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Modes of Occurrence of Rare-earth Elements (La, Ce, Sm, Eu, Tb, Yb, Lu) in Coals of Northern Asia[1]

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Abstract—The modes of occurrence of six rare-earth elements (La, Ce, Sm, Eu, Yb, and Lu) in low-rank coals (lignites and sub-bituminous coals; also referred to as brown coals) from different deposits of Siberia, the Russian Far East, Kazakhstan, and Mongolia were studied using two selective leaching methods. Selective extraction of organic compounds included the extraction of organic substances with minimal effects on the mineral matter was only used for low-rank coals. The second method of the selective leaching of rare-earth elements (REE) from mineral matter in brown and bituminous coals used ammonium acetate, conc. HCl, conc. HF and 10% HNO_3. The content of the six rare-earth elements in all phases (bitumen, humic acids, and residues) was determined by INAA. It was found that in the early stages of coal formation the bulk of the REE was associated with the organic matter primarily humic substances. Release of REE from humic substances during coalification results in the formation of authigenic minerals. The proportion of the REE in organic forms is gradually reduced in the coalification process until there is a complete REE transition to mineral phases in anthracite and graphite. These investigations showed that the alteration of modes of occurrence of La, Ce, Sm, Eu, Yb, and Lu from primary organic compounds to primary minerals occurred simultaneously with the organic matter alteration over the coalification process from peat to anthracite.

Keywords: Coal, rare earth elements, modes of occurrence, organic compounds, authigenic minerals, transformation of modes of occurrence

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INTRODUCTION

The modes of occurrence of chemical elements in coal can be important indicators of the conditions of their formation and the nature of geochemical anomalies. They are also important factors in determining the technology for the extraction of valuable elements from coal and coal by-products. Determining the modes of occurrence of elements in coal can be difficult due to the many different possible modes of occurrence and also due to the difficulty of quantifying the modes of occurrence. Determining the modes of occurrence is especially important for the rare earth elements (REE) because extracting them from coal and coal ash for use in a wide range of technological devices is receiving global attention [1–4].

There has been significant progress in the study of the modes of REE occurrence in coals for three decades after a publication of [5]. Until recently there has been the notion in the literature that the bulk of the REE in coal was concentrated in inorganic compounds, mainly adsorbed on clay minerals, as isomorphous components in various minerals (especially clays) and in the rare earth phosphates and aluminophosphates [5–15]. Calculations performed by Finkelman [5] for the bituminous Waynesburg coal (West Virginia, USA) based on electron-microscopy data showed that micro-inclusions (1-2 microns) of rare-earth phosphates (monazite, xenotime) and aluminophosphates (crandallite group minerals) were able to provide 100% of the total content of REE in the coal. Using a suite of bench samples from a Texas lignite strip mine, Finkelman estimated that no more than 10% of the total REE in the lignite had an organic association; the remaining 90% of the REE were associated with REE-bearing minerals.

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[1] The article was translated by the authors.

In a recent attempt to quantify the modes of occurrence of elements in coal R.B.Finkelman et al. [16] concluded that in bituminous coals 70% of the light REE (La, Ce, Nd, and Sm) and Y were in phosphate minerals, 20% in clays, and 10% in carbonates and organics. Whereas, 50% of the heavy REE (Yb and Lu) were in phosphates, 20% in clays and 30% in organics and carbonates. In a limited number (6) of low-rank coals they found that 60% of the light REE and Y were associated with clays, 20% in phosphates, and 20% in carbonates and organics. Of the heavy REE 50% were associated with clays, 25% in organics and carbonates, and 25% in phosphates.

Simultaneously with the foregoing ideas, assumptions about the possible REE accumulation in organic matter were proposed. They were based on indirect data on the REE distribution in coals and limited experimental studies on the sorption of individual REE by peat, humic acids and coal [17–27]. Convincing evidence that a large part of the REE concentration in brown coal is in the form of non-mineral stable complexes with humic acids has appeared [18, 28, 29]. Analysis of two samples of rare-metal rich Paleogene brown coals from the Russian Far East by V.V. Seredin and M.Ya. Shpirt [30] and M.Ya. Shpirt et al. [31] showed that in metal-rich coals from 78 to 88% of the REE were in the humic substances and only 11–22% was in mineral modes. These findings were supported by the results of the rare metal-bearing coals from Pavlovsky deposit (the Russian Far East) investigation by laser ablation ICP-MS [32]. She found that in the attritus vitrinite the REE concentrations were several times higher than their content in the coal minerals that were analyzed.

Such apparently contradictory findings on the modes of REE occurrence in the coals of different ranks, concentrations, and deposits require a detailed analysis of the nature of these differences by analysis of REE-rich coals as well as coals with typical REE contents. It is also necessary to assess the role of mineral and organic matter on REE modes of occurrence over the whole range of the coal formation: peat – lignite – subbituminous coal – bituminous coal – anthracite. In this study we generated quantitative data on the modes of REE occurrence in brown, and bituminous coals from different deposits of Northern Asia.

The collection of samples for this research was taken from different coal deposits of Siberia, Russian Far East, Mongolia, and Kazakhstan (Fig. 1). The sampling objective was to provide representative information from coals of these regions. The samples include coals of different ages – from Pennsylvanian to Paleogene, different coal ranks (from lignite to anthracite), different geological conditions of formation, different contents of mineral matter (different ash yields), and a wide range of REE concentrations.

DESCRIPTION OF SAMPLES AND METHODS

All samples were collected from coal seams in open-pit mines. The mass of every sample was between 1 and 2 kg. The main characteristics of the samples are presented in Tables 1 and 2.

Table 1 contains information on 39 coal samples most of which have extractable humic acids. These samples allow us to obtain different types of organic matter from the coal (bitumen, humic and fulvic acids), organically bound elements and minerals without the destruction of the minerals. This is only possible in low-rank coals (brown coals). In bituminous coals and anthracites, the extraction of organic matter without the destruction of the coal is not possible. The sum of REE concentrations (La, Ce, Sm, Eu, Tb, Yb, and Lu) in these samples ranges from 6.2 to 2100 ppm, and the ash yield ranges from 3.5 to 40.9%. The ranks range from subbituminous C to subbituminous A. As far as is known, the subbituminous A coals do not contain extractable humic acids. The coal of this rank was collected from the Chernogorskoe deposit with the purpose of assessing the role of the non-extractable humic acids on the REE concentration. Bituminous coals of the Saihan-Ovoo deposit (Mongolia) were weathered (oxidized under natural conditions) and have a high yield of humic acids. The alteration of the modes of REE occurrence in coal oxigenic water can be also observed for coals from the deposits Adun-Chulun (Mongolia), Itatskoe (Kansko-Achinsky basin), and Azeiskoe (Irkutskiy basin). The samples of coal which were not subjected to weathering, as well as oxidized coals with a high proportion of regenerated humic acids were collected with the purpose of assessing the role of regenerated humic acids on the REE accumulation. The remaining samples are from brown-coal deposits of different geologic ages, which were formed in different geological conditions (Tables 1and 2).

Table 2 contains information on eight samples for research on the mineral component of coals by selective leaching of the inorganic substances [33]. These samples were collected from coals of different geologic ages (Paleogene to lower Permian), different coalification extents – from lignite to low volatile bituminous coal, different ash yields and REE contents. The sum of the REE (La, Ce, Sm, Eu, Tb, Yb, and Lu) in these coals ranges from 9.0 to 148.5 ppm, and the ash yield ranges from 5.8 to 23.7%. Two lignites were sampled from the Paleogene coals of Rezhenskoe and Talovskoye deposits of the Zapadno-Sibirsky Basin. The subbituminous C coals are represented by the Paleogene coals of the Taldu-Durgun deposit (West Siberia) and by the Middle-Jurassic coals of the Itatskoe and Berezovskoye deposits (Kansk-Achinsk basin). The subbituminous A coals are represented by the coals of the Izyhskoe deposit of Minusinsk Basin late Permian age, and medium and low volatile bituminous coals are represented by the Early Permian

