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ORIGINAL ARTICLE

Features of rare earth elements geochemistry in coals of Central Kazakhstan

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Abstract This research presents the results of a comprehensive study of mineralogical and geochemical features of REE distribution in coals of Central Kazakhstan deposits—Karaganda coal basin and Shubarkol deposit, which have large hard coal reserves and are industrially important for the coal industry of Kazakhstan; the research is based on 205 samples of clayey interlayers and coal seams. It shows basic patterns of distribution and features of concentration for impurity elements, gives an estimate of the impurity elements concentration, including REE, defines conditions and factors of their accumulation, and studies features of their forms in coal and coal-bearing rocks, which allows estimating the mechanisms of their migration and conditions of accumulation. According to the results of geochemical indicators, the article establishes the factors of REE dislocation, reveals the composition of margin rocks that have influenced REE concentration in coal seams, and the presented latest data on mineralogy allowed to establish the ways of their transportation to the paleobasin during the syn- and epigenetic periods of formation of the coal deposits of Central Kazakhstan being researched. It was found that the coals are insignificantly enriched with heavy lanthanides from Ho to Lu. The distribution curves of UCC normalized REE values in the coals are similar and coincide, but they are less than the average value for world coal, and amount to only one-third of the UCC. It was found that the highest concentrations of all REE are characteristic of clayey interlayers and oxidized coals. The La/Yb ratio in this case increases upwards along the section, indicating mainly clastogenic mechanism of REE delivery to the coals. In coal and clay samples, the predominant mineral form of REE is light lanthanide phosphates. Identified particles of REE from minerals and their composition peculiarities suppose autigene nature of their formation. The formation of the bulk of autigene minerals occurred during the maturation of brown coals and their transformation into hard ones.

Keywords Coal · REE · Impurity elements · Accumulation conditions · Concentration factors

1 Introduction

Under the conditions of the global economy, science, and technology rapid development, the constant desire for accuracy and intellect increased the demand for mineral resources of rare metals (Arbuzov et al. 2007, 2008, 2014; Seredin and Dai 2001). However, due to the gradual depletion of resources of traditional metal minerals, their limited residual reserves make it relevant to search for new potential sources (Spears 2012; Seredin et al. 2013; Dai et al. 2011). Coal is an important mineral and economic resource in many countries of the world (Arbuzov et al. 2007, 2014; Seredin and Dai 2001) and plays an important role in the modern economic development (Oliveira et al. 2019). It is the main source of material for power generation, energy-intensive industries (steel industry, cement production, etc.), and heating of residential and commercial premises.

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It was established that many rare metals can be found in industrial values in coal seams in many regions (Popov et al. 2022; Dai et al. 2006, 2015; Sun et al. 2010), including Ge, Ga, U, V, Se, rare earth elements and Y, Sc, Au, and Ag.

Coal has been found to be significantly enriched with trace elements and in recent years, potential options for REE extraction from them have been proposed (Liu et al. 2019; Eterigho-Ikelegbe et al. 2021). However, despite the high content of these elements in coals, they pose an environmental problem. Potential environmentally hazardous elements can be directly emitted during the use of coal, coal mining or transportation, disposal of coal mining wastes, and coal combustion by-products (Baba and Kaya 2004; Hower et al. 2020). Therefore, it is vital to determine the content and distribution of the elements in coal. Obtaining rare elements from coal is an important embodiment of the green and efficient utilization of coal, which is of great strategic importance to the development of a green economy (Li et al. 2022).

This paper presents data on the distribution of impurity elements in coal deposits, including some rare elements (Ge, Ga, Se, Li and REE + Y), which play a key role in energy-efficient technologies. The main purpose of this research is to investigate the geochemical characteristics since there are many coal deposits with high Ge, Ga, Se, Li, and REE contents in the world. Rare metals are concentrated in both coals and the host rocks, and in basement rocks. The genesis of metal accumulation and the ways of their occurrence can vary. It is shown that enrichment with these metals can occur in coal seams and in host rocks. The article studies genesis of high concentrations of rare metals and patterns of their occurrence in coal basins.

This paper considers the Karaganda coal basin, which is the largest and most famous coal basin in Kazakhstan, and Jurassic age Shubarkol deposit known for its low-ash content.

1.1 Characteristics of research objects

More complete sets of elements are found in brown and hard coal deposits of almost any age and genetic type (Arbuzov et al. 2014; Hower et al. 2018). The main differences are due to the tectonic position of the metallogenic province, peculiarities of geochemical specialization of the margin rocks, which influenced conditions of formation of the coal basin or deposit (Arbuzov et al. 2008). Kazakhstan deposits are no exception. Kazakhstan has large reserves of stone and brown coal. The choice of the research objects was determined by the research objectives, such as estimation of the average content of element-impurities in coals formed during different geological ages in different geotectonic settings, study of the patterns of their accumulation in coal-bearing sediments, assessment of the influence of various factors of geological environment on their concentration in coals and clayey interlayers, study of the conditions of concentration and fractionation of individual rare earth elements in geological processes, as well as determination of forms of their occurrence in coals.

The present research is aimed at studying geochemistry of coals in Central Kazakhstan (Fig. 1), which according to tectonic zoning belongs to the western part of the Central Asian Orogenic Belt (CAOB). The two research objects are large in terms of hard coal reserves and are industrially significant in the country's coal industry.

Despite the quite large number of coal deposits in Kazakhstan, these objects supply most of the country's domestic demand and export significant volumes of coal products.

Karaganda coal basin in terms of its tectonics, corresponds to the middle part of the laterally elongated synclinorium that occupies a specific position in the structure of Central Kazakhstan, being located in the zone of connection of the regions of Caledonian and Hercynian foldings, i.e., between the Hercynian Dzhungaro-Balkhash geosynclinal in the south and the zone of the Caledonian solidification in the north. Along this area, the Devonian marginal volcanogenic belt stretches; its occurrence was facilitated by the presence of a system of deep-seated faults and echelon faults here, which are accompanied by contortion, crushing, and schistosity of the rocks. The basin extends for 120 km in latitude, with a width of 30 km. The basin covers an area of 3600 km, of which the Carboniferous coal-bearing deposits account for about 2000 km.

Three major synclines (from west to east) are distinguished within the Karaganda basin: Sherubai-Nurinskaya, Karaganda, and Upper-Sokurskaya. The Karaganda industrial region is most fully explored; the main number of operating mines is concentrated here. This paper presents the results of geochemical and mineralogical research of the seam k_7 of Karaganda series ($C_1V_{3\text{-nkrg}}$) of Visean age of Carboniferous age in the Karaganda industrial region of Karaganda coal basin at mine faces—Sranskaya, Aktasskaya, and Kuzembayev mines, since Karaganda series is the second productive series of the basin and is widely spread along the wings of the Sherubay-Nurinskaya and Karaganda synclines. In the Upper-Sokurskiy area, the series has not been stripped, although the possibility of its presence in the cores of synclinal structures covered by a thick cover of Mesozoic sediments cannot be ruled out.

