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Modes of Occurrence of Uranium and Thorium in Coals and Peats of Northern Asia

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Abstract—Modes of U and Th occurrence in coal and peat have been studied. By examples of different fields of Northern Asia, it has been shown that the scattered form of uranium and thorium occurrence dominates in peat and brown coal. Along with the scattered mode associated with organic matter, U and Th form minerals of their own, represented by uraninite, coffinite, and monazite, in brown and bituminous coals and there are minerals in which they are present as an isomorphic accessory (zircon, xenotime, etc.). New data on the ratio between the mineral and organic forms of occurrence of uranium and thorium in coals and peats have been obtained. The change in the mode of U and Th occurrence through the peat–lignite–coal sequence has been revealed.

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INTRODUCTION

Studying the modes of occurrence of chemical elements in coal is of great importance for determination of the coal formation conditions, simulation of the behavior of chemical elements during coal combustion in thermal power plants (TPPs), and development of an integrated coal and ash processing technology.

The modes of occurrence of uranium in coal have been investigated for more than half a century. At the early stage in the 1940–1950s, uranium-bearing coals were of interest as a possible source of U for the nuclear industry; thus, uranium–coal deposits were mainly studied at that time [1, 2]. Subsequently, the attention to the forms of U in coals was determined by the potential radioecological hazard associated with the use of coal in power generation. It was found that the uranium occurrence forms along with the combustion technology determine the U behavior in the processes of coal utilization in thermal power plants [3].

The geochemistry of thorium in coals has been studied to a lesser extent because of its low content and a low demand for this element in the industry. Anomalous Th concentrations in coals are rare and have no commercial value. At the same time, recent studies have shown that during coal burning in TPPs, a large proportion of the metal can be carried over with flue gases into the atmosphere and have a negative impact on the environment [3, 4]. It was found that its concentration in flue gases depends on the thermochemical stability of organic and mineral components of coal, the Th carriers.

Quite a long period of investigation of U and Th in coals has resulted in accumulation of numerous, often conflicting data on the forms of their occurrence in coal of different types. What has been established is only the idea that U in coals is primarily associated with organic matter [5–10]. According to the summarized information [11] based on extensive analysis of vast world literature, coals with the U content below the crustal abundance (clarke) value are mainly characterized by the mineral form of occurrence, whereas uranium-rich coals largely contain it in the organic matter. In accordance with the general concepts of Th geochemistry in the hypergenesis zone, which are confirmed by experimental data in some cases, the idea of thorium occurrence in the mineral form in coals has held sway. Its main carrier and concentrator in coals can be monazite according to some data [6, 11] or silicates and aluminosilicates according to other data [4, 12, 13]. At the same time, there is information suggesting the possibility of concentrating a significant amount of Th and in the organic matter as well [4, 13–16].

The assessment of the balance of U and Th by forms of their occurrence in different types of coal at their different contents is the main problem that still remains unresolved. In addition, it is not clear how the ratio between the forms of occurrence of radioactive elements varies during diagenesis and coal metamorphism.

Table 1. Uranium content in peats

Peatland	Peat species	Degree of decomposition, %	A^d, %	Uranium content, ppm
Poludenovskoe	High-moor Eriophorum–Sphagnum	30	1.4	0.09
Aigarovo	High-moor Scheuchtzeria–Sphagnum	30	2.8	0.35
Vasyuganskoe-11	Low-moor sedge	30	4.3	0.16
Berezovaya griva	Transition-moor Sphagnum	20	5.6	0.36
Gusevskoe	Low-moor grass	40	8.2	0.32

EXPERIMENTAL

The U and Th occurrence forms were studied with the use of a set of methods. The role of organic and mineral matter in the concentration of uranium was investigated by the standard techniques of peat and brown coal separation into group components. The group composition of peat was studied by successive extraction of bitumens, water-soluble and easily hydrolyzable substances (WSS and EHS), humic acids (HA), fulvic acids (FA), and lignin–cellulose residue (LCR) according to the Instorf (Peat Research Institute) procedure [17]. Bitumens and humic acids were extracted from brown coal. Humic substances and bitumens were isolated from brown coal according to *GOST* (State Standard) *9517-94* and *GOST 10969-87*, respectively. The U content of all the group components of peat and brown coal was determined and the balance calculations were made. Isolated fractions were studied by instrumental neutron activation analysis (INAA) in the nuclear and geochemical laboratory at the Environmental Geology and Geochemistry Department, Tomsk Polytechnic University (TPU) (analyst A.F. Sudyko). Quality control was carried out by a parallel study of the original sample and its ash residue obtained by ashing the sample at 800°C; standard reference samples were also used. Altogether, the group composition of 6 peat samples and 13 samples of brown coal was studied.

For the same purpose, experiments on chemical demineralization of nine coal samples were carried out according to two standard procedures using ammonium acetate and dilute and concentrated acids (HCl, HF, and HNO_3) [18, 19]. All the products, including solutions, were analyzed for uranium.

To determine the U occurrence and distribution modes, extensive research by f-radiography was performed. Coal petrographic sections were used for this purpose. Poly(ethylene terephthalate) (PET) was used as a detector of induced fission fragments. Specimens were irradiation with a neutron flux of 10^{14}–10^{16} n/(cm^2 s) depending on the concentration of fissile elements. A special composition based on a sodium silicate adhesive with a known U content [20] was used as a standard.

The mineral forms of occurrence of uranium in some coal and coal ash samples were studied using a Hitachi S–3400N scanning electron microscope with a Bruker XFlash 4010 energy dispersive spectrometer in the "Uranium Geology" International Innovative Research-and-Education Center at the TPU Environmental Geology and Geochemistry Department. This instrumentation makes it possible to identify and visualize micro- and nanosized mineral forms and to determine their elemental composition. Forty five samples from different deposits of Northern Asia were studied.

The given set of analytical methods allows the occurrence forms and the conditions of concentration of uranium and thorium in coals to be determined with high reliability.

RESULTS AND DISCUSSION

Forms of Occurrence of Uranium in Peat

To assess the modes of occurrence of uranium in the early stages of coal formation, the group composition of low-, high-, and transition-moor peats with different ash contents and U concentrations below the clarke value was studied (Table 1).

According to balance calculations, the major portion (~60%) of U in fen peats with a high degree of decomposition of organic matter is associated with alkali-extractable humic substances (Table 2). For example, 58.5% of U is recovered into the total alkaline extract (HA and FA) of peat from the Gusevskoe peatland, whereas only 12.9% is in the insoluble residue. Low-ash bog peat from the Aigarovo peatland gives 48.5% of U in an alkaline extract and as small an amount as 10.9% in the insoluble residue. A significant amount of the metal in all cases is stripped into the fraction of easy hydrolyzable and water-soluble substances. Since this peat component is extracted by treating a sample with 4% HCl, adsorbed uranium must transfer into it. This faction is the main source of forming uranium minerals of its own in a reducing

Table 2. Recovery of uranium from group components of peat

Peatland	Scope of study	Yield of group components, % on *daf* basis	Uranium content, ppm	Uranium recovery, wt %
Poludenovskoe	Benzene bitumens	7.5	<0.01	0.1
	Water-soluble and easily hydrolyzable substances	38.6	0.062	26.6
	Humic acids	16.7	0.091	17.0
	Fulvic acids	15.2	0.042	7.1
	Lignin–cellulose residue	22.0	0.201	49.2
Aigarovo	Benzene bitumens	5.3	0.600	9.1
	Water-soluble and easily hydrolyzable substances	38.9	0.280	31.5
	Humic acids	17.3	0.520	25.8
	Fulvic acids	24.2	0.320	22.7
	Lignin–cellulose residue	14.3	0.260	10.9
Gusevskoe	Benzene bitumens	1.7	0.15	0.1
	Water-soluble and easily hydrolyzable substances	40.6	0.220	28.5
	Humic acids	26.1	0.670	54.7
	Fulvic acids	19.5	0.062	3.8
	Lignin–cellulose residue	12.1	0.340	12.9

environment according to the mechanism detailed in [21].

