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Nature of ree accumulation in clayey interlayers and coals in Karaganda coal basin

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ABSTRACT
It is the first completed complex mineralogical and geological research of REE (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in the coals of Karaganda coal basin in Central Kazakhstan. This paper presents the results of the research of REE (from lanthanum to lutetium and Y) distribution in 85 samples of coal and clayey interlayers of stratum k7 of Karaganda coal basin in the faces of Saranskaya, T.Kuzembayev, Aktasskaya mines. The ultimate composition of clayey interlayer and coal samples was analyzed by the methods of inductively coupled plasma optical emission spectroscopy and inductively coupled plasma mass spectrometry (ICP-OES and ICP-MS). Research of the lateral and vertical discontinuity of the total REE concentration has indicated the presence of mixed types of REE distribution in coals, which supposes various forms of REE migration and different mobility of heavy and light lanthanides within the hypergenesis zone. The established lanthanum-ytterbium (La/Yb) ratio in the coal, which is normalized to UCC and equals La/Yb<1, relates to the coals with H type of REE distribution, and the one that equals La/Yb>1 and normalized to chondrite belongs to the coals with L type of REE distribution, which allows making conclusions on the presence of independent sources and different mechanisms of REE accumulation in the sediments of Karaganda coal basin. It is also established that the La/Yb ratio grows from coals to clayey interlayers, which indicates a predominantly clastogenic mechanism of REE input to the coals. The prevailing mineral form of the REE in the coal and clayey interlayer samples from the Karaganda coal basin is light lanthanide phosphates. Sparry crystals with CeLaNdPO composition were found in the coal and clayey interlayer samples. It was established that xenotime is the main deportment for Y in many coals.

Keywords: coal, clayey interlayer, Central Kazakhstan, Karaganda coal basin, rare earth elements, average content.

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Introduction

The growing demand for rare earth elements in the global market encourages many countries to search for alternative REE sources. In such countries as the USA, China and a range of other countries, the average content of all rare earth elements has already been estimated in the world coals [[1], [2]]. Coal and coal processing products have become an alternative for finding and extracting REE.

The main sources of REE are granite weathering crusts, carbonatite deposits and coastal-marine placers. In addition to traditional raw materials sources of lanthanides, metalliferous coals are also considered potentially promising [[3], [4]]. The factor of synchronous volcanism has a significant impact on the formation of the geochemical background of rare elements and impurities in coals (Finkelman, 1993). Volcanogenic material is found in coal seams mainly in the form of low–power clay interlayers - tonsteins. Volcanic pyroclastic, which forms tonsteins, serves as a source of accumulation of valuable metals and abnormal concentrations of impurity elements in coals. In areas with thick seams, the accumulation levels of these impurity elements in coals can reach industrially significant values (Seredin, 1994; Spears, 1999, Arbuzov et al., 2003, 2005, 2019).

The first references to the abnormal content of REE in coals were noted in 1933 by V.M. Goldschmidt and C. Peters. In the 1980s, V.V. Seredin for the first time described rare earth mineralization with commercial content of REE in coals. After publication in 1991 by V.V. Seredin, different research groups started to publish papers on abnormally rare earth coals in other deposits [Seredin, 2001, 2005; Seredin et al., 2011, 2012, 2013; Dai et al., 2007, 2008, 2010, 2011, 2016c; Arbuzov et al., 1997, 2003, 2007a; Hower et al., 1999; Mardon, Hower, 2004; Chekryzhov et al., 2016b; Dai et al., 2016c], which had lead to an increased interest to studying lanthanide geochemistry in coal deposits. It is known [[3], [5]], that REE content in all coals is lower than in UCC (upper continental crust). Countries with developed economies (USA, Europe, Australia, China) have partially estimated REE composition in the organic matter, and it is published in many publications, which show that coals and coal ashes can also contain high, in some cases commercial concentrations of REE. For the efficiency of REE extraction from coals, it is necessary to understand the mechanism of concentration, nature of accumulation, and deportments of REE in coals. In this regard, attention to geochemical research in coal deposits has increased dramatically, and coal deposits are considered potential sources of REE [[3], [5]].

However, despite comprehensive geochemical research of coal deposits in the world, the issues related to the conditions of accumulation, migration and fractionating of lanthanides in coals, their departments, and factors controlling the formation of rare earth metal-bearing coals remain open and require additional research [[4], [6]].

For the Republic of Kazakhstan, the industry of which is focused on the extraction, processing and consumption of mineral raw materials, the state of the mineral resource base is of key importance. The Karaganda coal basin is one of the largest and most promising basins in Kazakhstan. In his Message to the people of Kazakhstan [7], President of the Republic of Kazakhstan Kassym-Zhomart Tokayev on 01.03.2023 noted the high significance of studying and researching rare and rare earth metals: “One of priority tasks must be development of deposits of rare and rare earth metals that essentially have become a “new oil”. Countries that will be able to implement their potential in this sphere will define the vector of the technological progress for the whole world”, said the President of the Republic of Kazakhstan. The President's words once again confirm the relevance of research on the REE geochemistry in coal as an additional source of REE.

