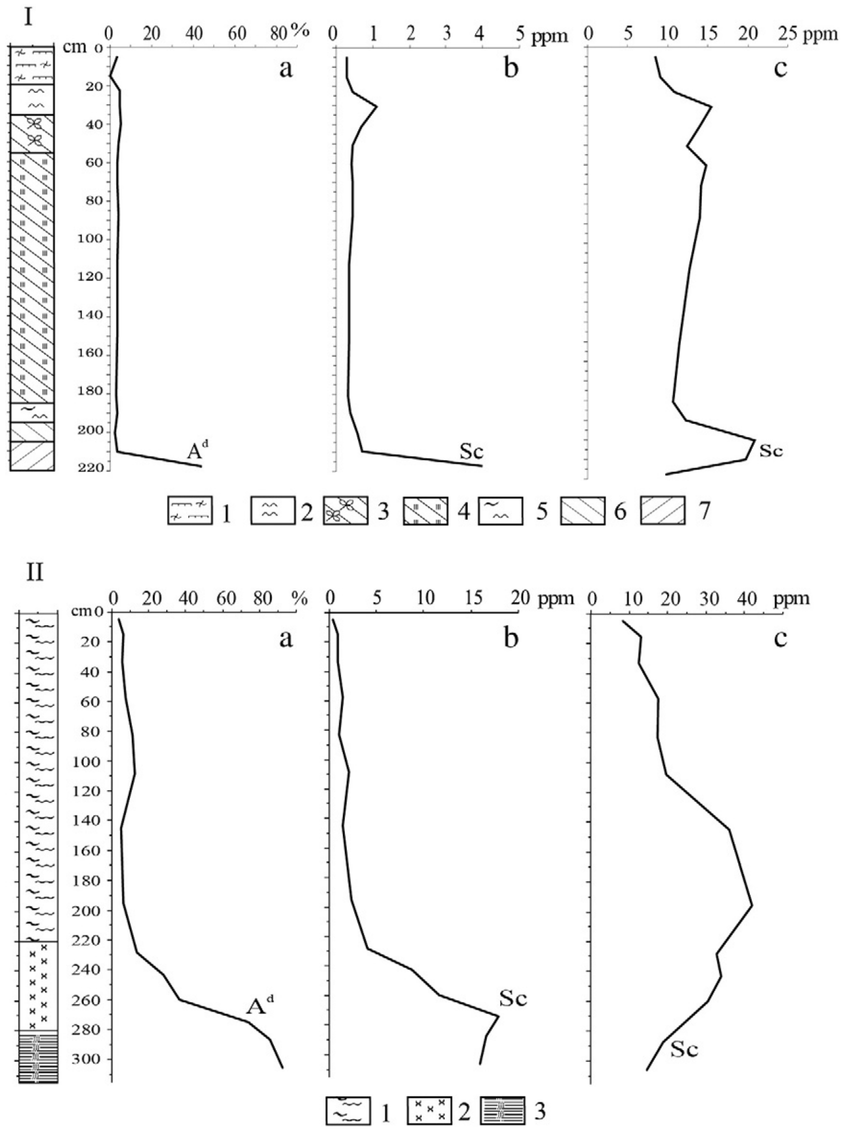

Fig. 7. Distribution of Sc and ash yield in vertical sections of peat deposits: I—ombrotrophic bogs (Vodorazdelnoe deposit, West Siberia), II—minerotrophic bogs (Pukhovskoe deposit, West Siberia). *Legend*: Vodorazdelnoe deposit: 1—sphagnum ombotrophic moss; 2—cotton-grass-sphagnum moss; 3—sedge-menyanthes peat; 4—scheuchzeria-sedge peat; 5—sphagnum mesotrophic peat; 6—sedge mesotrophic peat; 7—sedge minerotrophic peat. Pukhovskoe deposit: 1—sphagnum minerotrophic moss; 2—equisetum peat; 3—mineralised peat.

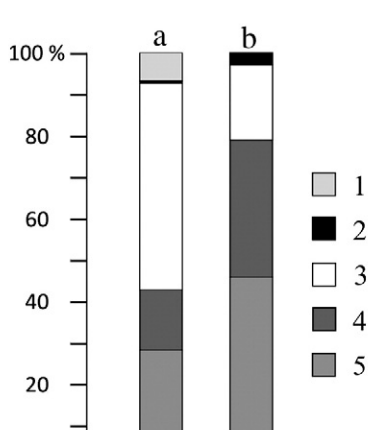

Fig. 8. Yield of Sc in the geochemical fractions of peat and brown coals: a) peat, and b) brown coal. *Legend*: 1—water-soluble and easily hydrolysable substances; 2—bitumen; 3—humic acids; 4—fulvic acids; 5—insoluble residue.

Correlation analysis of coal deposits with anomalously high Sc concentrations shows a significant negative correlation between the Sc content in coal ash and the ash yield, and an insignificant positive or negative correlation between the Sc content in coal and the ash yield. This observation attests to the accumulation of high Sc concentrations in coals from water solutions but not in clastogenic mineral formations. The contribution of clastogenic matter in the total element balance is insignificant. A significant positive correlation between the Sc content and the ash yield in the coals and a significant negative correlation between the Sc content and coal ash are characteristic of coals with ordinary levels of Sc accumulation. This observation suggests an equivalent role for clastogenic and biogenic metal accumulation in coals. In certain deposits with anomalously low Sc contents (relative to the mean data for coals of the world), there is no significant correlation between the Sc content in coal ash and the ash yield, whereas the correlation between the Sc content of the coal and the ash yield is positive. This result emphasises the dominant contribution of clastogenic matter and the secondary contribution of aquagenic and biogenic matter in the total balance of Sc in such coals.

Electron microscope imaging of brown and bituminous coals with different metal contents have revealed that the mineral matter is

Table 3
Scandium yield in fractions of the group composition of coal.