The role of bitumens in the concentration of uranium is negligible, emphasizing the leading role of the sorption mechanism of the initial accumulation of the metal in the organic matter.

In well-decomposed low-ash high-moor peat from the Poludenovskoe field, the role of humic acids in the concentration of uranium is much smaller. Here, the main mass of the metal (49.2%) contained in the residual fraction, which combines the mineral matter and the NaOH-insoluble lignin–cellulosic residue. But even in such a peat, humic acids (HA + FA) account for 24.1% of the metal. Together with uranium recovered with the WSS and EHS fraction (we believe the fraction to concentrate mainly the adsorbed metal), this makes total 50.7%. The residual fraction seems to contain U compounds with the organic matter along with the mineral form.

Consequently, well-decomposed peat with an ordinary uranium content is clearly dominated by occurrence forms associated with the organic matter. A decrease in the degree of decomposition is accompanied by lowering the contribution of humic acids to the concentration of uranium. In peats with a low degree of decomposition, especially with extremely low U accumulation levels, the role of organic matter in the concentration of the metal decreases. However, even in this case it is comparable with the role of the mineral matter.

Humic substances in most cases are U concentrators. A U carrier in weakly decomposed peats with a low yield of humic substances can be the residual fraction. However, since the total recovery of the metal into the alkaline extract (FA + HA) and the fraction of readily hydrolyzable substances exceeds 50% in all cases, we can conclude that the main U carrier in all types of low-ash peat is the organic matter. The metal concentrates both as strong complex humates and in the adsorbed form in this matter.

Thus, the results of the investigation of peats show that even in samples with a very low U content (0.09–0.36 ppm), the clastogenic material plays a secondary role in U accumulation. The further accumulation of uranium during the metamorphism of a peat deposit and its transformation into a coal seam can be due mainly to infiltrogenic processes, which are based on sorption concentration. Hence, it follows that the organic, rather than mineral, form of occurrence of uranium must largely prevail in low- and medium-ash immature brown coals with different U contents.

Forms of Occurrence of Thorium in Peat

The distribution of thorium in the group components of peat was studied using as examples five sam-

Table 3. Thorium content in peats

Peatland	Peat species	Degree of decomposition, %	A^d, %	Thorium content, ppm
Poludenovskoe	High-moor Eriophorum–Sphagnum	30	1.4	0.37
Vasyuganskoe-9	High-moor fuscum magellanicum	10	1.9	0.21
Vasyuganskoe-11	Low-moor sedge	30	4.3	0.44
Berezovaya griva	Transition-moor Sphagnum	20	5.6	1.1
Gusevskoe	Low-moor grass	40	8.2	0.32

Table 4. Recovery of thorium from group components of peat

Peatland	Group components	Yield of group components, % on daf basis	Thorium content, ppm	Thorium recovery, wt %
Poludenovskoe	Benzene bitumens	7.5	<0.010	0.1
	Water-soluble and easily hydrolyzable substances	38.6	0.043	4.4
	Humic acids	16.7	1.120	50.2
	Fulvic acids	15.2	0.302	12.3
	Lignin–cellulose residue	22.0	0.560	33.0
Vasyuganskoe-9	Benzene bitumens	2.8	<0.010	<0.1
	Water-soluble and easily hydrolyzable substances	52.5	0.016	4.0
	Humic acids	12.6	0.640	38.2
	Fulvic acids	10.6	0.240	11.7
	Lignin–cellulose residue	21.5	0.460	46.1
Vasyuganskoe-11	Benzene bitumens	5.0	0.005	0.1
	Water-soluble and easily hydrolyzable substances	33.0	0.066	5.0
	Humic acids	33.4	0.910	69.1
	Fulvic acids	8.6	0.010	0.2
	Lignin–cellulose residue	20.0	0.560	25.6
Berezovaya griva	Benzene bitumens	3.1	<0.01	0.1
	Water-soluble and easily hydrolyzable substances	46.0	0.180	7.5
	Humic acids	15.5	3.70	52.3
	Fulvic acids	20.1	0.98	18.0
	Lignin–cellulose residue	15.3	1.6	22.2
Gusevskoe	Benzene bitumens	1.7	0.017	0.1
	Water-soluble and easily hydrolyzable substances	40.6	0.011	1.2
	Humic acids	26.1	0.780	70.6
	Fulvic acids	19.5	0.110	7.3
	Lignin–cellulose residue	12.1	0.55	20.9

ples taken in peatlands southeast of the West Siberian Plain. The samples had different ash contents, degrees of decomposition, and formation environments. The ash content of the initial peat samples and the thorium content are shown in Table 3.

An analysis of the data presented in Table 4 shows that the major concentrators of Th in peat are alkali-extractable humic substances and residual fractions, which consist of the lignin–cellulosic residue nonhydrolyzable with 4% HCl and the mineral matter. The

Table 5. Thorium content in peats, humic substances, and their ashes

Peatland	Thorium content, ppm				ACF
	peat	HA	peat ash	HA ash	
Poludenovskoe	0.37	1.12	13.1	61.1	4.7
Vasyuganskoe-9	0.21	0.64	9.7	107	11.0
Vasyuganskoe-11	0.44	0.91	6.3	64.9	10.3
Berezovaya griva	1.10	3.70	17.1	368	21.5
Gusevskoe	0.32	0.78	3.6	66.0	18.3
Average	0.49	1.43	10.0	136	13.6

Note: ACF is the ash concentration factor (the ratio of the element concentration in the HA ash to that in the ash of original peat).

share of Th concentrated in the residual fraction varies from 20.9 to 46.1% and its accumulation factor in this fraction relative to the source peat ranges from 1.3 to 2.1. The highest recovery of the metal into this fraction is characteristic of low-ash, weakly decomposed high-moor peat.

Humic substances (HA) and fulvic acids (FA) concentrate 49.9 to 77.9% of total Th in peat. The highest recovery of the metal into this fraction characterizes samples of low-moor well-decomposed peat with an ash content of 5.6–8.3%.

The humic substances are main concentrators of thorium in peat. Its content in the ash of humic acids reaches 368 ppm, being on average 136 ppm (Table 5). The concentration factor in the fraction of humic substances relative to peat varies from 2.1 to 3.4. The ash concentration factor reaches 21.5. All these data provide convincing evidence for selective accumulation of Th by humic substances during peat formation.

The amount of Th recovered in the fraction of water-soluble and easily hydrolyzable substances is 1.2 to 7.5% of its total content in the samples. The bitumens concentrate a negligible fraction of the metal, not more than 0.1%. Consequently, humic substances (HA + FA) are not only a concentrator, but also the main carrier of Th in the peat, which account for more than half the mass of the metal in the studied samples.

The residual fractions are also Th concentrators, although they are of secondary importance as a carrier. In the residual fraction, thorium can occur in both mineral and organic forms, as a constituent of NaOH-insoluble substances.

From the experimental data obtained in this study, it can be concluded that the role of the mineral form of thorium in coals at the peat accumulation stage is greatly inferior to the role of the organic matter. The organic matter concentrates 50 to 78% of total Th in the test peat samples.