A comprehensive assessment of the contents of critical elements in coal is extremely important for understanding the geological processes affecting their enrichment with elements, which allows the full use of coal in an economical and environmentally friendly way. A reliable estimation of the average content of rare earth elements in coal for the majority of coal basins and deposits of Kazakhstan needs to be clarified using modern research methods. An analysis of the nature of the lateral distribution showed that the k7 coal seam can serve as a potential raw material for complex processing and utilization of many impurity elements. The restoration of economically valuable REE and critical elements that can contribute to the national economy, the introduction of advanced environmentally friendly technologies and the reduction of the risk of coal leaks in warehouses will limit disposal costs, as well as reduce the environmental impact, which should be taken into account and implemented by coal mining companies.

Deposit Characteristics. A distinctive feature of the Paleozoic coal accumulation in Central Kazakhstan, as a result of which the Karaganda coal basin was formed, is a significant influence on the carbon formation process of volcanic activity. This was reflected in the enrichment of coals with lithophilic, including moderate and weakly carbon fiber elements such as Hf, REE, Sr, Ta, Th and U [[5], [8]]. Their anomalies in Paleozoic coals are associated with the horizons of tonsteins, modified tuffites and scattered pyroclastic material, which were described above.

The Karaganda coal basin in the west is framed by the large meridional Tekten fault. In the east, its border is considered to be part of the synclinorium, where it abruptly turns into a narrow and shallow synclinal fold (Achshisu synclinorium), which comprises coal-bearing sediments with commercial strata. Beyond the basin, this synclinorium extends to the east along the valley of the Achshisu River for 200 km.

Within the Karaganda basin, three large synclinoria are distinguished (from west to east): Churubay-Nura, Karaganda and Upper-Sokur, which are divided by respectfully Alabas anticlinal fold and Maykuduk upheaval [9] (see Fig. 1).

This paper presents the results of the complex mineralogical and geochemical research of the stratum k7 of the Karaganda district of Karaganda coal basin in the faces of "Saranskaya", "Aktasskaya", Kuzembayev mines.

The listed mines belong to the Karaganda coal province. Today, all three mines are joined into the Saran field of Karaganda coal province. The field of T. Kuzembayev mine is located in the eastern part of Saran field. The fields of Saranskaya and Aktasskaya mines belong to the central and southwest parts of the Saran field of Karaganda coal province.

The Karaganda synclinorium, within which the Karaganda coal province is located, occupies the central part of the Karaganda basin. The northwestern wing of the synclinorium, where the T. Kuzembayev, Saranskaya and Aktasskaya mines are located features a comparatively simple structure and persistent east-north-eastern trending. The northwest flat dipping wing of the synclinorium has a general northeast trend with a pitch towards the southeast under the angle of 10-150. In the northeastern, part of the site in the area of synclinorium closure, the trending of the coal-bearing strata gradually changes from north-eastern to eastern. Pitch angles at outcrops are respectfully grown from 10-15 to 700. The southeastern wing of the synclinorium unlike the northwestern one has more upridging of strata.

Discontinuous faults are widely developed on the southeastern wing of the Karaganda synclinorium, and there are few of them on the northwestern flat dipping wing and this area is tectonically simple. The geological structure of the region comprises sediments of Carbonic, Jurassic, Neocene and Quaternary periods [9].

According to M.G. Chernovyants (1992), a high saturation of coal seams with tosteins has been established. Among them, coarse and crystalline varieties predominate, their thickness ranges from fractions of millimetres to 2 cm. It was also found that the k1 formation at the mine named after Gorbachev has up to 20 tonstein interlayers, and the k7 formation has 6 Tonstein horizons. In this regard, samples were taken in three operating mines, where the k7 formation is currently being worked out, these are directly in the bottom – the Saranskaya, Aktasskaya and Kuzembaev mines for a more detailed study of geochemical features and understanding of the mechanisms of accumulation of impurity elements in the coal-bearing deposits of the Karaganda syncline.

