

Scandium in the coals of Northern Asia (Siberia, the Russian Far East, Mongolia, and Kazakhstan)

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Abstract

We present new original data on the geochemistry of scandium in the coals of Asian Russia, Mongolia, and Kazakhstan. In general, the studied coals are enriched in Sc as compared with the average coals worldwide. Coal deposits with abnormally high, up to commercial, Sc contents were detected in different parts of the study area. The factors for the accumulation of Sc in coals have been identified. The Sc contents of the coals depend on the petrologic composition of coal basins (composition of rocks in their framing) and the facies conditions of coal accumulation. We have established the redistribution and partial removal of Sc from a coal seam during coal metamorphism. The distribution of Sc in deposits and coal seams indicates the predominantly hydrogenic mechanism of its anomalous concentration in coals and peats. The accumulation of Sc in the coals and peats is attributed to its leaching out of the coal-bearing rocks and redeposition in a coal (peat) layer with groundwater and underground water enriched in organic acids. The enrichment of coals with Sc requires conditions for the formation of Sc-enriched coal-bearing rocks and conditions for its leaching and transport to the coal seam. Such conditions can be found in the present-day peatland systems of West Siberia and, probably, in ancient basins of peat (coal) accumulation.

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Introduction

Over the last few decades, extensive studies of the trace elements of coal basins and coal deposits worldwide have shown that coals accumulate many valuable metals, including rare and disseminated elements. Scandium is of particular interest as an element almost not making up commercial deposits, which is usually extracted during the recovery of ores of other metals but often makes up geochemical anomalies in coal ashes, up to commercial contents (Arbuzov and Ershov, 2007; Arbuzov et al., 2003; Kashirtsev et al., 1999; Seredin and Finkelman, 2008; Seredin et al., 2006; Valiev et al., 1993; Yudovich and Ketris, 2006).

Despite the abundance of information about the Sc content of coals, the geochemistry of this element is poorly known. The most complete overview of its geochemistry is presented in (Yudovich and Ketris, 2002, 2006). The few works concerned with the occurrence of Sc in coals (Arbuzov and Ershov, 2007; Arbuzov et al., 1996, 1997, 2000, 2003;

Borisova et al., 1974; Eskenazi, 1996; Gordon et al., 1968; Guren et al., 1968; Kryukova et al., 2001; Menkovskii et al., 1968; Seredin et al., 2006; Swaine, 1964; Yudovich and Ketris, 2002, 2006; Yurovskii, 1968) deal only with some special issues of its geochemistry. Currently, there is no clear vision of the causes or conditions of accumulation of high Sc contents in coals. In consequence, no prospecting criteria for Sc-bearing coals have been developed. This is explained by the lack of interest in coals as a source of Sc in industry. The low demand for this element, mostly because of its extremely high cost, is satisfied by the available resources and does not stimulate the study of any other Sc sources. However, the ashes of some coals could compete with conventional Sc sources owing to their accessibility and high contents of the metal.

Description of the study area

The Sc geochemistry of coals was studied for Asian Russia, Mongolia, and Kazakhstan (Fig. 1). The selection of the study area was determined by the objectives of the study, which included not only the estimation of the Sc content of coals

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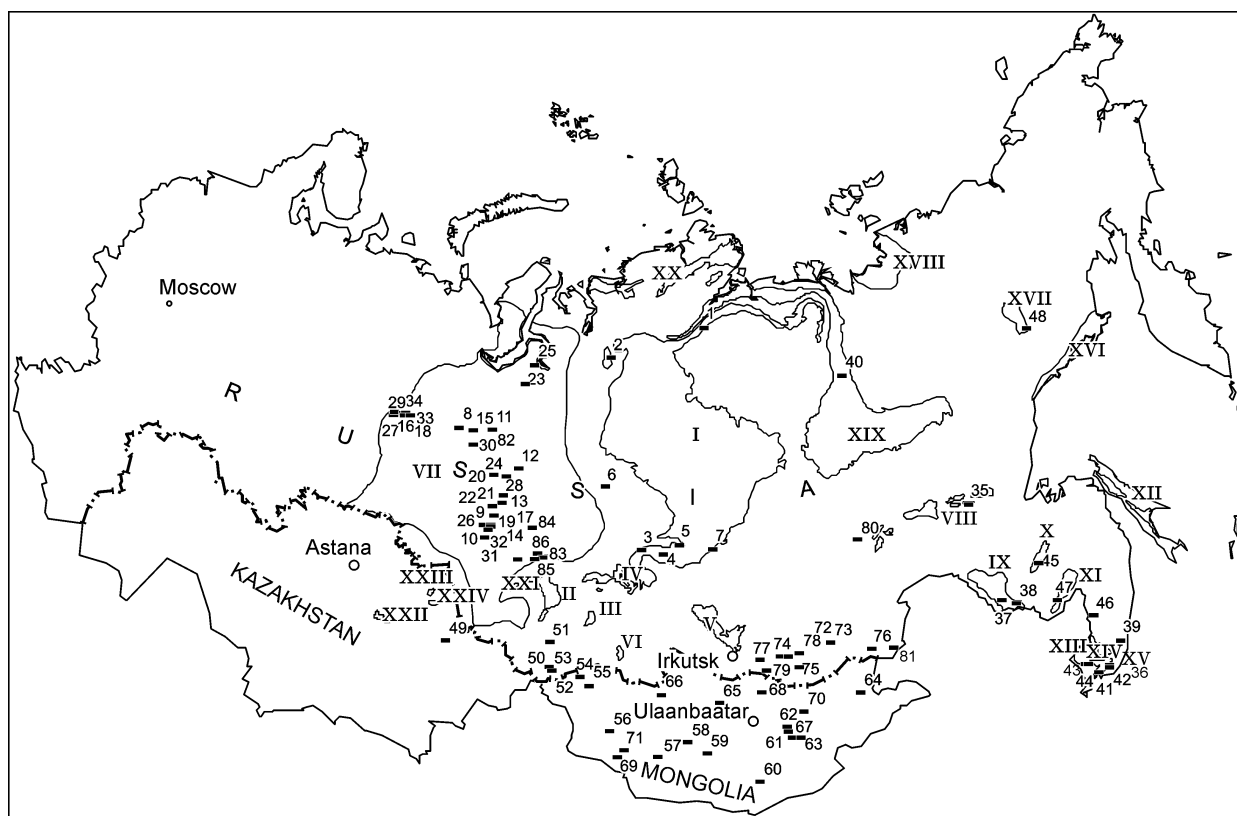


