International Journal of Coal Science & Technology (2022) 9:14
https://doi.org/10.1007/s40789-022-00486-0

RESEARCH

Structural and geochemical features of coal-bearing sediments and sources of rare element impurities in coals of the Rakovka depression, Primorsky Krai, Russia

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Received: 1 September 2021 / Accepted: 18 February 2022
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Abstract
There are known brown coal deposits in Primorsky Krai (Russian Federation), where coals contain rare elements (Ge, U, REE, etc.) up to industrial concentrations. One of the known metalliferous coals is the Rakovka coal-bearing depression, located on the southern edge of the Khanka (Prikhankaiskaya) Lowland, with an area of about 70 km^2. Rare-metal granites with a developed weathering crust are spread in its basement and flanks. The structural conditions forming the depression were studied using measurements of orientations of structural elements (layering, contacts, veins, and dikes) with regard to kinematic conditions of faulting. The coal and host rocks were sampled in sections in the cross strike of the coal seam. Granites and dikes cutting them were sampled by separate rock chip samples. The chemical composition and element content were determined for all samples. It was found that the adjacent rocks played a major role in the formation of the Rakovka rare-metal-coal deposit. The rare-elements enrichment is not associated with active tectonics, faults, and hydrothermal sources, as was previously assumed. Rather, it was caused by the hydrogenic and clastogenic removal of these metals from the weathering crust of granites of the depression's flanks and argillated basite dikes cutting the granites. The hydrogenic nature of the anomalous accumulation of U in sorbed form on organic matter of coals is confirmed by the predominant enrichment of low-ash beds. Rare earth elements entered coal seams both in mineral and dissolved forms. A model of REE and uranium input into the coal-bearing sediments of the Rakovka depression was proposed.

Keywords REE · Rare metal-coal deposit · Accumulation pattern · Tectonics

1 Introduction

There are known brown coal deposits in Primorsky Krai (Russian Federation), where coals contain rare elements (Ge, U, REE, etc.) up to industrial concentrations (Kostin and Meitov 1972; Seredin 2004, 2008; Kokovkin 2006, 2013; Sedykh 2008; Seredin and Dai 2012; Dai et al. 2016). These deposits of the rare-metal-coal type are unique complex objects. Previously, the reserves of some rare elements were calculated at several sites of these deposits. Now, there are contemporary analytical methods for assessing concentrations of rare elements. Due to this, it has become relevant to re-evaluate the reserves, study the factors of their accumulation, and create the models of formation of metalliferous coals. This work is focused on the partial solution of these issues.

The study of the Cenozoic coal-bearing depressions of the Southern Primorye began as early as the late nineteenth century and the first half of the twentieth century. The first data on the geological structure and coal-bearing deposits in Primorsky Krai date back to 1888–1894. The most fruitful stratigraphic research was carried out from the late 1960s to the late 1980s. During that period, the range of topics concerning the stratigraphy of Paleogene-Neogene deposits in Primorye, including coal-bearing ones, was considerably expanded and refined. A new stratigraphic scheme for the Paleogene-Neogene deposits of Primorye was published relatively recently (Pavlyutkin and Petrenko 2010). The issues of tectonics of Cenozoic depressions were discussed

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Published online: 16 March 2022

in (Golozubov et al. 2007, 2009; Zheldak et al. 2017). The metal content issues in the coals of Primorye were also addressed in a number of works (Kostin and Meytov 1972; Seredin 2004, 2008; Kokovkin 2006, 2013; Sedikh 2008; Seredin and Dai 2012; Kuzevanova 2014; Chekryzhov et al. 2016, 2017; Dai et al. 2016; Arbuzov et al. 2021).

In terms of significant accumulation of rare elements in coals and argillites accompanying coal-bearing depressions, researchers usually consider three main mechanisms: (1) weathering of metal-enriched granitoids and, and less frequently, other igneous and metamorphic rocks, their accumulation in residual weathering products and subsequent hydrogenic and clastogenic redeposition and accumulation; (2) explosive volcanism (more often alkaline) and enrichment of coals with rare-metal pyroclastics; and/or (3) endogenous hydrothermal activity. Ya.E. Yudovich (Yudovich 1978; Yudovich and Ketris 2006), who summarized numerous data for the world coals, believes that there are numerous factors influencing the geochemical background of coals, while the metal content in coals is caused, as a rule, by the predominant role of only a single factor. For example, the researchers who studied the rare-metal-coal objects in Primorye split into two groups, one of which believed the endogenous factor to be decisive in forming most of the studied ores (Kostin and Meytov 1972; Seredin 2004; Sedykh 2008), while the other group considered the exogenous factor as such (Kuzevanova 2014; Vyalov et al. 2021; Arbuzov et al. 2021).