Shubarkol deposit was formed in the inherited cavity of the folded regions formed on the Saryssu-Teniz upheaval. The deposit basin developed over the ancient sedimentary complexes, which is a part of the structural cage of the Caledonian accretionary-folded regions belonging to the

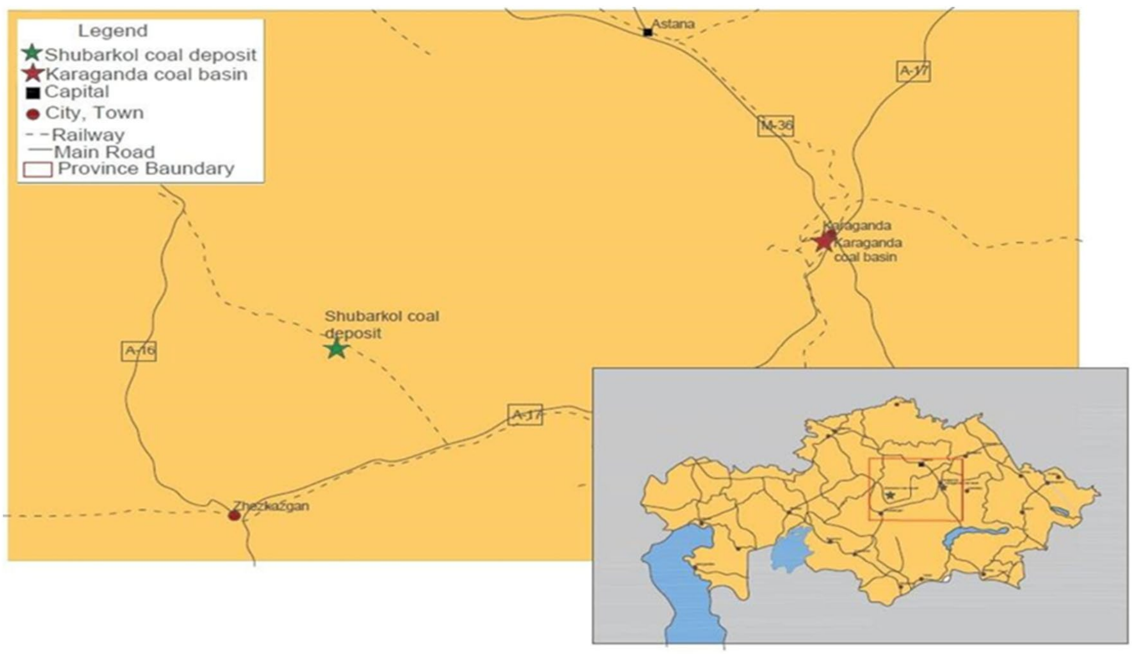


Fig. 1 Location of the Shubarkol deposit and Karaganda coal basin

central part of the Saryssu-Teniz upheaval or fault-shear zone Kopobayeva et al. (2021), the large tectonic structure of the Western part of the Central Asian orogenic belt (CAOB).

Coal-bearing strata are represented by the Jurassic sediments of Shubarkol basin. Lower Jurassic coal-bearing sediments with a thickness of up to 330 m form a basin with east–west trending (7 × 16 km) with gentle western and eastern (5–10° and 5–15°), and steeper southern (20–48°) and northern (40–90°) wings. In the internal part of the basin, the bedding angle does not exceed 3–5°. In the central part of the basin, low-angle transverse upheaval of coal-bearing stratum is observed, which flattens to the north from the long axis of the structure. It separates the basin into its western and eastern parts. In the first one, the top of the upper coal horizon has maximal depth from the daylight surface that is 127 m, and in the eastern part, it is 90 m. The field comprises three sites: Western, Central and Eastern. The composition of the coals from the Shubarkol deposit is diverse, they contain various impurity elements and rare metals. The research has shown (Parafilov et al. 2020; Amangeldykyzy et al. 2021a, b) that there are significant contents of Ba, Sr, Th, Rb, Fe, Co, Ce, Zn, and Sc at the deposit.

The commercial coal-bearing capacity of the field belongs to the lower part of the Jurassic sediments section and includes three coal horizons: Upper, Middle and Lower. The Upper horizon is of the greatest interest; it is taken for open pit mining. Thinner and more irregular Middle and Lower horizons are planned for underground mining.

Geology of the field is presented by terrigenous-carbonate sediments of Upper Devonian and lower Carboniferous periods, the terrigenous rock of the Middle Upper Carboniferous age (Palaeozoic sediments), as well as loose weathering products of Mesozoic and loose sediments of Cainozoic.

2 Materials and methods

The paper presents research based on 2 coal deposits of Central Kazakhstan, the most detailed geological and geochemical research was performed. The total number of coal samples studied in the region is 205.

For a more detailed understanding of geochemical features and mechanisms of impurity elements accumulation in coal-bearing sediments of the Karaganda basin, we performed sampling in three active mines, where at the moment the seam k7 is being mined, this was done directly in the mine face of mine Saranskaya, Aktasskaya and Kuzembayev mine, and also new data of mineralogical and geochemical researches of coals and clayey interlayers of Shubarkol deposit are given. Coal and clayey interlayers at the research objects were sampled vertically—by channel method, thickness of each sample was 0.05–0.20 m. The chemical composition of samples from the two deposits was determined in the analytical chemistry laboratory of the Collective Use Centre of the Far East Geological Institute of the Far

Eastern Branch of the Russian Academy of Sciences (FEGI FEB RAS). The ultimate composition of coal and clayey interlayers samples was determined by inductively-coupled plasma optical emission spectroscopy and inductively coupled plasma mass spectrometry (ICP-OES and ICP-MS) using Agilent 7500 (Agilent Techn, USA) and iCAP 7600 Duo (Thermo Scientific, USA) spectrometers. Electron-microscopic analysis of the samples from Karaganda basin was performed in the Laboratory for micro- and nano-research of the FEGI FEB RAS using two-beam scanning electron microscope Tescan Lyra 3 XMH + EDS AZtec X-Max 80 Standart. This method allows identifying and photographing mineral forms in micron and nanomicron sizes, and identify their ultimate composition. Minerals deportment in the samples of coals from Shubarkol deposit were studied using the method of scanning electron microscope SEM–EDX Hitachi S-3400N, which was performed in IIREC "Uranium Geology" at the Geoecology and Geochemistry Department of the TPU. Based on the data, tables were compiled for the content of individual rare elements, spider diagrams, diagrams for impurity elements average content with reference to their clarkes in hard coals were build.

3 Results and discussion

To reveal the main patterns and specifics of impurity elements concentrations, including REE concentrations, a complex analysis was carried out and the conditions of REE accumulation in coals and coal-bearing rocks were studied.