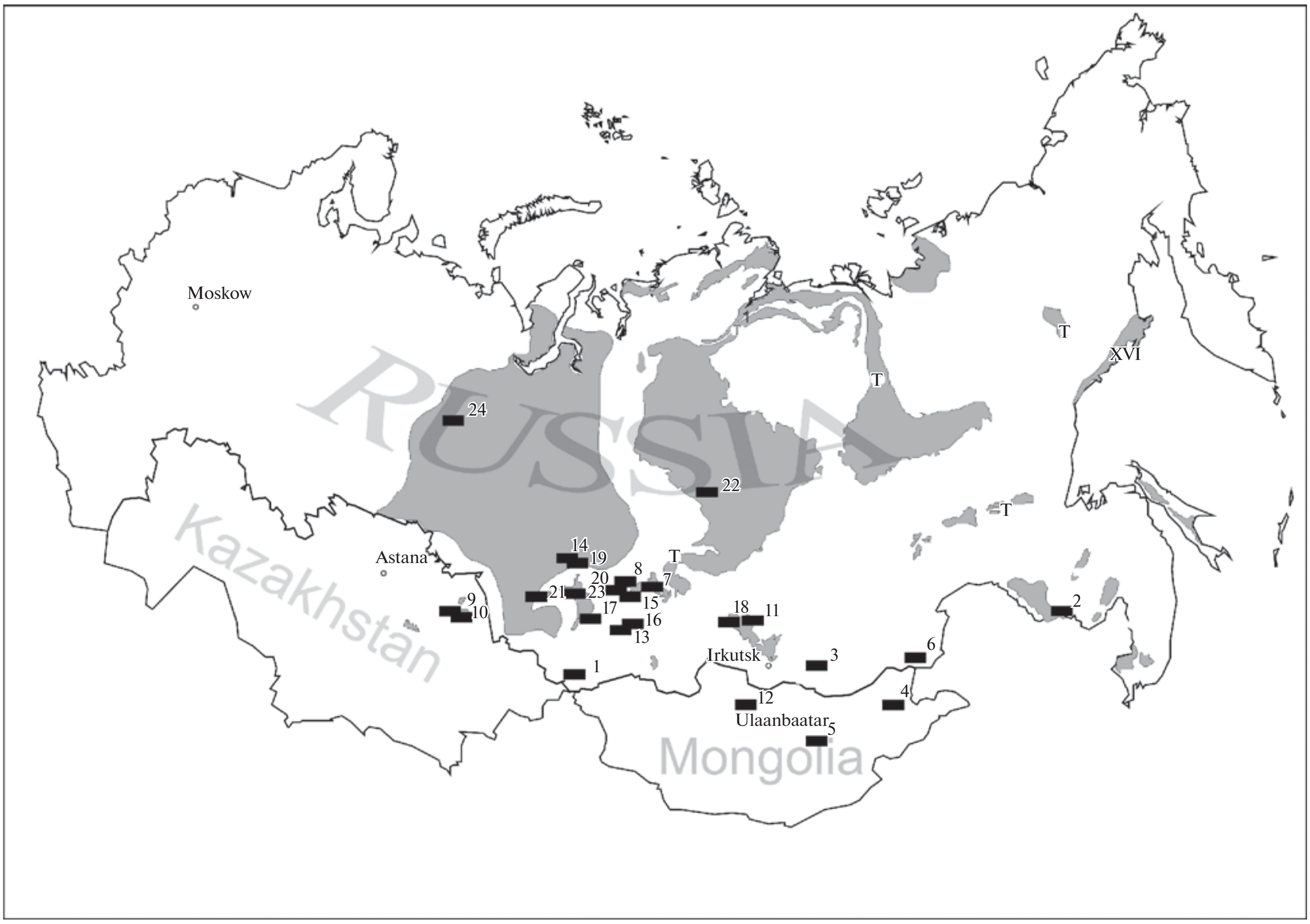

Fig. 1. Locations of the studied coal deposits in Northern Asia. *Studied Deposits:* 1 – Taldu-Dyurgunskoe, 2 – Raichichkinskoe, 3 – Tarbagataiskoe, 4 – Aduunchuluun, 5 – Baganuur, 6 – Chkaranorskoe, 7 – Latyntsevskoe, 8 – Itatskoe, 9 – Sarykol'skoe, 10 – Taldykol'skoe, 11 – Azeiskoe, 12 – Saykhan-Ovoo, 13 – Chernogorskoe, 14 – Talovskoe. 15 – Berezovskoe, 16 – Izykhskoe, 17 – Sibirginskoe, 18 – Mugunskoe, 19 – Rezhenskoe, 20 – Tisulskoe (Kaychaksky), 21 – Gorlovsky basin, 22 – Fatianikhinskoe, 23 – Uropskoe, 24-Lovinskoe.

coals from the Sibirginskoe deposit of the Kuzbass Basin.

ANALYTICAL PROCEDURES

Organic Association

Twenty-four samples of subbituminous C, eleven samples of subbituminous B, one sample of subbituminous A, and three samples of low volatile bituminous coals were subjected to the selective extraction of organic compounds. The REE and ash contents in the raw coal are shown in Table 1.

The modes of REE occurrence were studied using a range of analytical methods. The method of selective extraction of organic compounds included the extraction of different-types of organic substances without dissolution of the mineral matter. It was only implemented for the low-rank coals, because the extraction of organic substance from the bituminous coals without destruction of the organic molecules is not possible. The phase composition of brown coal was studied by selective extraction of bitumen, as well as extraction of humic acids (HA), fulvic acids (FA) and the insoluble residue. We use the term 'phase' to indicate raw coal, bitumen, humic acids, and the leaching residue.

Bitumen was extracted from the raw coal samples by benzene. The insoluble residue was then exposed to 1% NaOH in a water bath for 2 hour at 100°C followed with a one-time treatment with a solution of Na-humates. Addition of 5% HCl caused substitution of Na^+ by H^+ resulting in the precipitation of humic acids. Fulvic acids thus remain in the solution. The solution was evaporated for further study. In separate samples the extraction of total humic acids (the sum of free humic acids and humates) was made by treatment of samples with an alkaline solution of sodium pyrophosphate decahydrite ($Na_4P_2O_7 \cdot 10H_2O$).

La, Ce, Sm, Eu, Tb, Yb, and Lu contents were determined in the brown coal phases (raw coal, bitumen, humic acids, and the leaching residue) and mass

Table 1. REE and ash contents in the raw coal samples subjected to selective extraction of organic compounds

Coal field, Region	Age	Sample code	A^d, %	Coal rank	Elements content, ppm*							
					La	Ce	Sm	Eu	Tb	Yb	Lu	Sum
Taldu-Durgun, West Siberia	Pg	98–49	15.1	SubC	4.4	6.0	0.95	0.29	0.17	1.0	0.14	13.0
Raichihinskoe, Far East	Pg	Ray-9	16.4	SubC	38.5	67.3	9.0	1.58	1.43	5.0	0.77	123.6
		Ray-12	21.0	SubC	32.4	43.0	3.6	0.68	0.54	2.2	0.32	82.7
		Ray-22-1	7.5	SubC	5.1	13.1	1.0	0.18	0.14	0.57	0.07	20.2
		Ray-27	9.1	SubC	8.9	13.8	1.5	0.25	0.19	0.76	0.05	25.5
		Ray-30	9.9	SubC	4.4	9.7	0.76	0.10	0.08	0.45	0.06	15.6
Tarbagataiskoe, East Siberia	K_1	Tig-9	8.6	SubC	3.7	9.4	0.71	0.14	0.10	0.44	0.07	14.6
		Tig-18	11.9	SubC	4.0	11.4	0.74	0.16	0.12	0.46	0.08	17.0
Adun-Chulun, Mongolia	K_1	A-Ch-1	6.3	SubC	5.3	14.2	0.95	0.19	0.19	0.34	0.05	21.2
		A-Ch-2	13.1	SubC	4.2	11.3	0.85	0.23	0.21	0.38	0.08	17.3
		A-Ch-3	9.2	SubC	3.5	21.0	1.0	0.21	0.14	0.61	0.12	26.6
		A-Ch-4	11.4	SubC	3.7	13.4	0.43	0.09	0.13	0.28	0.04	18.1
		A-Ch-5	17.9	SubC	46.6	146	4.1	1.59	1.69	4.56	0.62	205.2
		A-Ch-6	40.9	SubC	727	1033	145	29.8	30.8	119	16.2	2100.8
		A-Ch-8	17.3	SubC	13.7	79.8	–	0.84	1.1	3.1	0.63	99.2
Baganur, Mongolia	K_1	B-1	9.5	SubC	3.3	8.9	0.82	0.11	0.16	0.45	0.05	13.8
		B-2	7.2	SubC	3.6	8.0	0.66	0.12	0.13	0.32	0.04	12.9
Kharanorskoe, East Siberia	K_1	Har-15	10.0	SubC	4.9	11.3	1.1	0.17	0.17	0.81	0.15	18.6
		Har-17	7.2	SubC	3.6	10.0	0.15	0.07	0.08	0.18	0.06	14.1
		Har-20	5.0	SubC	1.6	4.3	0.13	0.04	0.02	0.10	0.02	6.2
Latyntsevskoe, East Siberia	J_2	437	20.5	SubC	7.0	10.4	1.19	1.22	1.43	3.66	0.99	25.9
Itatskoe, West Siberia	J_2	06-4	8.7	SubC	14.8	32.9	3.4	1.21	1.30	5.40	0.86	59.9
		06-20	20.4	SubC	26.4	50.5	2.5	0.77	0.80	3.1	0.46	84.5
Sarykol'skoe, Kazakhstan	J_{1-2}	C-8	8.6	SubB	7.7	16.1	1.77	0.5	0.29	0.76	0.10	27.2
		C-12	14.1	SubB	6.3	16.1	1.85	0.54	0.37	1.04	0.14	26.3
		C-15	24.2	SubB	8.5	21.7	2.38	0.72	0.38	1.49	0.24	35.4
Taldykol'skoe, Kazakhstan,	J_{1-2}	T-6	22.6	SubB	10.3	27.2	2.0	1.05	0.70	2.37	0.34	44.0
		T-8	11.1	SubB	7.9	21.4	3.2	0.62	0.47	1.17	0.18	34.9
		T-12	16.2	SubB	8.9	22.4	2.5	0.68	0.42	1.38	0.20	36.5
		T-15	26.5	SubB	12.4	29.0	2.9	0.80	0.59	1.96	0.29	47.9
Azeiskoe, East Siberia	J_2	Az-41-09	14.3	SubB	87.1	173	14.0	3.1	2.1	5.4	1.60	286.3
		Az-31-09	5.2	SubB	13.9	25.9	3.0	0.76	0.68	2.4	0.32	47.0
		Az-29-09	9.6	SubB	34.5	60.0	5.5	1.3	0.91	2.4	0.31	104.9
		Az-19-09	11.9	SubB	21.9	39.9	4.7	1.1	0.83	2.7	0.42	71.6
Mugunskoe, East Siberia	J_2	Mg-21-09	9.2	SubB	5.4	19.1	2.2	0.30	0.45	1.18	0.36	29.0
Chernogorskoe, East Siberia	C_2	2046D	4.3	SubA	2.7	4.3	0.72	0.43	0.30	1.6	0.39	10.4
Saihan-Ovoo, Mongolia	J_{1-2}	CO-08-1	19.4	Lvb	29.4	53.3	4.89	1.5	0.54	2.12	0.22	92.0
		CO-08-3	5.9	Lvb	4.1	11.7	1.16	0.39	0.17	0.58	0.11	18.2
		CO-08-5	3.5	Lvb	9.6	17.4	2.62	0.37	0.18	0.60	0.060	30.8

Note: – not evaluated. * – determined by instrumental neutron activation analysis (INAA)

Table 2. The REE and ash contents of different rank coal samples subjected to selective leaching

Coal field	Age	Sample code	A^d, %	Coal rank	Elements content, ppm*							
					La	Ce	Sm	Eu	Tb	Yb	Lu	Sum
Rezhenskoe, West Siberia	Pg	R-1	15.6	LigB	17.8	37.5	5.5	1.1	0.64	2.9	0.60	66.0
Talovskoye, West Siberia	Pg	Tom-1	23.7	LigB	20.5	38.3	4.6	1.0	0.57	1.8	0.27	67.0
Taldu-Durgun, West Siberia	Pg	98-49	14.3	SubC	3.8	6.6	1.1	0.24	0.20	0.83	0.15	12.9
Itatskoe, West Siberia	J_2	BU-953	5.8	SubC	2.4	5.1	0.67	0.22	0.18	0.36	0.09	9.0
Berezovskoye, West Siberia	J_2	64-02	15.7	SubC	11.6	29.8	9.1	3.5	3.0	8.9	2.0	67.9
Izyhskoe, seam XXXnp, Eest Siberia	P_2	99-129	16.8	Sub A	49.6	80.4	8.8	1.1	1.2	6.2	1.2	148.5
Sibirginskoe, seam I, Kuzbass, West Siberia	P_1	O301	6.4	Mvb	5.9	9.4	0.92	0.38	0.34	0.84	0.13	17.9
Sibirginskoe, seam IV-V, Kuzbass, West Siberia	P_1	157-02	8.7	Lvb	21.6	44.7	2.9	0.45	0.3	1.2	0.16	71.3

Note: * – determined by the instrumental neutron activation analysis (INAA).

balance calculations were performed. All the isolated fractions were analyzed by instrumental neutron activation analysis (INAA) at the Nuclear-Geochemical Laboratory of the Department of Geoecology and Geochemistry of Tomsk Polytechnic University (TPU) (analyst A. F. Sudyko). The irradiation of the samples was carried out in the neutron research reactor (IRT-T) in the Physical-Technical Institute of TPU. Quality control was conducted parallel with the study of the original samples and their ash residues as well as through the use of standard reference samples [34].