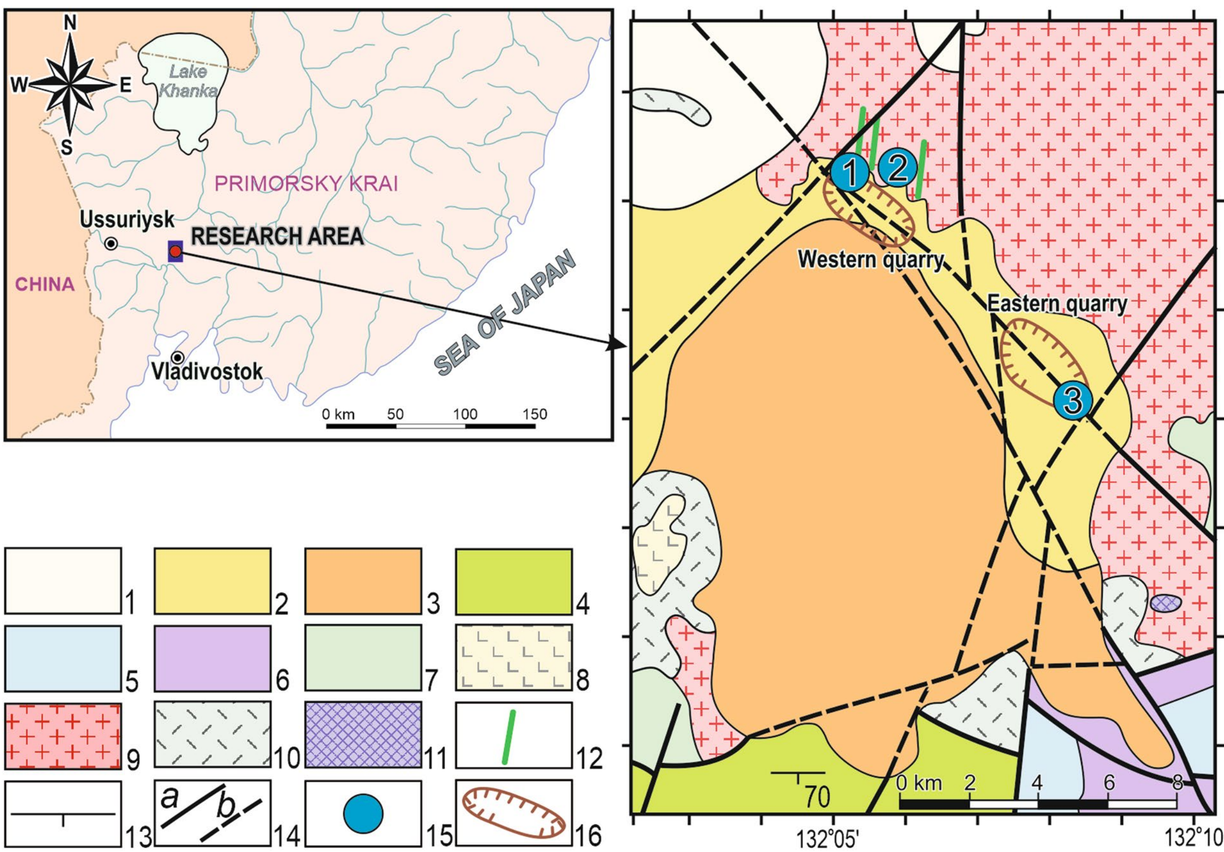

Fig. 1 The location and geological scheme of the Rakovka depression. 1—Quaternary deposits; 2—Late Miocene: poorly consolidated sandstones, pebbles, tuffites, diatomites; 3—Oligocene: sandstones, siltstones, tuffites, conglomerates, brown coals; 4—Early Cretaceous: sandstones, siltstones, conglomerates, gravelites, clayey limestones; 5—Middle Jurassic: sandstones, siltstones, tuffites; 6—Late Triassic: sandstones, siltstones, carbonaceous shales, hard coal beds; 7—Lower Cambrian: sandstones, quartzites. Magmatic rocks: 8—Pliocene basalts; 9—Late Permian granites; 10—Early Carboniferous rhyolites; 11—Early Carboniferous diorites; 12—Dikes of the basic composition; 13—Bedding elements; 14—Faults: proven (a) and probable (b); 15—Sampling points and their numbers; 16—Coal pits (Explanations are given in the text)

For the study we chose the Rakovka coal-bearing depression, known for metalliferous coals, with relatively active modern tectonics (Kokovkin 2006, 2013). Rare-metal granites with a developed weathering crust are spread in its basement and flanks.

The Rakovka coal-bearing depression (Fig. 1) including the Rakovka brown coal deposit, is located on the southern edge of the Khanka Lowland and has an area of about 70 km^2. There are several papers on this depression (Kokovkin 2006, 2013; Sedykh 2008; Seredin and Dai 2012; Chekryzhov et al. 2016), which provide some information on the genesis, stratigraphic partitioning, and elevated contents of valuable elements.

Magmatic rocks are widespread in the geological structure of the basement and flanks of the Rakovka depression. They are represented by the Late Permian granite complex and an Early-Middle Jurassic dike complex. There are very few magmatic rocks of the Early Carboniferous and Pliocene. Paleozoic and Mesozoic sedimentary and volcanogenic rocks are minor. The Cenozoic complex of the depression is subdivided into Oligocene coal-bearing strata and Upper Miocene sandy-pebble deposits with an admixture of pyroclastics. The Quaternary sediments are insignificant (Fig. 1).

Geologically and tectonically, the sediments of the central part of the depression lie predominantly horizontally, while the sides are inclined toward the center at an angle of 5°–10°. The southwestern and northeastern edges of the depression are complicated by tectonic faults with vertical displacement amplitudes of up to 50 m.

In the Rakovka brown-coal deposit, the main coal seams are represented by lignites with reserves of 220 Mt. In the section of the coal formation, the greatest continuity is found in coal seams contiguous with the middle monotonous sandy-clay horizon, and the least continuity is to the base and top of the section; the maximum coal saturation is observed in the central and northern areas of the depression. Uranium, REE, germanium, and a number of other rare elements anomalies were also found here (Sedykh 2008; Kokovkin 2013; Kuzevanova 2014; Chekryzhov et al. 2016).

Initially, the endogenous mechanism was assumed for uranium and REE enrichment in coals of the Rakovka depression (Kokovkin 2006, 2013; Sedykh 2008). Later, rare-metal granites and dikes were found on the northern edge of the depression (Seredin and Dai 2012). It was discovered that there are two types of rare elements input into coals within the Rakovka deposit: hydrogenic and clastogenic ones (Chekryzhov et al. 2016).

2 Methods

The main method for studying the structural conditions forming the depression was measurements of orientations of structural elements (layering, contacts, veins, and dikes) with regard to kinematic conditions of faulting. The displacement type and compression direction were determined by the morphology and features of the structural pattern and step-fold nature of layers. Conjugate systems, the orientation and paragenetic relations of shear and tension elements, and the character of contacts were considered.

The results of field observations were processed using the StereoNett 2.46 software (© Johannes Duster, Institute of Geology, Ruhr-Universitet-bochum. http://www.ruhr-uni-bochum.de). To estimate the distribution of maxima and identify dominant systems, the measurements were mapped on the upper hemisphere of the stereographic projection of the Wulff net. Rose diagrams were plotted for the steeply inclined (60°–90°) elements to identify the dominant directions of shear displacements most reliably, considering the kinematic characteristics, and to determine the stress field orientation based on the structural paragenesis of folded and faulted systems.

To understand in more detail the geochemical features and mechanisms of accumulation of rare elements in coal-bearing sediments in the Rakovka depression, we took samples in the operating coal pits in two areas of the depression: directly in the contact zone with the flanking rocks—the "West" section (Western quarry), and in the near-fault zone of the depression—the "East" section (Eastern quarry), where we carried out multiple measurements of orientations of the structural elements. Also, we took samples of granites flanking the depression and dikes that cut these granites. The dikes are of the basic composition with a developed weathering crust (Fig. 1).

The coal and host rock layers were sampled vertically; the thickness of each sample was 0.05–0.20 m. Granites and dikes cutting them were sampled by separate rock chip samples. The chemical composition was determined in the Laboratory of Analytical Chemistry of the Center for Collective Use of the Far East Geological Institute, Far Eastern Branch of the Russian Academy of Sciences (FEGI FEB RAS). Element content was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using an Agilent 7500 spectrometer (Agilent Techn, USA). The contents of 29 elements were also evaluated in parallel by the INAA method. The analysis was performed at the Nuclear Geochemical Laboratory of the International Research Scientific Educational Center (IRSEC) "Uranium Geology" at Tomsk Polytechnic Universtity (Tomsk, Russia). In the

"West" section, the REE group was analyzed by ICP-MS and the remaining elements—by neutron activation. In the "East" section, all elements were analyzed by ICP-MS only. Electron-microscopic analysis of samples was conducted in the Laboratory of Micro- and Nanoresearch FEGI FEB RAS using a dual-beam scanning electron microscope Tescan Lyra 3 XMH + EDS AZtec X-Max 80 Standart. The data were used to compile tables of contents of individual rare elements, create spider plots, graphs of average contents of impurity elements relative to their Clarkes in brown coal ash, and charts of the ash quantity to individual element quantities ratio.

3 Results

3.1 Structural features of the Rakovka depression

The results of previous studies of depressions of this type did not eliminate the possibility that the enrichment of coal deposits occurs due to their connection with ore-generating faults (Bersenev 1959; Kokovkin 2006, 2013; Sedykh 2008).