Fig. 1. Distribution of the studied coal basins and deposits in the territory of Northern Asia. Basins: I, Tunguska; II, Kuznetsk; III, Minusa; IV, Kansk–Achinsk; V, Irkutsk; VI, Ulugkhem; VII, West Siberian; VIII, South Yakutian; IX, Lower Zeya; X, Bureya; XI, Middle Amur; XII, Sakhalin; XIII, Razdol'naya; XIV, Bikin–Ussuri; XV, Partizansk; XVI, Okhotsk; XVII, Arkagala; XVIII, Yana–Omoloi; XIX, Lena; XX, Taimyr; XXI, Gorlovo; XXII, Karaganda; XXIII, Ekibastuz; XXIV, Maikube. Coal deposits and occurrences: 1, Kayak; 2, Kaierkan; 3, Kokui; 4, Gavrilovka; 5, Kodinsk; 6, Stony Tunguska; 7, Zheron; 8, Ai-Pim; 9, Archin'ya; 10, Upper Tara; 11, Upper Trom'egan; 12, East Permyaki; 13, Gerasimovka; 14, Grigor'evka; 15, Konitor; 16, Lazarev; 17, Letnyaya; 18, Lova; 19, Luginetskii; 20, Malaya Rechka; 21, Myl'dzhino; 22, Lower Tabagan; 23, Novyi Urengoi; 24, Prigranichnoe; 25, SG-7-397; 26, North Kalinov; 27, Tal'nikovaya; 28, Trassovoe; 29, Umyt'ya; 30, Fedorovka; 31, Shirotnoe; 32, South Tabagan; 33, Yakhlya; 34, Symor'yakh; 35, El'ga; 36, Sergeevka; 37, Erkovtsy; 38, Raichikha; 39, Voznovo; 40, Zhigansk; 41, Shkotovo; 42, Avangard; 43, Lipovtsy; 44, Pavlovka; 45, Urgal; 46, Bikin; 47, Ushumun; 48, Arkagala; 49, Karazhyra; 50, Kurai; 51, Pyzhina; 52, Taldu-Dyurgun; 53, Balkhash; 54, Nuursthotgor; 55, Khartarvagatai; 56, Khundlun; 57, Zeegt; 58, Uvurchuluut; 59, Bayanteeg; 60, Tavantolgoi; 61, Baganuur; 62, Tugrugnuur; 63, Alag-Togoo; 64, Aduunchuluun; 65, Saikhan-Ovoo; 66, Mogoin-Gol; 67, Shivee-Ovoo; 68, Sharyngol; 69, Manit; 70, Chandgantal; 71, Khurengol; 72, Olon'-Shibir'; 73, Tataurovo; 74, Tarbagatai; 75, Zashulan; 76, Kharanor; 77, Zagustai; 78, Burtui; 79, Okino-Klyuchevskoe; 80, Apsat; 81, Urtui; 82, Kavrin; 83, Tugan; 84, Kolpashevo; 85, Lagernyi Sad; 86, Talovka.

but also the study of (1) regularities in the accumulation of abnormal contents of metals; (2) influence of different factors of the geologic medium on the levels of Sc accumulation in coals and coal ashes; and (3) conditions of Sc accumulation and occurrence in coals showing different degrees of metamorphism.

Nine coal basins and 14 coal deposits were studied in Siberia. The region is characterized by the presence of coals of all ranks from lignites to anthracites, within a wide age interval from Devonian to Paleogene. Detailed geochemical studies were carried out for four basins: Kuznetsk, Minusa, Irkutsk, and Kansk–Achinsk. The data on the Gorlovo, Tunguska, West Siberian, Ulugkhem, and Taimyr basins are also representative, though not so abundant. Also, contact-metamorphic graphite rocks which formed after coals are observed here. Overall, 3285 coal samples and 1927 peat samples (a total of 5212 samples) were studied for Siberia.

The knowledge of the Russian Far East is not so detailed. Late Jurassic, Cretaceous, Paleogene, and Neogene coals are

observed here. The region is marked by the substantial role of volcanism in the formation of coal-bearing sediments. The numerous deposits and basins of the Russian Far East are insufficiently studied, so that the present conclusions are tentative. Part of the data were obtained from the study of the collections of coal samples provided by V.V. Ivanov, A.A. Kumar'kov, M.A. Klimin, V.N. Shvets, and V.A. Melkii. The coals of this region are represented by 291 samples from 13 deposits.

The first representative geochemical studies for Mongolia were carried out. In total, 327 coal samples were studied from 18 deposits of Carboniferous, Permian, Jurassic, and Cretaceous ages. The Mongolian coal deposits are distinguished by the wide interval of coal formation from Early Carboniferous to Cretaceous.

A small amount of data was obtained for the coal-bearing sediments of Kazakhstan. They are represented by the coals and coal-bearing rocks of the Carboniferous Ekibastuz and Karaganda basins and Jurassic Maikube basin and Karazhyra

deposit. The collection of samples from the Kazakhstan deposits was provided by S.Yu. Kalinina, A.Ya. Pshenichkin, and S.V. Azarova.

The collection of samples from Siberia, Russian Far East, Kazakhstan, and Mongolia includes the main types of coals which formed in different geotectonic and facies settings. Their ranks vary from immature brown coals to anthracites, and their ages vary from Devonian to Neogene. Besides, the present-day peat bogs of West Siberia were studied for comparison.