Additionally, the whole range of REE was investigated by inductively-coupled plasma/mass spectrometry (ICP-MS) in the phases (bitumen, humic acids and coal residue) of the Azeiskoe samples. The analyses were carried out at the Analytical Laboratory of the Far-East Geological Institute of Russian Academy of Sciences (analyst N.V. Zarubina) and at the Chemical-Analytical Center "Plasma" in Tomsk city (analyst N.V. Fedunina). The repeatability of the two methods of measurement for the REE was found to be satisfactory [35].

Mineral Association

Chemical demineralization (selective leaching) experiments were performed on eight samples of different coal ranks (Table 2). Standard leaching methods with ammonium acetate dilute and concentrated acids (HCl, HF and HNO_3) were described by [5]. Duplicate 5 gram coal samples, ground to pass 60 mesh, were sequentially leached at room temperature with 35ml each of 1N ammonium acetate (CH_3COONH_4), 3N hydrochloric acid (HCl), and concentrated hydrofluoric acid (HF; 48 percent) in 50 ml polypropylene tubes. Each tube was shaken for 18 hours using a motorized wrist shaker. Because gas can form during some of the leaching procedures due to decomposition of carbonates, sulfides, and other minerals, each tube was enclosed in a polyethylene bag closed with a plastic coated wire strap. In the final step of the process the residual material (primarily mineral free coal particles and pyrite) was placed in an Erlenmeyer flask and shaken with 2N HNO_3 for 18 hours.

The sequence of solvents was adopted so that exchangeable cations would be removed first by the ammonium acetate; cations associated with the carbonates and monosulfides would then be removed by the HCl; and cations associated with the silicates would be removed by HF. Moreover, the HCl influence on the organic matter lead to the hydrolytic splitting of the C-O-Ln associations in complex humates with further formation of soluble $LnCl_3$ and REE transition into water solution [31]. Finally, elements associated with the disulfides would be removed by using HNO_3. In this procedure unleached cations may be 'shielded' mineral grains that are completely encapsulated by the coal matrix, or they may be associated with insoluble mineral phases, or associated with the organic matrix.

All products obtained, including the solutions, were analyzed for their REE concentrations. Analysis of the REE (La, Ce, Sm, Eu, Tb, Yb, and Lu) in the initial coal and leaching products was conducted by INAA.

REE mineral modes of occurrence in some coal samples and coal ash were studied at the International Innovation Scientific-Educational Center "Uranium Geology", Department of Geochemistry and Geoecology of Tomsk Polytechnic University. A Hitachi S-3400N scanning electron microscope with a BrukerXFlash 4010 energy dispersive spectrometer was used to identify mineral occurrences and elemental composition of micron and nanometer particles. The identification of the REE mineral associations was made on the basis of chemical composition of the mineral phases. More than 100 samples were studied in this way. The samples included untreated coal and coal ash, coal remaining after the selective extraction of organic compounds, coal remaining after demineralization, the ash of remaining coal, and the ash of humic acids.

RESULTS AND COMMENTS

The analytical procedures designed to determine organic and mineral associations allowed us to assess the modes of REE occurrence and concentration mechanism in coals with high reliability.

SELECTIVE EXTRACTION OF ORGANIC COMPOUNDS

S.I. Arbuzov et al. [22, 23] concluded that the modes of occurrence of REE in peat indicate that their concentration in low rank coal is largely controlled by hydrogenic mechanisms. They noted that in the peat bog environment the REE generally are transformed into mobile forms and eventually accumulate in the organic matter.

The REE modes of occurrence in brown coal can be deduced from the results of the selective extraction of organic compounds (bitumen, humic acids and coal residue) (Table 3).

The procedure was carried out on 35 subbituminous (B, C) coal samples from 11 coal fields in Siberia, the Russian Far East, Kazakhstan and Mongolia and 1 sample of subbituminous A coal with residual humic acids from the Dvuharshinny seam of the Chernogorskoe coal field in Siberia. Also 3 samples of oxidized coal with a high yield of regenerated humic acids from the Saihan-Ovo (Mongolia) field were tested.

The data showed that the REE distribution determined by selective extraction of organic compounds was heterogeneous, even within a single coal field (Table 3). This is seen in the results from the Raichihinskoe deposit no apparent dependence of REE concentration on the ash content of the raw coal samples. Humic substances and residual coal can both play a major role for the REE modes of occurrence in the coals with the same ash content.

This is clearly shown by the examples of sample Ray 27-10 from the Raichihinskoe deposit and sample C-8-1 of the Sarykol'skoe deposit. The ash yields of these samples are similar but the REE distributions in the phases are different. In the Ray 27-10 sample there is a clear association of the REE with the humic substances but in the C-8-1 sample there is a stronger association of the REE with the residual coal (Table 3). However, we commonly observe similar behavior of the REE the coals with different ash contents. This can be seen in sample C-8-1 from the Sarykol'skoe deposit and sample T-6-1 from the Taldykol'skoe deposit. The ash yield of these samples differs by almost three times, yet the REE distributions in the phases are similar. The same is noted for the samples I-06-4 and Ray 12-10 (Table 3).

In general, it should be recognized that the role of humic substances in the accumulation of REE is substantial for brown coal. The proportion of REE associated with humic substances in our samples is as low as 20% for a few elements in several samples (Table 3) but generally the REE proportion is comparable to or greater than that in the residual coal phase. From 20 to 95% of the REE in the samples were found in the alkaline extracts (humic and fulvic acids). No more than 5% of the REE were in the bitumen. Excluding one sample (Ray 27-10) from the Raichihinskoe deposit, the other samples show that from 20 to 80% of REE are associated with the residue. It is important to understand that REE may be present in the residue not only in the mineral components but also in the organic components.

Organic modes of occurrence of the REE appear in the residuals when the bound humic substances (humates) are removed from the coal through extraction by alkaline sodium pyrophosphate (Table 4).

However, this process of extraction of humic acids, which are bound in humates, does not substantially influence the assessment of REE yield in the remaining phases. A distinct association of HREE (Yb and Lu) with humic acids is apparent. Their yield into the phase of the free humic acids is substantially higher than the light REE (La and Ce) and middle REE (Sm and Eu). It thus appears that a substantial part of the REE in the remaining coal is concentrated in the minerals or in the form of organic compounds which are not leached by the alkaline extract.

Table 5 shows the yield of 6 REE (La, Ce, Sm, Eu, Yb and Lu) in the low-rank coals from the Adun-Chulun field.

These coals were subject to oxidation with the formation of complex uranium-rare-metal mineralization [36]. All five samples were collected from one 25 m seam from the bottom upwards. The first three samples were taken by the furrow method with the interval length of 7 meters. Sample A-Ch-5 represents the upper 1.5 m of the seam and sample A-Ch-6 represents a 10-cm interval in the near-roof part of the seam. These two samples are anomalously enriched in U and REE (Table 1).

Table 3. The calculated yield of REE in the phases of brown coals, normalized to 100%

Phase	Phase percentage	La	Ce	Sm	Eu	Yb	Lu
Tig-9-10 Tarbagataiskoe ($A^d = 8.6\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.50	4.3	2.6	3.2	4.6	4.5	2.9
Humic Acids	14.0	29.5	28.1	39.1	31.4	33.3	36.2
Residue	84.5	66.2	69.3	58.7	64.0	62.3	60.9
C-8-1 Sarykol'skoe ($A^d = 8.6\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	0.7	1.6	4.1	4.1	2.8	2.2	0.5
Humic Acids	8.8	46.9	37.2	28.8	27.7	22.7	23.2
Residue	90.5	51.5	58.6	67.1	69.5	75.2	76.3
IT-06-4 Itatskoe ($A^d = 8.7\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.0	0.6	0.3	0.1	6.6	1.0	1.0
Humic Acids	52.4	70.2	79.6	74.3	72.6	66.0	51.5
Residue	47.6	29.0	20.1	25.6	20.8	33.0	47.5
Ray 22-10 Raichihinskoe ($A^d = 7.5\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.2	5.1	5.1	2.6	2.8	3.9	1.2
Humic Acids	36.6	61.6	63.1	67.6	59.5	59.4	59.8
Residue	61.6	33.3	31.8	29.8	37.7	36.7	39.0
Ray 27-10 Raichihinskoe ($A^d = 9.1\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	2.1	3.2	0.9	4.4	1.5	0.2	0.6
Humic Acids	91.4	94.3	96.5	93.7	94.8	96.5	96.4
Residue	6.5	2.5	2.6	2.0	3.7	3.3	3.0
Ray 12-10 Raichihinskoe ($A^d = 21.0\%$)							
Raw coal	100.0	100.00	100.0	100.0	100.0	100.0	100.0
Bitumen	1.5	4.6	2.6	5.5	2.4	3.6	3.5
Humic Acids	62.2	73.7	76.6	74.0	66.9	74.3	73.1
Residue	34.7	21.7	20.8	20.5	30.8	22.1	23.4
437 Latyntsevskoe ($A^d = 20.5\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Humic Acids	61.0	78.1	78.8	79.6	82.4	79.2	90.6
Residue	38.0	21.9	21.2	20.4	30.8	20.8	9.4
T-6-1 Taldykol'skoe ($A^d = 22.6\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	0.7	1.4	0.5	0.3	6.2	0.3	0.6
Humic Acids	6.3	19.5	25.9	18.0	26.7	24.4	18.5
Residue	93.0	79.0	73.6	81.7	67.0	75.4	80.9

Table 3. (Contd.)

Phase	Phase percentage	La	Ce	Sm	Eu	Yb	Lu
Az 19-09 Azeiskoe ($A^d = 11.9\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumens	0.64	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Humic Acids	46.39	38.6	36.9	21.7	23.2	29.1	39.7
Insoluble residue	52.49	60.3	64.3	77.6	76.2	70.2	59.6
Az 31-09 Azeiskoe ($A^d = 5.2\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	0.31	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Humic Acids	40.2	21.7	18.2	30.7	37.5	23.7	33.1
Residue	59.5	73.4	73.5	69.0	62.2	75.9	66.6
Az 41-09 Azeiskoe ($A^d = 15.8\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.5	1.6	1.3	1.3	2.0	0.1	1.9
Humic Acids	40.9	20.3	23.0	26.0	15.8	45.3	46.0
Residue	57.6	78.1	74.7	72.7	82.2	54.6	52.1

There is an interesting REE distribution in the Adun-Chulun sample A-Ch-6 with the abnormally high content of REE exceeding 0.2%. The residual phase contains approximately 80–90% of the six REE which is 20–30% more REE than the raw coal. The humic substances accounts for only about 20% of the REE. The unusually high concentration of the REE and the exceptionally high proportion in the residual coal indicates that a substantial amount of the REE in this sample may be in minerals.