Structural studies were conducted in the Rakovka depression to identify traces of tectonic processes. As a result, the evidence of tectonic activity was found in the Southeast (SE) and Northwest (NW) sections in the Western pit of the Rakovka lignite deposit.

In general, the coal seams lie flat, but there are intensely dislocated areas with faults that show signs of displacement.

To identify the stress field that deformed the Cenozoic coal-bearing strata, we made structural observations. For this purpose, the orientation of layering and faults was measured, and the data were mapped on the upper hemisphere of the stereographic projection of the Wulff net.

One notable example of plicative dislocations is a sloping asymmetric anticlinal fold in the SE section of the field. It has a NW strike with a southwestward vergence and is complicated by a thrust in the axial part (Fig. 2a). The hanging wall is denuded and angularly unconformably overlain by Quaternary sediments more than 1-m thick (Fig. 2a). The distribution of stratification measurements, with a very wide range of dip angles, from gentle to steeply inclined to overturned, has a fairly consistent NW (300°–330°) strike (Fig. 2c), which, combined with the thrust, indicates their formation under the action of NE (30°–60°) compression.

Other examples of the coal seam dislocations are a series of NE (40°–50°) faults with amplitudes of about 1–2 m with bed reversals near the fault plane in the NW section of the deposit (Fig. 2b).

A comparison of the orientation of fault displacements with thrust in both sections of the deposit showed a paragenetic relationship of these dislocations formed under the action of NE (30°–60°) compression (Fig. 2c).

This means that the determined paragenetic connection between the folded and ruptured structures in the Rakovka lignite deposit formed in the NE stress field is consistent with the previously established regional Early Cenozoic stress field for Primorye and the Sikhote Alin as a whole (Golozubov et al. 2007, 2009; Zheldak et al. 2017).

3.2 Geochemical features of coals and flanking rocks of the Rakovka depression

The analytical data obtained from coal ashes and rock interlayers (Tables 1, 2) and granites flanking the depression (Table 3) were used to make plots of mean contents of elements-impurities in coal ashes in the "West" (Fig. 1, No. 1) and "East" (Fig. 1, No. 3) sections (Fig. 3) relative to their Clarkes in brown coals (Yudovich and Ketris 2006). We also created spider plots of REE distribution (Fig. 4) in coal ash from these sections and the flanking granites (Fig. 1, No. 2) normalized to UCC (Taylor and McLennan 1985).

By interpreting the obtained data, we can trace a number of patterns of rare elements distribution in the study area. There is a clear spatial and geochemical relationship between uranium- and REE-enriched coals and granites on the flanks of the depression, as well as argillated dikes that cut them. In the graphs of the average content of elements-impurities in ash coals (Fig. 3) there is a noticeable elevation of REE elements and uranium (compared to similar rocks in a similar geological environment), and associated components in the coals and rock interlayers of both sections. But the most enriched are coals of the "West" section located closer to the granites. Coal and rock interlayers sampled to the southeast ("East" section at some distance from the granite massif) have a slightly lower content of REE elements, despite the fact that sampling was carried out in the vicinity of the fault zone active in the Cenozoic.

Spider plots of REE content (Fig. 4) indicate a similar pattern of REE distribution in coals, rock interlayers and granites.

To study the REE distribution patterns in coal-bearing sediments of the Rakovka depression, we also plotted variations of ash content and concentrations of individual rare elements in the "West" and "East" sections (Fig. 5).

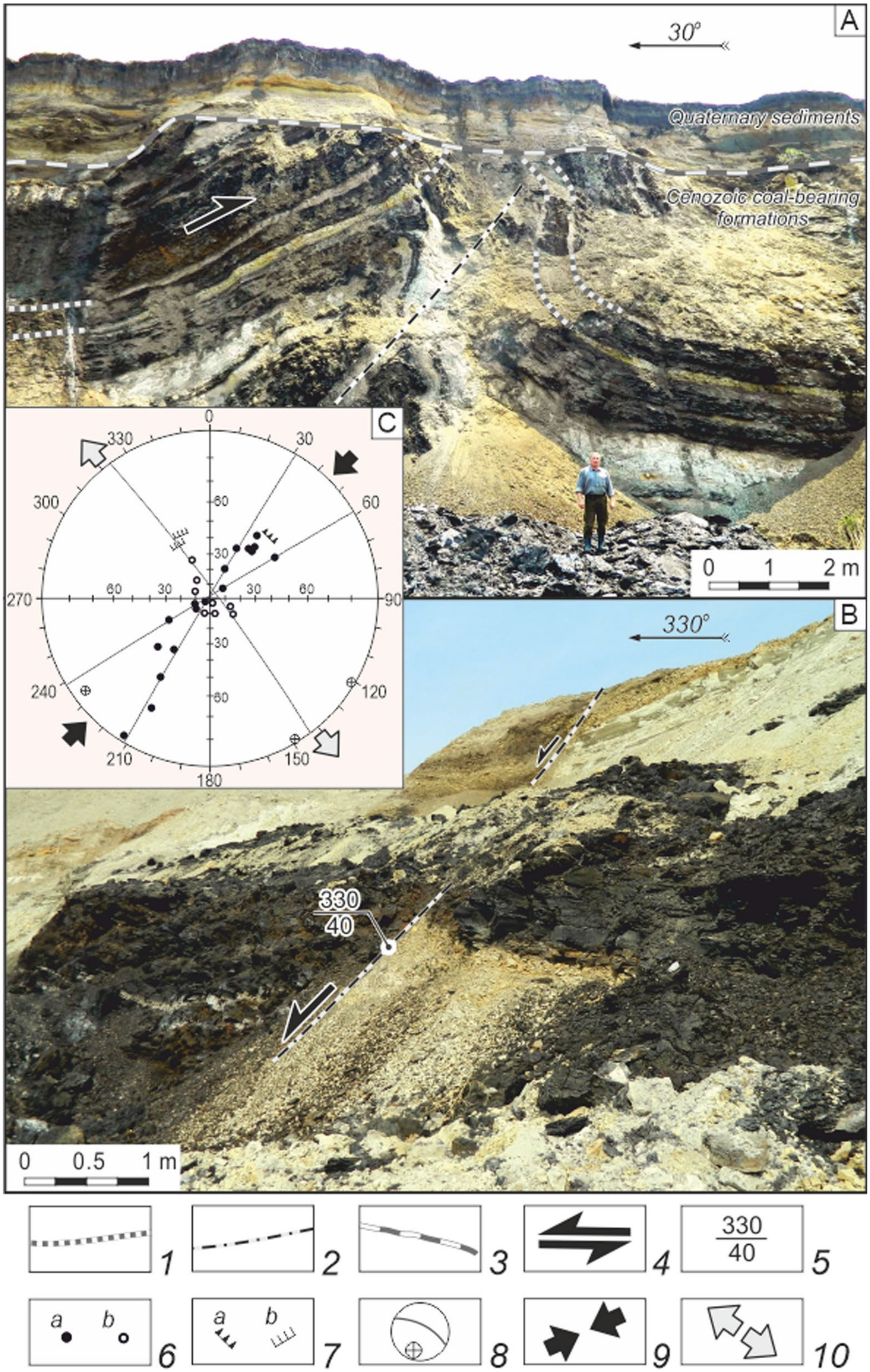

Fig. 2 Longitudinal compression **a** and extension **b** deformations formed by the northeastern (30°–60°) stress field. The diagram of structural elements **c**: 1—marker clay interlayers; 2—faults; 3—angular unconformity; 4—displacement direction; 5—elements of the fault plane: azimuth (numerator) and angle (denominator) of incidence. The diagram mapped on the upper hemisphere (Wulff net) shows: 6—poles of stratification planes in the southeastern (**a**) and northwestern (**b**) areas; 7—poles of thrust (**a**) and faults (**b**); 8—equators of layering belts (big circle arcs) and their axes; 9—compression orientation; 10—extension orientation