Note that the peats examined in this study had formed in harsher climates compared with the source organic matter of fossil coals.

However, it is known that there is a general trend of the degree of peat decomposition and, hence, the role of humic substances in peat mass to increase with changing climatic conditions from subarctic to subtropical. This correlation also suggests the increasing role of organic matter in the accumulation of U and Th in the warmer climate of Late Paleozoic and Mesozoic, compared to the current climate of Siberia.

Forms of Occurrence of Uranium in Brown and Bituminous Coals

The important role of organic matter in the concentration of uranium in coals is supported by the data obtained in the investigation of coals from different deposits of Northern Asia. Comparing the U content in coal ash and coal-bearing rocks of various coalfields and basins, we can conclude that the role of organic matter in the accumulation of uranium for coal is not less important than for peat. For example, the ash of coal from various deposits of the Minusinsk basin contains U in an amount of 3.3–4.2 times that in coal-bearing rocks [22]. If the host rocks are considered a source of clastogenic U in the coal of this basin, it is clear that most of the metal has accumulated as a result of sorption on the organic matter from aqueous solutions.

From the general concepts of the geochemistry of uranium, it can be concluded that the clastogenic matter does not play a determining role in its accumulation in ordinary coals. Taking the average ash content of coal to be 20% and the average U content to be 2.4 ppm in coals [23] and 3.2 ppm in sedimentary rocks [24], we can approximately calculate that the clastogenic matter contains on average about 27 wt % of the metal in coal. Even if we assume that the formation of coal involves only argillaceous sediments with a U content of 3.7 ppm, the contribution of clastogenic

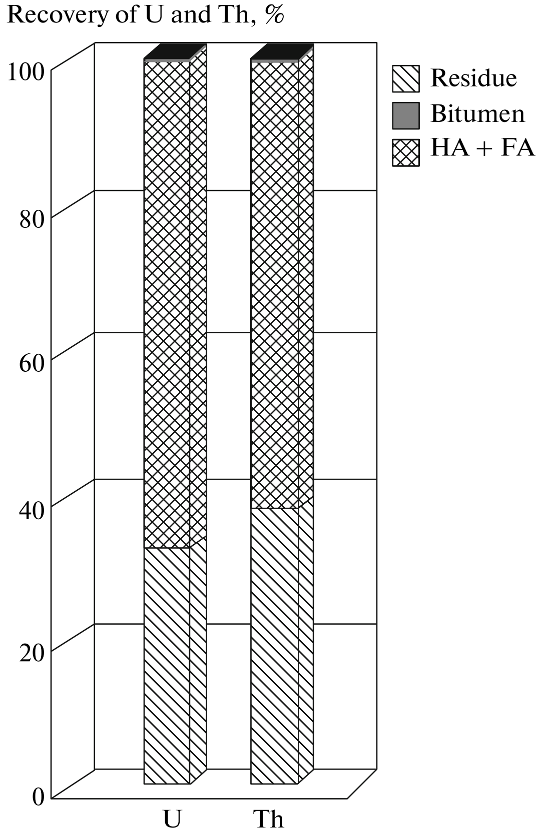

Fig. 1. Recovery of uranium and thorium into group fractions of brown coal.

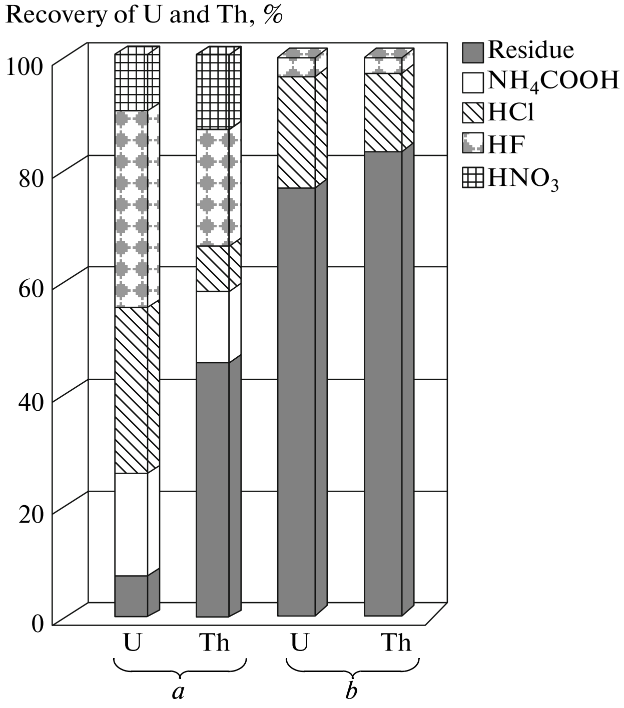

Fig. 2. Recovery of uranium and thorium into chemical demineralization products:
(a) brown coal and (b) bituminous coal.

matter will not exceed 31%. Thus, it follows that detrital uranium-bearing minerals, such as zircon and xenotime, are not the main form of its occurrence in coals. Clastogenic material cannot be a significant factor responsible for U accumulation in coals unless they have a high ash content or a very low U content.

Therefore, depending on the conditions of formation of coal seams, U can accumulate in them either as a result of sorption on organic matter or as a constituent of clastogenic material. However, even in the organic matter of coal, uranium can occur not only in the form of organometallic complexes and in the adsorbed state, but also in authigenic trace mineral form.

The type of mineral matter and its role in the accumulation of uranium can be estimated by studying the group composition and the chemical demineralization of coal and by radiographic techniques.

A study of the group composition of brown coal has shown that U in the coal is concentrated mainly in the organic matter (Fig. 1). Alkali-extractable humic and fulvic acids incorporated about 70% of the metal, whereas the residual fraction contained only 30%. According to data reported by various research groups, organic forms of occurrence of uranium associated mainly with humic substances prevail even in uranium-bearing lignite and brown coals [25–27].

Demineralization of brown coals has shown that the adsorbed U forms and simple and complex humates recovered from coal with ammonium acetate and concentrated hydrochloric acid play a significant role in these coals (Fig. 2). Sometimes, considerable amounts of U are associated with HF-soluble aluminosilicates and silicates.

Demineralization of bituminous coal by its treatment with concentrated HCl and HF did not result in full recovery of uranium (Fig. 2). The concentration of uranium in ash of the residual coal having an ash content of less than 1% exceeded 100 ppm in all cases, with its initial content in ash of the untreated samples varying from 1.7 to 3.2 ppm. The residual fraction retained about 3/4 of the total amount of U in the sample. It is characteristic that a significantly greater amount of U (35.1 ppm of dry residue) is leached with hydrochloric acid from grade D (long-flame) coal than from higher rank coal of the OS (hard caking) grade (20.6 ppm) despite the fact that its content in the untreated coal in the latter case is almost two times that in the former case. It is likely that as a result of coal metamorphism, the proportion of sorbed U forms decreased as a result of changes in the structure of