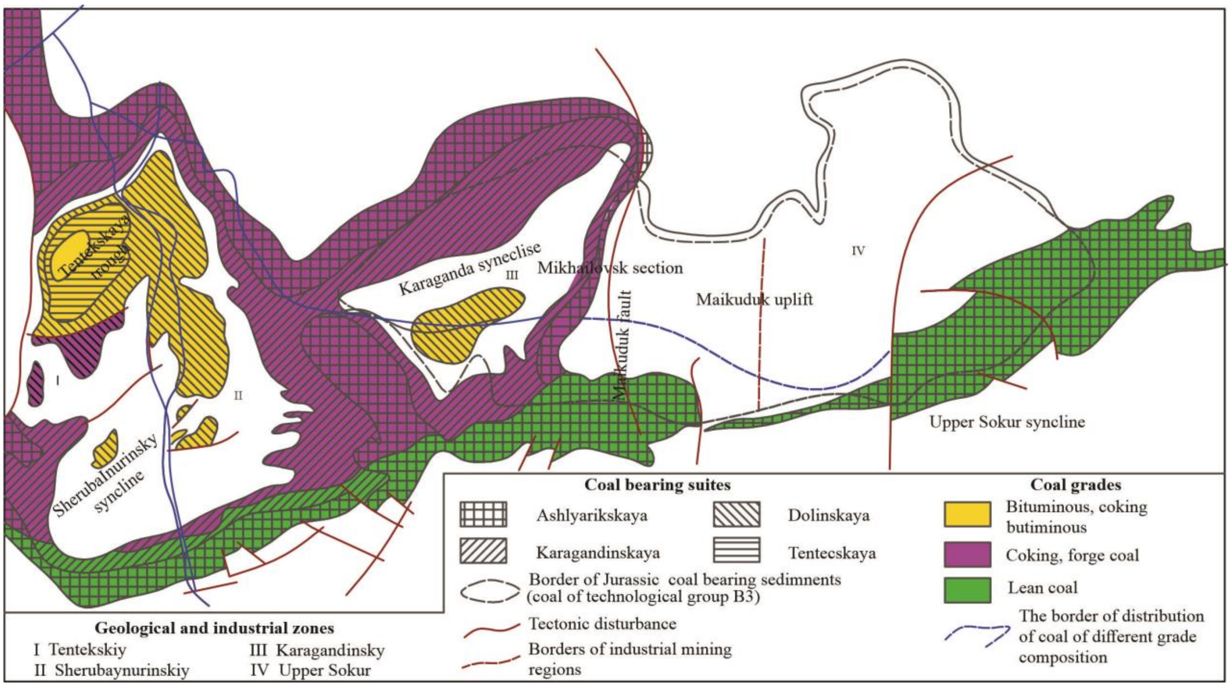


Figure 1 – Geological and Industrial Zoning of Karaganda Coal Basin

Research Methods

The grounds for this article are complex geochemical and mineralogical research of coals and clayey interlayers of stratum k_7 of the Karaganda coal basin. Coal strata sampling was performed by the channel method with differentiated sampling in the faces of Saranskaya, T. Kuzembayev, and Aktasskaya mines. 85 samples of coals and hosting rocks have been taken in vertical sections. In each section, 5 samples were taken to trace the lateral and vertical variation in the mineralogical and geochemical features of stratum k_7: coals – UC (upper coal – upper part of the section) and BC (bottom coal – bottom part of the section); clayey interlayers – CI and contact zones of coal and clayey interlayers – UCn (upper contact in the upper part of the section) and of clayey interlayer with coal – BCn (bottom contact in the bottom part of the section). The length of the sampling interval was chosen depending on the thickness and complexity of the stratum structure; it on average varied from 10 m to 200 m. The depth of the sampling points varies at the three mines, the depth of the formation varies from 600 to 650 m.

All samples were subjected to sample preparation, laboratory and analytical tests in accredited, leading laboratories that specialize in coal research. The ultimate composition of clayey interlayer and coal samples was analyzed by the methods of inductively coupled plasma optical emission spectroscopy and inductively coupled plasma mass spectrometry (ICP-OES and ICP-MS). To study the distribution of the minerals, their form, and morphological features in the coals and clayey interlayers, analytical scanning electron microscopy along with energy-dispersive X-ray spectroscopy (SEM-EDS) were used. All researches were performed in the Federal State Budget Enterprise of Science Far East Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (FEGI FEB RAS).

Discussion of the results 85 coal samples were studied: 25 coal samples at Saranskaya mine, 40 coal samples from Kuzembayev mine, 20 coal samples at Aktasskaya mine; total content of REE (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) are presented in Table 1, Table 2, and Table 3.

Based on these data, the total amount of REE in clayey interlayers and contact zones varies within the range of ∑REE = 53.18-102.53 g/t. And their total content in the coal is within the range ∑REE = 28.48-65.78 g/t. These data on REE amounts in the coals and clayey interlayers indicate that increased content of REE relates to the clayey interlayers and contact zones of the coal-clayey interlayer.

Table 1 – Results on the REE Contents for Saranskaya Mine

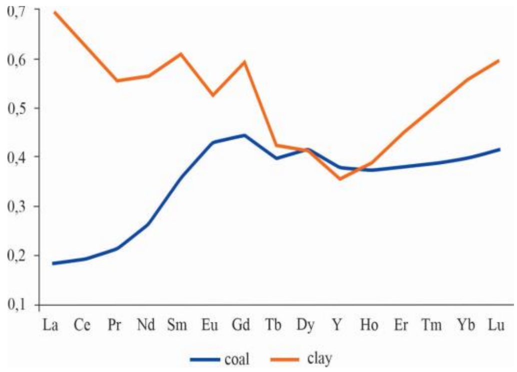
Saranskaya Mine					
	Sampling Point No. 1				
	UC	UCn	CI	BCn	BC
∑REE	65.78	68.01	104.89	75.81	35.86
	Sampling Point No. 2				
∑REE	62.44	57.34	107.18	62.19	41.04
	Sampling Point No. 3				
∑REE	35.52	64.52	96.19	60.61	46.8
	Sampling Point No. 4				
∑REE	60.52	47.99	90.45	36.26	30.59
	Sampling Point No. 5				
∑REE	33.07	58.46	89.04	49.59	30.34

Table 2 – Results on the REE Contents for T. Kuzembayev

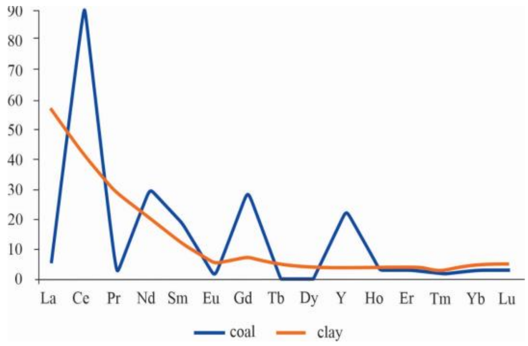
Mine Aktasskaya Mine					
	Sampling Point No. 1				
	UC	UCn	CI	BCn	BC
∑REE	38.89	56.29	92.72	63.2	41.35
	Sampling Point No. 2				
∑REE	36.23	44.69	89.11	49.06	33.1
	Sampling Point No. 3				
∑REE	46.5	47.15	86.82	51.63	29.47
	Sampling Point No. 4				
∑REE	38.37	64.62	89.3	51.73	35.47