Assessment of the degree of enrichment of the Jurassic (Fig. 2a) and Carboniferous sediments (Fig. 2b) of Central Kazakhstan has shown that the concentrations of trace elements are close to the average values for world coals (0.5 < KK < 2) according to (Dai et al. 2015). Analysis of distribution of impurity elements in the coal samples of Shubarkol (Jurassic) deposit has shown (Fig. 2a) that the largest concentration belongs to ion lithophilic elements (Ba, Sr, Sc, Zr, V), and the rest of rare earth elements have relatively average concentration, while in the coal samples of Karaganda basin the highest concentration belongs to ion lithophilic (Li, Sc, V, Zr, Hf, Y) and chalcophylic (Ag, Cu, Co) elements. The coals of the Karaganda basin are also

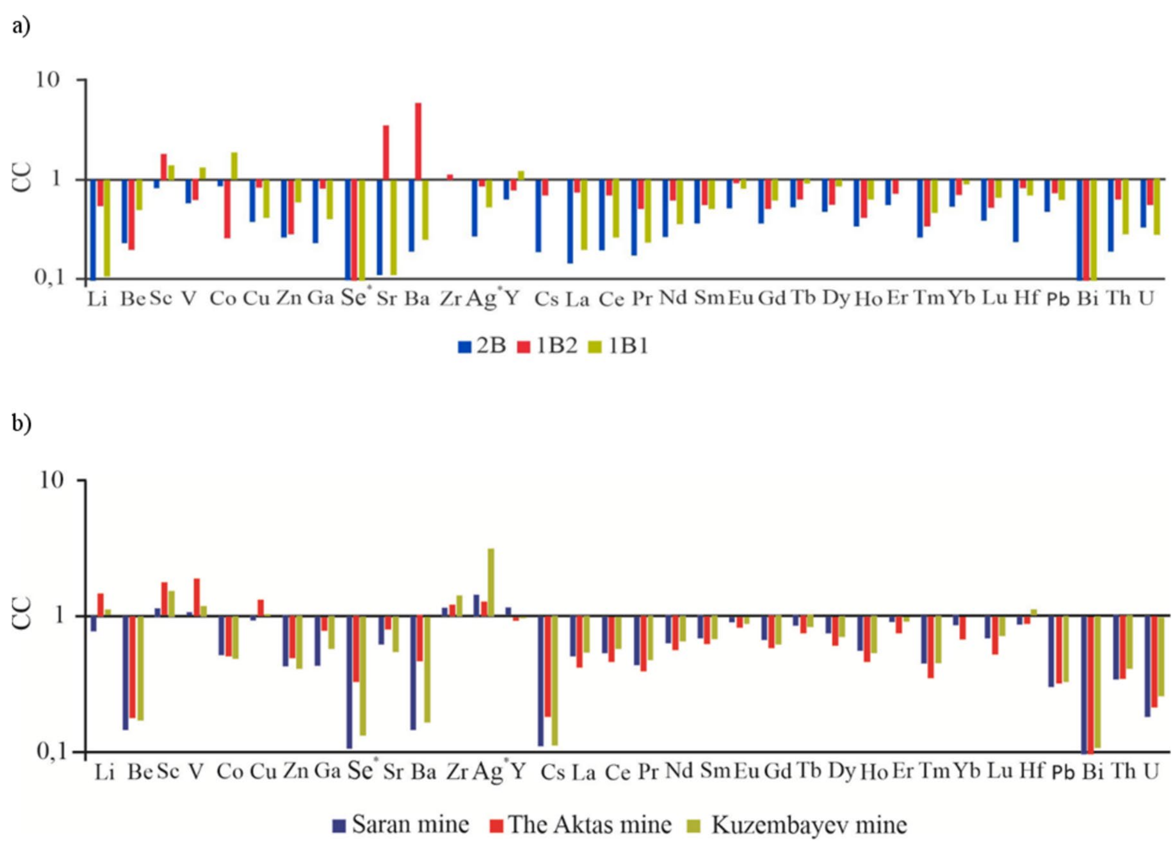


Fig. 2 Concentration coefficients (CC) of trace elements in the coals of seams **a** 2B, 1B2, 1B1 of Shubarkol deposit and **b** seam k_7 of Karaganda basin

enriched with As, Sb, Hg, which is allegedly consistent with the presence of epithermal deposits of Cu, Sb, Hg, Pb, As associated with volcanites.

Increased contents of Sr and Ba at Shubarkol deposit have apatite associations that can be obtained from bauxites on the weathered basement in the area of the sedimentation source.

Analysis of the impurity elements distribution in clayey rocks of the research objects showed that large ion lithophilous (Sc, Ba, Sr) and transit (Cr, Zn) elements has the greatest concentration, and the rest elements (As, Ca, Fe, Sb) are relatively average.

Based on the results of the REE distribution analysis along the CC in Jurassic and Carboniferous coals, it was established that the coals are depleted in LREE: La–Nd; insignificantly depleted in MREE: Sm-Dy, and insignificantly enriched with NREE: Ho-Lu. Thus following the sequence La → Lu, the ion radius of REE decreases, and the alkalinity of the REE gradually reduces. According to (Chen et al. 1990), the ability of REE to form complexes increases in the sequence La → Lu, and ability of heavy REE to form complexes is greater than that of light REE, so that the migration ability of heavy REE is higher than that of light REE in nature. Thus, it is assumed that the possible sources of heavy REE in the coals of Central Kazakhstan are a decrease in the pH value of terrigenous materials when entering the peat bog and an increase in the absorption capacity of REE from La to Lu, which led to their accumulation in the peat bog (Shao-Qing et al. 2021).

To establish the specifics of REE distribution in coals, the paper analyses the normalized to UCC (Taylor and McLennan 1985) REE values for world coals (link), and Jurassic and Carboniferous coals of Central Kazakhstan. Based on the data obtained (Fig. 3, Table 1) there is a trend of coincidence of the REE distribution (< 1.0) in nature, despite the differences in age and conditions of coal formation. Similarity is observed in relation to world coals with a predominance of significant decrease in some REE.

The similarity of the character of REE distribution in world and different-age coals of Central Kazakhstan is also confirmed by the sum of REE, which varies from 13.3 to 90.6, with the average value of 56.38 in Jurassic coals and 28.2–65.4 in Carboniferous coals with the average value of 42.50. The established contents are lower than the average value for coals in the world (Ketris and Yudovich 2009), and amount to only a third part of the UCC (Table 1).

Within the studied deposits, the lateral and vertical distribution of REE has been studied. Analysis of the vertical distribution of La and Yb in seams 2B and 1B2, 1B1 in three sections on the western and central sites of the Shubarkol deposit and in seam k7 of Karaganda basin (Fig. 4) has shown that the highest concentrations of all REE are characteristic of clayey interlayers and oxidized coals. The La/Yb ratio in this case increases upwards along the section, indicating mainly clastogenic mechanism of REE delivery to the coals (Arbuzov et al. 2007).