Table 4. REE yield in the phases after the leaching of free and general humic acids, normalized to 100%

Phase	Phase percentage	La	Ce	Sm	Eu	Yb	Lu
Tig-18-10 Tarbagataiskoe ($A^d = 11.9\%$)							
Raw coal	100	100	100	100	100	100	100
Bitumen	1.5	1.6	5.2	4.0	0.3	0.7	1.5
Free Humic Acid	2.4	1.4	5.0	4.2	3.1	24.5	19.3
Humates	8.8	20.8	15.0	43.8	14.5	2.3	10.0
Residue	87.33	76.2	74.7	48.5	81.9	72.6	67.2
Tig-9-10 Tarbagataiskoe ($A^d = 8.6\%$)							
Raw coal	100	100	100	100	100	100	100
Bitumen	1.5	4.3	2.6	3.2	5.9	4.5	2.9
Free Humic Acid	12.7	28.5	27.0	36.0	15.0	32.3	35.3
Humates	0.1	0.1	1.8	0.5	2.4	2.3	9.1
Residue	59.37	67.2	68.5	60.3	76.7	61.0	52.8
Az-41-09 Azeiskoe ($A^d = 14.3\%$)							
Raw coal	100	100	100	100	100	100	100
Bitumen	1.5	1.6	1.3	1.3	2.0	0.1	1.9
Free Humic Acid	40.7	20.3	23.0	26.0	15.8	45.3	46.0
Humates	17.1	1.4	1.0	<0.1	<0.1	1.2	6.6
Residue	36.2	76.7	74.7	72.7	82.2	43.4	45.5

Table 5. The REE composition in phases of low-rank coals from Adun-Chulun (Mongolia) coal field with high REE concentrations, normalized to %

Phase	Phase percentage	La	Ce	Sm	Eu	Yb	Lu
A-Ch-1 Adun-Chulun (sum of REE = 21.1 ppm)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.4	0.1	1.3	1.3	1.4	1.4	1.4
Humic Acid	57.6	69.2	60.0	70.4	58.4	74.1	71.5
Residue	41.0	30.7	39.0	28.3	40.2	24.5	27.1
A-Ch-3 Adun-Chulun (sum of REE = 26.6 ppm)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.2	0.1	0.1	0.1	1.3	3.2	1.2
Humic Acid	31.2	57.1	48.3	66.0	33.6	30.1	35.2
Residue	67.6	42.8	51.6	33.9	65.1	66.7	63.6
A-Ch-4 Adun-Chulun (sum of REE = 18.1 ppm)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	1.5	0.1	1.6	1.9	1.7	1.5	1.5
Humic Acid	38.7	53.7	66.9	52.2	67.6	61.7	59.7
Residue	59.8	46.2	31.5	45.9	30.7	36.8	38.8
A-Ch-5 Adun-Chulun (sum of REE = 205 ppm)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	2.2	1.8	2.2	2.2	2.4	1.0	1.5
Humic Acid	53.6	46.2	57.7	75.3	61.2	45.9	35.2
Residue	44.2	52.0	40.1	22.5	36.4	53.1	63.3
A-Ch-6 Adun-Chulun (sum of REE = 2100 ppm)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Humic Acid	36.4	20.7	22.6	18.7	22.5	17.2	14.2
Residue	63.5	79.2	77.3	81.2	77.4	82.7	85.7

The organic mode of REE occurrence may be, to a great extent, retained in the early coalification stages and in oxidized coals. This is indirectly supported by the study of the phases of the strongly oxidized Lvb coals from Saihan-Ovoo coalfield in Mongolia (Table 6).

The oxidized coals of the Saihan-Ovoo deposit are characterized by an 80% yield of humic acids. We studied the sum of sevan REE (La, Ce, Sm, Eu, Tb, Yb, Lu) in three coal samples with the low, moderate, and high contents of these elements in relation to the mean content in world coals [37]. The ash yield of the coal samples also differs substantially. In all cases the main REE carrier is the organic matter – regenerated humic acids. They account for more than 80% of the total REE in the coals. From this information we may conclude that in these brown coals and oxidized bituminous coals the REE can predominantly occur in the organic complexes.

However, another interpretation of this observation is possible. REE may be imported with carbonate water and may be sorbed on humic substances. Alternatively, it is possible that dissolution of soluble minerals during coal oxidation by the carbonate water may result in REE redistribution in the complex humates. The enrichment of carbonatious water by REE is known [38], and high sorption capability of humic acids of brown coals relatively to some REE has been investigated [18, 28, 29].

MINERAL MATTER IN COAL SUBJECTED TO SELECTIVE EXTRACTION OF ORGANIC COMPOUNDS

A detailed study of the 800°C ash sample by scanning electron microscopy of the mineral content of sample A-Ch-5 from the Adun-Chulun coal seam with a total of 205 ppm for seven REE (La, Ce, Sm, Eu, Tb, Yb, Lu) in the raw coal (0.12% in the ash) was conducted. Only a single micron-sized grain of an alumino-phosphate REE mineral, presumably a crandal-

Table 6. The REE composition in phases of oxidized Lvb coal from Saihan-Ovoo (Mongolia) coal field, normalized to 100%

Phase	Phase percentage	La	Ce	Sm	Eu	Yb	Lu
SO-08-1 (sum of REE=92.0 ppm; $A^d = 19.4\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	4.2	2.2	2.9	2.0	2.5	0.6	1.5
Humic Acids	82.0	84.2	83.3	85.9	86.8	87.6	86.8
Organic-leach residue	13.8	13.6	13.8	12.1	10.7	11.8	11.7
SO-08-3 (sum of REE=18.2 ppm; $A^d = 5.9\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	3.5	1.5	1.5	0.6	0.1	4.4	3.5
Humic Acids	80.8	79.2	81.8	84.2	87.5	81.6	89.0
Organic-leach residue	15.7	19.3	16.7	15.2	12.4	14.0	7.5
SO-08-5 (sum of REE=30.7 ppm; $A^d = 3.5\%$)							
Raw coal	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Bitumen	2.1	0.1	0.1	1.7	2.6	2.1	2.1
Humic Acids	80.1	83.7	80.6	89.6	81.3	88.0	85.0
Organic-leach residue	17.8	16.2	19.3	8.7	16.1	9.9	12.9

lite group mineral, was detected. The absence of any significant amounts of minerals containing REE indicates mainly organic modes of REE occurrence in these coals with high contents of REE. As noted above and in Table 5, sample A-Ch-6 with a higher REE content than in sample A-Ch-5, likely has a significant mineral mode of occurrence

Similar results were obtained in the study of a brown coal from the Azeiskoe coal field (sample Аз 41-09, Tables 3 and 4). The sample had an ash yield of 14.3% and the sum of the seven REE was 242 ppm in the coal (0.26% in the ash). Rare single grains of what we interpret to be mendeleyevite ($(Ca,U)_2(Ti,Nb,Ta)_2O_6(OH)$) and the rare-earth phosphate monazite were found in the raw coal and in the residual phase after the extraction of bitumen and humic acids. The small number of these minerals likely does not provide a substantial share of total REE in the sample. In addition, in the ash of some brown coals film-like mineral modes of REE were found (Fig. 2). The presence of such material in the coal ash and their absence in the coal allows us to suppose that they formed from organic compounds during ashing. It is interesting that phosphates (goyazite, monazite) and aluminosilicates form the same film-like residues after ashing of humic acids extracted from the REE-enriched coals.

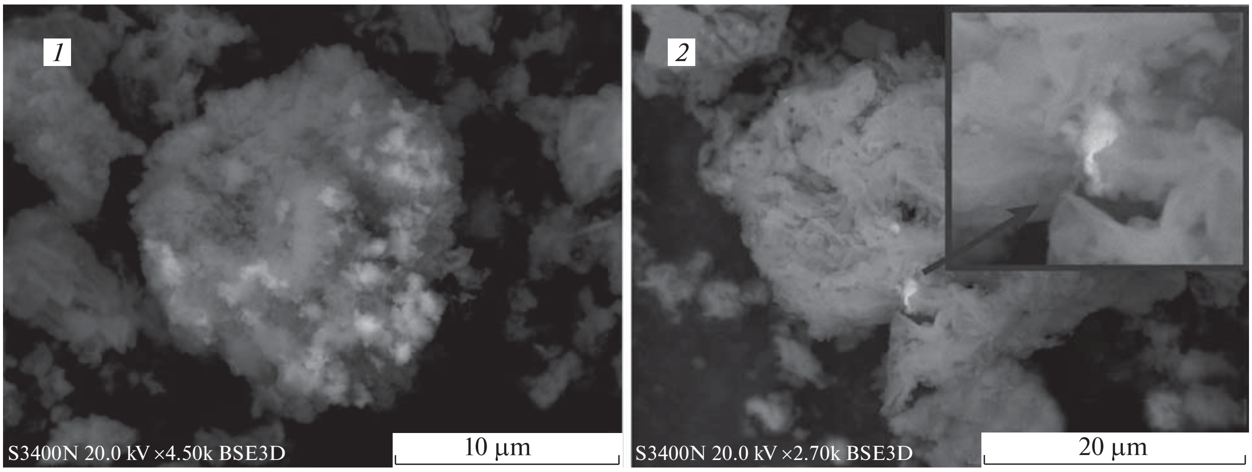

Fig. 2. Film-like mineral phases of REE phosphates (light) in the coal ash. Subbituminous B coal of Azeiskoe coalfield, Irkutsk Basin (sample Az 41-09) *1* – Rare earth phosphate minerals (light) in the coal ash; *2* – Inclusion of rare earth phosphate mineral in film-like material.

SELECTIVE LEACHING INORGANIC REE FROM BROWN AND BITUMINOUS COALS

The evaluation of the quantitative contribution of mineral matter to the total REE balance in subbituminous B, A and bituminous coals is a rather complicated task. To evaluate the role of minerals and sorbate modes of occurrence in bituminous and brown coals we carried out sequential chemical demineralization described above. This procedure removed practically all of the minerals in the coal except some grains of zircon and REE phosphates resistant to acids. However, this method is indirect and allows only for the estimation of possible or probable modes of occurrence. The results of the demineralization procedure are given in Tables 7 and 8.