Table 3 – Results on the REE Contents for Aktasskaya

Mine Kuzembayev Mine					
	Sampling Point No. 1				
	UC	UCn	CI	BCn	BC
∑REE	29.99	48.46	90.46	62.17	48.59
	Sampling Point No. 2				
∑REE	65.31	67.69	89.04	54.87	42.41
	Sampling Point No. 3				
∑REE	55.9	57.15	97.67	68.1	38.74
	Sampling Point No. 4				
∑REE	59.32	63.22	112.45	87.2	35.67
	Sampling Point No. 5				
∑REE	47.11	75.7	107.01	64.03	36.26
	Sampling Point No. 6				
∑REE	51.42	78.99	106.66	69.23	28.48
	Sampling Point No. 7				
∑REE	43.36	76.46	107.99	79.19	31.09
	Sampling Point No. 8				
∑REE	47.71	64.65	108.94	66.36	42.72



a) normalized to UCC



b) normalized to chondrite

Figure 2 – Rare Earth Elements Distribution in Coals and Clayey Interlayers of Karaganda Coal Basin

Seredin and Dai [4] divided REY (REE) in coal into light (LREY: La, Ce, Pr, Nd and Sm), medium (MREY: Eu, Gd, Tb, Dy and Y) and heavy (HREY: Ho, Er, Tm, Yb and Lu) groups. This classification is more convenient than other classifications for describing REE distribution in coals. When interpreting the obtained results, REE contents were considered as normalized to the chondrite composition [10] and normalized to UCC [10], and the following criteria for lanthanide estimation were used:

$$Eu_{an} = Eu/Eu^* = Eu_N/(Sm_N + Gd_N) \times 0.5 \quad (1)$$

$$Ce_{an} = Ce/Ce^* = Ce_N/(La_N + Pr_N) \times 0.5 \quad (2)$$

The distribution curve normalized to UCC in clay shows depletion of medium lanthanides and predominance of light lanthanides over heavy ones, and vice versa enrichment of medium lanthanides and predominance of heavy lanthanides over light ones in coal (Fig. 2). Estimated Eu - and Ce - anomalies in the coal and clay showed negative europium and cerium anomalies (0.24 and 0.26, respectively). This type of REE distribution is characteristic of clayey interlayers formed with the participation of ash material of acidic composition. Four main types of REE distribution are characteristic of the world coals: N–type (normal for earth crust), L –, M – and H – types feature an accumulation of light, medium and heavy lanthanides [[11], [12]]. It is considered that coals with N- and L-type distributions are formed when most of REE were introduced with terrigenous material and coals with M- and H-type distributions are formed when most REE were introduced with water solutions [[11], [12], [13]].

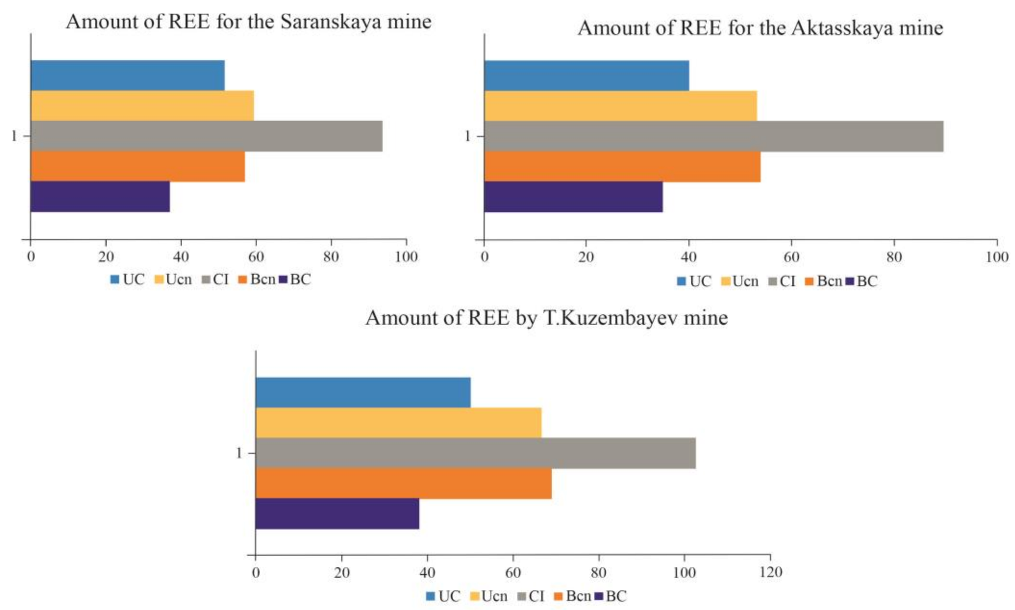


Figure 3 – Vertical Distribution of rare Earth Elements in Clayey Interlayers CI, Contacts of CI and Coal in Karaganda Coal

Basin Note. UC – upper coals, UCn – upper contact of coal and clayey interlayer, CI – clayey interlayer, BCn – bottom contact of clayey interlayer and coal, BC – bottom coals.