Such a REE distribution is explained by different sorption capacity of clayey minerals. Also Seredin (Seredin 1996) claims that adsorption of clayey and fine-grained minerals is of secondary importance. Due to the difference in chemical properties of REE, fractionating is possible when REE come to the peat bog in their ion state,

Fig. 3 Normalized diagrams of REE distribution in the coals of the upper bench of the seam

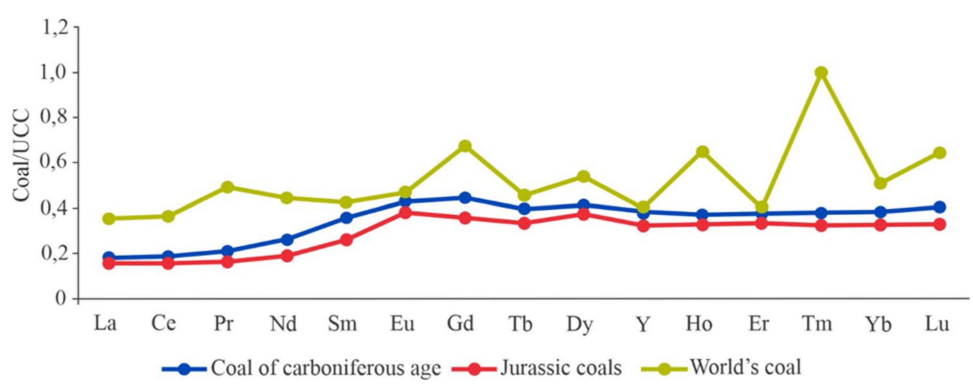


Table 1 Average REE value for the coal of Early Carboniferous and Middle Jurassic in Central Kazakhstan, UCC, and world coal

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	∑REE
Jurassic coal	8.06	17.5	2.11	9.0	1.97	0.4	2	0.31	1.79	10.1	0.38	1.13	0.17	1.19	0.18	56.4
Carboniferous coal	5.55	12.4	1.52	6.9	1.62	0.4	1.70	0.26	1.47	8.37	0.30	0.88	0.13	0.88	0.13	42.5
UCC	30.0	64.0	7.1	26.0	4.50	0.9	3.80	0.64	3.50	22.0	0.80	2.30	0.33	2.20	0.32	168.4
World's coal	11.0	23.0	3.4	11.0	2.40	0.43	2.70	0.31	2.10	8.20	0.57	1.00	0.30	1.00	0.20	67.6

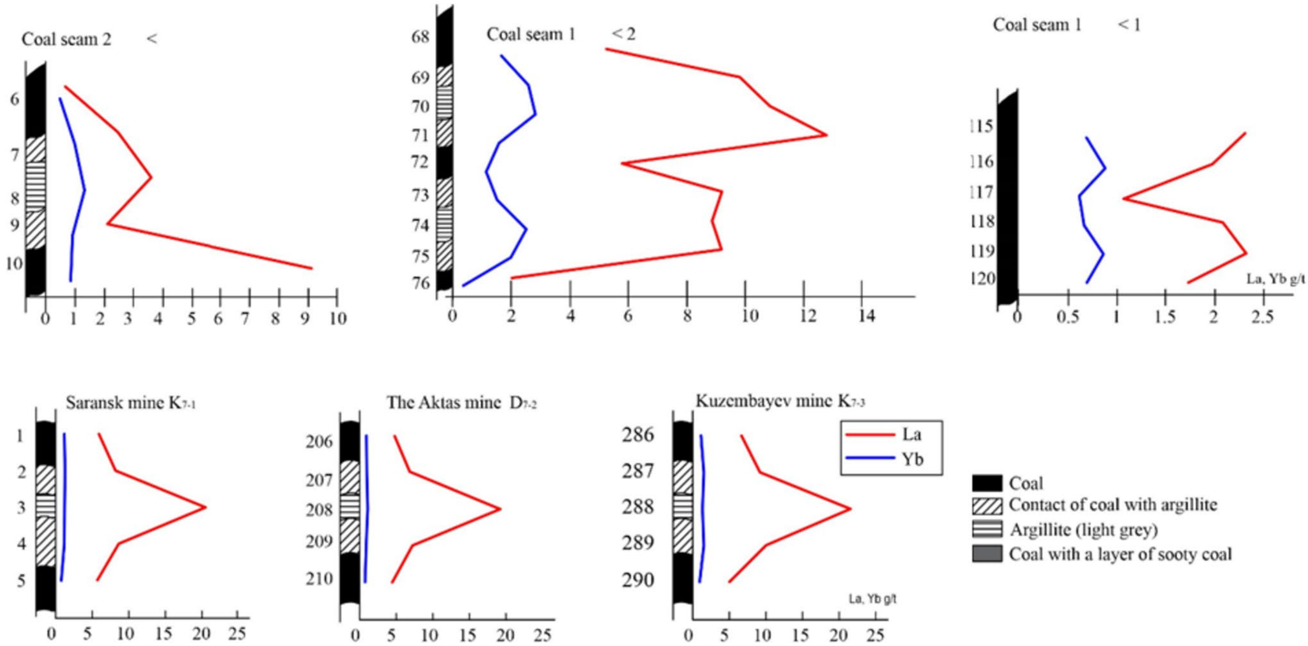


Fig. 4 Vertical distribution of La and Yb in seams 2B, 1B2, 1B1 of shubarkol deposits and in seam k_7

which is mainly manifested in the difference in the nature of REE distribution in coals and hosting rocks. HREE in coals are relatively enriched. The above fractionating may not occur during the REE transfer to a peat bog in form of fragments. Therefore, it is assumed that the REE inclusions in Carboniferous coals in this research are mainly brought into coal with debris facies, which mainly exist in inorganic minerals. While for Jurassic coals it is likely that REE would come into the coal basin mainly in a dissolved state, since there are differences between the patterns of distribution and content of REE in coal and empty rock.

Lateral variability within coal seam k_7 of Karaganda basin and coal seams 2B (section 1–2), 1B2 (section 4–3), 1B1 (section 6–5) of Shubarkol deposit is less distinctly manifested (Fig. 5).

It was established that the sum of REE in coals of seam k_7 at different sites of Karaganda coal basin do not differ. It is shown that at a fairly significant distance, the content changes weakly, and increases in general from west to east. At the same time, their content clearly decreases from margins to the centre (Fig. 5a, b), according to (Yudovich and Ketris 2006), this fact indicates a certain role of water solutions in REE accumulation in colas, presence of such a distribution pattern is characteristic for carbonificated elements (Li, Rb, Sr, Ba, Be, Sc and etc.).