Table 1 Concentration of rare elements (g/t) in coal ash and rocks of coal-bearing sediments of the "West" section (analyzed by neutron activation and for REE group—by atomic emission spectrometry)

Sample	Ad (%)	Sc	Cr	Co	Zn	As	Rb	Sr	Sb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
9/1	4.49	31.7	122.0	21.6	125.0	72.2	< 2.0	1538	4.60	1.21	4152	424	734	86.4	324	60.5	3.29
9/2	5.73	23.6	122.0	55.9	70.9	117.0	< 2.0	1388	6.99	3.37	1699	302	548	61.5	226	40.1	2.93
9/3	4.90	40.4	166.0	32.9	78.8	102.0	56.3	629	5.17	5.49	2491	325	629	72.4	269	49.3	3.16
9/4	26.20	12.4	36.4	13.2	72.5	59.6	101.0	< 150	0.73	18.20	375	62.2	124	14.1	51.5	9.94	0.73
9/5	10.50	50.8	128.0	28.9	62.1	71.1	71.9	720	4.90	8.25	1825	276	586	64.5	236	44.2	2.93
9/6	6.91	32.9	121.0	93.0	112.0	99.6	47.7	815	3.57	7.46	2159	319	685	73.1	274	52.5	3.47
9/7	8.12	33.9	104.0	86.8	81.6	67.4	72.3	659	4.32	10.10	1993	265	583	61.4	245	50.3	4.94
9/8	13.90	15.5	57.9	40.3	75.9	30.2	91.2	346	0.93	15.70	831	137	305	33.5	140	31.6	4.24
9/9	7.16	49.1	132.0	86.8	74.1	88.5	89.6	547	16.70	12.80	1359	199	490	57.1	257	66.3	10.20
Cross-sectional average	9.77	32.3	110.0	51.1	83.7	78.6	75.9	831	5.32	9.17	1876	257	520	58.2	225	45.0	3.99

Sample	Ad (%)	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	Hf	Ta	Th	U	Br	Fe	Ca
9/1	4.49	62.70	10.50	66.4	462.0	12.60	37.60	5.73	36.80	5.27	7.85	3.94	54.7	697	60.8	23.60	10.8
9/2	5.73	37.80	5.97	37.5	251.0	7.32	21.50	3.40	23.70	4.88	6.16	< 0.10	20.8	2526	37.0	24.40	8.77
9/3	4.90	46.40	7.40	46.7	288.0	8.82	26.70	4.30	29.40	4.60	34.6	8.56	45.4	795	29.8	19.10	8.41
9/4	26.20	8.67	1.59	10.8	59.5	2.02	6.61	1.13	8.16	1.20	6.15	7.02	34.5	243	15.3	4.55	1.52
9/5	10.50	38.50	6.84	44.9	244.0	8.14	25.20	4.17	29.50	4.29	49.6	13.10	48.4	443	24.4	14.10	5.60
9/6	6.91	50.50	8.29	52.5	341.0	9.69	29.10	4.54	30.30	4.42	7.00	1.54	77.1	810	33.5	19.20	6.50
9/7	8.12	58.20	9.34	60.2	479.0	12.20	35.20	5.03	31.00	4.69	8.45	3.75	151.0	584	34.7	16.60	6.70
9/8	13.90	40.80	6.83	45.8	322.0	9.60	28.90	4.07	26.60	4.59	4.68	2.34	33.9	117	17.6	8.27	3.26
9/9	7.16	93.80	16.80	121.0	790.0	26.50	82.50	12.10	81.70	12.40	6.56	3.85	73.1	382	22.8	16.80	5.68
Cross-sectional average	9.77	48.60	8.17	54.0	360.0	10.80	32.60	4.95	33.00	5.15	14.60	5.51	59.9	733	30.7	16.30	6.36

The graphs (Fig. 5) show that concentrations of ytterbium, yttrium, and uranium rise with decreasing ash content, which is associated with the hydrogenous mechanism of coal enrichment, while light REE and zirconium could be introduced both in dissolved form and as a part of the clastogenic suspension during formation of coal deposits from the weathering crust of the flanking granites. Earlier it was suggested that there are two mechanisms for REE contribution to the coals of the Rakovka depression. The conclusion was based on the difference in the thorium-uranium ratio in different coal sections: a low ratio being characteristic of hydrogenous mineralization and a normal ratio being typical in most terrigenous sedimentary rocks (Chekryzhov et al. 2016).

A mostly hydrogenic mechanism of coal enrichment with heavy REE and uranium is also confirmed by the electron microscopy data. It was found that the coals contain no evident mineral forms of uranium and very few mineral forms of heavy REE and yttrium (only single xenotime grains). At the same time, there are many mineral phases (monazite and zircons)—carriers of light REE and zirconium (Fig. 6).

In the altered granites adjacent to the lignite, in addition to monazite observed in large quantities in the coals, there are also cerite and amorphous excretions in the form of ore crusts containing increased content of cerium and uranium (Fig. 7) formed by weathering of granites.

4 Discussion

The sampled coals and rock interlayers within the Rakovka depression are more enriched in REE and uranium in the "West" section. The section is located approximately 500-m away from the tectonic fault, but near the granite massif flanking the depression, which also has increased REE and uranium content. The samples collected in the "East" section are located directly in the zone of influence

Table 2 Concentration of rare elements (g/t) in coal ash and rocks of coal-bearing sediments of the "East" section (analyzed by atomic emission spectrometry)