Coal rank	Spirit-toluol extract	Humic and fulvic acids	Insoluble residue
Subbituminous C	2.3	48.2	49.5
Subbituminous B	0.1	25.4	74.5
Subbituminous A	0.1	5.3	94.6
Very oxidised low volatile bituminous coal	3.5	84.0	12.5

generally poor in Sc. Even the anomalously Sc-bearing coals rarely contained minerals enriched in Sc. In this study, we found Sc-containing zircon (2% of Sc), Sc-bearing Y phosphate (according to the chemical composition identified as xenotime, up to 5% Sc), and unidentified minerals of a complex composition (Fig. 9). These materials represent single authigenic mineral formations, but their contributions are quite small and do not contain the total quantity of Sc determined in the samples, especially in the anomalously Sc-bearing coals containing up to 0.23% of the metal.

The bulk of the Sc in the brown and bituminous coals is hypothetically concentrated in various metal–organic complexes. The presence of specific formations of a complex composition (Si–Al–Na–Ca–Zr–Sc–Ti–V–Fe–O), with anomalously high concentrations of Zr, Sc, Ti, V, Cr, and Fe as well as S and P in the coal ash (laboratory ashing at 800 °C), is an indication of this concentration distribution (Fig. 9). Such compounds are rarely found in coals, but they can be detected in coal ash. Thus, we hypothese that they are formed during the laboratory ashing of coal because of the oxidisation of organic substances, which concentrates this group of elements. This assumption is in agreement with the results of a study on Sc and P association in bituminous coal (Guren et al., 1968). According to the data reported by Guren et al., approximately 80% of the Sc and 65% of the P have been determined to occur in humic acid substances extracted with alkali after the oxidative treatment of bituminous coal. This result allowed the authors to draw conclusions based on the association between significant fractions of Sc and P in coals and organic matter, and also on their concentration in coal due to the presence of humic acids (Guren et al., 1968). Humic and fulvic acids may concentrate a wide range of chemical elements. The multiple-charge ions of certain elements compete with other elements, replacing them in humic acids. Certain slaggy modes of Sc-containing minerals, which are often detected in coal ash, also indicate their possible secondary nature (Figs. 9.1, 9.3). Crystal forms of these complex mineral compounds, enriched with Sc, Zr, Ti, V, and Cr (Fig. 9.4), demonstrate their independent mineral phase. This observation suggests their initial accumulation in organic matter rather than in kaolinite.

6. Factors that control Sc accumulation in coals

Among the variety of factors that determine the accumulation and regular distribution of Sc in coal seams, the composition of the sediment source area of coal basins (especially the chemistry of the source rocks, as discussed by Yudovich and Ketris, 2002), sedimentary facies, hydro-geochemical processes, and coal metamorphism are highly significant.

6.1. Chemistry of the sediment-source rocks

An analysis of the geological location of the Sc-bearing coals indicates their connection with regions containing Sc-concentrating rocks (geochemically specialised complexes), primarily mafic materials.

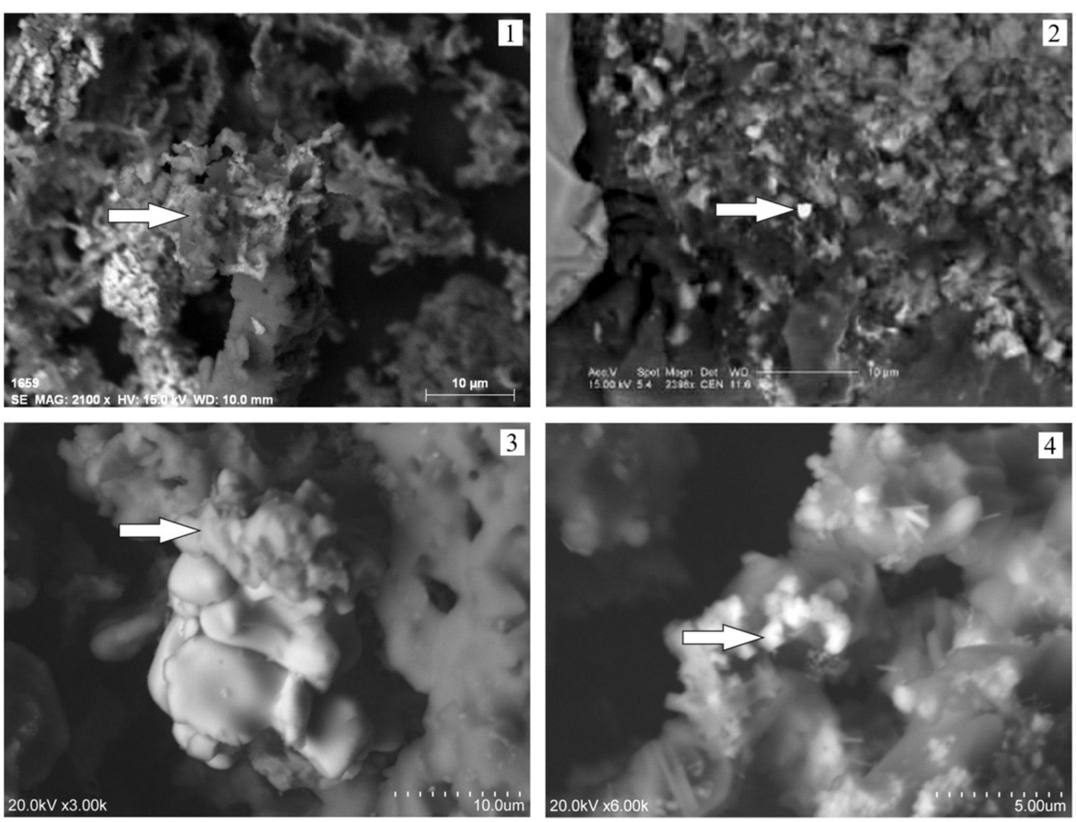

Fig. 9. Electron microscopy images of Sc-containing minerals: 1—slaggy aggregate composed of Sc-containing zircon (3% Sc) in an aluminium–silicate matrix (coal ash); 2—xenotime with Sc in kaolin-chlorite aggregate (coal); 3—slaggy aggregate of complex composition (Si, Zr, Al, Ca, Ti, V, Cr, Fe, Ni, O) in contact with Cu oxide containing less than 1% Sc (coal ash); 4—crystals of a Zr-mineral of complex composition (<1% Sc) in an aluminium–silicate matrix (coal ash).