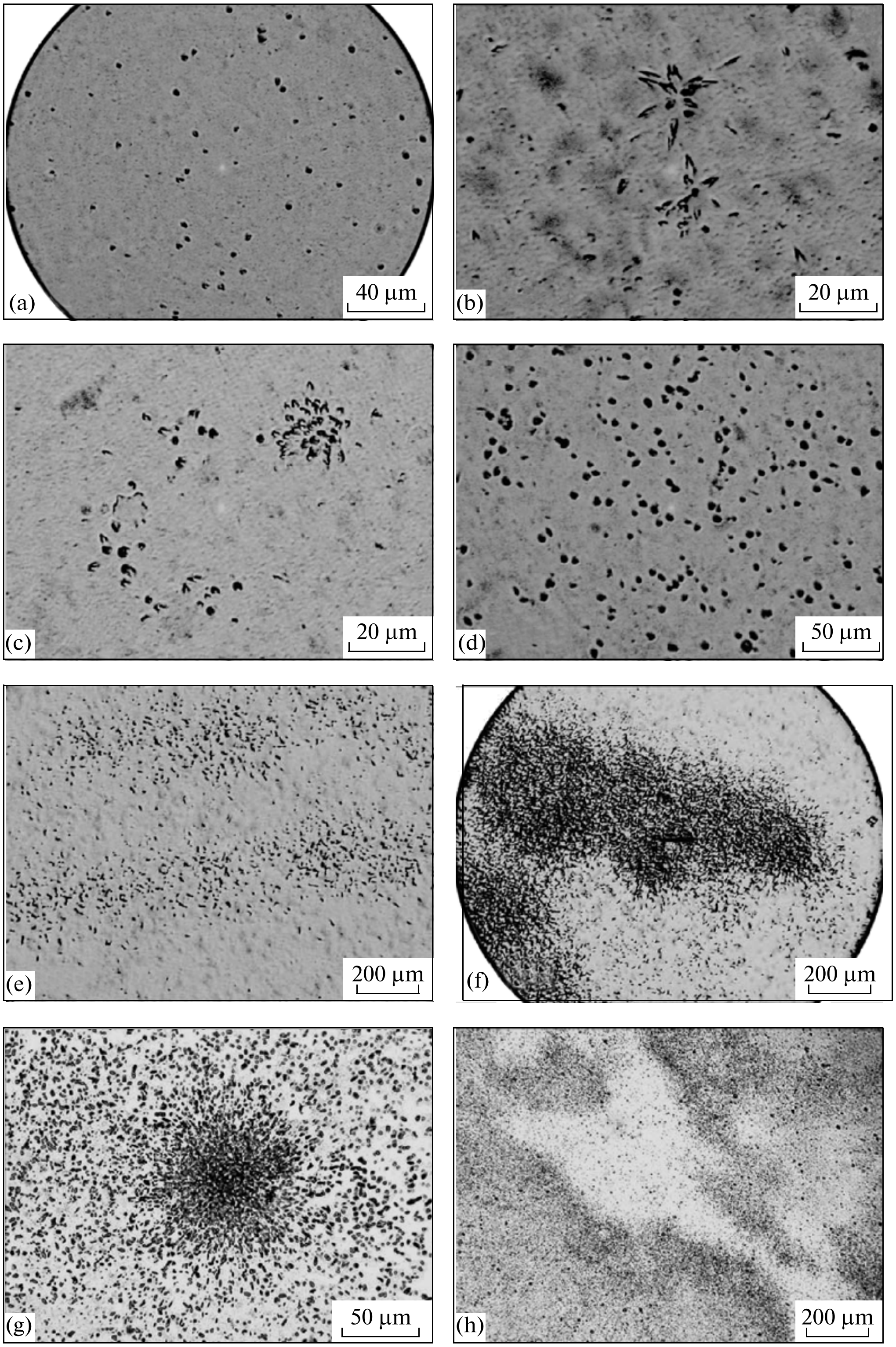

Fig. 3. Uranium distribution pattern in coals according to the f-radiography data (detector, PET): (a) Dvukharshinnyi bed. Uniform distribution; (b) Dvukharshinnyi bed. Inclusions of uranium-bearing accessories ("stars"); (c) bed I. Inclusions of uranium-bearing accessories ("stars") with a uranium-enriched zone; (d) bed III. Reticular distribution of uranium; (e) bed III. Linear uranium-enriched zones, (f) bed III. Clustering of tracks over phosphate; (g) Itatskii bed. Local clustering of tracks in uranium-bearing coals; and (h) Itatskii bed. Inhomogeneous distribution of tracks in uranium-bearing coals.

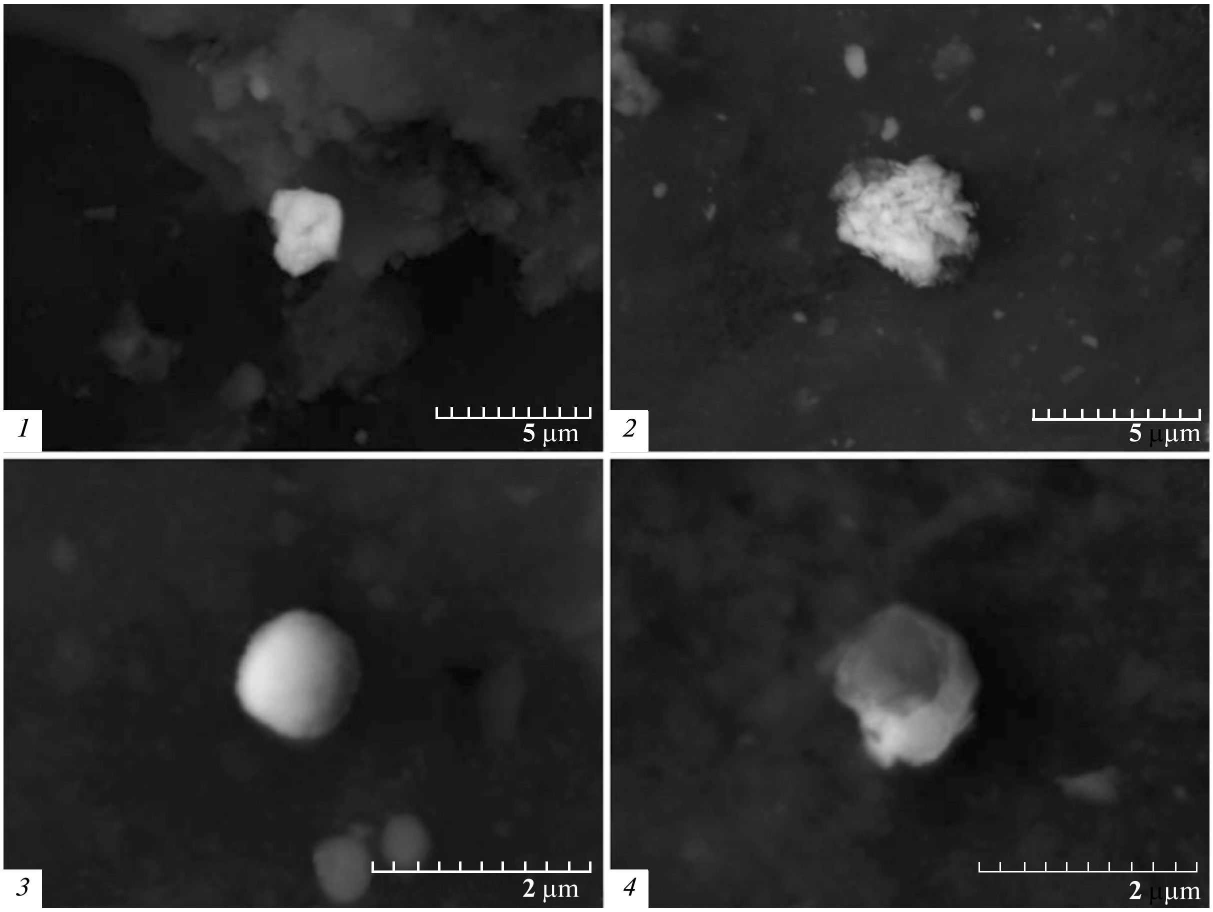

Fig. 4. Inclusions of uranium minerals in coals of the Irkutsk-basin Azeiskoe field: (*1*, *2*) coffinite and (*3*, *4*) uraninite.

organic matter, a reduction in its sorption capacity, and the formation of authigenic minerals.