Sample	Ash (%)	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Zr
RAK-1-1-18	70.3	3.99	22.7	119.0	46.9	4.06	6.48	28.2	72.3	51.7	164.0	49.6	53.9	188.0
RAK-1-2-18	36.1	11.50	36.1	157.0	67.5	18.70	24.00	58.4	152.0	55.5	121.0	104.0	134.0	179.0
RAK-1-3-18	46.1	6.61	27.4	163.0	69.2	11.20	6.41	57.5	91.0	49.2	150.0	73.9	90.5	227.0
RAK-1-4-18	83.6	3.38	16.2	88.5	31.8	2.63	10.40	20.6	80.2	37.2	158.0	42.2	37.2	215.0
RAK-1-5-18	39.2	7.09	28.1	134.0	51.0	14.30	20.80	64.5	63.5	52.7	112.0	77.4	113.0	117.0
RAK-1-6-18	77.2	3.33	21.9	101.0	39.8	3.66	1.30	38.1	62.7	53.4	186.0	38.6	55.3	189.0
RAK-1-7-18	23.2	9.38	35.0	96.6	42.5	21.80	8.78	124.0	79.3	72.6	76.3	120.0	159.0	119.0
RAK-1-8-18	7.64	43.90	62.1	190.0	66.5	121.00	33.70	88.8	45.1	41.3	43.9	420.0	497.0	201.0
RAK-1-9-18	91.4	2.43	14.7	71.1	30.8	3.84	13.70	18.7	74.9	28.5	151.0	49.8	30.7	289.0
RAK-1-10-18	22.8	20.20	33.1	128.0	56.2	25.20	22.30	66.3	39.2	45.8	131.0	166.0	198.0	208.0
RAK-1-11-18	34.1	75.90	69.8	183.0	66.8	219.00	53.9	127.0	145.0	46.5	48.2	458.0	634.0	182.0
RAK-1-12-18	94.7	2.49	10.7	54.3	23.1	2.46	7.19	35.9	91.3	22.6	131.0	68.2	36.1	396.0
RAK-1-13-18	72.9	1.07	3.58	18.7	5.81	3.27	8.98	28.6	173.0	6.55	16.7	9.0	10.6	21.9
RAK-1-14-18	26.6	11.50	27.5	145.0	58.2	15.70	13.50	55.0	244.0	50.9	101.0	79.5	159.0	149.0
RAK-1-15-18	88.4	3.46	18.6	95.9	36.7	2.79	11.40	41.0	42.9	38.4	175.0	44.1	55.5	215.0
Cross-sectional average	54.3	13.80	28.5	116.0	46.2	31.40	16.20	56.8	97.1	43.5	118.0	120.0	151.0	193.0

Sample	Ash (%)	Nb	Mo	Cd	Sn	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu	Gd
RAK-1-1-18	70.3	19.60	5.91	0.59	10.50	16.90	315.0	71.30	132.0	14.60	55.50	10.30	1.20	12.98
RAK-1-2-18	36.1	20.90	14.70	2.23	11.30	10.90	438.0	110.00	201.0	23.90	94.80	19.30	2.52	26.20
RAK-1-3-18	46.1	19.60	8.60	0.37	8.07	10.40	378.0	81.80	149.0	16.70	64.10	14.00	1.66	16.90
RAK-1-4-18	83.6	20.70	1.40	4.41	6.49	10.80	443.0	58.60	111.0	12.60	41.10	8.93	0.98	8.32
RAK-1-5-18	39.2	16.20	10.10	0.83	13.70	10.40	337.0	228.00	446.0	48.80	170.00	31.80	3.15	31.90
RAK-1-6-18	77.2	22.60	2.79	0.54	11.80	12.70	326.0	100.00	189.0	22.00	77.50	13.80	1.62	15.30
RAK-1-7-18	23.2	23.50	25.70	0.96	13.00	6.21	375.0	265.00	561.0	62.20	232.00	43.20	4.11	43.10
RAK-1-8-18	7.64	21.50	32.00	0.23	11.00	3.52	1219.0	158.00	309.0	42.70	206.00	60.10	8.18	77.50
RAK-1-9-18	91.4	18.00	0.47	0.24	4.33	10.60	521.0	46.80	91.1	10.20	37.50	7.59	0.84	6.79
RAK-1-10-18	22.8	16.30	21.20	1.27	9.74	16.10	577.0	145.00	309.0	36.20	151.00	34.70	4.51	40.40
RAK-1-11-18	34.1	23.20	84.60	0.70	12.80	4.59	1062.0	170.00	349.0	46.00	224.00	62.10	10.00	91.30
RAK-1-12-18	94.7	12.80	0.48	24.10	3.27	5.25	588.0	43.40	87.2	10.60	37.90	7.29	1.03	8.10
RAK-1-13-18	72.9	2.85	0.19	0.26	0.57	0.61	85.9	9.87	19.3	2.35	9.39	2.05	0.28	2.26
RAK-1-14-18	26.6	20.10	8.21	1.35	11.00	7.05	386.0	296.00	631.0	67.80	242.00	47.40	4.34	48.70
RAK-1-15-18	88.4	22.60	0.67	0.52	6.16	14.50	502.0	101.00	204.0	21.60	76.60	12.70	1.50	14.40
Cross-sectional average	54.3	18.70	14.50	2.57	8.91	9.38	503.0	126.00	253.0	29.20	115.00	25.00	3.06	29.60

Sample	Ash (%)	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U
RAK-1-1-18	70.30	1.20	9.14	1.84	5.37	0.73	4.98	0.69	5.14	1.63	2.83	53.9	38.90	13.10
RAK-1-2-18	36.10	3.54	22.10	4.41	12.20	1.83	10.30	1.27	5.58	1.58	2.70	82.1	64.50	30.00
RAK-1-3-18	46.10	2.48	14.30	3.22	8.39	1.31	7.74	1.04	6.68	1.47	2.55	42.8	54.30	15.40
RAK-1-4-18	83.60	1.04	6.99	1.19	3.64	0.64	3.80	0.45	5.94	1.73	2.17	46.1	31.40	11.00
RAK-1-5-18	39.20	3.75	23.40	3.86	9.43	1.30	7.66	1.10	2.96	1.07	1.89	71.4	61.60	17.60
RAK-1-6-18	77.20	1.87	10.80	1.71	4.98	0.93	4.60	0.73	5.01	1.65	2.46	64.9	44.50	15.50
RAK-1-7-18	23.20	5.67	30.20	5.57	14.50	2.07	12.10	1.54	3.29	1.57	3.04	98.7	106.00	53.80
RAK-1-8-18	7.64	11.50	76.50	15.30	45.10	6.30	38.00	5.20	4.24	1.13	4.38	98.5	117.00	39.50
RAK-1-9-18	91.40	0.77	5.14	1.04	3.06	0.51	3.17	0.55	7.49	1.46	2.31	37.9	23.90	7.64
RAK-1-10-18	22.80	5.69	35.40	7.26	20.70	2.81	18.00	2.73	7.07	1.58	3.09	64.5	94.90	52.90
RAK-1-11-18	34.10	14.40	97.40	21.40	62.40	9.38	52.20	8.27	6.03	1.67	10.10	164.0	182.00	87.30
RAK-1-12-18	94.70	0.98	6.10	1.13	3.53	0.65	3.32	0.59	9.98	1.16	1.50	25.8	19.20	6.24
RAK-1-13-18	72.90	0.33	2.10	0.40	1.18	0.17	1.04	0.13	1.15	0.21	0.24	10.7	3.86	0.98
RAK-1-14-18	26.60	6.17	34.10	6.18	16.30	2.36	15.30	2.12	4.65	1.69	2.09	63.3	119.00	34.80
RAK-1-15-18	88.40	1.83	12.10	2.07	5.47	0.76	5.35	0.73	6.23	1.73	3.28	39.9	30.90	10.70
Cross-sectional average	54.30	4.09	25.70	5.11	14.40	2.12	12.50	1.81	5.43	1.42	2.97	64.3	66.10	26.40