Methods

The paper is based on the results of quantitative determinations of Sc in 5891 coal and peat samples and >2000 samples of coal-bearing rocks from different deposits. The coal seams were sampled by the trench method with differentiated recovery of samples at coal-mining enterprises from open pits and mines as well as from outcrops and well core. The average sampling interval, selected depending on the seam thickness and structure, varied from 0.15 to 2.0 m. Some cross sections were studied in more detail, at intervals of 0.5–10.0 cm. Lateral variation in Sc content was estimated from a network of seam sections.

In most of the samples, Sc content was determined by instrumental neutron activation analysis (INAA) directly in coal, without its preliminary concentration to prevent the loss of some metal on ignition. Laboratory determination of the Sc content of the coals, coal ashes, and rocks was carried out in the Nuclear–Geochemical Laboratory (Department of Geocology and Geochemistry (DGG), Tomsk Polytechnic University) (analyst A.F. Sudyko). The Sc detection limit in the coals for the INAA was 0.02 ppm. For control, parallel determinations of Sc contents were carried out for the coals and coal ashes, with corresponding recalculations in ash for coal and vice versa. The quality of the INAA was tested against different standards for coal ash and rocks (Table 1).

For part of the samples, the Sc content of the coal ash was determined by ICP-MS at the Institute of the Problems of the Technology of Microelectronics and Ultrapure Materials (Chernogolovka) (analyst V.K. Karandashev) and at the center of shared use “Analytical Center of the Geochemistry of Natural Systems” (Tomsk State University) (analyst Yu.V. Anoshkina). The results obtained by different methods show satisfactory convergence (Fig. 2).

Table 1. Determination of Sc in standard samples

Standard sample	Specification, ppm	DGG
Rhyolite JR-1	5.07 ± 0.54	5.4 ± 0.1
Rhyolite JR-2	5.59 ± 1.22	5.5 ± 0.1
Granite JG-2	2.42 ± 0.42	2.4 ± 0.04
Granodiorite JG-3	8.76 ± 0.55	8.7 ± 0.12
ZUK-1 GSO 7125-94	11.0 ± 1.0	11.1 ± 0.3
GBPg-1 (garnet-biotite plagiogneiss)	14.3 ± 2.2	14.5 ± 0.2
SLg-1 (black shale)	20.0 ± 3.0	21.0 ± 0.5

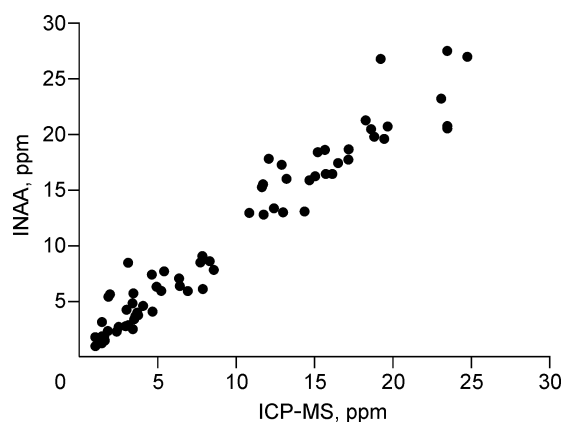


Fig. 2. Convergence of determinations of Sc content by instrumental neutron activation analysis (INAA) and ICP-MS.

The average Sc content of the coals was estimated by successive averaging of the data. The average Sc contents of the coal seams were calculated as mean weighted values for the thickness of the sampling intervals; those of the deposits, as mean weighted values for the thickness of the seams; and those of the basins, as mean weighted values for the mass (resources) of coal at the deposits (Arbuzov and Ershov, 2007).

The selected set of analytical methods permits a reliable estimation of the content, distribution, and conditions of concentration of Sc in coals.

Results and discussion

Scandium content of the coals. The average Sc content of the studied coals is 4.3 ppm, and the average ash content is 13.1% (Table 2). The average content was calculated as a mean weighted value for the coal resources. The modal estimate of the average Sc content of 67 deposits and basins is 4.6 ppm, and the median content is 4.2 ppm. These data, consistent with the estimated geometric mean Sc content of the coals of China (Dai et al., 2012; Ren et al., 1999), are close to data on its average content in the coals of the United States (Finkelman, 1993). On the other hand, this estimate is higher than that of the average Sc content of the coals worldwide (3.9 ppm), after (Ketris and Yudovich, 2009), which shows the Sc enrichment of the coals in the study area as compared with the world average.

The average Sc content of the coals of some deposits in the region varies from 0.85 ppm (Urtui deposit, Transbaikalia) to 16.0 ppm (West Siberian basin, Mesozoic coals). In some samples from the Pereyaslovka deposit (Kansk–Achinsk basin), its contents reach 230 ppm (Arbuzov et al., 2008).

The average Sc content of the coal ash varies from 7.3 ppm (Aduunchuluun deposit, Mongolia) to 150 ppm (West Siberian basin, Mesozoic coals). The Sc contents of some samples of coal ash from the West Siberian basin reach 0.23%.

Coals of different ages differ in Sc content even region-wide. Devonian coals have a uniform Sc content, which is