These results also indicate that clay and other aluminosilicate minerals cannot be main U carriers in mature black coal, since the treatment of a sample with hydrofluoric acid, which dissolves these minerals, has led to the recovery only about 9% of the metal into solution. The treatment of coal with hydrochloric acid led to transfer on average less than 20% of total U to the dissolved state. This finding shows that the percentage of uranium sorbed on both the organic and mineral matter is small and the role of carbonates and certain silicates decomposable by concentrated HCl in its accumulation is minor. In the residual demineralized coal, U can concentrate in either acid-resistant accessory minerals or, presumably, in the form of complex humates. In addition, unstable authigenic minerals that are non-decomposable and inaccessible to acids because of too small dimensions could also be preserved in the coal matrix. Electron microscopic examination of the ash of these samples revealed the presence of numerous grains of zircon, monazite, and xenotime. Moreover, the zircon often had the form of allothigenic debris, whereas monazite and xenotime are characterized by a distinct character of authigenic precipitation.

Similar results were obtained by a group of American researchers [19], who studied ten samples of coals of different maturity collected from different US coalfields and basins using a different procedure of stepwise leaching. They found that extraction with hydrochloric acid recovers 40–60% of uranium from coals with a low degree of coalification (brown coals and lignite) and not more than 18% from bituminous coals. A 48% HF solution leached 26–27% of U in the former case and not more than 23% in the latter case. These results enabled them to conclude that U mainly occurs in the form of chelates in low-mature coals, about 25% in silicates or to a lesser degree in oxides.

One of the most reliable and illustrative methods for assessment of the forms of uranium occurrence in coals is f-radiography, which is extensively used for studying the distribution and levels of accumulation of U in rocks and minerals. This method has not been

Table 6. Average Th content in coals, coal ashes, and coal-bearing rocks from various fields of the Minusinsk coal basin

Coalfield	A^d, %	Thorium content, ppm			Accumulation factor*
		in coal	in coal ash	in cola-bearing rock	
Beiskoe	11.8	2.4	20.3	8.5	2.4
Izykhskoe	20.5	3.5	17.0	5.2	3.3
Chernogorskoe	14.6	2.6	17.8	4.6	3.9
Average over basin	17.6	3.1	17.6	6.4	2.8

* The ratio of thorium concentration in the coal ash to that in the coal host rock.

Table 7. Recovery of thorium into group fractions of grade D coal from the Minusinsk-basin Chernogorskoe field

Group composition of coal	Yield of fraction, % on *daf* basis	Thorium content, ppm	Th recovery into fraction,%
Original coal	100	0.65	100
Alcohol–toluene extract (bitumen)	4.7	0.018	0.1
Humic and fulvic acids	0.6	30.8	28.5
Residual coal	94.7	0.49	71.4

widely used in coal investigation practice in view of certain technical difficulties in its implementation [28].

Radiographic studies have shown that the bulk of U in coals with its low contents (close to the clarke value) occurs in the scattered form. Evenly scattered tracks are the most typical, although another type of distribution is met as well. Figure 3 exemplifies different types of uranium distribution in coal sampled from several coal seams of the Minusinsk, Kuznetsk, and Kansk–Achinsk basins. In coals with an ordinary U content, uniform scattering of the tracks dominates (Fig. 3a), but there are also single clusters (“stars”), indicating the presence of uranium-bearing accessories in the coal (Fig. 3b). In addition, single islets of irregularly distributed track clusters are observed (Fig. 3c) and, less frequently, microveinlet segregations (Fig. 3d), indicating postdiagenetic redistribution of U in the coal matrix. In the under-roof part of the seam, clusters of tracks in the form of linear zones are found (Fig. 3e). High-density clusters are noticed over certain areas sometimes (Fig. 3g).

In coals with an abnormal U content, the scattered form is prevalent as well. In this case, U is also characterized by inhomogeneous distribution, but it mainly concentrates as clusters in the organic matter (Figs. 3g, 3h), rather than in minerals of its own, not to mention occurrence as an isomorphic impurity in accessories.

Thus, the radiographic studies reveal the predominantly scattered distribution of uranium in coals with its both nearly crustal and anomalous abundances. Star-like uranium clusters are not widespread and play a secondary role in the overall balance of U in coal.

However, f-radiography does not make it possible to identify micro- and nanosized minerals.

The presence of radiographically undetectable micro- and nanominerals in coals was confirmed by examination of coals with different U accumulation levels with a high-resolution scanning electron microscope. It was found that U can form minerals of its own even in the case of its ordinary concentration in coals. This fact was established for the first time and requires detailed theoretical elaboration. So far, it has been assumed that uranium does form minerals of its own in coal at low U contents of up to 0.1%—the idea expressed as early as the middle of the last century [2]. In later studies, uraninite and coffinite were discovered in coals with a lower, although still abnormally high U content (>10 ppm) [11].

The size of mineral inclusions of uranium oxides and silicates in the test samples generally does not exceed 1.5 μm and only occasionally reaches 3 μm (Fig. 4). The shape of mineral segregations differs, although irregular isometric, sometimes shelly, entities are more frequently met.

Forms of Occurrence of Thorium in Brown and Bituminous Coals

The important role of organic matter in the concentration of thorium during coal accumulation,

Table 8. Thorium concentration in products of stepwise demineralization of coal

Product characteristic	Th content, ppm		
	bed XXX (grade D)	bed I (grade K)	bed IV–V (grade OS)
Original coal	2.7	1.1	11.5
Ash of original coal	16.2	9.6	53.9
Coal after treatment with conc. HCl	1.6	1.2	10.1
Ash of residual coal after treatment with conc. HCl	10	12	51.7
Residue after evaporation of HCl	32	1.6	32.9
Coal after treatment with conc. HF	1.4	1.3	11.7
Ash of residual coal after treatment with conc. HF	136	304	641
Residue after evaporation of HF	3.3	No data	2.7

which has been revealed for peat, is also confirmed by the results of the study of brown and bituminous coals. The relative contribution of organic matter to the concentration of the element can be estimated on the basis of regression equations derived for correlation of the Th content of coal with that of coal ash [29, 30]. Conditionally assuming that coals with an ash content of 2% contain only organic ash, we find on average about 65% of Th to be associated with organic matter in coals from the Minusinsk basin with an average ash content of 17.6%. This approximate calculation of the proportion of Th attributable to organic matter is in good agreement with the data on the Th contents in coal, coal ash, and coal-bearing rocks (Table 6).

For the Kuznetsk basin, the amount of thorium associated with organic matter is about 40% of the total amount in coal [22]. However, this does not mean that organic compounds in bituminous coals bound 40 to 65% of Th. It is more likely that Th had accumulated in the organic matter at the early stages of coal formation was later released as a result of changes in the structure of organic matter during the coalification process and joined the newly formed micro- and nanosized mineral phases. To verify this hypothesis, we determined the group composition of brown coal and performed electron-microscopic study of brown and black coals.