Table 3 Concentration of rare elements (g/t) in altered granites (GR-2-1-18, GR-2-2-2-18, GR-2-8-18), dike (GR-2-3-18, GR-2-5-18), and ore crust (GR-2-7)-18 from the depression flanks (analyzed by atomic emission spectrometry)

Sample	Be	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	As	Rb	Sr	Y
GR-2-1-18	9.15	2.40	4.94	2.31	0.92	2.63	18.00	32.2	22.2	4.01	393	20.5	82.9
GR-2-2-18	19.10	3.00	9.00	4.42	2.83	7.63	11.80	41.7	29.2	16.60	469	16.8	128.0
GR-2-3-18	38.40	18.90	105.00	94.40	22.30	28.70	26.50	456.0	25.7	17.10	528	54.0	541.0
GR-2-5-18	29.70	16.90	114.00	58.00	13.70	19.40	32.60	262.0	38.4	22.00	560	34.1	849.0
GR-2-7-18	54.40	12.50	90.20	27.20	94.50	35.90	49.00	223.0	178.0	78.60	520	30.9	2066.0
GR-2-8-18	12.20	1.40	3.01	2.04	0.62	1.47	9.90	457.0	23.9	6.53	390	22.8	57.3

Sample	Zr	Nb	Mo	Cd	Sn	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
GR-2-1-18	118	24.30	0.45	0.32	9.17	3.94	101.0	112.0	227.0	25.10	85.3	17.50	0.42
GR-2-2-18	177	53.90	1.56	0.44	23.90	4.50	125.0	77.6	608.0	18.90	67.3	17.80	0.36
GR-2-3-18	151	6.47	1.37	0.37	0.02	15.40	328.0	592.0	225.0	138.00	487.0	103.00	2.58
GR-2-5-18	175	39.10	1.28	0.58	9.44	17.20	180.0	383.0	600.0	80.00	297.0	63.00	1.66
GR-2-7-18	159	41.80	23.40	2.75	10.50	17.40	1043.0	539.0	26,280.0	169.00	641.0	220.00	4.88
GR-2-8-18	142	28.90	0.68	0.66	12.70	4.63	94.4	46.5	84.9	9.21	28.6	5.53	0.07

Sample	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Pb	Th	U
GR-2-1-18	17.50	2.70	15.60	2.87	8.50	1.42	8.47	1.14	5.98	1.68	1.62	40.9	39.40	10.7
GR-2-2-18	20.20	3.15	21.00	4.62	14.80	2.76	17.70	2.73	11.20	5.67	1.95	263.0	39.80	28.2
GR-2-3-18	77.40	12.70	74.50	15.30	45.00	7.28	45.30	6.95	3.12	0.23	4.21	136.0	2.95	79.7
GR-2-5-18	81.50	12.80	88.00	20.40	65.50	10.70	73.10	11.10	6.08	2.56	6.13	75.7	35.40	56.9
GR-2-7-18	297.00	57.10	380.00	78.50	247.00	41.60	288.00	38.10	6.77	3.73	12.30	3756.0	35.80	256.0
GR-2-8-18	5.92	1.08	8.34	1.79	6.34	1.17	7.02	1.00	6.44	1.76	1.23	28.3	42.40	12.8

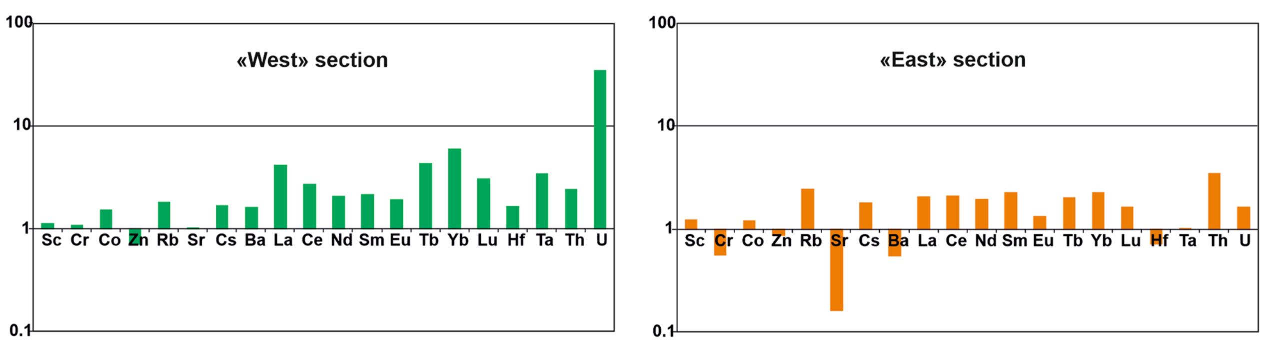

Fig. 3 Average content of impurity elements in ash of the Rakovka depression coals relative to Clarkes in ash of lignite coals of the world (Yudovich and Ketris 2006)

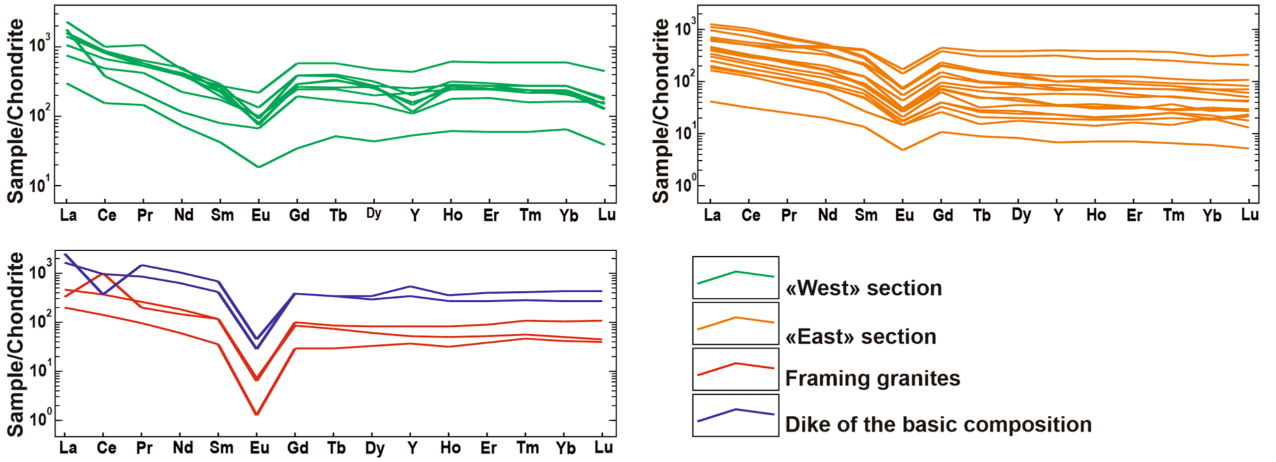

Fig. 4 REE distribution in coal ash, granites, and dike in the Rakovka depression normalized to UCC (Taylor and McLennan 1985)

of the fault, 1.5-km away from the granites. Coals here are very dislocated, being in an active tectonic zone. These two observations lead to the conclusion that the enrichment of coal seams with rare earth elements and uranium is associated primarily with the removal of elements from the weathering crust of granite massif and argillated dikes of the basic composition in suspended and dissolved form that cut the massif, rather than active tectonics and hydrothermal sources.