Table 7. The REE composition in phases of selective leaching normalized to 100%

Coal rank (coal field)	Component	La	Ce	Sm	Eu	Yb	Lu
Lig A (Talovskoe)	Raw coal	100	100	100	100	100	100
	NH_4COOH	10.7	1.7	39.4	3.0	17.4	15.9
	HCl	46.3	61.5	33.4	69.1	17.8	5.4
	HF	20.9	21.2	5.0	3.3	13.7	22.0
	HNO_3	15.6	8.4	0.6	8.0	11.6	10.8
	Acid residue	6.4	7.3	21.7	16.6	39.5	45.9
Lig A (Rezhenskoe)	Raw coal	100	100	100	100	100	100
	NH_4COOH	<0.1	<0.1	20.9	8.4	3.8	6.1
	HCl	74.2	69.6	63.1	71.2	40.2	50.3
	HF	7.4	2.5	1.9	2.2	17.5	0.7
	HNO_3	6.6	12.1	6.7	9.5	11.6	12.6
	Acid residue	12.0	15.8	7.4	8.6	27.3	30.3
Lig A (Taldu-Durgunskoe)	Raw coal	100	100	100	100	100	100
	NH_4COOH	6.0	0.8	16.7	13.8	13.8	6.9
	HCl	37.3	63.2	49.2	43.9	56.8	64.3
	HF	13.8	22.9	8.5	17.7	4.0	0.4
	HNO_3	5.6	3.9	1.6	2.4	3.8	0.7
	Acid residue	37.3	9.1	24.0	22.2	21.5	27.7
Sub C (Berezovskoe)	Raw coal	100	100	100	100	100	100
	NH_4COOH	19.5	9.4	17.9	8.6	8.0	1.1
	HCl	68.6	88.3	67.7	84.3	85.7	92.5
	HF	1.0	0.1	4.7	1.4	0.9	2.3
	HNO_3	7.3	1.2	5.1	2.4	2.4	0.8
	Acid residue	3.5	1.0	4.6	3.3	3.0	0.8
Sub C (Kaychaksky)	Raw coal	100	100	100	100	100	100
	NH_4COOH	40.9	27.5	17.4	16.5	0.9	3.6
	HCl	14.6	37.3	27.7	43.9	62.0	48.5
	HF	7.9	22.3	4.8	25.8	21.7	1.9
	HNO_3	22.0	19.7	29.9	11.0	11.0	13.8
	Acid residue	14.7	2.6	18.4	2.7	4.3	32.2
Mvb (Sibirginskoe)	Raw coal	100	100	100	100	100	100
	HCl	5.9	5.8	15.8	26.2	18.6	32.8
	HF	6.0	3.9	5.3	6.6	6.5	0.8
	Acid residue	88.1	90.3	78.9	67.2	74.9	66.4

Arbuzov et al., [22] has shown that REE in modern peats prevail in water-soluble and easy-hydrolized forms. However, the treatment of brown coals with ammonium acetate, with rare exceptions, doesn't lead to any significant extraction of REE. As the ammonium acetate makes possible the extraction of mobile and weakly bound sorbate forms, these results indicate that, when passing from the peat phase to the brown-coal phase, REE change their mode of occurrence. This is indicated by the predominant yield of REE in the hydrochloric-acid extract (Table 7). In the opinion of Finkelman et al. [39] the high share of the REE leached with HCl may indicate a chelate mode of occurrence. This fact agrees well with the data of the composition of brown coal. Some small amount of REE in brown coals appears to be contained in silicates and alumosilicates as it is rather constantly (from 1 to 30%, on the average 5-10%) extracted with hydrofluoric acid. It is necessary to take into account that clay minerals, destroyed by hydrofluoric acid, often contained fine-grained inclusions of phosphates and other rare-earth minerals (Fig. 3). These nanometer and micron mineral inclusions are accessible to solution after the removal of clay matrix.

The treatment of samples with 10% HNO_3 also results in REE leaching, but it is difficult to interpret these data. It is possible that the nitric acid leaches REE from phosphates [39] or extracts them from the organic matter breaking the organic matrix of coal. It is known that dilute nitric acid oxidizes brown and bituminous coal [40].

In brown coals, where the REE organic mode of occurrence prevails, minerals were found to be prevalent in some cases. The nature of REE association with clays is not clear. REE are not included in the structure of kaolinite and other clay minerals and sorbate modes are extracted by ammonia acetate. The most probable explanation is the presence of fine-grained rare-earth minerals in the clay matrix (see, for example, Fig. 3). Relatively large clay particles limit the access of acids to included micro-minerals which may contain REE. After the destruction of the aluminosilicates by HF the rare-earth bearing inclusions are exposed and became accessible to leaching. The presence of micro-inclusions of rare-earth minerals in coal kaolinite was established earlier in the research of subbituminous A coals containing dispersed pyroclastic, in the Minusinsk Basin [21]. This observation is also supported by data for other lower rank coals (Fig. 3). Micro-inclusions are usually phosphates, aluminophosphates (florencite) and rarely silicates. The asso-

Table 8. Concentration of REE in the products of coal subjected to selective leaching

Products features	Elements concentration, ppm							La/Yb
	La	Ce	Sm	Eu	Tb	Yb	Lu	
Izykhskoe deposit, XXXnp seam								
Raw coal	49.6	80.4	8.8	1.1	1.2	6.2	1.2	8.0
Coal after HCl treatment	16.2	20.6	2.3	0.38	0.78	6.2	1.1	2.6
Residue after HCl evaporation	1143	1735	217	25.0	16.0	38.6	6.8	29.6
Coal after HF treatment	14.2	20.8	2.2	0.46	0.97	6.2	1.2	2.3
Residue after HF evaporation	12.6	13.0	0.91	0.3	0.33	2.1	0.49	6.0
Sibirginskoe deposit, IV-V seam								
Raw coal	21.6	44.7	2.9	0.45	0.30	1.2	0.16	18.0
Coal after HCl treatment	20.8	43.1	2.5	0.34	0.26	1.0	0.11	20.8
Residue after HCl evaporation	37.8	72.3	17.7	4.0	5.3	15.2	2.2	2.5
Coal after HF treatment	23.3	49.4	2.8	0.37	0.26	1.1	0.13	21.2
Residue after HF evaporation	5.6	8.2	0.38	0.03	0.13	0.08	0.01	70.0
Sibirginskoe deposit, I seam								
Raw coal	8.2	15.2	1.40	0.51	0.34	0.51	0.19	16.1
Coal after HCl treatment	4.5	12.4	0.84	0.40	0.18	0.48	0.06	9.4
Residue after HCl evaporation	0.95	<0.5	0.66	<0.1	<0.1	1.6	0.45	0.6
Coal after HF treatment	2.5	18.9	0.87	0.53	0.21	0.39	0.07	6.4

ciation of such specific clay-associated rare-earth minerals with dispersed pyroclastics is likely, as redeposited crusts of weathering are lean in REE in comparison with the initial rocks [41].

The Subbituminous A coal from the XXXnp bed of the Minusinsky Basin, enriched in REE, lost about 70–75% of the cerium after treatment with concentrated HCl. The content of yttrium did not change (Table 8). The hydrochloric extract was strongly enriched in light and intermediate REE (La, Ce, Sm, Eu). The lanthanum-ytterbium ratio after this treatment increased from 8 in the original coal to 29.6 in the extract. In the residual coal it decreased to 2.6. Therefore, the treatment by concentrated HCl leads to the selective dissolution of minerals bearing light REE. They may be carbonates, sulphates, hydrophosphates, and some silicates. The presence in coal of minerals such as bastnesite ($CeCO_3F$), parisite ($CaCe_2(CO_3)_3F_2$), and minerals of the crandallite group is supported by our electron microscopy data.

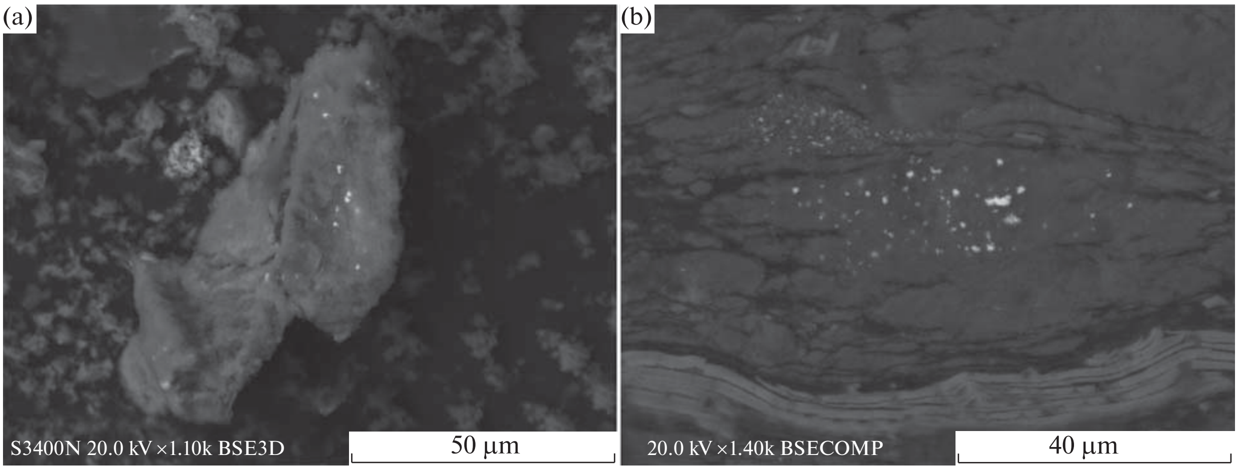

Fig. 3. Inclusions of rare-earth phosphates (bright white points in the gray background) in kaolinite *1* – Azeiskoe coalfield, Irkutsk Basin (sample Az 27-09); *2* – Ningwu coalfield, Ordos Basin, China.

Table 9. Contents of REE in the 800°C ash of raw coal and coal subjected to chemical demineralization

Products features	Elements content, ppm						
	La	Ce	Sm	Eu	Tb	Yb	Lu
Izykhskoe deposit, XXXnp seam (Subbituminous A)							
Coal ash	340	490	57.5	7.4	8.3	44.5	8.3
Coal ash after HCl treatment	113	122	14.5	2.8	4.9	38.3	7.4
Coal ash after HF treatment	1457	1688	196	45.3	60.4	549	106
Sibirginskoe deposit, IV–V seam (low volatile bituminous coals)							
Coal ash	187	214	20.5	2.4	1.9	10.9	1.3
Coal ash after HCl treatment	266	389	26.0	3.7	2.6	10.8	1.1
Coal ash after HF treatment	1940	3393	176	31.8	13.8	74.8	9.6
Sibirginskoe deposit, I seam (medium volatile bituminous coals)							
Coal ash	92.9	147	14.4	5.9	5.3	13.1	2.1
Coal ash after HCl treatment	85.5	118	10.7	3.6	2.9	7.7	0.97
Coal ash after HF treatment	807	3490	273	82.3	42.8	92.8	20.9

Probably, the REE contained in the organic matter in the ion-exchange mode as well as the sorbate phase, also pass into the HCl extract. Influence of HCl on the organic matter lead to the hydrolytic splitting of the C-O-Ln associations in complex humates with further formation of soluble $LnCl_3$ and REE transition into water solution [43].

In more metamorphically altered coals of Lvb rank (seams IV-V) the HCl treatment results in the leaching of 5 to 30% of individual REE (less than 10% on average: Table 8). There is a higher yield of heavy REE into the extract as compared with light REE. It is possible that the HCL soluble cerium minerals characteristic of the XXXnp seam are absent here, but the acid-soluble minerals of yttrium and heavy REE are common. Electron-microscopic study showed the presence of xenotime and intergrowths of zircon and xenotime in these coals [21]. The same tendency is characteristic of the sample of low-ash coals of Mvb rank from seam I of the Sibirginskoe deposit. The yield of light REE into the hydrochloric extract is 10–20% and for the heavy REE – 45–55% (Table 8).