The indicative ratio is the lanthanum-ytterbium (La/Yb) ratio. The estimated lanthanum-ytterbium (La/Yb) ratio in coal, which is equal to La/Yb<1, allows referring the coals to H-type distribution coals, indicating the participation of water-soluble forms of lanthanides in REE accumulation in coals. Lanthanum-ytterbium ratio in clay equal to La/Yb>1 allows the conclusion of the existence of independent sources and different mechanisms of REE accumulation in the sediments of the Karaganda coal basin. For the Karaganda coal basin, the main supplier of debris material during different periods of basin formation was the mountain structures located to the south of the basin. A smaller volume of material (thinner one) came from the hilly uplands to the north (Ishina T.A., 1954).

Lanthanide normalization to chondrite differs significantly from UCC normalization: in clays, it shows a predominance of light lanthanides over heavy ones, the concentration ratio decreases from lanthanum (57.3) to ytterbium (4.9). The estimated Eu - and Ce - anomalies showed negative europium and cerium anomalies (0.1 and 0.2, respectively); there are more light lanthanides in the coal, with a positive cerium (5.6) anomaly and a negative europium anomaly (0.01) present. The lanthanum-ytterbium ratio in clay and coal equal to La/Yb>1 allows attributing coals to L-type REE distribution coals, which allows the conclusion that in the formation of L-type coals of the Karaganda coal basin with near-clark REE contents, a clayey matter of terrigenous ash as a carrier of REE prevailed [[12], [13], [14]].

According to [[15], [16]], the presence of mixed types of REE distribution implies different forms of REE migration and different mobility of heavy and light lanthanides in the hypergenesis zone. It is necessary to be cautious in interpreting these data for hard coals, since in the process of coal formation, intra-stratum migration of significant masses of excess moisture occurs, temperatures reach 200^0 C and higher, and stratal waters are also saturated with organic matter and carbon dioxide. Jointly these factors facilitate the migration of lanthanides and, consequently, can lead to significant redistribution and even their removal outside the coal stratum.

Complex processes of REE distribution in coals are indicated by the results of detailed geochemical research of the coal stratum k_7. Analysis of vertical REE distribution in stratum k_7 of the Karaganda coal basin (Fig.3) showed that the highest concentrations of all REE are characteristic of clayey interlayers and zones of coal and clayey interlayer contact.

Fig. 3 shows that lanthanides are equally enriched in the contact zones between coal and clayey interlayer. Detailed research of the coal stratum will make it possible to identify and evaluate the role of the main factors of REE accumulation in coal.

In terms of REE content in coal, the increase is seen in the REE content from the bottom (BC) towards the top (UC). La/Yb ratio in this case also grows from coals (6.31) to clayey interlayers (17.06), which indicates a predominantly clastogenic mechanism of REE input to the coals.

Distribution of lanthanum and ytterbium in coal showed that the La/Yb ratio in the stratum bottom (BC) decreases from west to northeast, and in the stratum top (UC) on the contrary increases from west to northeast. A sharp decrease in the lanthanum-ytterbium ratio indicates the participation of water-soluble forms of lanthanides in REE accumulation in the coals [[16], [17], [18]]. At the same time, the increase in the lanthanum-ytterbium ratio indicates a predominantly clastogenic mechanism of REE ingress into the coals [[19], [20]]. The La/Yb ratio from bottom to top decreases in the two mines, and towards the northeast the La/Yb ratio from BC to UC increases (Fig. 4). The latter is conditioned by the heterogeneous composition of the alimentation zones of individual regions of the basin. The nature of this phenomenon is multifactorial and requires special analysis.

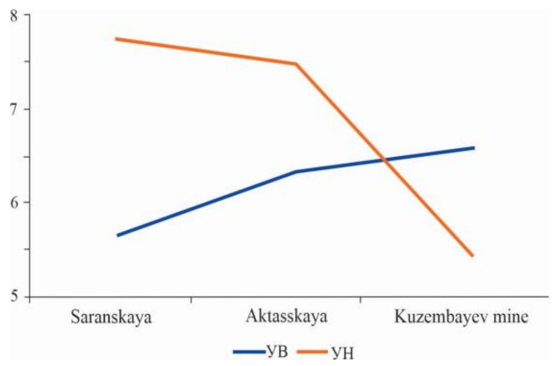


Figure 4 - Distribution of Lanthanum and Ytterbium in the Coal of Karaganda Coal Basin

Analysis of REE distribution showed increased total concentrations of light and medium lanthanides in the Karaganda coal basin, which represents an interest in researching the nature of their accumulation in the coals (Table 4).

Analysis of REE distribution showed increased total concentrations of light and medium lanthanides in the Karaganda coal basin, which represents an interest in researching the nature of their accumulation in the coals (Table 4).

Assessment of lateral variability of element concentrations makes it possible to reveal the influence of rocks in the source area on the accumulation of abnormal REE concentrations in the coals. Within a single coal stratum, the distribution of lanthanides is often very uneven and is conditioned by the role of various factors responsible for REE accumulation in the coal.