First, in the West Siberian basin, especially the region behind the Urals, the materials show a mean Sc content of 16 ppm in coal and 150 ppm in ash, including the Sakhalinskiy, Minusinskiy, and Irkutskiy basins and the deposits of Mongolia (Bayanteeg, Shariingol, Chandgan Tal). All of these deposits have geochemically specialised complexes of mafic material in the source rock areas of the basins. For the coals of the Shaimskiy region of the West Siberian basin, the Ural zone is anomalously enriched in Sc. Studies by Fedorov et al. (2009) and Frolova et al. (2011) have suggested a leading role of basic rocks in the formation of terrigenous deposits of the coal-bearing Tyumeskaya suite of the Shaimskiy region. For the Irkutskiy basin, the Sc-bearing traps of the Siberian platform are examples of such zones. The high Sc contents in the coals of the Azeiskoe deposit are spatially related to the northern boundaries of the basin, which are composed of terrigenous carbonate deposits of Ordovician age with thick covers and trap sills of Triassic age with a weathered crust (Arbuzov et al., 2012). The Sc-bearing coals of the Minusinskiy basin are also distinctly related to boundary blocks, with a wide development of femic rocks (Arbuzov and Ershov, 2007).

Hence, all cases of anomalous or simply high Sc contents in coals and coal ash are associated with particular types of complexes within the boundaries of the coal deposits and basins. Therefore, the chemistry of the source rock in a coal basin is a leading factor that determines the accumulation levels of Sc in the coal deposits.

6.2. Facies factors

Sedimentary facies also play an important role in the formation of the geochemical background of coal seams. Higher initial Sc concentrations, as well as high ash yields, are characteristic of the coals formed in minerotrophic bogs (Table 4). This process allows for the accumulation of a substantial portion of the Sc in coals as early as the peat formation stage. These data (Table 4) also show that, even if the peat has a similar ash yield, the Sc content in a deposit can differ considerably. This observation illustrates the important role of source rock type, and possibly hydro-geochemistry as well, in the accumulation of Sc in peat and coal. Minerotrophic peat is enriched in Sc compared to ombrotrophic peat (Arbuzov et al., 2009; Mezhibor et al., 2003), but the ash of ombrotrophic peat is enriched with Sc relative to that of minerotrophic peat, as is the ash of low-ash coals relative to that of high-ash coals.

6.3. Hydro-geochemical factors

Hydro-geochemistry, together with the nature of the source rocks, is the determining factor for Sc accumulation in coals. Scandium is weakly soluble under the conditions of the hypergenesis zone and is weakly transported by surface waters. The mean Sc content in surface fresh water is 0.004 μg/L (Shvartsev, 1998), but its concentrations under different conditions and in various regions can vary considerably. According to the same data set, the Sc concentration reaches up to 0.045 μg/L in the surface waters of Sweden, but in bog and swamp waters the Sc concentrations are often considerably higher. For example, the water from a drainage canal of the Vasuygan Swamp in Western Siberia contains 0.18 μg/L of Sc (Savichev, 2003). In underground waters, the Sc concentration is higher than that in surface waters. The Sc concentration in the hypergenesis zone depends on climatic characteristics. The highest Sc concentration found in the waters of the mountain-taiga regions is 0.08 μg/L (Shvartsev, 1998). In the current acid mining waters of the Kizelovskiy basin (pH range from 2 to 4), the Sc concentration reaches up to 45 μg/L (Torikova et al., 1966), which is approximately 1000 times higher than that in surface fresh waters. In the cold and carbonated mineral waters of the Primorie, the Sc contents reach 8 μg/L (Chelnokov and Kharitonova, 2008). High Sc concentrations in the ground waters of the hypergenesis zone, compared with those of the surface waters, can be explained by the presence of reducing agents

Table 4
Sc content and average ash yield of peat deposit of the south-western part of West-Siberian plain.

Peat deposit type	Deposit	A^d%	Sc content, ppm	
			Peat	Peat ash
Ombrotrophic	Petropavlovskiy Ryam	2.2	0.83	37.7
	Zapadno-Moiseevskoe	2.7	0.56	20.7
	Malaya Icha	1.9	0.36	18.9
	Semiozerie	3.9	0.46	11.8
	Vasyuganskoe 397	2.3	0.27	11.7
	Vasyuganskoe, Section 3	2.3	0.59	25.7
	Zalesnoe	1.4	0.23	16.4
	Poludenovskoe	3.2	0.23	7.2
	Kolpashevskoe	3.9	0.48	12.3
	Saim	3.2	0.7	21.9
	Aigarovo	2.5	0.37	14.8
	Bakcharskoe	4.1	0.49	12.0
	Iksinskoe	3.8	0.55	14.5
	Sosnovo-Makhninskoe	2.9	0.62	21.4
	Vodorazdelnoe	3.7	0.43	11.6
	Kirsanovskoe	2.4	0.35	14.6
Mean for the ombrotrophic peat		3.2 ± 0.3	0.56 ± 0.06	17.6
Minerotrophic	Pukhovskoe	14.9	3.5	23.5
	Sukhovskoe	12.43	0.52	4.2
	Vasyuganskoe, Section 1	5.2	1.2	23.1
	Zharkovo	5.8	1.3	22.4
	Vilkinskoe	16.9	1.8	10.7
	Klyukvennoe	12.9	1.6	12.4
	Berezovaya Griva	8.7	1.7	19.5
	Gusevskoe	14.6	0.54	3.7
	Chistoe	8.1	0.9	11.1
	Arkadievo	20.7	0.6	2.9
	Ishkol	10.0	2.1	21.0
Mean for the minerotrophic peat		13.4 ± 1.4	1.4 ± 0.2	10.3
Mean for the peat		7.3 ± 0.9	0.88 ± 0.17	12.2

and organic matter in their composition (Shvartsev, 1998). This observation is in agreement with data indicating a high Sc content in swamp waters. Scandium is assumed to migrate in the form of organic complexes under these conditions.