Table 2. Scandium content of the coals and coal ash

Coal basins and deposits	Number of samples	$A^{d,}$ %	Sc content, ppm	
			coal	coal ash*
Siberian region				
Devonian coals				
Barzas	14	32.5	6.4 ± 0.7	19.7
Ubrus	6	49.2	8.7 ± 1.3	17.7
Average	20	35.3	6.8 ± 0.8	19.2
Carboniferous–Permian coals				
Gorlovo	24	7.0	2.9 ± 0.5	41.4
Kuznetsk	1394	13.5	3.9 ± 0.1	28.9
Minusa	490	16.9	8.2 ± 0.6	48.5
Tunguska	67	14.1	4.6 ± 1.4	32.6
Taimyr	51	24.4	7.4 ± 0.6	30.5
Kurai	12	25.2	6.9 ± 0.9	27.4
Average	2038	13.5	4.5 ± 0.8	33.2
Mesozoic coals				
Pyzhina	6	6.5	2.9 ± 1.4	44.6
Kansk–Achinsk	524	9.8	2.9 ± 0.5	29.6
Irkutsk	129	14.3	6.7 ± 0.9	46.9
Ulugkhem	45	9.3	2.3 ± 0.5	44.6
West Siberian	172	10.6	16.0 ± 2.1	150
Tunguska	30	12.6	3.9 ± 0.6	23.8
Kuznetsk	3	17.3	6.4 ± 1.4	37.0
Olon’–Shibir’	40	15.3	4.6 ± 0.5	32.8
Tataurovo	31	13.3	1.3 ± 0.4	9.8
Tarbagatai	34	10.9	1.5 ± 0.5	13.8
Zashulan	18	7.3	1.2 ± 0.4	16.4
Kharanor	41	10.0	1.2 ± 0.2	12.0
Zagustai	13	18.2	4.0 ± 1.1	22.0
Burtui	18	9.5	2.8 ± 0.4	29.5
Okino–Klyuchevskoe	8	19.2	4.7 ± 1.3	24.5
Urtui	8	7.9	0.85 ± 0.13	10.8
Apsat	5	12.3	2.7 ± 0.3	22.0
Average	1125	12.0	3.9 ± 0.9	32.5
Paleogene coals				
West Siberian	73	30.7	13.3 ± 0.6	43.3
Taldu-Dyurgun	29	19.8	9.1 ± 0.8	46.0
Average	102	30.7	13.3 ± 0.6	43.3
Present-day peat				
West Siberian	1927	7.3	0.88 ± 0.17	12.2
Far Eastern region				
Late Jurassic–Lower Cretaceous coals				
Erkovtsy	23	14.2	2.0 ± 0.7	14.1
Raichikha	19	13.6	3.5 ± 0.8	25.7
El’ga	47	16.1	2.1 ± 0.7	13.0
Urgal	58	25.7	5.1 ± 0.3	19.8
Lipovtsy	4	32.7	4.2 ± 0.5	12.8
Average	151	17.9	2.8 ± 0.6	15.4
Paleogene–Neogene coals				
Shkotovo	7	16.2	6.4 ± 1.3	39.5

(continued on next page)

Table 2 (continued)

Coal basins and deposits	Number of samples	A^d , %	Sc content, ppm	
			coal	coal ash*
Paleogene–Neogene coals				
Pavlovka	40	14.2	4.6 ± 0.6	32.4
Bikin	16	17.4	10.5 ± 2.5	60.3
Ushumun	9	10.1	2.9 ± 0.6	28.7
Yana–Omoloi	16	33.0	4.6 ± 1.0	13.9
Sakhalin	39	16.2	9.1 ± 0.7	56.2
Vozново	6	21.1	2.3 ± 0.8	10.9
Sergeevka	7	15.8	3.0 ± 0.4	19.0
Average	140	23.5	6.8 ± 0.9	28.9
Kazakhstan				
Carboniferous coals				
Karaganda	3	9.8	6.0 ± 1.7	61.2
Ekibastuz	41	36.1	8.3 ± 0.4	23.0
Average	44	23.0	7.2 ± 0.5	31.3
Jurassic coals				
Karazhyra	7	11.2	8.9 ± 0.9	79.7
Maikube	10	25.5	8.1 ± 1.6	31.8
Average	17	18.4	8.5 ± 1.3	46.3
Mongolia				
Carboniferous coals				
Nuurshotgor	122	18.2	3.4 ± 0.3	18.7
Khartarvagatai	10	18.7	2.7 ± 0.2	14.4
Khundlun	8	9.4	1.8 ± 0.3	19.1
Zeegt	10	12.5	1.2 ± 0.2	9.6
Average	150	14.7	2.3 ± 0.5	15.6
Permian coals				
Tavantolgoi	10	9.8	1.8 ± 0.2	18.4
Manit	16	20.2	4.9 ± 0.5	24.3
Uvurchuluut	5	17.2	7.9 ± 2.5	45.9
Khurengol	28	38.9	4.8 ± 0.3	12.3
Average	49	21.2	4.9 ± 1.2	22.5
Jurassic coals				
Saikhan-Ovoo	6	9.7	3.9 ± 0.9	40.2
Mogoin-Gol	15	14.8	4.2 ± 1.5	28.4
Bayanteeg	8	14.8	11.6 ± 1.8	78.4
Sharyngol	29	12.2	6.0 ± 0.5	52.7
Average	58	12.9	6.4 ± 2.5	49.9
Cretaceous coals				
Alag-Togoo	10	28.6	3.0 ± 0.8	10.5
Aduunchuluun	10	12.5	0.9 ± 0.1	7.3
Baganuur	2	8.1	1.1 ± 0.1	13.6
Tugrugnuur	7	13.3	2.3 ± 0.3	17.3
Shivee-Ovoo	28	N.d.	1.3 ± 0.4	N.d.
Chandgantal	13	21.3	11.2 ± 3.5	52.6
Average	70	16.8	3.3 ± 1.6	19.7
Average for Northern Asia	5891	13.11.1	4.3 ± 0.4	32.8
Average for coals worldwide**	8400		3.9	23.0

Note. N.d., Not determined; A^d , ash content. The analyses were carried out by INAA at the Department of Geoecology and Geochemistry, Tomsk Polytechnic University (analyst A.F. Sudyko). * Recalculated for ash; ** after (Ketris and Yudovich, 2009).

higher than the world average. However, the peculiar conditions of the coal accumulation during that period determined the elevated ash content of the coals and, correspondingly, their low Sc content (19.2 ppm).

Carboniferous–Permian coals show wider variations in Sc content. In Siberia, the content of this element varies from 2.9 ppm in the anthracites of the Gorlovo basin to 8.2 ppm in the hard coals of the Minusa basin. The Kazakhstan coals (Karaganda basin and Ekibastuz) have an elevated Sc content. The Carboniferous coals of Mongolia are generally poor in Sc. However, Permian deposits contain coals with elevated Sc contents (Table 2).

Mesozoic coals, which can be found throughout the study area, show the widest variations in Sc content. Abnormally Sc-bearing coals are observed in the West Siberian and Irkutsk basins of Siberia and at the Bayanteg, Sharyngol, and Chandgantal deposits of Mongolia. The Jurassic coals of Kazakhstan also have high Sc contents. The Mesozoic coals are characterized not only by abnormally high but also by abnormally low Sc contents of 1–2 ppm (Urtui, Zashulan, Kharanor, and Tataurovo deposits of Transbaikalia).