The treatment by HF causes the dissolution of a large part of the ash-forming minerals remaining after the hydrochloric treatment, mainly silicates and alumosilicates. Following HF leaching the ash yield of the sample decreases to 0.2–0.6%. In the residual coal the REE content increases slightly or does not change. The relative enrichment of REE in the demineralized coal is due to the dissolution of minerals with little to no REE (quartz, most clay minerals) and thus due to the relative increase of the acid-resistant REE bearing minerals (monazite, xenotime, zircon, and others) in the coal. This conclusion is supported by the study of the residual coal ash. In all cases the ash of the demineralized coal contains REE concentrations an order of magnitude higher than in the ashes of the original coal (Table 9).

MINERAL MATTER IN THE COAL SUBJECTED TO SELECTIVE LEACHING

Calculations show that the hosts and concentrators of REE in the mature coals of bed IV-V are the minerals resistant to hydrochloric and hydrofluoric acids or, probably, metal-organic compounds. In less mature coals of the XXXnp seam, together with minerals stable in acids, the soluble compounds of REE (likely, carbonates and silicates) are present in comparable amounts. SEM/EDX analysis of coal samples and products of the chemical demineralization support these conclusions. For example, monazite, xenotime, and other REE-bearing phosphates have been found in the products of demineralization [21]. Palmer and others [42] examined the leached residue of the Broaz coal from eastern Kentucky, USA using SEM-EDX and the electron microprobe. In the Broaz leached residue they found crandallite and goyazite (calcium and strontium aluminum phosphate, respectively). According to Willett et al. [25], the presence of the rare earth phosphates probably accounts for most of the rare earth elements in coals.

In our samples the REE mineralogy is quite variable. Rare-earth cerium and yttrium phosphates were identified in subbituminous and bituminous coals and in the coal ash. Monazite was identified (Fig. 4) in all samples and phosphates similar in composition to xenotime are widespread. Usually, they are found as isolated (1–5 μm) inclusions of yttrium phosphate with heavy REE (Fig. 5). In some cases phosphate rims are developed around the zircon grains that are, most likely, caused by the isomorphic replacement of Zr and Si by Y and P [43].

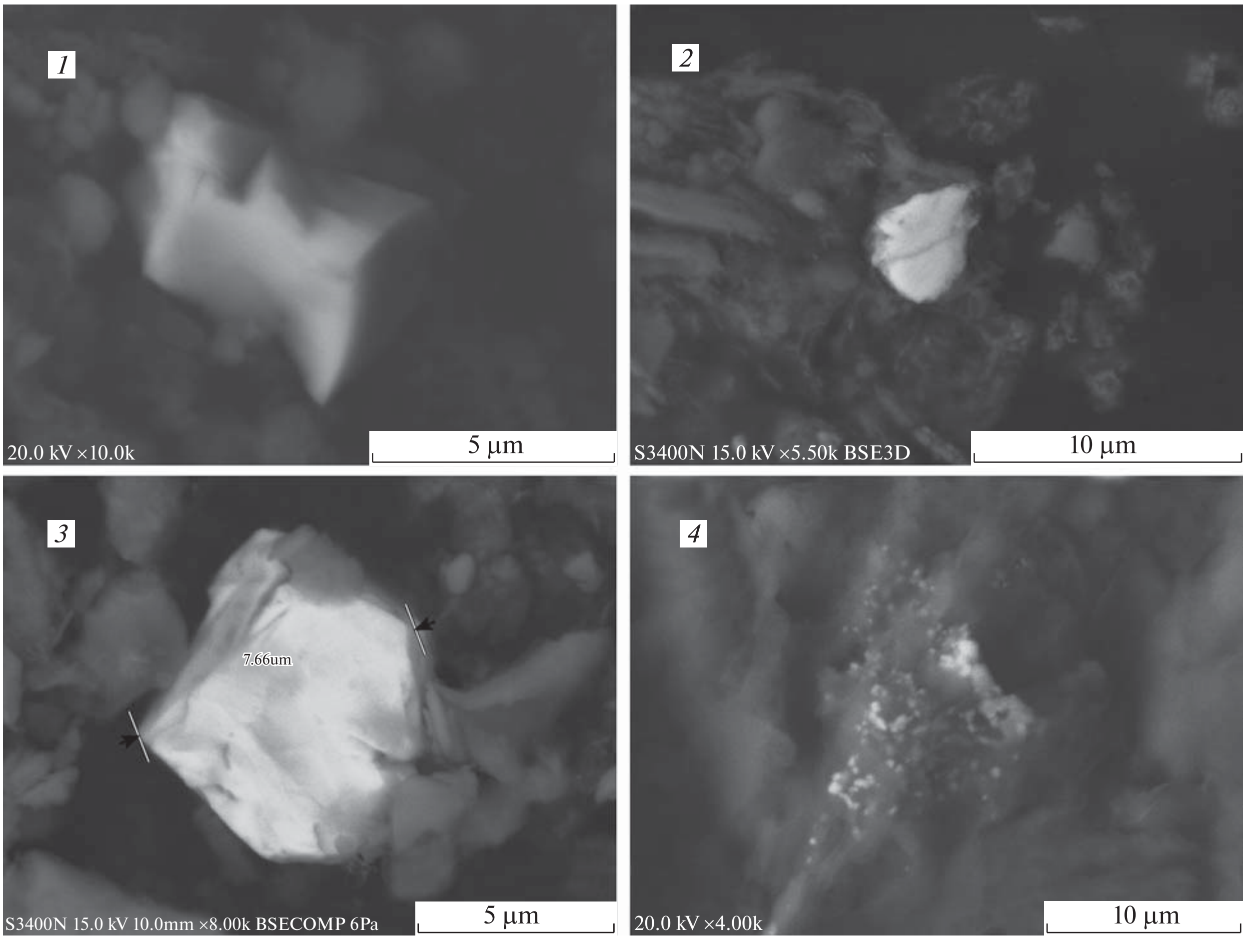

Fig. 4. Monazite in coals and coal ash *1* – Subbittominous C coal Tarbagataiskoe deposit (Tig 18-10), *2*– ash subbituminous B coal Azeiskoe deposit (Az 41-09), *3* – ash subbituminous A coal, seam Dvukharshinnyy Chernogorskoe deposit Minusinsk basin (DK-15), *4* – graphitic coal, Fatyanihinskoe deposit, Tungusky basin.

Authigenic carbonate minerals of different compositions were found in bituminous and sub-bituminous B coals of the Irkutsky Basin and in subbituminous and bituminous coals of the Kuzbass and Minusinsky Basins (Fig. 6). Globular rare-earth minerals of fluorine-carbonate composition, identified as bastnaesite [(Ce,La)(CO_3)F], parisite [Ca$(Ce,La)_2(CO_3)_3F_3$], as well as unidentified mineral aggregates of carbonate composition (Ce-La-Fe-C-O), are the most common forms of light REE in the sub-bituminous rank coals of the Azeiskoe deposit [44]. Similar globular inclusions of the REE fluorine-carbonates and carbonates of 1 to 20 microns have been observed in coals of the Kuznetsky and Minusinsky Basins. Three REE-bearing minerals from different basins are shown at Fig. 6. All of these minerals had from 3.0 to 8.5% Fe admixture. The spherical particles had a modular-granoblastic surface. The detailed mapping of the spherical inclusion surface showed that an iron-bearing mineral fills the space between the particles of fluorine-carbonates. The nature of these formations is not understood. Perhaps, microorganisms participate in their formation.

In the coals from the XIth seam of the Sibirginskoe deposit, known for high contents of Nb, Ta, Zr, and the rare-earth element group [19, 45] Ca-Ce-Nd carbonates have been found. Due to the high content of neodymium they are tentatively identified as synchysite (CaNd$(CO_3)_2$F) (Fig. 7).

Finally, in coals and coal ash from different deposits of North Asia unidentified rare-earth minerals have been found with compositions corresponding to alumophosphates, silica-alumophosphates, and other complex compounds (Fig. 8).

DISCUSSION

The existence of coals containing 100–200 ppm total REE producing coal ash with 0.2–1.0% REE [1, 2, 4, 21, 36, 45–54] requires the presence of mineral or organic components concentrating these elements. Some studies show that the ratio of different elemental modes of occurrence can vary greatly in the