The peculiarities of the Sc distribution in the coal seams provide evidence for the accumulation of Sc at the boundaries of the coal seams (or peat deposits). A low capacity for Sc migration in the water of the hypergenesis zone contradicts the model of long-distance transportation of soluble forms of Sc out of the weathering crust and its loss and redistribution within the limits of a coal deposit. Sc accumulation in coal was caused by the formation of terrigenous deposits in the sedimentary basin, with a considerable role played by basic rocks following extraction with organic acids in aqueous solution, migration inside the deposit, migration into the peat deposit and coal seam, and final deposition. Such a model of Sc accumulation is confirmed by the Sc distribution in the coal seams, the established facts regarding the high Sc contents in acid ground and peat waters, and the capacity of Sc for forming stable complexes with humic and fulvic acids (Komissarova, 2006).

The Sc content in the coal-bearing strata and the characteristics of the basins' hydro-geochemistry suggest a possibility of above-background Sc accumulation in coals. Coal deposits and basins with anomalous Sc concentrations show 1.5–3 times higher Sc concentrations compared with the mean content of Sc in coal-containing rocks of the world.

6.4. Metamorphism factors

The influence of metamorphism is represented by the change in Sc concentration as a result of the metal's redistribution and loss during rank advance. The comparison of the Sc concentrations in coals of different rank indicates the loss of Sc during metamorphism. The reason for Sc loss is not always well defined because the concentration of the metal in coals depends on many factors. An example of a case in which this ambiguity is observed is in the comparison of coals with different degrees of coalification (coals of different rank) within one deposit or basin with a common source rock area. Thus, in the coal of Kuzbas (Fig. 10), the Sc concentration distinctly decreases from subbituminous coals to anthracites. These data correlate well with data from studies on the coal-bearing section at Allan (Alberta, Canada) (Goodarzi and Cameron, 1987) and with data on the Tabas basin (Central Iran). Thus, regional coal metamorphism leads to Sc loss.

Sc loss during contact metamorphism is more evident, but the zones of Sc loss and redistribution are quite thin (directly near the contact with an intrusion) compared with that observed during regional metamorphism, thus causing a great loss of metal. At small distances, the Sc concentration in coal increases simultaneously with the ash yield (Arbuzov and Ershov, 2007).

7. Nature of the anomalous Sc content in coal

Because Sc has not attracted the same attention as Ge, the nature of the anomalous Sc concentrations in coal has not been as actively discussed as the nature of Ge-bearing coals. This problem is associated with same issues of metal source type, method of transportation, and concentration mechanisms. However, these issues are more important because the migration capacity of Sc in the hypergenesis zone is greater than that of Ge. Therefore, the classic model for Ge in coals, involving metal leaching from the surrounding rocks during weathering crust formation, transportation in soluble or suspended form, and deposition under peat bog conditions, cannot be accepted for Sc without many limitations. First, Sc is weakly mobile in the weathering crust due to its chemical properties, which are similar to those of aluminium (Stryapkov, 1997). Second, these properties drive low Sc contents in surface and ground waters. Via this connection, the Sc accumulation in peat out of such waters seems improbable, but it is especially relevant for the thin seams of low-ash coals formed from ombrotrophic peat deposits. It is known that the highest Sc contents of up to 0.1–0.2% in the ash are found in the thin seams of coals with a low-ash yield, usually ranging from 1% to 3% but no more than 5% (Arbuzov et al., 2003a, 2003b, 2006; Kashirtsev et al., 1999; Seredin et al., 2006). Additionally, the coals are also anomalous, containing up to 50–80 ppm of Sc. Considering the accumulation mechanism exhibited in the source rocks of the peat bogs from which the thin low-ash coal seams were formed, such an anomalous Sc concentration is impossible to explain as the accumulation out of aerosols or ultra-fresh atmospheric precipitation at the peat deposition stage.

Due to this connection, the model of Sc accumulation in coals (which excludes the leading model of transportation of solute Sc out of the weathering crust to a coal seam or its accumulation in coals as a fine suspension) seems more reliable. Adopting the water transportation model assumes that the mechanisms of Sc transportation are known, and the model concerning transportation in the form of a suspension assumes a high ash yield for the Sc-bearing coals. Although high Sc contents are found in stagnant waters (Savichev, 2003), stagnant waters contain a substantial amount of organic matter, including humic and fulvic acids. Thus, the stagnant waters of the west Siberian plate contain 25 mg/L to 165 mg/L of organic acids (Shvartsev et al., 2012), primarily humic and fulvic acids. For example, the water of the Timiryazevskoe bog in the southern region of the west Siberian plate contains 154 mg/L of fulvic acids and 34 mg/L of humic acids (Savichev and Shmakov, 2012). It is possible that Sc migrates in the water of the peat (coal)-accumulation areas and enters the coal seam due to the presence of the organic acids. When such waters are present in coal-accumulation areas, there is no need to explain the long-distance transportation of Sc in water solutions from the source rock zone to a coal seam. The transportation and deposition of Sc-enriched minerals in clastogenic form in coal-bearing strata, their subsequent transfer to water solutions as humates or fulvates, and their eventual re-deposition in a coal seam are more probable. In part, this process occurs at the stage of peat formation. The presence of contrasting enrichment zones in the near-bottom region and weak contrasting zones in the top region of the peat deposits illustrate this point (Arbuzov and Ershov, 2007). The Sc concentrations in the bottom portions of the modern peat deposits of Western Siberia reach up to 100 ppm. These data agree with the deductions of Yudovich and Ketris (2006) on the predominant Sc accumulation at the peat formation stage. It is possible that the formation of the enrichment zones continues at the diagenesis