The group composition of brown coal was studied in 13 samples from different fields in Siberia and Mongolia. In these samples, 63% of Th is associated with alkali-extractable humic substances (HA + FA) and only 36% is found in the residual coal (Fig. 1). The role of bitumens in the concentration of the metal is negligible and accounts for as low as 1.0% of its mass in the sample. Since the initial samples had different ash contents (ranging from 6 to 30%) and different metal contents (of 0.9 to 7 ppm), it can be concluded that the organic matter at the brown-coal stage can be the major concentrator and carrier of thorium. These data indicate that Th can be prevalently bound to the organic matter not only in low-ash [4], but also in medium-ash coals. In this case, Th in both peat and brown coal forms stable coordination compounds, rather than undergoes simple physical adsorption on the organic matter. This conclusion is confirmed by an insignificant recovery of thorium into the fraction of easily hydrolyzable peat substances obtained by treating the samples with a 4% HCl solution. This treatment leads to the transfer of the ion-exchange forms of metals to the solution.

The role of humic substances in the concentration of Th is preserved until their final conversion into NaOH-insoluble compounds. This is evidenced by its unusually high content in residual humic acids extracted from the grade D coal (Table 7). The yield of humic substances (HA + FA) is as low as 0.6%, but their Th content reaches 30.8 ppm, which exceeds 3000 g per ton of ash at their ash content of about 1%; therefore, despite the low yield of humic substances, they bind 28.5% of the total amount of Th in the sample.

Thus, our data on the distribution of Th in the group composition of peats and brown coals show that humic substances act its main concentrator and, presumably, carrier until their complete disappearance due to condensation and transformation into the condensed structures of black coal.

The further transformation of the organic matter is accompanied by the loss of active functional groups, the release of associated metals, and the formation of individual mineral phases. Studying the forms of occurrence of Th in coals is complicated by a small size of the mineral phases, the complexity of their isolation from the coal matrix, and the impossibility of tangible evaluation of the contribution of organic complexes to its accumulation. To resolve this prob-

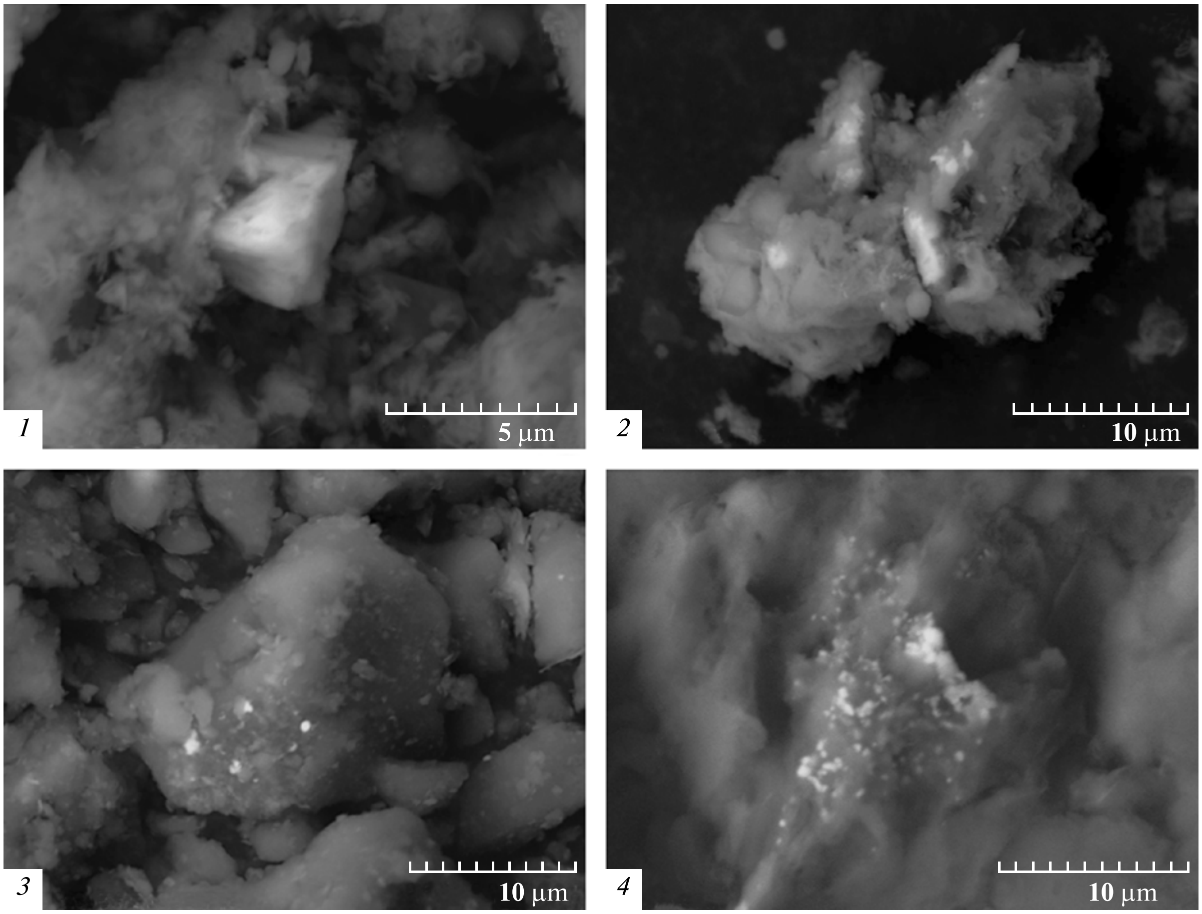

Fig. 5. Inclusions of thorium minerals (bright segregations) in coals and coal ashes:
(*1*) cheralite, coal ash, Azeiskoe field; (*2*) monazite, coal ash, Azeiskoe field; (*3*) monazite, coal, Azeiskoe field; and (*4*) monazite, graphitized coal, Tunguska-basin Fat'yanikhinskoe field.

lem, different indirect (selective dissolution, density separation of fractions, correlation analysis) and direct methods (electron microscopy) were used.

For an approximate assessment of the forms of thorium occurrence in bituminous coal, stepwise demineralization of samples of grade D (long flame), K (coking), and OS (hard caking) coals was carried out (Table 8).

The amount of Th in these samples varies from 1.1 to 11.5 ppm; that is, they represent coals with a Th content below, equal to, and above the crustal abundance.

In the first case, the grade D coal from the Kuzbas (bed XXXnp) lost about 40% by weight of its Th during the treatment with concentrated HCl. The amount of Th in the hydrochloric acid extract reached 32 ppm on a dry mass basis. The subsequent treatment of the coal sample with hydrofluoric acid did not lead to transfer of the metal to the solution. The amount of Th in the ash of demineralized coal with an ash content of the residual fraction of about 1% was 136 ppm. Its significant leaching from the coal during the treatment of the samples with concentrated HCl can be due to the occurrence of Th in rare-earth carbonates, in the adsorbed form on both the organic and mineral matter, and in the form of organic chelates. The assumption on chelation is consistent with the significant role of residual humic substances in Th buildup in coals of this grade (Table 7).

In the second case, the treatment of Th-lean grade K coal having a relatively low ash content (bed I of the Kuznetsk basin) with concentrated HCl and HF has not led to the leaching of the metal together with other ash-forming components and its contents in the residual low-ash product ($A^d = 0.4\%$) exceeded 300 g per ton of ash. This suggests that Th in the sample is bound in compounds non-decomposable by strong acids. Such compounds may be rare-earth, yttrium, and zirconium phosphates detected by electron microscopy study of ash of the residual fraction, as well as organometallic complexes.