Paleogene–Neogene coals occur in Siberia and the Far East. In general, they have elevated Sc contents, but the Sc content of the ash is often lower than the average for the study area owing to high ash content. Young coals are observed in the West Siberian and Sakhalin basins as well as at the Taldu-Dyurgun (Gorny Altai) and Bikin (Primorye) deposits with a high Sc content. The Sakhalin coals contain 9.1 ppm Sc, and the coal ash contains 56.2 ppm Sc.

Patterns of the Sc distribution. The considerable variations in the average Sc content of the deposits and basins indicate the nonuniform distribution of this element in space and time. Also, wide lateral variation in Sc content within the region is evidenced by its nonuniformity in coeval coals. For example, the average content of this element in the Carboniferous–Permian coals of Siberia varies from 2.9 ppm in the Gorlovo basin to 8.2 ppm in the Minusa basin. The average Sc content of the Paleogene–Neogene coals of the Russian Far East varies from 2.3 ppm (Voznovo deposit) to 10.5 ppm (Bikin deposit). In all the cases, high Sc contents in the coals are observed in regions where mafic rocks (basaltoids, gabbro, and amphibolites) with an elevated Sc content are abundant in the provenance area of the coal-bearing basin.

Scandium content and distribution within coal deposits and basins also depend on the presence of Sc-enriched rocks in the provenance area. Besides, a clear zoning is observed, which is expressed in a decrease in Sc content from provenance area to basin center.

The vertical distribution of Sc is as nonuniform as its lateral distribution. Note that Sc content within stratigraphic units shows regular variation from the bottom up the coal-bearing section. Different patterns are possible, based on the geology of the study area, but the lower and upper parts of the section within the boundaries of stratigraphic units are generally enriched in Sc with respect to the central part (Arbutov and Ershov, 2007).

The Sc distribution in the vertical section of a coal seam is still more differentiated. Like other coal-philous elements (those enriching coal ash as compared with the host rocks (Yudovich and Ketris, 2002)), Sc ensures obvious enrichment of the near-contact zones of coal seams—the areas near the seam top and bottom (Fig. 3). The Sc content of these areas can differ from that of the inner zones by more than an order of magnitude. The thickness of the zones with elevated contents of the metal does not depend on that of the coal seam. This determines the known pattern of Ge–Sc content in thin seams is higher than in thick ones (Lomashov and Losev, 1962; Yudovich, 2003). This is explained by the higher portion of Sc-enriched near-contact intervals in the section of the thin seams as compared with the thicker ones. A significant negative correlation is observed between the seam thickness and the Sc contents of the coal and coal ash. For example, in the abnormally Sc-bearing coals of the West Siberian basin, the coefficient of correlation between Sc content and the seam thickness is -0.31 for 49 intersections. The study of present-day peat bogs shows that the formation of enriched near-contact zones begins as early as the stage of peat accumulation. The lack of a direct relationship between the ash content of the coal indicates that these near-contact anomalies are hydrogenic. Note that the near-contact zones of Sc accumulation are not detected in all the studied coal-bearing sections but coal seams with such zones enriched in Sc clearly predominate. Analysis of more than a hundred vertical sections of the coal seams shows that the presence or lack of such zones are not influenced by the composition of the over- or underlying sediments. They are equally distinct for the sandy, siltstone, and mudstone compositions of the host rocks. In the studied present-day peat bogs of West Siberia, enriched near-contact zones are more rare and, often, less distinct. However, even here, at the base of the peat deposit, the Sc content of peat ash sometimes exceeds 100 ppm (background value for the section, 5–10 ppm). Such enriched zones are observed both in lowland and raised peat bogs.

Factors controlling the Sc accumulation in the coals. The leading factors which determine the Sc content and distribution patterns in the coal seams are the composition of the provenance area of the coal-bearing basin (factor of petrology, according to Ya.E. Yudovich (Yudovich and Ketris, 2002)), the facies factor, the hydrogeochemical factor, and the factor of coal metamorphism.

Petrology factor. Analysis of the geologic position of the Sc-bearing coals shows their relationship with areas with Sc-enriched rocks (geochemically specialized complexes), mainly mafic ones. First and foremost, this is the West Siberian basin, particularly its Trans-Urals part with an average Sc content of 16 ppm in coal and 150 ppm in ash. Such basins include the Sakhalin, Minusa, and Irkutsk basins and some deposits of Mongolia (Bayanteg, Sharyngol, and Chandgantal). All these deposits are characterized by the presence of geochemically specialized mafic rocks in the provenance area of the coal-bearing basin. The Urals are a provenance area for the abnormally Sc-enriched coals of the Shaim district of the West Siberian basin. According to some