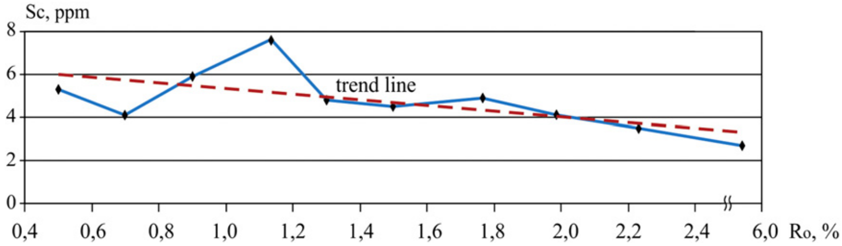

Fig. 10. Graph and trend line showing the change in Sc concentration in coals as a function of the degree of metamorphism (Kuzbas, Russia).

stage. The upper zone of enrichment can be formed when a peat deposit is buried under terrigenous deposits, and later during the diagenesis and coalification stages due to Sc redistribution at high temperatures (100–200 °C), according to the mechanism proposed by Ivankin and Trufanov (1987). The following determined mechanisms confirm this model of formation of Sc-bearing coals:

(a) Negative correlation between the Sc content of coal ash and the ash yield and the insignificant association between the Sc content of the coal and ash yield. This observation indicates the absence of a dependence between the accumulation of terrigenous ash in coal and the Sc concentration. Therefore, the terrigenous material arriving in a peat deposit is not the primary factor effecting the accumulation of anomalously high Sc contents in coal seams.
(b) Coals with anomalously high Sc contents have only been found in basins and deposits in which the source rock areas are rich in Sc-bearing rocks (mainly gabbro–basalt rocks). These areas include the deposits of the Zapadno-Sibirskiy basin near the Urals, the Minussinskiy basin, Sakhalin Island, the Irkutskiy basin, and selected deposits of Mongolia and Kazakhstan. These observations indicate the important role of the general Sc geochemical peculiarities of the regions in the Sc-bearing coal distribution.
(c) The distribution of Sc in coal seams is typical of that expected for coal-philous chemical elements. To be exact, Sc is concentrated in the near-contact portions of seams (near-top and near-bottom areas), which indicates a predominantly hydrogenous mechanism of Sc accumulation. The near-top portion is often more heavily enriched in Sc than the near-bottom portion, and vice versa in peat deposits. This evidence suggests a possible redistribution of Sc during coalification, in diagenesis and catagenesis after the formation of the original peat deposit.
(d) The correlation between the Sc content of coal ash and coal seam thickness is negative. The coefficient of correlation for the Zapadno-Sibirskiy basin is −0.13. This result, together with the data regarding the enrichment of the near-contact areas of the seams, provides evidence for the hydrogenous mechanism of the Sc concentration.
(e) In peat and brown coal, Sc is concentrated in the organic matter as humates and fulvates. Such modes of occurrence are formed by metabolic processes in the presence of water solutions.
(f) The Sc-enriched coal seams in the basins of coal formation usually adjoin coal-containing rocks with high Sc values (Arbuzov and Ershov, 2007; Arbuzov et al., 2003b; Eskenazy, 1996), which exceed the mean content observed in coals of the world by 1.5–2.5 times. It is likely that these rocks were the source of the Sc anomalies in the coals. A favourable hydro-geological environment and hydro-geochemical conditions were necessary for the leaching, transportation, and concentration of Sc in the coal seams. Similar conditions are characteristic for modern-day mire and bog systems.

8. Conclusion

The studied coals of the Asian regions of Russia, Mongolia, Kazakhstan, and Iran are enriched in Sc compared with the mean values for coals of the world. In different areas of the studied regions, we observed deposits with anomalous Sc concentrations, up to commercially significant quantities. These deposits are related to rock blocks in the sediment source area saturated with mafic complexes having high Sc contents. The composition of the surrounding rocks and the hydrogeochemical conditions of the basins and deposits determine the accumulation levels of Sc in the coals. Scandium was determined to be redistributed and become partially lost from the coal seams during coal metamorphism. The element is typically concentrated in the near-top and near-bottom zones of the seams. Therefore, thin coal seams always contain more Sc than thicker seams. An organic mode of Sc occurrence is predominant in peats and brown coals. The peculiarities of the Sc distribution in the deposits and coal seams and the modes of its occurrence illustrate a predominantly hydrogenous mechanism for accumulation of anomalous Sc concentrations in coal and peat. The Sc accumulation is assumed to be caused by Sc leaching from coal-containing rocks and re-deposition in the coal (peat) seam via processes that involve soil and ground waters enriched with organic acids. The formation conditions of the Sc-enriched coal-containing rocks and the conditions of Sc leaching and transportation to the coal seams are necessary for the accumulation of high Sc concentrations in coals. Such conditions are realised in the present-day mire systems of Western Siberia, and could have been present in ancient basins of peat (coal) accumulation.