Table 9. Thorium distribution in coal fractionation products

Specific gravity, g/cm^3	Yield of fraction, %	A^d, %	Th content, ppm		Th recovery into fraction, %
			in coal	in coal ash	
Grade 1B (Vtoroi bed of the Taldu–Dyurgun field)					
<1.2	82.99	10.7	0.7	6.5	68.9
1.2–1.3	11.86	13.7	1.4	10.2	19.7
1.3–1.4	1.24	32.8	2.2	6.7	3.2
1.4–1.5	0.60	38.0	1.7	4.5	1.2
1.5–1.6	0.06	36.5	1.8	4.9	0.1
1.6–1.7	0.16	43.3	1.5	3.5	0.3
1.7–1.8	0.44	65.7	2.2	3.4	1.1
>1.8	2.67	79.2	1.7	2.2	5.4
Grade D (Dvukharshinnyi bed of the Chernogorskoe field)					
<1.3	23.25	3.88	0.62	19.3	10.0
1.3–1.4	42.00	8.48	1.1	12.1	32.0
1.4–1.5	13.25	16.61	1.9	11.5	17.5
1.5–1.6	3.50	26.43	2.0	10.1	4.9
1.6–1.7	4.25	27.50	2.4	9.7	7.1
1.7–1.8	1.00	29.97	2.2	7.2	1.5
1.8–2.0	9.50	48.98	2.7	7.1	17.8
>2.0	3.25	88.17	4.1	5.1	9.2
Grade Zh (fat coal) (bed E-10 of the Osinovskoe field)					
<1.2	75.00	3.53	1.1	31.2	35.5
1.2–1.3	2.90	9.20	2.6	28.3	3.2
1.3–1.5	1.00	27.08	3.6	13.3	1.5
1.5–1.8	1.20	48.68	10.0	20.5	5.1
>1.8	9.80	83.27	13.0	15.6	54.7
Grade K (bed I of the Sibirginskoe field)					
1.2–1.3	96.06	2.81	1.1	41.5	78.0
1.3–1.4	0.48	11.90	1.6	19.3	0.6
1.4–1.5	0.38	17.33	2.1	16.0	0.6
1.5–1.6	0.20	33.42	5.7	15.8	0.8
1.6–1.7	0.38	48.01	7.2	12.9	2.0
1.7–1.8	2.24	48.70	10.0	19.6	16.5
>1.8	0.26	54.51	7.9	13.6	1.5
Grade OS (bed IV–V of the Ol'zherasskoe field)					
<1.3	32.8	4.6	1.6	35.0	9.7
1.3–1.4	21.9	10.1	2.8	24.0	11.3
1.4–1.5	9.4	20.0	5.1	20.0	8.8
1.5–1.6	6.1	29.0	7.2	27.0	8.1
1.6–1.8	9.0	40.9	9.6	14.0	15.9
>1.8	20.9	78.3	12.0	12.0	46.2
Grade T (lean coal) (bed II of the Aralichevskoe field)					
1.3–1.4	50.0	6.5	3.1	47.7	32.2
1.4–1.5	20.2	13.5	5.3	39.3	22.2
1.5–1.6	11.9	19.3	6.9	35.8	17.0
1.6–1.7	5.95	30.3	8.6	28.4	10.6
1.7–1.8	2.40	36.1	11.0	30.5	5.5
1.8–1.9	3.60	42.5	9.4	22.1	7.0
>1.9	5.95	43.4	4.4	10.1	5.4

The treatment of grade OS coal (bed IV–V) with concentrated HCl led to the recovery of as low as 8% of Th, and the subsequent treatment with HF recovered another 3%. An insignificant recovery of the metal from this coal, as in the previous case, is explained in terms of the occurrence of Th in acid-resistant minerals (rare-earth phosphates, zircon) and in part, presumably, in organometallic complexes.

The electron microscopy study confirms these conclusions. Numerous rare-earth phosphates, such as monazite, xenotime, and crandallite, were found in the ash of demineralized coal. These data agree with the results of study of bituminous coals from the United States. [11, 19].

The same minerals were also found in substantial quantities in samples of coal and coal ash from various fields of Siberia (Fig. 5). The most numerous small mineral inclusions of thorium-containing phosphates were detected in the ash of coals enriched abnormally in Th. Most frequently, such coals are found in contact with tonsteins. The size of the mineral segregations usually does not exceed 10 μm, most frequently being 1–5 μm. The amount of Th in phosphates considerably varies, ranging from a few fractions of percent to 17%. A mineral that has been identified as monazite according to its composition prevails (Fig. 5, images *2–4*). High-thorium phosphates from the monazite group similar to cheralite in composition are met rarely (Fig. 5, image *1*).

In order to substantiate the reason why Th in coals primarily occurs in the mineral form, it is necessary to explain the facts of distinct enrichment in thorium of low-ash coal and the ash of light coal fractions (Table 9). Analysis of fractions with different densities is commonly used to justify the association of the element with the organic or mineral matter of coal [31]. Its accumulation in the light or heavy fractions is considered an indication of the relation with the organic or mineral matter, respectively.

Ashes of the light fractions of coal are significantly enriched in the metal relative to those of heavy fractions. The amount of Th in the ash of light fractions in all the samples without exception is substantially, by a factor of 2–4, higher than that in the ash of heavy fractions. This suggests its selective accumulation in the coal organic matter. Calculations show that the light fractions (<1.5 g/cm^3) contain 10 to 93% of Th mass in coal. The maximum falls on Th-lean, low-maturity grade B1 brown coals with a medium ash content and low-ash coals of the K grade, and the minimum content is in high-ash coals of the OS grade. The data in Table 9 show that there is no correlation between the amount of Th in the fractions and the coal grade.

The association of Th with the light fractions of coal and the predominantly mineral form of its occurrence in bituminous coal do not contradict each other and reflect the evolution of thorium concentration modes. In the early stages of coal formation, the bulk of Th in low- and medium-ash peats accumulated in humic substances; consequently, the connection of the greater amount of the metal to the organic matter of coal is quite natural. During the course of coal evolution, Th was released from the organic mass. Its occurrence form changed accordingly, but the formation of minerals proceeded directly on the site because of a low migratory ability of Th. The small size of the minerals and their presence in pores and microcracks do not allow them to be isolated from the organic matter by the conventional gravity separation of coal into fractions.

The results of correlation analysis also support this mechanism of Th accumulation in coals. In general, thorium abundance is characterized by highly significant positive correlation with the ash content. For the coal ash, either weak negative correlation of Th with the ash content [29] or the lack of a significant relationship [30] is noted. This character of relationship suggests that Th accumulation in the organic matter was largely due to the decomposition of peat in the corrosive environment of clastogenic material. During the decomposition of the minerals, ash-forming elements that are the most mobile in an acidic medium were either driven out of the deposit or were utilized by peat-forming plants and hydrolyzate elements having a low mobility in the acidic environment accumulated. Migration of elements took place at the coal formation stages as well, which is evidenced by the formation of late carbonate and siliceous nodules, carbonate microveinlets, clastic siderite dikes, etc. This can explain the connection of elevated abundances of Th in the ash mainly with medium-ash coals. In low-ash coals, the amount of the original mineral matter is insufficient for accumulation of high concentrations of Th; in high-ash coals, the intensity of decomposition of clastogenic material decreases because of high alkalinity.

Note that this mechanism does not rule out Th getting into a peat bog in the dissolved state or in the form of colloids with surface and ground waters. The ability of an aquagenic inflow of the element to a coal seam is confirmed by the presence in the area of the West Siberian plate of low-ash peats with a Th content of up to 300 ppm in ash in the absence of other sources of its income to the peat bog. The abnormal Th-bearing capacity can be due to the presence of zircon–ilmenite and monazite placers in underlying Cretaceous–Paleogene sediments [32].