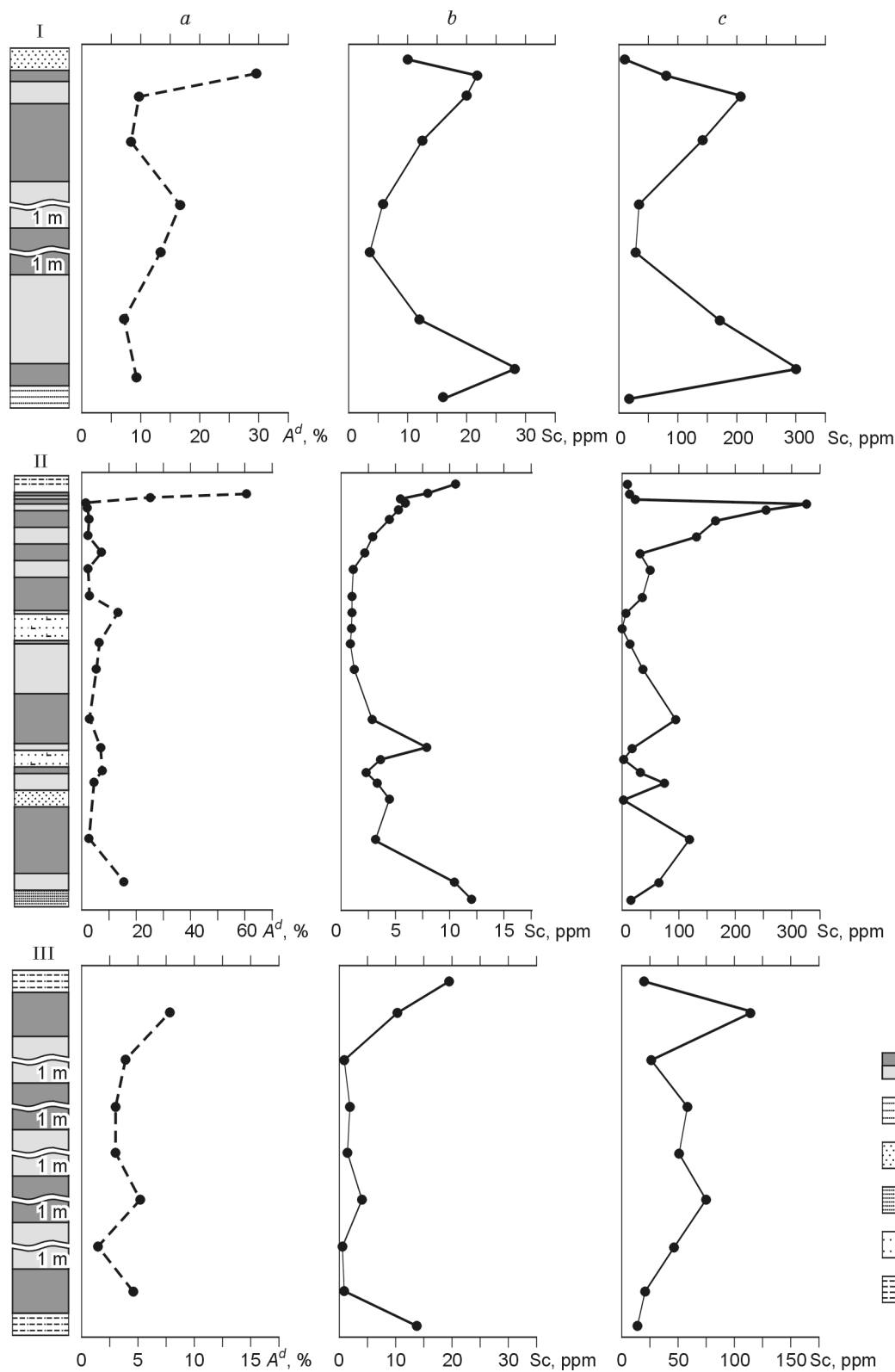


Fig. 3. Distribution of ash content (a) and Sc in coal (b) and coal ash (c) in a vertical profile of the coal seam. I, brown coal. Rybinskii II seam, Borodino deposit, Kansk–Achinsk basin; II, hard coal. Dvukharshinnyi seam, Minusa basin; III, anthracite. Glavnyi II seam, Urgun deposit, Gorlovo basin. 1, coal; 2, mudstone; 3, siltstone; 4, sandstone; 5, tonstein; 6, silty sandstone. A^d , Ash content.

studies (Fedorov et al., 2009; Frolova et al., 2011), mafic rocks played the leading part in the formation of the terrigenous sediments of the coal-bearing Tyumen' Formation (Shaim district). The Sc-bearing traps of the Siberian Platform are a provenance area for the Irkutsk basin. The high Sc contents in the coals of the Azei deposit are concentrated on the northern margin of the basin, which is composed of Ordovician terrigenous carbonate sediments with thick sheets and sills of Triassic traps with weathering crusts which formed after them (Arbuzov et al., 2012). The Sc-bearing coals of the Minusa basin are also clearly confined to the blocks of the framing structures with widespread occurrence of femic structure-facies complexes (Arbuzov and Ershov, 2007).

Thus, in all the cases of the abnormal or simply elevated Sc contents of the coals and coal ashes, their relationship with the mafic rocks on the framing of the coal deposits and basins.

Facies factor. The facies factor also plays an important role in the formation of the geochemical background of the coal seams. Like elevated ash content, higher initial Sc contents are typical of coals which formed from lowland peat bogs. Lowland peat is richer in Sc than peat from raised bogs (Arbuzov et al., 2009). Note that the ash of the raised-bog peat is enriched in Sc with respect to the lowland peat, as is the case with the ash of low-ash coals with respect to coals with an elevated ash content. This indicates that a considerable part of Sc accumulates in the coals as early as during the stage of peat accumulation. Also, these data suggest a similar ash content of the peat, while the Sc contents of the peat deposit can differ considerably, indicating the importance of the petrology factor and, probably, hydrogeochemical factor in the accumulation of the metal in the peat and the coal which formed from that peat.

Hydrogeochemical factor. The hydrogeochemical factor, along with the petrology factor, is decisive for the Sc accumulation in the coals. Scandium is poorly soluble in water in the supergene zone and is poorly transported by surface waters. The average Sc content of nonsaline surface waters is only 0.004 µg/L (Shvartsev, 1998). Note that contents of this element can vary widely under different conditions and in different regions. According to the same data, its content in the surface waters of Sweden reaches 0.045 µg/L. The Sc content of bog waters is often considerably higher. For example, the waters from the drainage channel of the Vasyugan bog, West Siberia, contain 0.18 µg/L Sc (Savichev, 2003). The content of this element in groundwater and underground waters is higher than that in the surface waters. The highest Sc content (on average, 0.08 µg/L) is observed in the waters of mountain taigas (Shvartsev, 1998). The Sc content of the present-day acid mine waters of the Kizel basin (pH = 2–4) is up to 45 µg/L Sc (Torikova et al., 1996), which is almost 10,000 times higher than that in the nonsaline surface waters. The high Sc contents in the groundwater of the supergene zone as compared with those in the surface waters are explained by the presence of reducing agents and organic matter (Shvartsev, 1998). This agrees with the data on the high Sc content of the bog waters. It is presumed that Sc

migrates in the form of soluble organic complexes under these conditions.