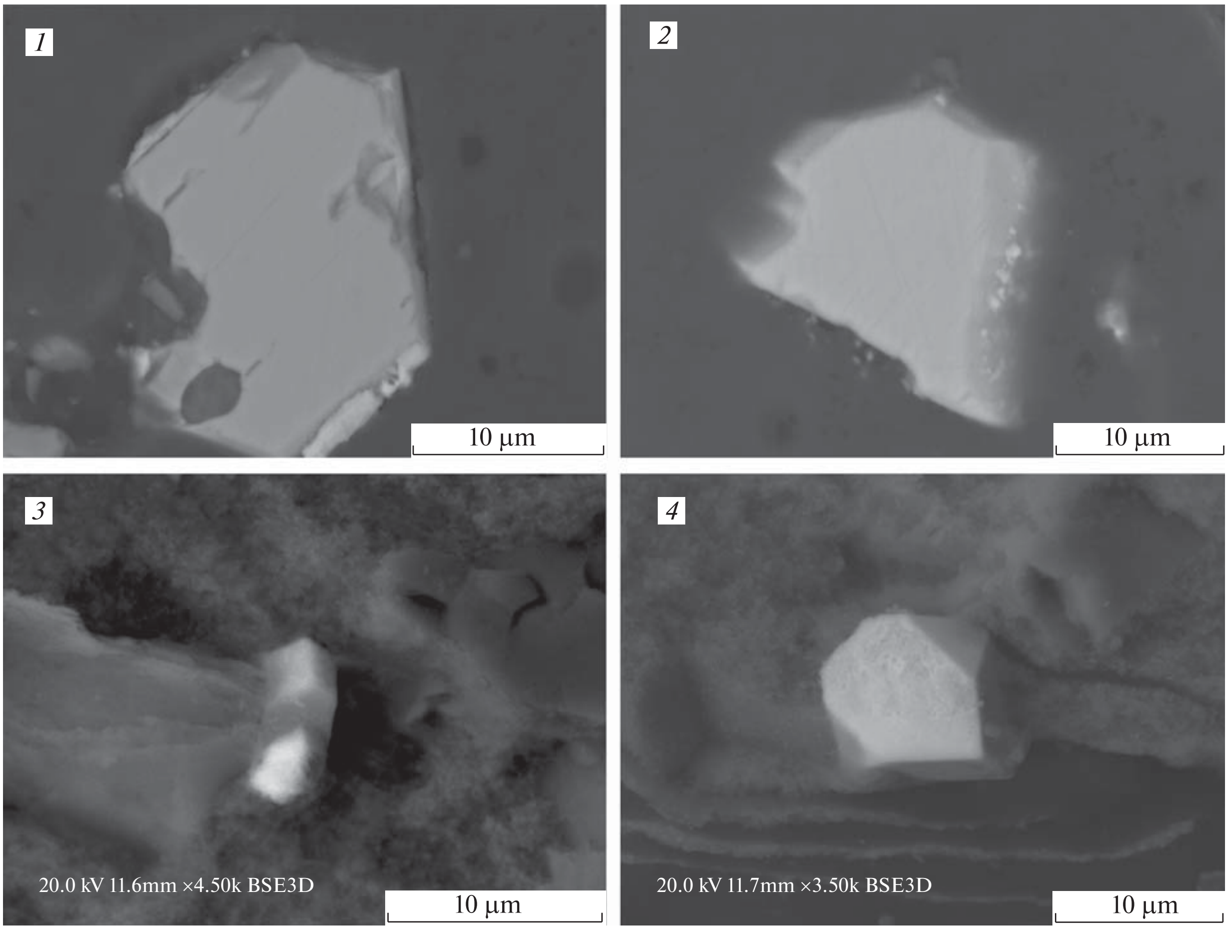

Fig. 5. Xenotime in coals *1* – Xenotime (white rim) on a zircon grain in the bituminous rank coal, Chernogorsk coalfield, Minusinsk Basin; *2* – Xenotime (bright white inclusions) on zircon grain in the bituminous rankcoal, Tomusinskoe coalfield, Kuzbass; *3* – Xenotime (white inclusion) on the zircon grain in Fire Clay tonstein (sample of D.A. Spears); *4* – Xenotime (white inclusion) in the coal ash of Velican seam, Chernogorsk coalfield, Minusinsk Basin.

process of coalification [21, 55–57]. These observations apply to all stages of the coal formation – from peat to bituminous coal to anthracite.

Modern modes of REE occurrence in coals are the result of long-term transformation occurring in the organic and mineral matter of paleo-peat during the coalification process. In this longstanding process with changing physical-chemical conditions, the modes of occurrence are reasonably supposed to change. The research of this directional process is necessary to begin from the peat-formation stage and to study it gradually until anthracites.

In the modern peats of northern Eurasia the REE contents are usually much lower than in coals, even though REE concentration levels in the peat ash is often comparable with the coal ash [58, 59]. Peat bogs are known in Finland in which the sum of the light REE (La, Ce, Pr, Nd, Sm) in the peat ash exceeds 0.1% and in some areas it is up to 0.5% [60]. The REE content is lower in the underlying granites and gneisses than in the peat and almost an order of magnitude lower than in the peat ash. For instance, in the Rapakivi granite the La, Ce and Nd content was reported as 128, 270 and 100 ppm respectively. But in the overlying peat, the La, Ce and Nd contents in separate horizons are as high as 1268, 2598 and 1766 ppm in the respective ash [60]. Therefore, with certain assumptions, modern peat bogs of the northern hemisphere can be considered as a precursor of coals and the origin of the rare earth elements distribution can also be assumed to derive primarily from the ancient peat bogs.

During peat accumulation, REE mostly accumulate in water-soluble and highly-hydrolized substances, probably partly in amino acids and in minor quantities in humic acids, composing 60–80% of the total [22, 23]. Mineral matter does not play a significant role in the accumulation of REE in peat. However, small portions of the REE do occur in stable REE minerals (e.g. monazite, xenotime, zircon, crandallite).

As noted above, from 20 to 95% of REE in the brown coal samples were found in the alkaline extracts

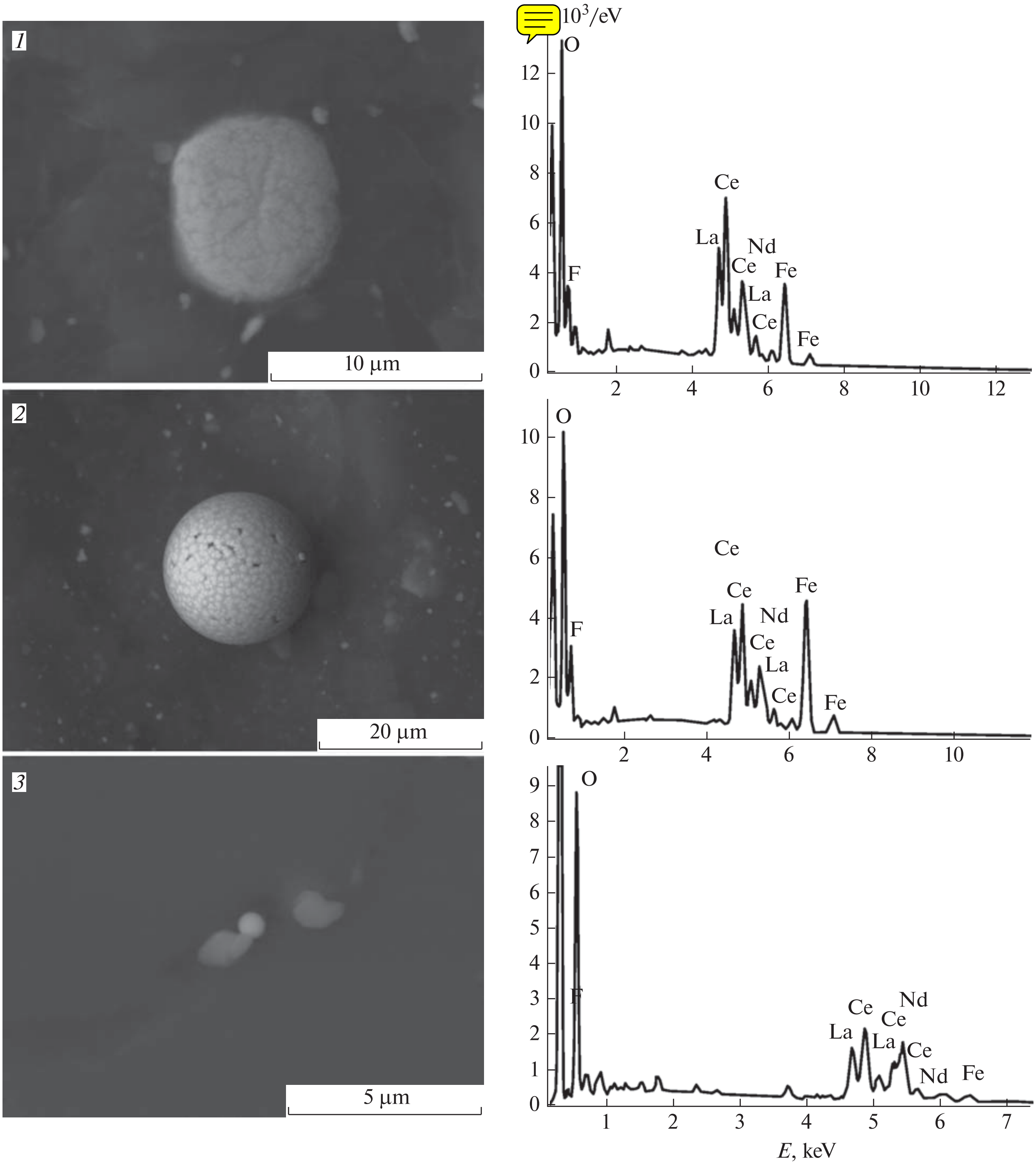

Fig. 6. REE carbonates in coals and EDX spectrums *1* – Subbituminous B brown coal, IIth seam of the Azeiskoe coalfield, Irkutsky basin; *2* – Subbituminous A coal, Velican Ith seam, Chernogorskoe coalfield, Minusinsky basin; *3* – Anthracite, Gorlovsky basin.

(humic and fulvic acids). In general, the role of humic substances in the accumulation of REE is substantial for brown coal. It is as low as 20% in rare cases but generally the REE proportion associated with humic substances is comparable to or greater than that in the residual coal phase. Thus, the fact that a large proportion of the REE is associated with humic substances in low-rank coals with different REE contents, demonstrates the important role of organic matter in the REE accumulation in coal regardless of its bulk content.

The residual phases of brown coals can contain REE either in minerals or as insoluble NaOH humins.

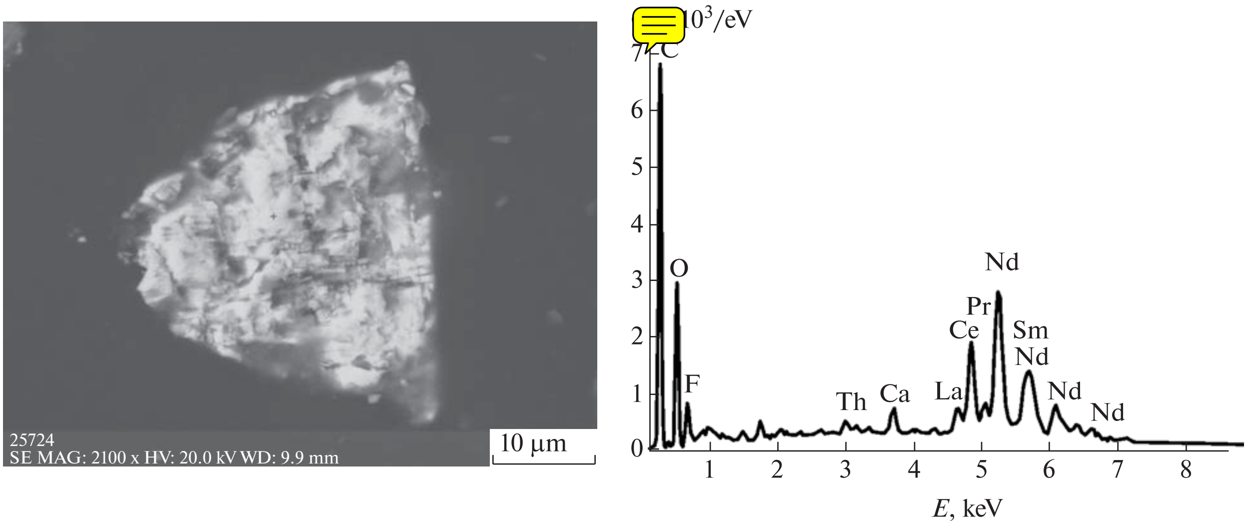

Fig. 7. Nd- synchysite in coal heavy fraction of XIth seam of Sibirginsky deposit, Kuzbass.