CONCLUSIONS

The integrated study of the forms of occurrence of U and Th in coals and peats has shown that the organic matter plays an important role in their concentration in all types of coal and peat. In the early stages of coal formation, the greater portion of U and Th in the majority of medium-ash peats and brown coals accumulates in the adsorbed form and in the form of strong humate complexes in the organic matter. During the course of coalification, the ratio between the U and Th occurrence forms varies because of alteration in the structure of the organic matter. The role of the mineral forms of their occurrence increases primarily owing to newly formed accessory minerals (uraninite, coffinite, zircon, monazite, apatite, xenotime, etc.).

In bituminous coals, the main Th concentrator minerals are rare-earth phosphates and other accessory minerals. Uranium in bituminous coals occurs in both mineral and scattered forms. Under certain conditions, uranium can form minerals of its own (oxides and silicates) in coals even with its very low content (<2 ppm). The main ash-forming aluminosilicate, silicate, and carbonate minerals (kaolinite, hydromicas, siderite, etc.) do not play a significant role in the concentration of U and Th in coals.

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REFERENCES

1. Breger, J.A., Deul, M., and Rubinstein, S., *Econ. Geol.,* 1955, vol. 50, no. 2, p. 206.
2. Vine, J.D., in *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy: Held in Geneva 8 Aug–20 Aug 1955*, vol. 6*: Geology of Uranium and Thorium*, New York; United Nations. 1956, p. 405.
3. Kizil'shtein, L.Ya., *Ekogeokhimiya elementov-primesei v uglyakh* (Environmental Geochemistry of Impurity Elements in Coals), Rostov-on-Don: SKNTs VSh, 2002.
4. Kizil'shtein, L.Ya. and Levchenko, S.V., *Geokhimiya,* 1995, no. 6, p. 874.
5. Finkelman, R.B., *U.S. Geol. Surv. Open-File Rep.*, 1981, nos. 81–99, p. 322.
6. Finkelman, R.B, in *Organic Geochemistry,* Engel, M.H. and Masco, S.A., Eds., New York: Plenum, 1993, p. 593.
7. Finkelman, R.B, in *Environmental Aspects of Trace Elements in Coal*, Swaine, D.J. and Goodarzi, F., Eds., Dordrecht: Kluwer Academic, 1995, p. 24.
8. Swaine, D.J., *Trace Elements in Coal*, London: Butterworths, 1990.
9. Vassilev, S.V., Eskenszy, G.M., Tarassov, M.P., and Dimov, V.I., *Geol. Balcanica,* 1995, vol. 25, no. 3/4, p. 111.
10. Karayagit, A.I., Gayer, R.A., Ortae, F.F., and Goldsmith, S., *Int. J. Coal Geol.*, 2001, vol. 47, p. 73.
11. Yudovich, Ya.E. and Ketris, M.P., *Neorganicheskoe veshchestvo uglei* (Inorganic matter of Coal), Yekaterinburg: UrO RAN, 2002.
12. Queral, X., Fernandez-Turiel, J.L., and Lopez-Soler, A., *Fuel,* 1995, vol. 74, no. 3, p. 331.
13. Dai, S., Li, D., Chou, C.L., et al., *Int. J. Coal Geol.*, 2008, vol. 74, no. 3/4, p. 253.
14. Ryazanov, I.V. and Kapaturin, G.G., in *Materialy po geologii i poleznym iskopaemym Severo-Vostoka evropeiskoi chasti SSSR. Sb. 8* (Papers on Geology and Mineral Resources of the Northeast of the European Part of the Soviet Union), Syktyvkar: Komi Knizhnoe Izd., 1976, p. 409.
15. Eskenazi, G., *Godishnik na Sofiiskii Universitet "Sv. Kliment Orkhidski." Geologo-Geografski Fakultet*, book 1: *Geology*, vol. 1, p. 43.
16. Dai, S., Ren, D., Chou, C.L., Li, S., and Jeang, Y., *Int. J. Coal Geol.*, 2006, vol. 66, no. 4, p. 253.
17. Lishtvan, I.I. and Korol', N.T., *Osnovnye svoistva torfa i metody ikh opredeleniya* (Basic Properties of Peat and Methods for Their Determination), Minsk: Nauka i Tekhnika, 1975.
18. Radmacher, W. and Mohrhauer, P., *Brennstoff-Chem.,* 1955, vol. 36, no. 15/16, p. 236.
19. Finkelman, R.B., Palmer, C.A., Krasnow, M.R., et al., *Energy Fuels,* 1990, vol. 4, no. 6, p. 755.
20. Sarnaev, S.I. and Rikhvanov, L.P., Abstracts of Papers *3-e Vsesoyuznoe Radiogeokhimicheskoe soveshchanie, Tomsk, 1991* (The 3rd All-Union Conference on Radiogeochemistry), Novosibirsk: OIGGM SO AN SSSR, 1991, p. 75.
21. Kochenov, A.V., Korolev, K.G., Dubinchuk, V.T., and Medvedev, Yu.L., *Geokhimiya,* 1977, no. 11, p. 1711.
22. Arbuzov, S.I. and Ershov, V.V., *Geokhimiya redkikh elementov v uglyakh Sibiri* (Geochemistry of Rare Elements in Siberian Coals), Tomsk: D-Print"P, 2007.
23. Ketris, M.P. and Yudovich, Ya.E., *Int. J. Coal. Geol.,* 2009, vol. 78, no. 2, p. 135.
24. Grigor'ev, N.A., *Geochem. Int.*, 2003, no. 7, p. 711.
25. Ilger, J.D., Ilger, W.A., Zingaro, R.A., and Mohan, M.S., *Chem. Geol.,* 1987, vol. 63, no. 3/4, p. 197.
26. Meunier, J.D., Landais, P., and Pagel, M., *Geochim. Cosmochim. Acta*, 1990, vol. 54, no. 3, p. 809.
27. Khomentovskii, B.N., Ovseichuk, V.N., and Vakhrushev, V.A., *Gornyi Zh.,* 1993, no. 3, p. 40.
28. Volostnov, A.V. and Arbuzov, S.I., in *Radioaktivnost' i radioaktivnye elementy v srede obitaniya cheloveka: Materialy II Mezhdunarodnoi konferentsii, Tomsk, 2002* (Proceedings of II International Conference on Radio-

activity and Radionuclides in the Environment, Tomsk, 2002), Tomsk: Tandem Art, 2004, p/ 119.

29. Arbuzov, S.I., Ershov, V.V., Potseluev, A.A., and Rikhvanov, L.P., *Redkie elementy v uglyakh Kuznetskogo basseina* (Rare Elements in Kuznetsk Basin Coals), Kemerovo, 2000.
30. Arbuzov, S.I., Ershov, V.V., Rikhvanov, L.P., et al., *Redkometall'nyi potentsial uglei Minusinskogo basseina* (Rare-Element Potential of Minusinsk Basin Coals), Novosibirsk: Filial "GEO", 2003.
31. Shpirt, M.Ya., Kler, V.R., and Pertsikov, I.Z., *Neorganicheskie komponenty tverdykh topliv* (Inorganic Components of Solid Fuels), Moscow: Khimiya, 1990.
32. Rikhvanov, L.P., Kropanin, S.S., Babenko, S.A., et al., *Tsirkon-il'menitovye rossypnye mestorozhdeniya kak potentsial'nyi istochnik razvitiya Zapadno-Sibirskogo regiona* (Zircon—Ilmenite Placer Deposits as a Potential Source of Development of the Western Siberia Region), Kemerovo: OOO "Sars", 2001.