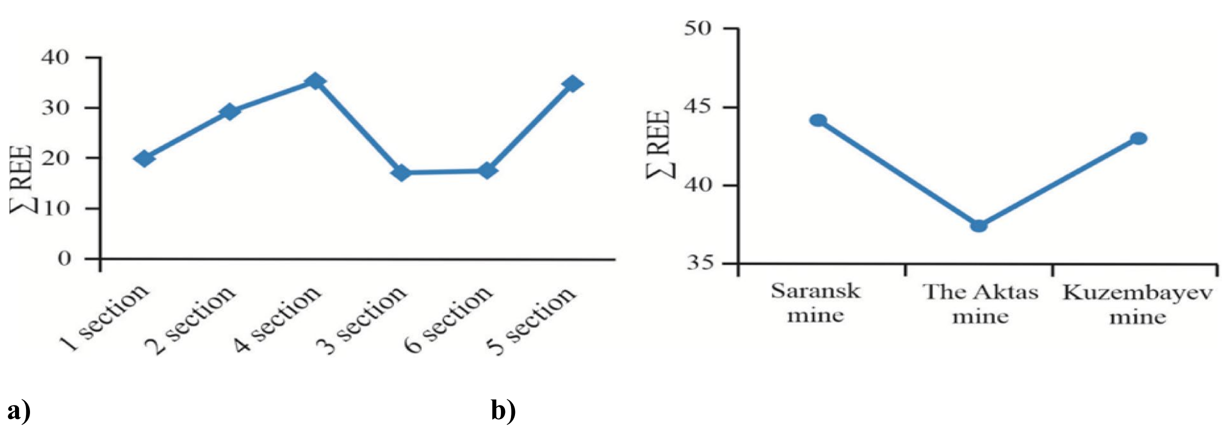


Fig. 5 Lateral distribution of the sum of lantanoids in coals from west to east according to the coordinate grid: **a** Shubarkol deposit at sites (2B) Western and (1B2, 1B1) Central; **b** Karaganda basin (k_7–1)—Saranskaya mine, (k_7–2)—Aktasskaya mine, (k_7–3)—Kuzembayev mine

The analysis of the geochemical data shown below indicates the existence of a number of independent sources and various REE accumulation mechanisms в sediments of the deposits in Central Kazakhstan. All data on REE are normalized to the content of the UCC. According to different ages of coal formation, data for the deposits are given in Table 2.

According to geochemical classification, suggested by Seredin and Dai (2012) and normalized to the REE average

Table 2 Geochemical parameters of rare earth elements in coal and clayey interlayer samples of Shubarkol deposit and Karaganda basin

In coals								In clayey interlayers					
Coal stratum	Sample	∑REE	La_n/Lu_n	La_n/Yb_n	δEu	δCe	Enrichment type	Sample	∑REE	La_n/Lu_n	La_n/Yb_n	δEu	δCe
Jurassic coals (Shubarkol)													
2B	6	15.3	0.099	0.101	1.212	0.206	H type	7	23.4	0.237	0.234	1.121	0.826
	10	13.3	0.081	0.080	1.162	0.160	H type	8	26.1	0.254	0.248	1.133	0.807
	41	15.0	1.005	1.028	1.178	0.800	H type	9	14.5	0.223	0.225	1.092	0.777
	50	24.2	0.244	0.238	1.203	0.330	H type	42	66.2	0.836	0.867	1.143	0.858
	59	29.3	0.224	0.222	1.138	0.337	H type	43	133.9	1.052	1.052	1.122	0.855
1B2	68	33.8	0.225	0.227	1.110	0.478	Type M	69	40.5	0.278	0.288	1.156	0.815
	72	31.7	0.410	0.427	1.201	0.694	Type M	70	40.5	0.268	0.281	1.177	0.778
	76	15.6	0.461	0.493	1.131	0.642	Type M	71	48.7	0.598	0.632	1.397	0.873
	85	56.5	0.987	1.018	1.354	1.203	Type M	83	48.8	0.209	0.220	1.097	0.891
	86	90.6	2.744	2.981	1.745	0.879	Type M	88	55.8	0.255	0.267	1.126	0.858
	100	52.1	1.051	1.063	1.584	0.860	Type M	89	40.0	0.284	0.309	1.074	0.802
	104	52.7	1.471	1.456	1.552	0.967	Type M	91	38.3	0.316	0.328	1.140	0.815
	105	37.8	0.818	0.805	1.592	0.808	Type M	92	49.4	0.317	0.331	1.133	0.806
	109	36.4	0.621	0.627	1.494	0.711	Type M	93	38.2	0.374	0.407	1.119	0.792
1B1	115	33.5	0.200	0.202	1.207	0.316	H type	118	32.3	0.216	0.228	1.183	0.386
	116	31.0	0.169	0.170	1.210	0.278	H type	119	32.8	0.180	0.179	1.242	0.272
	117	27.2	0.117	0.113	1.246	0.234	H type	120	27.0	0.164	0.168	1.182	0.257
Carboniferous coals (Karaganda basin)													
k_7	1	65.4	0.451	0.488	1.663	1.766	H type	3	104.63	1.251	1.453	1.493	1.537
	5	35.3	0.453	0.488	1.843	1.472	H type	8	106.91	1.128	1.324	1.572	1.581
	6	62.1	0.371	0.403	2.088	1.74	H type	13	95.91	0.971	1.085	1.794	1.49
	10	40.9	0.564	0.655	1.979	1.632	H type	18	90.14	0.979	1.092	1.665	1.544
	11	35.3	0.307	0.333	1.946	1.65	H type	23	88.76	1.020	1.163	1.63	1.532
	15	46.5	0.429	0.491	2.138	1.614	H type	203	92.48	1.13	1.301	1.43	1.51
	16	60.2	0.488	0.522	1.695	1.707	H type	208	88.92	1.43	1.542	1.31	1.49
	20	30.4	0.626	0.735	1.653	1.455	H type	213	86.62	1.34	1.558	1.31	1.52
	21	32.8	0.272	0.288	2.332	1.56	H type	218	89.08	1.32	1.443	1.36	1.51
	25	30.2	0.495	0.551	1.735	1.489	H type	278	112.09	1.186	1.198	1.534	2.211
	201	38.6	0.32	0.342	2.01	1.75	H type	283	106.69	1.415	1.361	1.449	2.253
	205	41.1	0.48	0.531	1.90	1.76	H type	288	106.40	1.330	1.323	1.380	2.334
	206	36.0	0.39	0.419	1.99	1.62	H type	293	107.73	1.526	1.512	1.368	2.318
	210	32.9	0.61	0.663	1.80	1.67	H type	298	108.66	1.436	1.457	1.356	2.256
	211	46.2	0.50	0.516	1.89	1.73	H type	281	46.9	0.554	0.565	1.988	2.154
	215	29.3	0.50	0.520	1.97	1.64	H type	285	36.0	0.352	0.347	1.868	2.098
	216	38.1	0.62	0.655	1.97	1.64	H type	286	51.1	0.384	0.388	1.925	2.283
	220	35.3	0.46	0.504	1.91	1.69	H type	290	28.2	0.318	0.311	1.780	2.041
	276	58.9	0.416	0.401	2.160	2.421	H type	300	43.1	0.408	0.402	1.712	2.159
	280	35.5	0.383	0.367	1.809	2.030	H type		-		-	-	-