The distribution of Sc in a coal seam indicates its accumulation from aqueous solutions at the seam boundary (peat deposit). The low migration capacity of Sc in the waters of a supergene zone permits rejecting the model for its long-distance transport from weathering crust in dissolved form and presuming its removal and redistribution directly within the coal-bearing series. The accumulation of Sc in coal is due to the formation of a terrigenous series in a sedimentary basin with a significant portion of mafic rocks; the subsequent extraction of this element into an aqueous solution with the participation of organic acids; its transport within the series; migration into a peat deposit and coal seam; and deposition. This model for the accumulation of Sc in coals is confirmed by its distribution in a coal seam, recorded high contents of this element in acid groundwater and soil waters, and its capability to make up stable complexes with humic and fulvic acids (Komissarova, 2006).

The Sc content of the coal-bearing sediments and the basin hydrogeochemistry determine the possibility of its exceeding the background value in the coals. The host rocks of coal deposits and basins with an abnormal Sc content have Sc contents exceeding the clark by a factor of 1.5–3.0 (Arbuzov and Ershov, 2007; Arbuzov et al., 2003; Eskenazi, 1996).

Factor of metamorphism. The factor of metamorphism consists in the fact that the content of Sc in coals changes owing to redistribution and removal during their metamorphism. The removal of Sc during metamorphism is evidenced by comparison of its contents in coals of different ranks. The evidence for the removal is not always convincing enough, because the content of the metal in the coals depends on many conditions and the assessment of the significance of this factor calls for a comparison of coals showing different degrees of metamorphism, other conditions of formation being equal. It is informative to compare coals showing different degrees of coalification (of different ranks) within one deposit or basin with a single provenance area of the basin of peat (coal) accumulation. Examples include the coals of the Kuznetsk Basin (Arbuzov et al., 2000). A well-defined decrease in Sc content is observed here in passing from long-flame coals to anthracites (Fig. 4). Similar results were obtained from the study of Canadian (Alberta) Cretaceous coals showing different degrees of metamorphism (Goodarzi and Cameron, 1987). Thus, the regional metamorphism of the coals causes a loss in Sc.

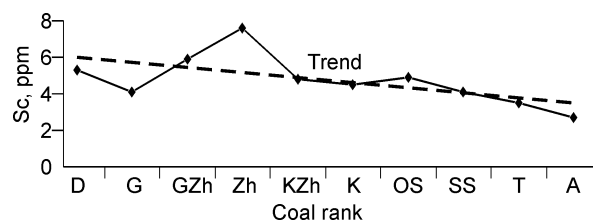


Fig. 4. Plot and trend of variation in the Sc content of the coals with changing degree of metamorphism (Kuznetsk Basin, Russia).

The results of removal of Sc during contact metamorphism are even more conspicuous. However, as distinct from regional metamorphism, which causes mass removal of the metal, thin zones of its removal and redeposition immediately near the contact with an intrusion are detected here. At a short distance, the coal is enriched in Sc and, simultaneously, has a higher ash content (Arbuzov and Ershov, 2007).

Conclusions

In general, the coals of Asian Russia, Mongolia, and Kazakhstan are enriched in Sc as compared with the average coals worldwide. Coal deposits with abnormally high, up to commercial, Sc contents were detected in different parts of the extensive study area. These deposits are confined to blocks of rocks with an elevated Sc content. The Sc contents of the coals depend on the composition of rocks in the framing of coal basins, the facies conditions of ancient coal accumulation, and the hydrogeochemical conditions of basins and deposits. We have established the redistribution and partial removal of Sc from a coal seam during coal metamorphism. The distribution of Sc in deposits and coal seams indicates the predominantly hydrogenic mechanism of its anomalous concentration in coals and peats. The accumulation of Sc in the coals and peats is attributed to its leaching out of the coal-bearing rocks and redeposition in a coal (peat) layer with groundwater and underground water enriched in organic acids. The enrichment of coals with Sc requires conditions for the formation of Sc-enriched coal-bearing rocks and conditions for its leaching and transport to the coal seam. Such conditions can be found in the present-day peatland systems of West Siberia and, probably, in ancient basins of peat (coal) accumulation.