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References

Arbuzov, S.I., Ershov, V.V., 2007. Geochemistry of Rare Elements in the Coals of Siberia. Publisher house "D-Print" (468 pp. (in Russian)).
Arbuzov, S.I., Potseluev, A.A., Rikhvanov, L.P., 1996. Rare-earth elements and scandium in the coals of Aralichevskiy area in Kuzbas. Geol. Geophys. 3, 68–73 (in Russian).
Arbuzov, S.I., Ershov, V.V., Potseluev, A.A., Rikhvanov, L.P., Sovetov, V.M., 1997. Rare-earth elements and scandium Sc in the coals of Kuzbas. Lithol. Miner. Resour. 3, 315–326 (in Russian).
Arbuzov, S.I., Ershov, V.V., Potseluev, A.A., Rikhvanov, L.P., 2000. Rare Elements in the Coals of Kuznetsk Basin. Publisher House KPK, Kemerovo (246 pp. (in Russian)).
Arbuzov, S.I., Ershov, V.V., Rikhvanov, L.P., 2003a. Scandium Sc in the coals of Minusinskiy coal basin. Geology of coal deposits. Interuniversity scientific thematic digest, vol. 13. Publisher House UGGA 216–231 (in Russian).
Arbuzov, S.I., Ershov, V.V., Rikhvanov, L.P., Usova, T.Yu, Kyargin, V.V., Bulatov, A.A., 2003b. Rare-metal Potential of the Coals of Minusinskiy Basin. Publisher House SO RAN, "Geo", Novosibirsk (347 pp. (in Russian)).
Arbuzov, S.I., Rikhvanov, L.P., Maslov, S.G., Arhipov, V.S., Belyaeva, A.M., 2006. Anomalous gold contents in brown coals and peat in the south-eastern region of the Western-Siberian platform. Int. J. Coal Geol. 68, 127–134.
Arbuzov, S.I., Volostnov, A.V., Ershov, V.V., Rikhvanov, L.P., Mironov, V.S., Mashenkin, V.S., 2008. Geochemistry and Metal-bearing of Coals of Krasnoyarsk District. STT, Tomsk (300 pp. (in Russian)).
Arbuzov, S.I., Arhipov, V.S., Bernatonis, V.K., Bobrov, V.A., Maslov, S.G., Mezhibor, A.M., Preis, Yu.I., Rikhvanov, L.P., Sudyko, A.F., Syso, A.I., 2009. Average content of several elements–admixtures in peats of south-east part of Western-Siberian plate. Bull. Tomsk Polytech. Univ. 315 (1), 44–48 (in Russian).
Arbuzov, S.I., Volostnov, A.V., Ilenok, S.S., Rybalko, V.I., 2012. Nature of the tonsteins of Azeiskoe deposit of Irkutskiy coal basin. Bull. Tomsk Polytech. Univ. 321 (1), 89–97 (in Russian).
Baruah, M.K., Kotoky, P., Borah, G.C., 1998. Gold in high sulphur Indian coals. Fuel 77, 1867–1868.
Borisova, T.F., Guren, G.F., Komissarova, L.N., Shatskiy, V.M., 1974. Scandium distribution in the coal matter. Chem. Solid fuel 5, 10–13 (in Russian).
Bouška, V., Pešek, J., 1999. Quality parameters of lignite of the North Bohemian Basin in the Czech Republic in comparison with the world average lignite. Int. J. Coal Geol. 40, 211–235.
Chelnokov, G.A., Kharitonova, N.A., 2008. Carbon Mineral Waters of the South of Russian Far East. Dalnauka, Vladivostok (165 pp. (in Russian)).
Coal base of Russia, 2004. Volume VI: General Regularities of Coal Formation and Coal-bearing Location in Russia. Geoinformmark, Moscow (779 pp. (in Russian)).
Dai, S., Zhou, Y., Zhang, M., Wang, X., Wang, J., Song, X., Jiang, Y., Luo, Y., Song, Z., Yang, Z., Ren, D., 2010. A new type of Nb (Ta)–Zr(Hf)–REE–Ga polymetallic deposit in the late Permian coal-bearing strata, eastern Yunnan, southwestern China: possible economic significance and genetic implications. Int. J. Coal Geol. 83, 55–63.
Dai, S., Jiang, Y., Ward, C.R., Gu, L., Seredin, V.V., Liu, H., Zhou, D., Wang, X., Sun, Y., Zou, J., Ren, D., 2012a. Mineralogical and geochemical compositions of the coal in the Guanbanwusu Mine, Inner Mongolia, China: further evidence for the existence of an Al (Ga and REE) ore deposit in the Jungar Coalfield. Int. J. Coal Geol. 98, 10–40.
Dai, S., Wang, X., Seredin, V.V., Hower, J.C., Ward, C.R., O'Keefe, J.M.K., Huang, W., Li, T., Li, X., Liu, H., Xue, W., Zhao, L., 2012b. Petrology, mineralogy, and geochemistry of the Ge-rich coal from the Wulantuga Ge ore deposit, Inner Mongolia, China: new data and genetic implications. Int. J. Coal Geol. 90–91, 72–99.
Dai, S., Ren, D., Chou, C.-L., Finkelman, R.B., Seredin, V.V., Zhou, Y., 2012c. Geochemistry of trace elements in Chinese coals: a review of abundances, genetic types, impacts on human health, and industrial utilization. Int. J. Coal Geol. 94, 3–21.

Dai, S., Seredin, V.V., Ward, C.R., Jiang, J., Hower, J.C., Song, X., Jiang, Y., Wang, X., Gornostaeva, T., Li, X., Liu, H., Zhao, L., Zhao, C., 2013. Composition and modes of occurrence of minerals and elements in coal combustion products derived from high-Ge coals. Int. J. Coal Geol. 121, 79–97.

Du, G., Zhuang, X., Querol, X., Izquierdo, M., Alastuey, A., Moreno, T., Font, O., 2009. Ge distribution in the Wulantuga high-germanium coal deposit in the Shengli coalfield, Inner Mongolia, northeastern China. Int. J. Coal Geol. 78, 16–26.

Eskenazy, G., 1996. Scandium in the Bulgarian coals. Part 1. Geology, vol. 89. Year-Book of Sofia University 205–217 (in Russian).

Fedorov, Yu.N., Maslov, A.V., Ronkin, Yu.L., 2009. Systematization of rare-earth elements in the Jurassic sandstones of Shaimskiy petroleum district (Western Siberia). Lithology and Geology of Fuels: Interuniversity Scientific Thematic Digest, vol. III (19). Publisher House UGGA, Ekaterinburg 45–56 (in Russian).