Comments. interchange: ∑REY = La + Ce + Nd + Sm + Eu + Tb + Yb + Lu; δEu = Eu N/Eu N * = Eu N/[(Sm N × 0,67) + (Tb N × 0,33)], δCe = Ce N /Ce N * = Ce N /[(La N × 0,67 + Nd N × 0,33)]; Sm N, Eu N, Gd N, Tb N, La N, Lu N, Ce N, Nd N——normalized ratio of rare earth elements in the Upper Continental Crust. The formulas are taken from (Taylor and McLennan 1985) concentration in UCC (Taylor and McLennan 1985), REE enrichment patterns in coals of the studied deposits were divided into three groups (Table 2): light (type L) (La_N/Lu_N > 1), medium (type M) (La_N/Sm_N< 1,) and heavy (type H) (La_N/Lu_N<1). Averaged for Central Kazakhstan deposits and presented in this paper ratio values La_N/Lu_N ~1 insignificantly exceed one unit. Ratio La_N/Lu_N in coals of the researched deposits of both ages varies from 0.16 to 2.74 (Table 2), which indicates the characteristic predominance of of heavy lanthanides over the light ones. REE in coals have low concentrations and are characterized by distinct enrichment of type H (Fig. 3). Formation of type H coals with near clarke levels of REE accumulation, according to V. V. Seredin (Yudovich and Ketris 2006), occurs during long-term discharge of carbonic acid waters with increased HREE content into the peat bog, with subsequent banding of REE by turf organic substance, the same situation was possible during the formation of metal bearing coals of Central Kazakhstan.

The diagrams of REE distribution in Jurassic and Carboniferous coals of Central Kazakhstan also confirm that the coals of deposits belong to H-M type (Table 2) and are characterized by the absence of a negative Eu anomaly.

Eu anomalies in sedimentary rocks are inherited from parent rocks or are exposed to high-temperature hydrothermal fluids influence. Value of Eu/Eu^* in argillites is also an indicator of the composition of rock complexes eroded on the paleo encatchment area. In this paper, samples of Carboniferous and Jurassic coals have positive Eu anomalies (Eu/Eu^*, average value of 1.1–2.3), which indicate a hydrogenic mechanism of lanthanides accumulation.

Despite the close spatial arrangement of the research objects, the geochemical specifics of the rocks have significant differences. The Jurassic coals of Shubarkol deposit are characterized by occurrence of a negative ceric anomaly δCe in seams 2B, 1B2, 1B1 of the deposit (it varies within 0.1–0.8), which is explained by the presence of autigene minerals (Kopobayeva et al. 2022), and coal forming peat bog in under oxidation conditions. If we consider mineralogical and geochemical conditions, these concentrations can be caused by the exposure to seawater or hydrothermal processes (Arbuzov et al. 2014), which could in their turn affect the occurrence of the ceric minimum in Jurassic coals due to the presence of autigene minerals (e.g., clay minerals that inherit the ceric minimum from seawater) (Ayupova et al. 2002), also REE may have entered the sedimentation area as a part of debris material, which confirms the influence of rocks of the alimentation zone on the formation of the geochemical background of the deposit.

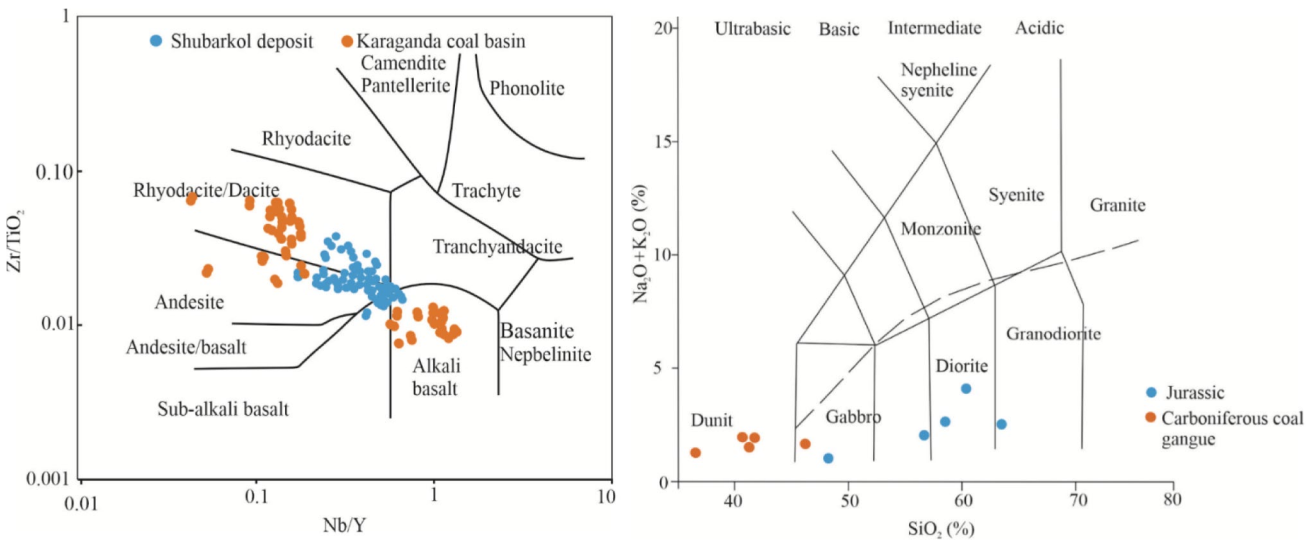
The enrichment of peat bog with rare lands could occur during infiltration of acidic natural waters into the epigenetic period, as evidenced by the positive cerium anomaly. Anomaly δCe is also an effective oxidation and reduction indicator that can be used to analyse sedimentary environments and paleowater conditions. It was revealed that only in coal samples of Karaganda basin, the ceric anomaly is positive, which could affect rocks with a slight admixture of the "background" debris material. Presence of the positive ceric anomalies in this field confirms the peculiarity of the composition of the original rocks and the way of REE migration to sediments under the reduction conditions. It is known that cerium migrates well in acidic waters and precipitates in the alkalized environment (Yudovich 2003).

To reconstruct the features of the rocks composition in the provenance areas, the ratios of a number of petrogenic and chemical elements (Na_2O, K_2O, SiO_2; Zr/TiO_2, Nb/Y) were used, and the corresponding diagrams (Fig. 6a, b) show that the source of the rare earth elements for the studied rocks are both rather mature rocks (presence of clay minerals in the original sediments), and the less altered material of the basic and ultrabasic composition.

During the research (Fig. 6a, b), it was found that the formation of the geochemical background of the research objects was influenced by the presence of intrusive rocks (granodiorites, diorites, gabbro, dunites, peridotites, granosyenites, sinenite porphyre, granite-porphyre) and volcanic (dacites, rhyodacites, andesites, andesite-basalts, alkali-basalts, quartz albitophyres, trachyte porphyre) of the Devonian age forming volcanic-plutonic complex (VPC) in Central Kazakhstan, which is also indicated by a high Sc contents. It is known that (Arbuzov et al. 2014), high concentrations of scandium belong to the areas with a significant distribution of basitic rocks in the composition of the coal bearing basin provenance area, which are geochemically specialized for Sc.