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References

- Arbuzov, S.I., Ershov, V.V., 2007. Geochemistry of Trace Elements in Siberian Coals [in Russian]. D-Print, Tomsk.
- Arbuzov, S.I., Potseluev, A.A., Rikhvanov, L.P., 1996. Rare-earth elements and scandium in the coals of the Aralichevo District in the Kuznetsk Basin. *Geologiya i Geofizika* (Russian Geology and Geophysics) 37 (3), 68–73 (65–70).
- Arbuzov, S.I., Ershov, V.V., Potseluev, A.A., Rikhvanov, L.P., Sovetov, V.M., 1997. Rare earth elements and scandium in Kuznetsk Basin coals. *Litologiya i Poleznye Iskopaemye* 32 (3), 275–285.
- Arbuzov, S.I., Ershov, V.V., Potseluev, A.A., Rikhvanov, L.P., 2000. Trace Elements in the Coals of the Kuznetsk Basin [in Russian]. Izd. KPK, Kemerovo.
- Arbuzov, S.I., Ershov, V.V., Rikhvanov, L.P., Usova, T.Yu., Kyargin, V.V., Bulatov, A.A., Dubovik, N.E., 2003. Rare-Metal Potential of the Coals of the Minusa Basin [in Russian]. Izd. SO RAN, Filial "Geo," Novosibirsk.
- Arbuzov, S.I., Volostnov, A.V., Ershov, V.V., Rikhvanov, L.P., Mironov, V.S., Mashen'kin, V.S., 2008. Geochemistry and Metal Content of the Coals of the Krasnoyarsk Territory [in Russian]. STT, Tomsk.
- Arbuzov, S.I., Arkhipov, 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 contents of some trace elements in the peats of the southeastern West Siberian Plate. *Izv. Tomsk. Politekh. Univ., Nauki o Zemle*, 315 (1), 44–48.
- Arbuzov, S.I., Volostnov, A.V., Il'enok, S.S., Rybalko, V.I., 2012. Origin of tonsteins from the Azei deposit of the Irkutsk coal basin. *Izv. Tomsk. Politekh. Univ., Nauki o Zemle*, 321 (1), 89–97.
- Borisova, T.F., Guren, G.F., Komissarova, L.N., Shatskii, V.M., 1974. Distribution of Sc in coal substance. *Khimiya Tverdogo Topliva*, No. 5, 10–13.
- Dai, S., Ren, D., Chou, C.-L., Finkelman, R.B., Seredin, V.V., Zhou, Y., 2012. 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.
- Eskenazi, G., 1996. Scandium in Bulgarian coals, in: *Annals of Sofia University, Faculty of Geology and Geography, Book 1: Geology*, Vol. 89, pp. 205–217.
- Fedorov, Yu.N., Maslov, A.V., Ronkin, Yu.L., 2009. Classification of rare-earth elements in the Jurassic sandstones of the Shaim petroliferous region (West Siberia), in: *Lithology and Geology of Fossil Fuels* [in Russian]. Izd. Ural'sk. Gos. Gorn. Univ., Yekaterinburg, Issue III (19), pp. 45–56.
- Finkelman, R.B., 1993. Trace and minor elements in coal, in: Engel, M.H., Macko, S.A. (Eds.), *Organic Geochemistry*. Plenum, New York, pp. 593–607.
- Frolova, E.V., Khasanova, K.A., Alekseev, V.P., 2011. Verification of paleogeographical reconstructions by analyzing geochemical data on the sediments of the Tyumen' Formation of the Shaim petroliferous region, Yamburg field (West Siberia), in: *Lithology and Geology of Fossil Fuels* [in Russian]. Izd. Ural'sk. Gos. Gorn. Univ., Yekaterinburg, Issue V (21), pp. 84–89.
- Goodarzi, F., Cameron, A.R., 1987. Distribution of major, minor and trace elements in coals of the Kootenay Group, Mount Allan, Alberta. *Can. Miner.* 25, 555–565.
- Gordon, S.A., Guren, G.F., Komissarova, L.N., Shatskii, V.M., 1968. Distribution of Sc in coal, in: *Studies on Rock Chemistry* (Trans. MGI) [in Russian]. Nedra, Moscow, pp. 32–37.
- Guren, G.F., Komissarova, L.N., Menkovskii, M.A., Shatskii, V.M., 1968. Distribution of Sc and P in coal. *Khimiya Tverdogo Topliva*, No. 6, 148–151.
- Kashirtsev, V.A., Zueva, I.N., Suknev, V.S., Mitronov, D.V., Syunduykov, Sh.A., Andreeva, G.V., Kapysheva, G.I., Livshits, S.Kh., Popov, V.I., 1999. Parageneses of rare-earth elements in the Mesozoic coals of the northern Lena basin. *Otechestvennaya Geologiya*, No. 4, 65–68.
- 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 (2), 135–148.
- Komissarova, L.N., 2006. Inorganic and Analytical Chemistry of Scandium [in Russian]. Editorial URSS, Moscow.
- Kryukova, V.N., Vyazova, N.G., Latyshev, V.P., 2001. Distribution of Sc in East Siberian coals. *Khimiya Tverdogo Topliva*, No. 3, 73–76.
- Lomashov, I.P., Losev, B.I., 1962. Germanium in Fossil Coals [in Russian]. Izd. AN SSSR, Moscow.
- Menkovskii, M.A., Komissarova, L.N., Guren, G.F., Shatskii, V.M., 1968. Distribution of Sc in the products of acid demineralization of hard coal, in: *Studies on Rock Chemistry* (Trans. MGI, No. 38) [in Russian]. Nedra, Moscow, pp. 38–42.
- Ren, D., Zhao, F., Wang, Y., Yang, S., 1999. Distributions of minor and trace elements in Chinese coals. *Int. J. Coal Geol.* 40 (2–3), 109–118.
- Savichev, O.G., 2003. Rivers of the Tomsk Region: State, Utilization, and Conservation [in Russian]. Izd. Tomsk. Politekh. Univ., Tomsk.
- Seredin, V.V., Finkelman, R.B., 2008. Metalliferous coals: A review of the main genetic and geochemical types. *Int. J. Coal Geol.* 70 (4), 253–289.
- Seredin, V.V., Arbuzov, S.I., Alekseev, V.P., 2006. Sc-bearing coals from Yakhlink deposit, Western Siberia. *Dokl. Earth Sci.* 409A (6), 967–972.
- Shvartsev, S.L., 1998. Hydrogeochemistry of the Supergene Zone [in Russian]. Nedra, Moscow.

- Swaine, D.J., 1964. Scandium in Australian coals and related materials. *Am. Chem. Soc. Preprints, Division of Fuel Chemistry*, 8 (3), 172–177.
- Torikova, M.V., Kudinov, Yu.A., Timofeev, P.V., 1996. Rare metals in oils, fossil coals, the products of their processing, and mineralized waters. *Razvedka i Okhrana Nedr*, No. 8, 21–23.
- Valiev, Yu.Ya., Gofen, G.I., Pachadzhayov, D.N., 1993. Trace elements in the Jurassic anthracites of the Nazar-Ailok deposit (central Tajikistan). *Geokhimiya*, No. 2, 243–251.
- Yudovich, Ya.E., 2003. Notes on the marginal enrichment of Germanium in coal beds. *Int. J. Coal Geol.* 56 (3–4), 223–232.
- Yudovich, Ya.E., Ketris, M.P., 2002. *Inorganic Substance of Coals* [in Russian]. UrO RAN, Yekaterinburg.
- Yudovich, Ya.E., Ketris, M.P., 2006. *Valuable Trace Elements in Coals* [in Russian]. UrO RAN, Yekaterinburg.
- Yurovskii, A.Z., 1968. *Mineral Components of Solid Fossil Fuels* [in Russian]. Nedra, Moscow.

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