Filby, R.H., Shah, K.R., Sautter, C.A., 1977. A study of trace element distribution in the solvent refined coal (SRC) process using neutron activation analysis. J. Radioanal. Chem. 37 (2), 693–704 (Part 2).

Finkelman, R.B., 1981. Modes of occurrence of trace elements in coal. U.S. Geol. Surv. Open-File Rep, pp. 81–99 (322 pp.).

Finkelman, R.B., 1993. Trace and Minor Elements in Coal. Organic Geochemistry. In: Engel, M.N., Macko, S.A. (Eds.), NY: Plenum Press, New York, pp. 593–607.

Finkelman, R.B., Palmer, C.A., Krasnow, M.R., Aruscavage, P.G., Sellers, G.A., Dulong, F.T., 1990. Combustion and leaching behaviour of elements in the Argoonne Premium coal samples. Energy Fuels 4, 755–767.

Frolova, E.V., Khasanova, K.A., Alekseev, V.P., 2011. Verification of the palaeo-geographic reconstructions by the analysis of geochemical data of the deposits of Tyumenskaya suite of Shaimskiy petroleum district (Western Siberia). Lithology and Geology of Fuels: Interuniversity Scientific Thematic Digest, vol. 21. Publisher House UGGA, Ekaterinburg 84–89 (in Russian).

Given, P.H., Miller, R.N., 1987. The association of major, minor and trace inorganic elements with lignites. III Trace elements in four lignites and general discussion of all date from this study. Geochim. Cosmochim. Acta 51, 1843–1853.

Gluskoter, H.J., Ruch, R.R., Miller, W.G., Cahill, R.A., Dreher, G.B., Kuhn, J.K., 1977. Trace Elements in Coal: Occurrence and Distribution. III. Geol. Circ. 499 (154 pp.).

Goodarzi, F., Cameron, A.R., 1987. Distribution of major, minor and trace elements in coals of the Kootenay Group, Mount Allan, Alberta. Can. Mineral. 25, 555–565.

Goodarzi, F., Sanei, H., Stasiuk, L.D., Baghery-Sadeghi, H., Reyes, J., 2006. A preliminary study of mineralogy and geochemistry of four coal samples from northern Iran. Int. J. Coal Geol. 65, 35–50.

Gordon, S.A., Guren, G.F., Komissarova, L.N., Shatskiy, V.M., 1968. About the peculiarities of the scandium distribution in coal. Research on the Chemistry of Solid RocksNedra, Moscow 32–37 (in Russian).

Guren, G.F., Komissarova, L.N., Menkovskiy, M.A., Shatskiy, V.M., 1968. About the peculiarities of the scandium and phosphorous distribution in coal. Chem. Solid fuel 6, 148–151 (in Russian).

Hower, J.C., Ruppert, L.F., Eble, C.F., 1999. Lanthanide, yttrium, and zirconium anomalies in the fire clay coal bed, Eastern Kentucky. Int. J. Coal Geol. 39, 141–153.

Hower, J.C., Ruppert, L.F., Williams, D.A., 2002. Controls on boron and germanium distribution in the low-sulfur Amos coal bed, Western Kentucky coalfield, USA. Int. J. Coal Geol. 57, 27–42.

Ivankin, P.F., Trufanov, V.N., 1987. About the hydrocarbon fluidization of coals. Rep. Acad. Sci. USSR 292 (5), 1214–1216 (in Russian).

Kashirtsev, V.A., Zueva, I.N., Suknev, V.S., Mitronov, D.V., Syundyukov, Sh.A., Andreeva, G.V., Kapysheva, G.I., Livshits, S.Kh., Popov, V.I., 1999. Paragenetic associations of rare-earth elements in the Mesozoic coals of the northern part of Lenskiy basin. Nativ. Geol. 4, 65–68 (in Russian).

Ketris, M.P., Yudovich, Ya.E., 2009. Estimations of Clarkes for carbonaceous biolithes: world averages for trace element contents in black shales and coals. Int. J. Coal Geol. 78, 135–148.

Komissarova, L.N., 2006. Inorganic and Analytical Chemistry of Scandium. Editorial URSS, Moscow (512 pp. (in Russian)).

Kryukova, V.N., Vyazova, N.G., Latyshev, V.P., 2001. Distribution of scandium in the coal matter of Eastern Siberia. Chem. Solid Fuel 3, 73–76 (in Russian).

Lishtvan, I.I., Korol, N.T., 1975. Major Properties of Peat and the Methods of Their Determination. Science and Technique, Minsk 320 pp. (in Russian).

Lomashev, I.P., Losev, B.I., 1962. Germanium in Coals. Publisher House of Academy of Science of USSR, Moscow (258 pp. (in Russian)).

Lyons, P.C., Palmer, C.A., Bostick, N.H., Fletcher, J.D., Dulong, F.T., Brown, F.W., Brown, Z.A., Krasnov, M.R., Romankiv, L.A., 1989. Geochemistry and origin of minor and trace elements in vitrinite concentrates from a rank series from the Eastern United States, England and Australia. Coal: classification, coalification, mineralogy, trace-element chemistry and oil and gas potential. Int. J. Coal Geol. 13, 481–527.

Mastalerz, M., Drobniak, A., 2012. Gallium and germanium in selected Indiana coals. Int. J. Coal Geol. 94, 302–313.

Menkovskiy, M.A., Komissarova, L.N., Guren, G.F., Shatskiy, V.M., 1968. Distribution of scandium Sc in the products of the acid demineralization of bituminous coal. Research on the chemistry of rocks. Proc. Mosc. State Univ. 38, 38–42 (in Russian).

Mezhibor, A.M., Arbuzov, S.I., Arkhipov, V.S., 2003. Trace elements in peat bogs of Tomsk region (South Siberia, Russia). Energy Explor. Exploit. 31, 629–644.

Papanicolaou, C., Kotis, T., Foscolos, A., Goodarzi, F., 2004. Coals of Greece: a review of properties, uses and future perspectives. Int. J. Coal Geol. 58, 147–169.