It is confirmed by the fact that in the south (Karamendinskiy complex) and in the south-west (Algabasskaya series) in the margins of Shubarkol coal deposit (Jurassic) (Amangeldykyzy et al. 2022) plutonic rocks of various composition: granodiorites, quartz diorites, diorites, alaskites and gabbro are spread, and for Karaganda basin (Carboniferous), Tekturmasskiy segment occupies an axial position and extends from south-west to north-east for the distance exceeding 40 km, and includes serpentine melange in the bottom and sediments of Karamusun, Tekturmas and Sarytau series. Composition of the serpentine melange includes harzburgites, dunites, eutaxic gabbro, gabbro-amphibolites, gabbro-greenstones, fragments of rodingites, basalts and siliceous rocks submerged into serpentine groundmass (Gurov et al. 2022).

It is established that impurity elements entered the coals via faults formed from basement rocks due to subtraction and resedimentation with syn- and epigenetic processes of subsoil and ground waters (Blyalova et al. 2023).



a) **b)**

Fig. 6 **a** Position of the figurative points of compositions on the discriminatory diagram; **b** sources of delivery of impurity elements to the coals of Central Kazakhstan

Based on the results of the research done using the scanning electronic microscope for the coal and clayey interlayer samples of Shubarkol deposit (Tomsk, TPU) and Karaganda coal basin (Vladivostok, FEGI FEB RAS), mineral deportments for the impurity elements, including REE, were identified.

During detailed electron-microscopic studies, well-faceted crystals of zircon, native silicon, and brazilite are found in the clayey interlayers of Shubarkol deposit. Separate grains of zircon contain an admixture of scandium, titanium, yttrium, or other heavy REE. Brazilite is less commonly found than zircon. The mineral was detected in rocks and coals on contact with them. This nature of mineral isolation indicates a sparing regime of transportation of a substance and eliminates its transfer with water flows. This once again indicates different ways of REE migration to the coals and carbonaceous rocks of the field (Kopobayeva et al. 2021).

The identified forms of rare earth elements in the coals of the Shubarkol field are in the form of aggregates of plate, laminal, sparry crystals, and fragments of prismatic crystals, which allows assuming the autogene nature of their formation (Fig. 7) (Amangeldykyzy et al. 2021a, b).

The coal and clayey interlayer samples from the Karaganda coal basin were studied using a highly local method of analytical scanning electron microscopy (SEM–EDS), which characterizes the morphometry of solid-phase components in the provided samples and determines the content of chemical elements in them. In addition, an automated search for mineral phases with specified characteristics was carried out using program modules AZtecFeature, including electronic documentation of pictures (images) in different modes under the scanning electron microscope, and dispersive spectra of their composition were obtained using the X-ray spectrometer.

REE deportments in coals are quite diverse, the most common ones are phosphates, alumophosphates, and carbonates. High carbonification of REE suggests an important role of organic matter in their concentration in coals. Autigene mineral forms of REE, which highly prevail in hard coals, including phosphates, are formed during the destruction of organic complexes in the process of converting organic matter during the process of coal formation (Yudovich and Ketris 2006). In the coal and clay samples from the Karaganda coal basin, the predominant mineral form of REE is phosphates of light lantanoids. Sparry crystals of CeLaNdPO composition (Fig. 8) are found in coal and clayey interlayer samples.

Reasoning from teh literature data, it is considered that the prevalent mineral form of REE presence in coals is phosphates concentrating light lanthanides (Arbuzov et al. 2019). Phosphates and carbonates enriched with yttrium and heavy lanthanides are found more rarely, in spite of their high content in coals. Although, according to (Seredin and Dai 2001; Arbuzov et al. 2019), this is not the initial form, since in diagenesis, transformation from organic into phosphatic form took place.

The REE particles found in the minerals in the samples from Shubarkol deposit and Karaganda coal basin and the specifics of their composition allow assuming autigene nature of their formation. The formation of the bulk of

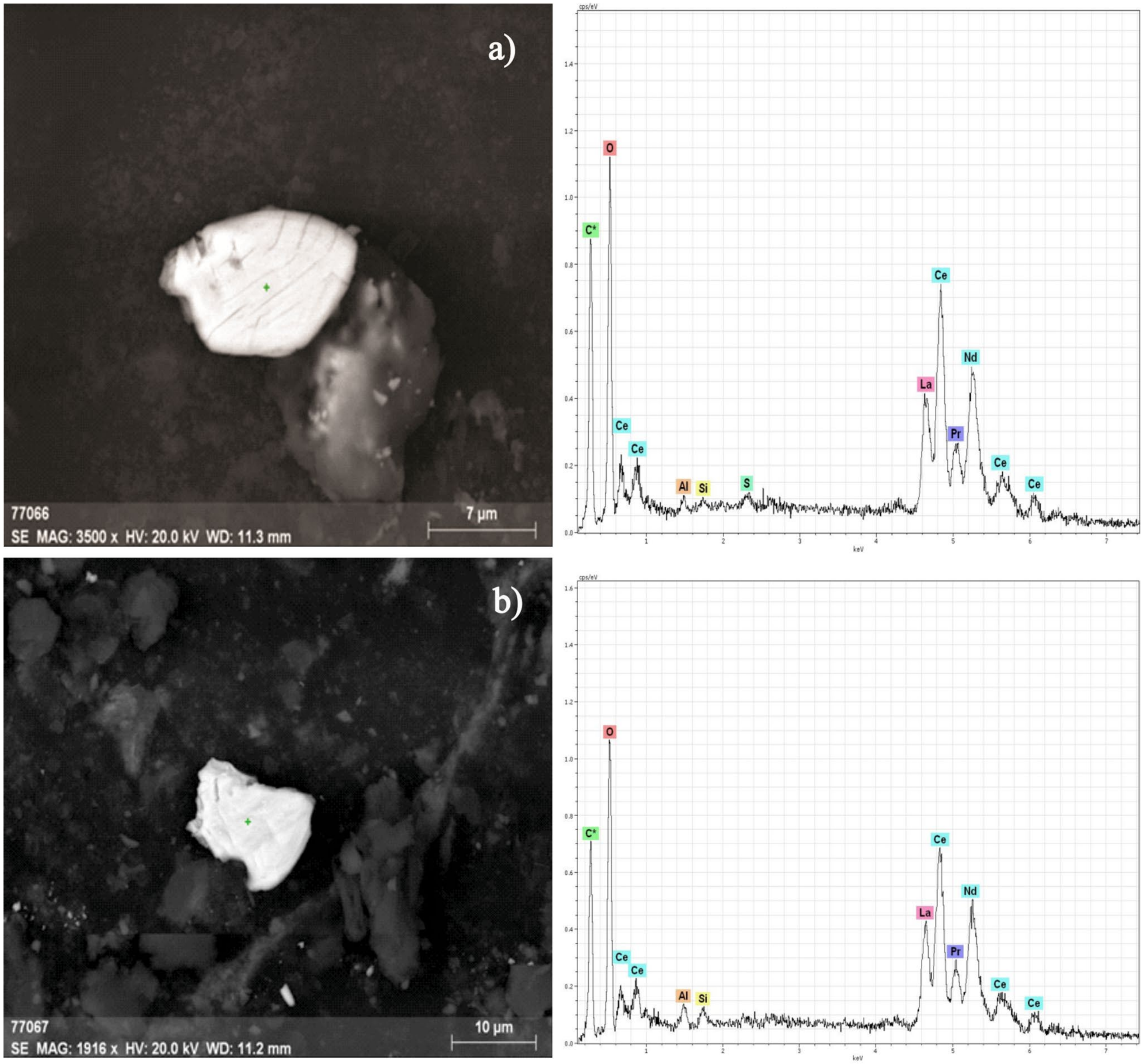


Fig. 7 **a** REE phosphates in the form of prismatic crystals, **b** REE in the form of aggregates of laminal crystals

autigene minerals occurred during the maturation of brown coals and their transformation into hard ones. In mature coals of the carboniferous stage, the role of mineral phases increases; due to the carboxyl, hydroxyl and other functional groups that are released during carbonification, autigene minerals are formed.