Table 4 – Total REE Content in Coals for the Three Mines

Group	Element	∑coal Saranskaya Mine	∑coal Aktasskaya Mine	∑coal T. Kuzembayev Mine	Total Amount
Light	La	56.341	37.10	95.43	188.87
	Ce	123.522	85.24	212.59	421.35
	Pr	15.050	10.73	25.96	51.74
	Nd	69.973	49.74	115.35	235.06
	Sm	16.662	12.15	26.26	55.07
Medium	Eu	3.941	2.87	6.12	12.93
	Gd	18.083	12.65	27.05	57.78
	Tb	2.667	1.88	4.15	8.70
	Dy	15.856	10.26	23.73	49.85
	Y	95.809	61.49	127.37	284.67
Heavy	Ho	3.190	2.11	4.92	10.21
	Er	9.151	6.05	14.78	29.99
	Tm	1.349	0.85	2.18	4.37
	Yb	8.677	5.42	15.80	29.90
	Lu	1.388	0.84	2.31	4.54

Rare earth elements are distributed rather unevenly in the Karaganda coal basin. An increase in REE elements from the west (at Saranskaya mine) to the northeast (at T. Kuzembayev mine) is observed, with the minimum REE content found at the Aktasskaya mine (Fig. 5).

To explain the reduced REE content at the Aktasskaya mine, it is recommended to research the tectonic situation of stratum k_7 at the sites of these mines.

In all three mines, the Lu - Tm and Er - Yb contents are similar and range from 0.84-2.31 up to 5.42-15.80 g/t, respectively. The highest values of REE content in the coal are observed in the northeast of the Karaganda synclinorium at the T. Kuzembayev mine.

A high total content of Se, Y, Nd and La should be noted in all three mines (Table 4).

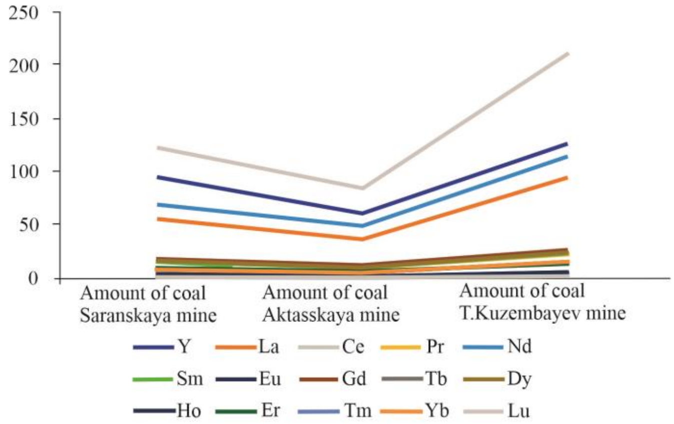


Figure 5 - Lateral Heterogeneity of REE Amount at Saranskaya, Aktasskaya, T. Kuzembayev Mines

Correlation analysis showed positive correlations of Y with light and medium lanthanides, and correlation with Y increases with light elements - La, Ce, Pr, Nd, Sm, the strongest correlation is with medium elements - Eu, Gd, Tb, Dy, and it decreases for heavy elements - No, Er, Tm, Yb, La. The correlation of cerium with light lanthanides is very strong and decreases towards heavy ones (Fig. 6).

To define trace mineral deportments of impurity elements in the rocks of the Karaganda coal basin, researches were performed using the highly local method of analytical scanning electron microscopy along with energy-dispersive X-ray spectroscopy (SEM-EDS), automated search for mineral phases with the set characteristics was performed using the AZtecFeature program modules.

By SEM-EDS method, 13 samples of coals, clayey interlayers and samples taken at the contact of the coal and host rocks were studied, and dispersion spectra were obtained for the composition using an X-ray spectrometer.

According to the research results, trace mineral inclusions of REE were found. Also, with a single occurrence, yttrium (Y) inclusions were found in the samples of coal, and argillite, and also in the samples taken at the contact of coal and clayey rocks.