Thus, based on the studies of the anomalous content of REE and uranium in the coal-bearing sediments of the Rakovka depression, the following conclusions can be made:

(1) According to the structural studies, the modern active tectonics has no effect on the enrichment of coals with rare metals in the Rakovka depression and the main mechanism of contribution of elements is the terrigenous removal of these metals from granites subsynchronous to the coal formation.
(2) The enrichment of coals with a number of elements depends on their location relative to the granite massif, the composition of granites, and the presence of weathering crusts.
(3) At least two mechanisms of terrigenous enrichment with REE are present in the depression (clastogenic and hydrogenic), as indicated by the thorium-uranium correlation and the ratio of these elements to the ash content of coals.
(4) The anomalous enrichment of coals with uranium has a typically hydrogenic nature.

Based on the reconstruction of the stages of magmatism, sedimentation and metallogenesis, a generalized model of REE and uranium input into the coal-bearing sediments of the Rakovka depression is proposed (Fig. 8).

Late Permian rare-metal granites were cut by dikes of the basic composition in the Jurassic. After this, the granite massif and dikes were argillated and weathered with the formation of weathering crusts. Then, in the Oligocene, the

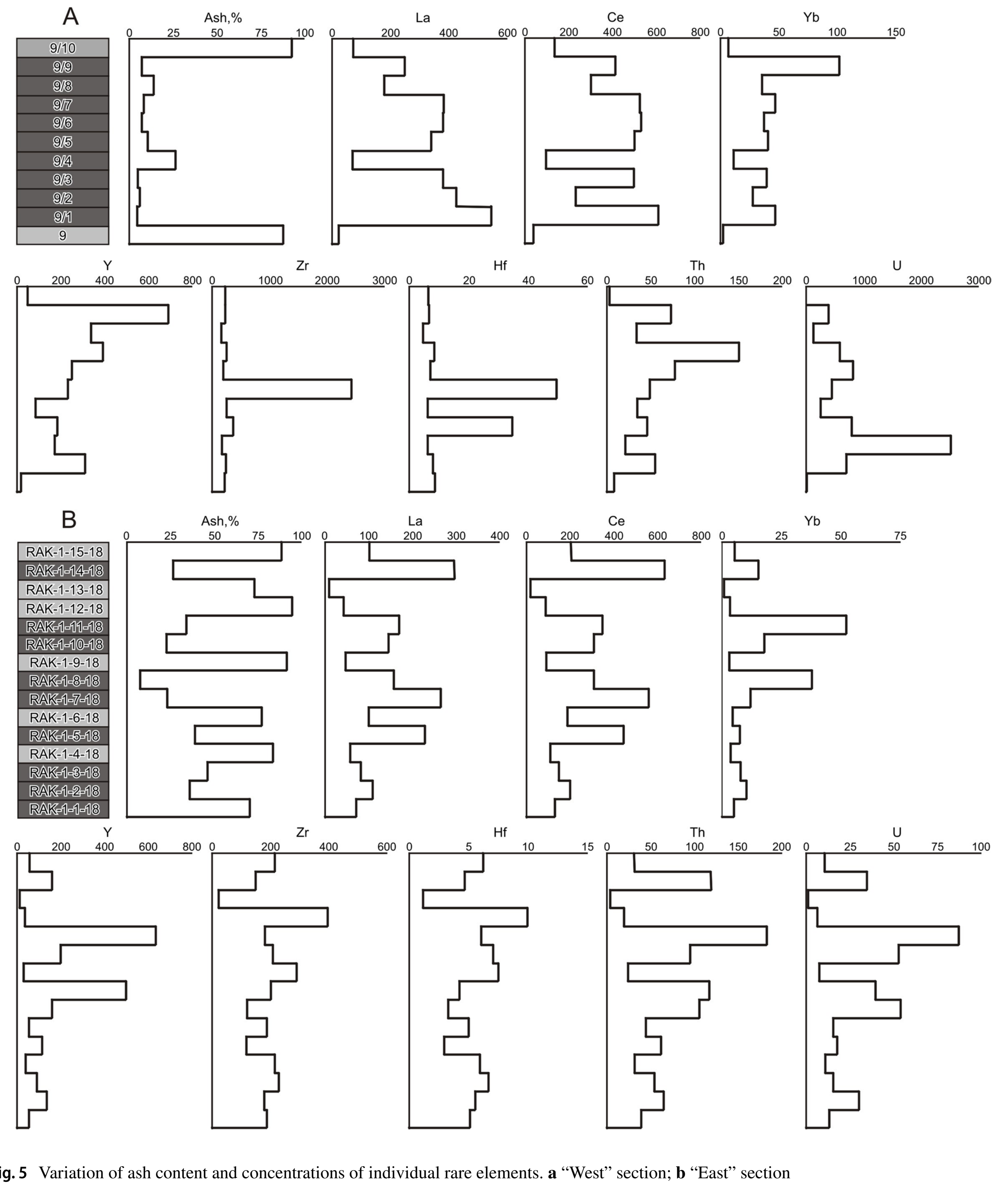

Fig. 5 Variation of ash content and concentrations of individual rare elements. **a** "West" section; **b** "East" section

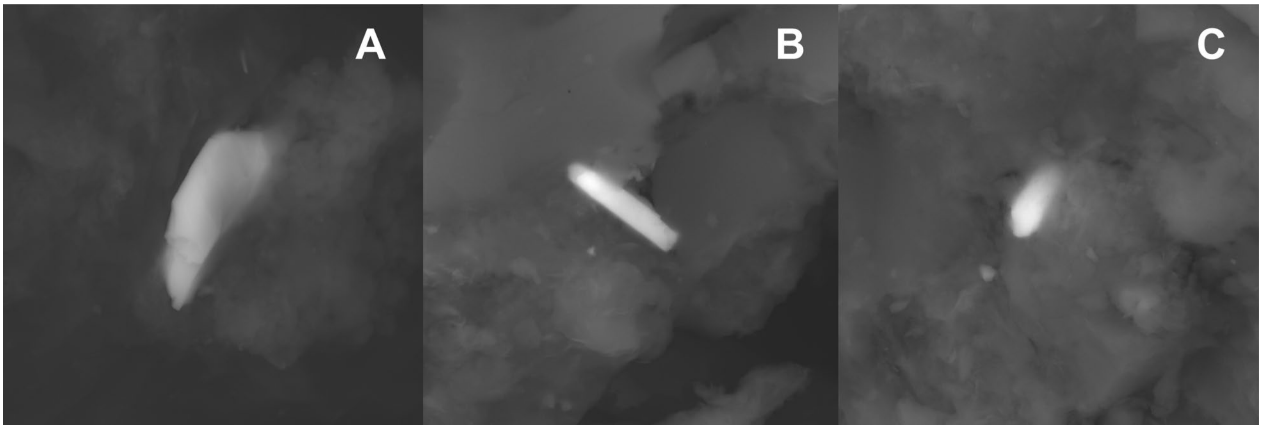

Fig. 6 Rare-metal microphases from metalliferous coals of the Rakovka brown coal deposit: **a** REE phosphate (monazite); **b** Zircon; **c** Yttrium phosphate (xenotime)