4 Conclusion

This article presents the results of summarized material that characterize the processes of accumulation and distribution of impurity elements, including REE in the coals of Central Kazakhstan. The identified main patterns of the distribution and features of concentration of impurity elements, REE in the coals of Shubarkol deposit and Karaganda coal basin evidence the existence of a number of independent sources and various mechanisms for REE accumulation.

It was established that the most of the trace element contents in the coals of Central Kazakhstan are depleted. The concentration is close to the appropriate average indicator for coals in the works. In Karaganda coal basin (Carboniferous), the interconnection of the metallogenic specialization of the provenance area on lithophilous and chalcophylic metals with geochemical features of the basin coals is clearly manifested (Gussev et al. 2010).

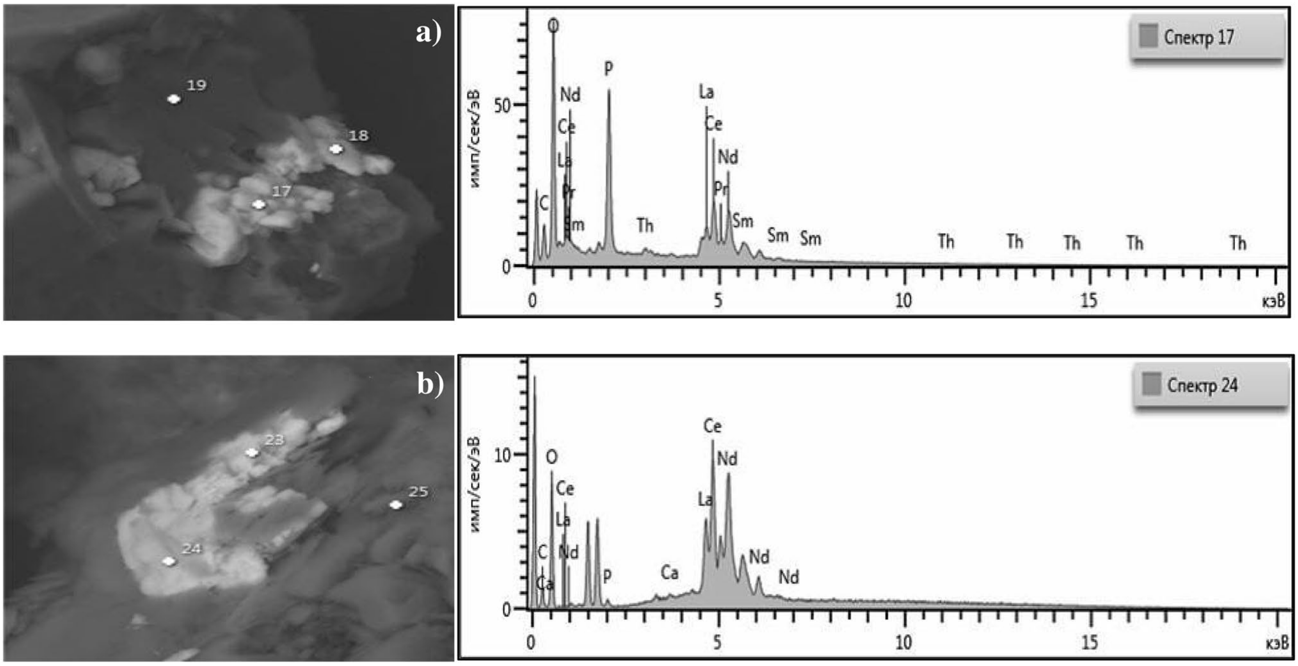


Fig. 8 Mineral inclusions of CeLaNdPO composition **a** in coals; **b** clayey interlayers of Karaganda coal basin

High contents of lithium, which are uncharacteristic for Paleozoic coals, emphasizes the role of pyroclastics in the accumulation of rare earth elements. The coals of the basin are also enriched with As, Sb, Hg, which is consistent with the presence of epithermal deposits of Cu, Sb, Hg, Pb, As associated with volcanites. Shubarkol deposit is enriched with Zn, Ba, and Sr, as such, this is consistent with the fact that deposits of Attassu Ba-Pb–Zn type are located nearby. The coals contain elements characteristic of alkaline rocks and granitoids, in increased quantities, such as Zr, Hf, Ta, Nb, and Sr.

The nature of the REE distribution in the Carboniferous and Jurassic coals is similar and tends to coincide, which indicates that the values of the REE content in the Carboniferous and Jurassic coals of Central Kazakhstan are the same.

The ratio of La_N/Lu_N of the coals of both ages indicates characteristic predominance of heavy lanthanides over light ones in coals of the deposits researched, and is featured by a distinct accumulation of H type. The absence of a negative Eu anomaly indicates hydrogenous mechanism of the lantanoids accumulation. Research of the lateral variability of the REE amount in the Carboniferous and Jurassic coals has shown that the contents are distinctly reduced from the margins to the centre, and this indicates a certain role of water solutions in the REE accumulation in the coals. A similar pattern of distribution is characteristic of carbonificated elements.

The results of analysing the established δCe anomaly confirm the specifics of the initial rocks composition and REE ingress way to the sediments under the conditions of reduction in Karaganda basin, and in the Jurassic seams of Shubarkol deposit, it indicates the presence of autigene minerals, and the fact that the coal forming peat bog was under the conditions of oxidation.

The identified particles of the REE minerals in the samples from Shubarkol deposit and Karaganda coal basin, and the features of their composition allow assuming the autigene nature of their formation with different ways of REE migration into the coals: this research found that in Carboniferous coals they were mainly brought into coal with debris rocks, which mainly exist in inorganic minerals, while for Jurassic coals, the ingress of REE into the coal basin occurred mainly in the dissolved state. The predominant mineral form of REE in hard coals and clayey layers of Karaganda coal basin and Shubarkol deposits are phosphates of light lantanoids (CeLaNd), the formation of which is conditioned by the destruction of organic complexes during the transformation of organic matter in the process coal formation.

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Data availability The data that support the findings of this study are available on reasonable request from the corresponding author.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

Consent to publication All authors read and approved the final manuscript.

Ethical approval Not applicable in this work.

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