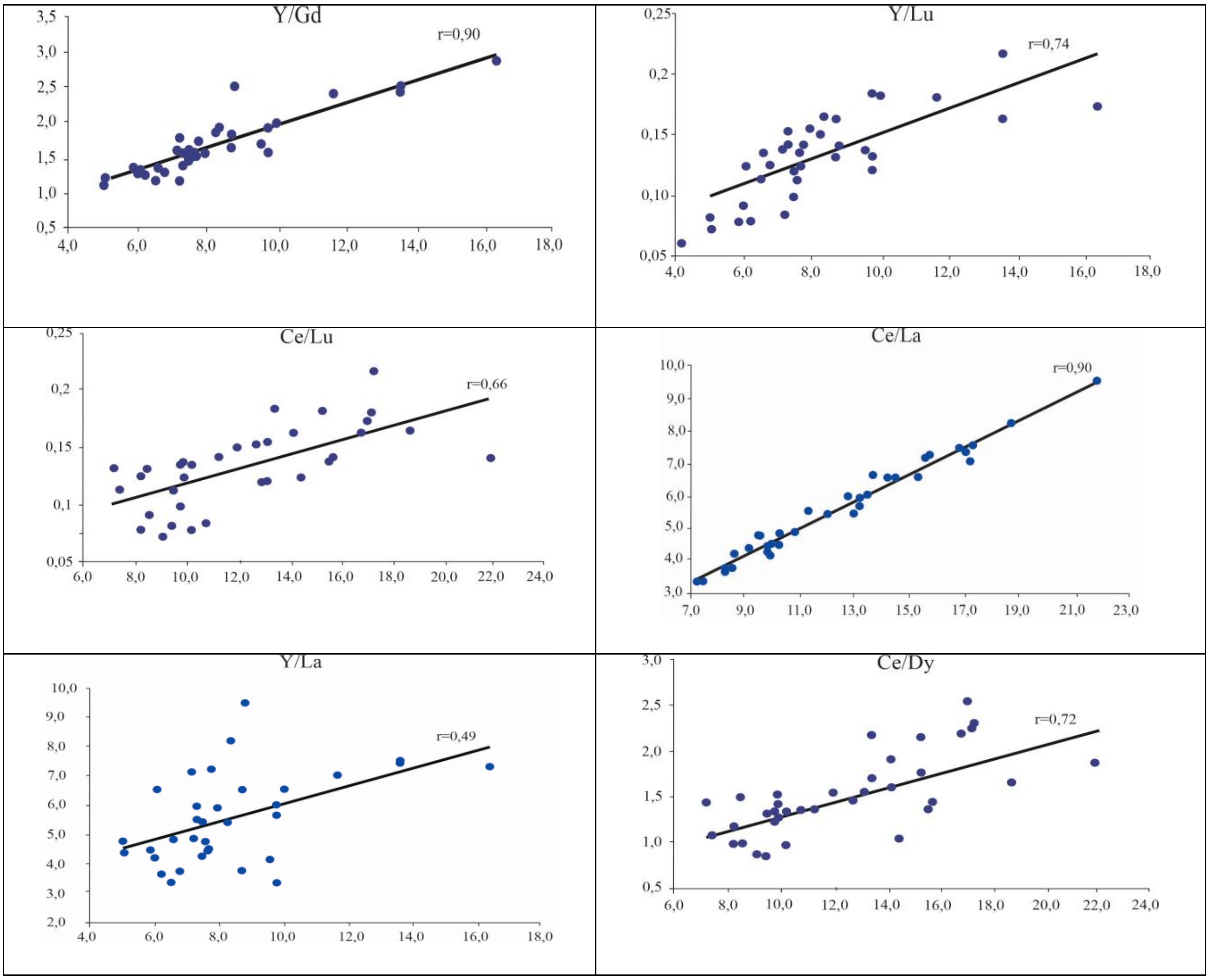


Figure 6 - Correlation Diagrams of Y and Ce and REE in the Coals of Karaganda Coal Basin

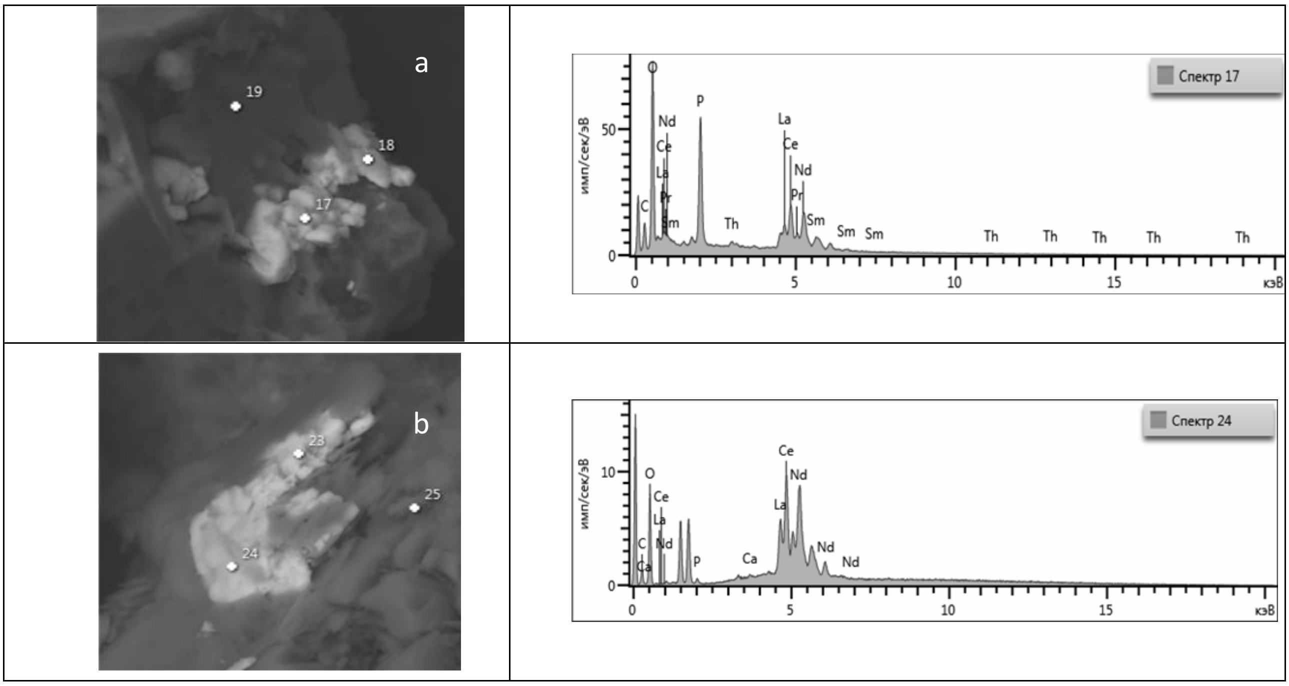


Figure 7 – Mineral Inclusions of CeLaNdPO Composition in Coals (a) and Clayey Interlayers (b) of Karaganda Coal Basin