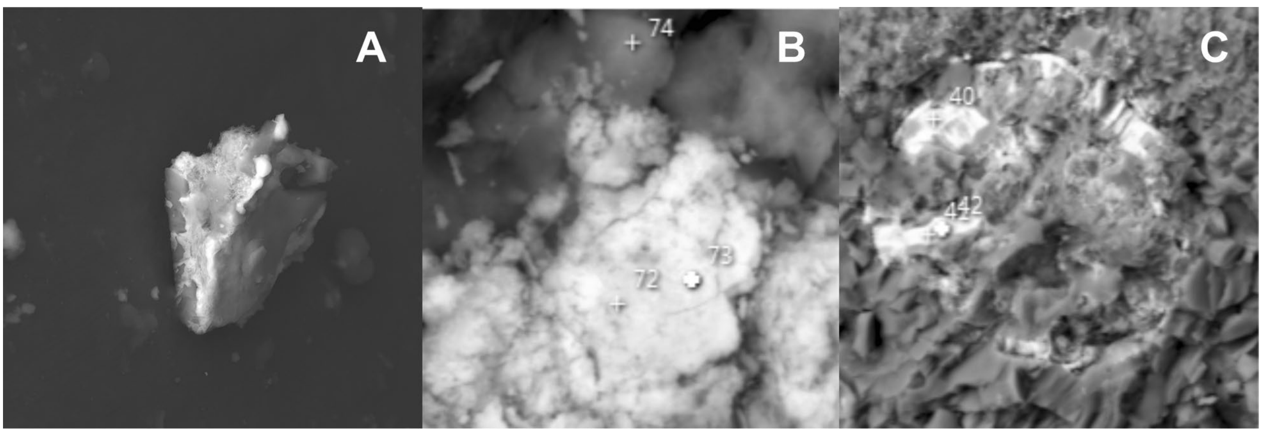

Fig. 7 Rare-metal phases from granites of the Rakovka massif: **a** Cerium silicate (cerite); **b** Manganese crusts with cerium; **c** REE fluorocarbonate (bastnasite)

sedimentation in the Rakovka Depression and formation of coal-bearing sediments began. At this time, peatlands received water draining weathering crusts of granites and dikes developed on the flanking of the depression. The water was enriched with REE, U, and other components in mineral and dissolved forms. The water-enriched peatlands with trace elements led to the formation of metalliferous coal near the granite massif (No. 6 in Fig. 8).

5 Conclusions

Based on the study of structural and geochemical features of coal-bearing sediments of the Rakovka depression, it was found that the flanking rocks played a major role in the formation of the Rakovka rare-metal-coal deposit. The enrichment with a number of rare elements is not associated with active tectonics, faults, and hydrothermal sources, as was previously assumed. It is caused by the hydrogenic and clastogenic removal of these metals from the weathering crust of granites of the depression's flanks and argillated basite dikes cutting the granites. The hydrogenic nature of the anomalous accumulation of U in sorbed form on organic matter of coals is confirmed by the predominant enrichment of low-ash beds. Rare earth elements entered coal seams both in mineral and dissolved forms. A model of REE and uranium input into the coal-bearing sediments of the Rakovka depression was proposed.

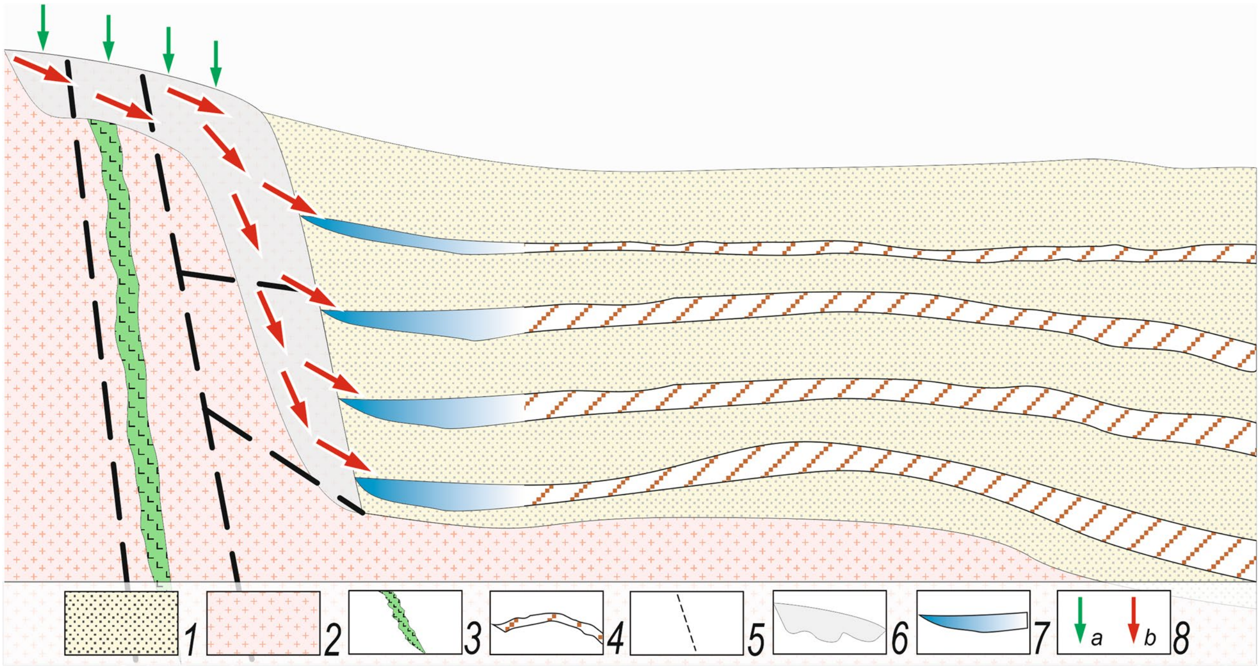

Fig. 8 A model of REE and uranium input into coal-bearing sediments of the Rakovka depression: 1—cenozoic sediments; 2—granites; 3—basic composition dike; 4—peat layers; 5—fractures; 6—argillated granites; 7—REE and uranium enrichment zones; 8—meteoric water (**a**), mineralized water (**b**)

Acknowledgements None.

Authors' contributions N. Popov and I. Chekryzhov, investigation, data curation, methodology, formal analysis. I. Chekryzhov, I. Tarasenko, S. Kasatkin and A. Kholodov, conceptualization, validation, supervision, writing review and editing. N. Popov, I. Tarasenko and I. Chekryzhov writing-original draft preparation. N. Popov and S. Kasatkin, software, formal analysis.

Funding The reported study was funded by RFBR and NSFC, Project Number 21-55-53013.

Availability of data and materials All data is included in the manuscript.

Declarations

Competing interests Authors declare that there are no competing interests.

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