Qi, H., Hu, R., Zhang, Q., 2007. Concentration and distribution of trace elements in lignite from the Shengli Coalfield, Inner Mongolia, China: implications on origin of the associated Wulantuga Germanium Deposit. Int. J. Coal Geol. 71, 129–152.

Ren, D., Zhao, F., Wang, Y., Yang, S., 1999. Distribution of minor and trace elements in Chinese coals. Int. J. Coal Geol. 40, 135–148.

Savichev, O.G., 2003. Rivers of Tomsk Region: State, Use and Protection. Publisher House of Tomsk Polytechnic University, Tomsk (202 pp. (in Russian)).

Savichev, O.G., Shmakov, A.V., 2012. Vertical regularities and year changes of the chemical composition of the water of Timiryazevskoe bog (Tomsk, Western Siberia). Bull. Tomsk Polytech. Univ. 320 (1), 156–161 (in Russian).

Seredin, V.V., Dai, S., 2012. Coal deposits as potential alternative sources for lanthanides and yttrium. Int. J. Coal Geol. 94, 67–93.

Seredin, V.V., Dai, S., 2013. The occurrence of gold in fly ash derived from high-Ge coal. Miner. Deposita. http://dx.doi.org/10.1007/s00126-013-0497-9.

Seredin, V.V., Finkelman, R.B., 2008. Metalliferous coals: a review of the main genetic and geochemical types. Int. J. Coal Geol. 70, 253–289.

Seredin, V.V., Arbuzov, S.I., Alekseev, V.P., 2006. Scandium Sc-bearing coals of Yakhlinskoe deposit, Western Siberia. Rep. Acad. Sci. 409 (5), 677–682 (in Russian).

Seredin, V.V., Dai, S., Sun, Y., Chekryzhov, I.Yu., 2013. Coal deposits as promising sources of rare metals for alternative power and energy-efficient technologies. Appl. Geochem. 31, 1–11.

Shvartsev, S.L., 1998. Hydrogeochemistry of the Hypergenesis Zone. Nedra, Moscow (366 pp. (in Russian)).

Shvartsev, S.L., Serebrennikova, O.V., Zdvizhkov, M.A., Savichev, O.G., Naimushina, O.S., 2012. Geochemistry of wetland waters from the Lower Tom Basin, Southern Tomsk Oblast. Geochem. Int. 50, 367–380.

Sorokin, A.P., Kuz'minykh, V.M., Rozhdestvina, V.I., Zhmodik, S.M., Anoshin, G.N., Mitkin, V.N., 2013. The regularities of formation of noble- and rare-metal mineralization in Cenozoic coaliferous deposits in the southern Far East. Russ. Geol. Geophys. 54, 671–684.

Stryapkov, A.V., 1997. Sorption of scandium Sc and REE as a reason of their accumulation in the weathering crust. Geochemistry 9, 930–936 (in Russian).

Suárez-Ruiz, Flores, D., Marques, M.M., Martinez-Tarazona, M.R., Rubiera, J., Pis, F., 2006. Geochemistry, mineralogy and technological properties of coals from Rio Maior (Portugal) and Peñarroya (Spain) basins. Int. J. Coal Geol. 67, 171–190.

Swaine, D.J., 1964. Scandium Sc in Australian coals and related materials. Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 8 (3), 172–177.

Swaine, D.J., 1990. Trace Elements in Coal. Butterworths, London (278 pp.).

Torikova, M.V., Kudinov, Yu.A., Timofeev, P.V., 1966. Rare metals in oil, coal, products of their treatment and mineralized waters. Prospect. Prot. Bowels 8, 21–23 (in Russian).

Valiev, Yu.Ya, Gofen, G.I., Pachadzhanov, D.N., 1993. Trace elements in Jurassic anthracites of Nazar-Ailokskoe deposit (Central Tajikistan). Geochemistry 2, 243–251 (in Russian).

Vassilev, S.V., Yossifova, M.G., Vassileva, C.G., 1994. Mineralogy and geochemistry of Bobov Dol coals, Bulgaria. Int. J. Coal Geol. 26, 185–213.

Ward, C.R., Spears, D.A., Booth, C.A., Staton, I., Gurba, L.W., 1999. Mineral Matter and Trace Elements in Coals of the Gunnedah Basin. , 40. New South Wales, Australia 281–308.

Yazdi, M., Esmaeilnia, S.A., 2003. Dual-energy gamma-ray technique for quantitative measurement of coal ash in the Shahroud mine, Iran. Int. J. Coal Geol. 55, 151–155.

Yazdi, M., Esmaeilnia, S.A., 2004. Geochemical properties of coals in the Lushan coal field of Iran. Int. J. Coal Geol. 60, 73–79.

Yudovich, Ya.E., 2003. Notes on the marginal enrichment of germanium in coal beds. Int. J. Coal Geol. 56, 223–232.

Yudovich, Ya.E., Ketris, M.P., 2002. Inorganic Matter of Coals. NISO UrO RAN, Ekaterinbourg (420 pp. (in Russian).

Yudovich, Ya.E., Ketris, M.P., 2006. Noble Trace Elements in Coals. Ural Department of Russian Academy of Sciences, Ekaterinburg (538 pp. (in Russian)).

Yudovich, Ya.E., Shastakevich, Yu.G., 1966. Ash yield of coals and the contents of rare elements in coals. Izvestie vuzov. Geol. Prospect. 9, 68–76 (in Russian).

Yurovskiy, A.Z., 1968. Mineral Components in Solid Fuels. Nedra, Moscow (214 pp. (in Russian)).

Zhuang, X., Querol, X., Alastuey, A., Juan, R., Plana, F., Lopez-Soler, A., Du, G., Martynov, V.V., 2006. Geochemistry and mineralogy of the Cretaceous Wulantuga high germanium coal deposit in Shengli coal field, Inner Mongolia, Northeastern China. Int. J. Coal Geol. 66, 119–136.