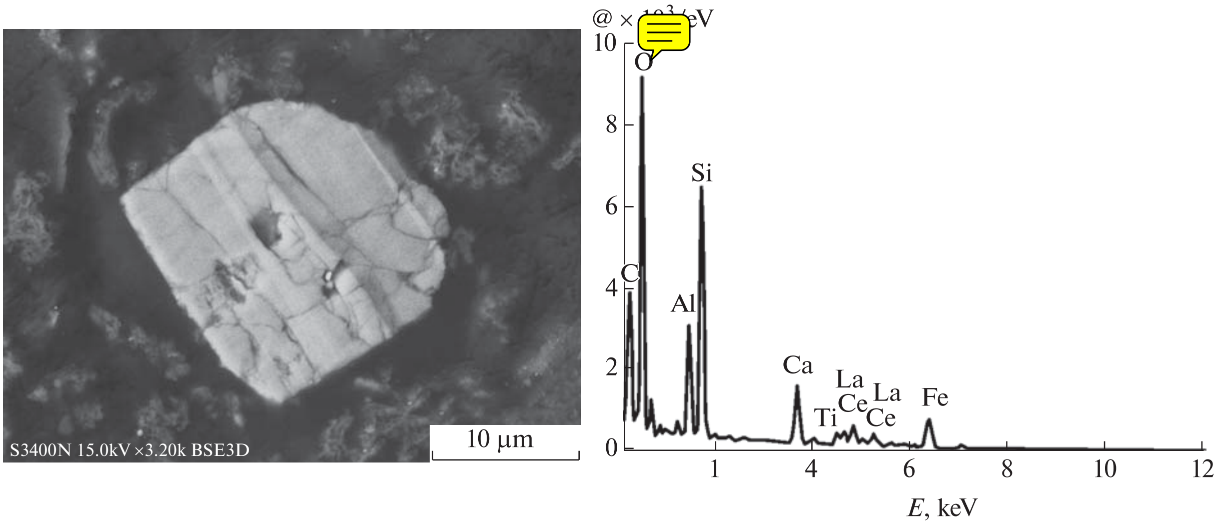

Fig. 8. REE-Ca-aluminum silicate in the ash of oxidized coal, Azeiskoe coalfield, Irkutsk basin and EDX spectrums.

According to Shpirt et al. [31], about 40% of the total amount of La and Yb is accounted for in the insoluble complex humates in the REE-enriched metalliferous brown coal of Primorye. No more than 10–20% is in rare-earth minerals and 1-2% is in the form of isomorphous components of various minerals.

It is notable that for most of our samples with both typical and elevated REE contents, significant amounts of the REE are concentrated in humic substances (humic and fulvic acids). The leading role of humic substances in the accumulation of the REE is obvious in brown coal while for peat the light REE are mainly concentrated in the water soluble phase and hydrolysable substances [22, 23]. Heavy REE tend to accumulate in the high-molecular weight humic acids. The condensation of low-molecular amino acids and other organic substances, concentrators of REE in the water soluble and hydrolysable substances, occurs in the process of coalification. Fulvic acids form first and then macromolecular humic acids appear [61]. There is a complexation of high-molecular humic acids followed by the simultaneous formation of insoluble humins. REE concentrated in peat in low-molecular hydrolysable substances readily pass into fulvic and humic acid by carbonization and then to insoluble NaOH-humins. Hence, the REE propensity to form strong insoluble complexes with humic acids causes their selective accumulation in the process of coal and peat formation – first in humic and fulvic acids, and then during carbonization in the residual carbon in the form of insoluble organic complexes (humins).

Our studies have revealed that the accumulation of REE in brown coal occurs mostly in the organic mode, most likely in strong complexes of chelates or in metal-organic complexes. The formation of such complexes indicates a predominantly hydrogenic mechanism for the REE concentration in coals. The presence of the organic modes of REE in brown coals is shown by the occurrence of film-like mineral phases in the coal laboratory ash, which are not detected in the coals (Fig. 2). Similar mineral phases were found in scandium-bearing brown coals [56] and [62] found similar amorphous film-like formations (crumpled thin films) of Ti-Al composition in low-temperature coal ash of the seam no.6 of the Illinois basin. Based on the structural features of such particles they concluded that the films likely formed from organic matter during the low-temperature ashing process.

The prevalence of these organic REE modes of occurrence results in changes in form during coal maturation and metamorphism. Coal metamorphism causes changes in the structure of the organic substances and reduction of the functional groups that should lead to the release of the REE and other elements associated with the organic matter and the formation of new compounds or removal of the elements.

According to our results, the extraction of insoluble humates by the alkaline extract is not generally followed by a substantial REE yield (Table 4). At the same time, in the oxidized bituminous coals of the Saykhan-Ovoo deposit a substantial part of the REE passed into the alkaline extract. It is possible that during the coalification process REE appear in the form of authigenic minerals when humic acids turn into insoluble humates. These authigenic minerals are dissolved again during the process of natural coal oxidation and then form complexes with humic acids.

Experiments showed that while heating the humic acid solution containing REE, a gradual leaching of the REE and formation of solid phases occurred [57]. About 25% of the REE passed into the solution at temperature of 80°C, 80% – at temperature of 160°C. No fractionation of the REE was observed. The REE extraction and distribution experiments by Nakada et al. [57] showed that REE adsorbed on humic acid were released and re-distributed to the solid phase (shale) in association with a decrease in the concentration of carboxyl groups. This supports the possibility of the alteration of modes of REE occurrence during coalification from chelates in the organic matter to minerals.

The poor permeability of coal seams, low migration capacity of REE in the waters of the supergene zone [63] and the absence of significant REE removal during carbonization and coal metamorphism [21] suggest a preferential binding of the released REE (during the autolysis of humic substances) in authigenic mineral forms directly in the coals or with the host rocks. The migration ability of REE in coals can be substantially higher than the traditionally accepted migration ability of the REE in freshwater of the supergene zone due to saturation by carbon dioxide and organic matter [38, 64, 65]. There also may be removal of REE during the up-ranking. It is especially evident in the anthracite stage [21].

However, the role of REE-bearing minerals in coals should not be disregarded. Their presence in sub-bituminous coals in important and is especially significant in bituminous coals and anthracites. Both the clastic and authigenic rare-earth minerals may be present in coal seams. In coals from different deposits of the world, a significant diversity of the REE minerals of both clastic and authigenic origin have been observed [1, 5, 21, 39, 44, 66, 67]. The calculations of Finkelman [5] for the Carboniferous Waynesburg seam (West Virginia, USA), based on the data of electron-microscopic investigations, showed that the micro-inclusions (1-2 mcm) of the rare-earth phosphates and alumophosphates (monazite, xenotime, crandallite) could provide 100% of the REE content in this mineral-rich coal.

The role of the authigenic minerals is most clearly demonstrated in zones where the coal is enriched in REE, uranium, and thorium at the contact with tonsteins [35, 44, 69]. The study of two coal samples from East Kentucky (USA), underlying tonsteins, were anomalously enriched in REE, yttrium, and zircon, showed that newly-formed rare-earth phosphates filled the fissures in clays and pores in clarain and vitrain [69].

Diverse REE minerals were recognized in tonsteins: phosphates (monazite, crandallite, xenotime, cheralite (Ca, Ce, Th)(P, Si)O_4), carbonates (bastnesite, parisite), oxides (cerium hydroxypyrochlore), and other accessory minerals containing REE (zircon, baddeleyite) [44]. Also, Il'enok and Arbuzov [44] found numerous small inclusions of the rare-earth phosphates (monazite, cheralite) at the contact with tonsteins in brown coals of the Azeiskoe deposit, Irkutsky Basin.

As Zou et al. [27] published unique pictures of authigenic goyazite and rhabdophane ($CePO_4 \cdot H_2O$) from a coking coal from southwestern China. Based on correlation analysis, the authors found that the REY (rare-earth elements+Y) mainly occur in the organic matter. It is possible that during coalification the REE reformed from organic complexes into authigenic minerals, within the organic matrix.

Coal metamorphism, up to the formation of anthracite and graphite, results in some REE loss from coal [21] and transformation of all organic compounds of REE into authigenic mineral forms (Fig. 5). Some of the stable minerals (monazite, xenotime and zircon) may be of primary clastogenic origin. This is evidenced by the presence of some finely dispersed rare-earth minerals in modern peat [22, 23].

We offer the following model to explain the alteration of modes of occurrence of REE during the coal formation process. At the early stage, during the peat accumulation the dissolution of minerals containing REE occurs. A substantial part of the REE becomes mobile, generally concentrating in the organic matter. A small proportion remains in mineral phases. Over the coalification and organic matter transformation processes, REE first pass into humic acids and then over the condensation process – into authigenic minerals. In bituminous coals and anthracites the REE mineral modes prevail.

CONCLUSION

This study showed that in the process of coal formation from "peat – brown coal – bituminous coal" an evolutional change of modes of REE occurrence takes place.

At the early stage of the coal formation (peat formation) mobile (water soluble) modes of REE occurrence prevail. The proportion of organically complexed REE compounds is substantial. Mineral matter does not play a substantial role in the REE occurrence in peat; even though rare-earth minerals (xenotime, zircon and monazite) are present.

At the brown-coal stage (from lignite to subbituminous B), the organic mode of REE occurrence is also dominant. It was observed for coals with different ash yields and with different levels of REE accumulation: from typical contents to anomalously high contents. The main forms of the REE are organic complex compounds of chelate type. The role of minerals in the total balance of REE is generally minor. The exceptions are some metal-bearing coals with rare-earth mineralization of hydrothermal origin [66] and, probably, the near-contact zones of tonsteins that are anomalously enriched in REE. In the humic matter of brown coal, in contrast to peat, the REE fractionation has not been observed.

In the mature coals of the bituminous stage, the role of minerals increases significantly [21, 68]. Due to the metal release through carbonification with the loss of carboxylic, hydroxylic, and other functional groups of humic matter authigenic minerals are formed. In the weak-metamorphically altered bituminous coal, a significant portion of the REE occurs as organic complexes; probably as unstable minerals easily extracted by concentrated HCl. Through the oxidation of such coals under natural conditions, the bulk of the REE is found in the regenerated humic acids. The higher the coal metamorphism grade, the greater the role of the newly formed minerals in REE accumulation. In the process of the coal metamorphism the share of the organic modes gradually decreases up to the full transformation into mineral phases in anthracite and graphite.

Among the REE minerals in coals diverse phosphates (monazite, crandallite, xenotime, goyazite, florencite) predominate, carbonates (bastnaesite, parisite, synchysite) and unidentified minerals of complicated compositions also occur. In addition, REE were observed in different accessory minerals in the form of isomorphic admixtures.

The modes of REE occurrence indicate that their concentration in coal is governed by hydrogenic mechanisms. Independently of the source of the REE supplied to the basin of coal accumulation, under conditions of the aggressive environment of a peat bog they change to a mobile form and finally are concentrated in the organic matter. In brown coals, in addition to the clastogene-volcanogene source, the REE may also accumulate in the organic matter due to their supply from the hypergene zone or thermal water. The subsequent transformation of the organic matter through the carbonification process results in the formation of authigenic REE minerals. The role of the organic modes of the REE occurrence in coals should be considered in the development of technology for the extraction of REE from coal and coal ash.

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