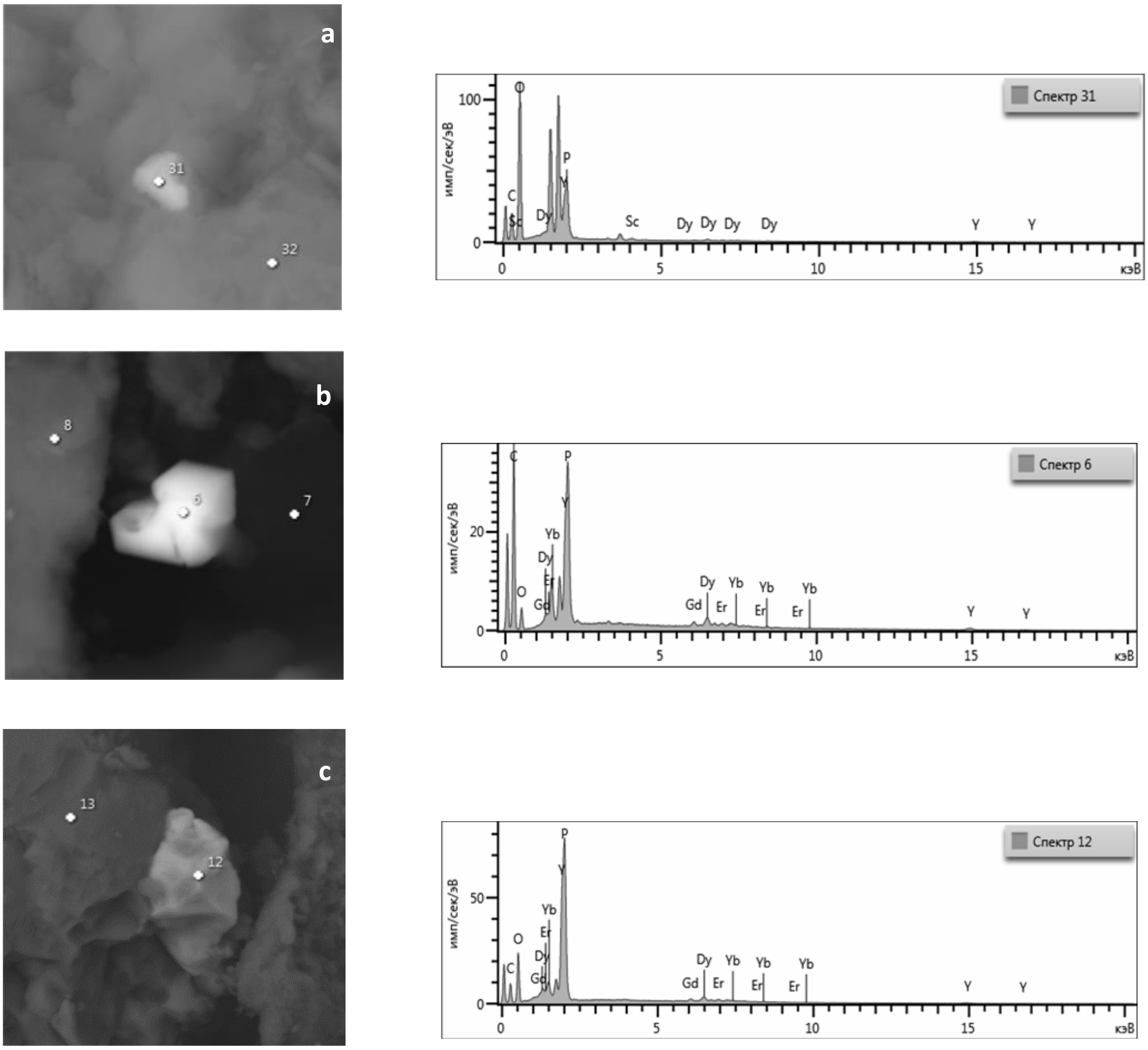


Figure 8 – Grain YPO of the Composition (xenotime?) in Coal (a), and Contact(b) Samples, in Argillite (c)

The REE deportments in coal are quite diverse; the most common ones are phosphates, aluminophosphates and carbonates. High carbonification of REE suggests an important role of organic matter in their concentration in the coals. Autigene mineral forms of REE that are sharply predominant in hard coals, including phosphates, are formed during the destruction of organic complexes in the process of organic matter transformation during the coal formation process [[21], [22]]. In coal and clay samples from the Karaganda coal basin, the predominant mineral form of REE is light lanthanide phosphates. Sparry crystals of CeLaNdPO composition (Fig. 7) were found in coal (Fig. 7a) and clayey interlayer samples (Fig. 7b).

The first data on Y contents in the coal appeared in 1931: 4 g/t of Y were found in the ashes of two samples of Silesian and English coal (Goldschmidt, 1931). It is known [20] that by its chemical properties, Y is very close to lanthanides, in particular, it is an almost complete geochemical analogue of the heavy lanthanoids Yb. According to [20], the carbonification coefficient of Y that exceeds one, as well as its high concentrations in coal inclusion ashes, indicate the presence of antigens yttrium impurity of organic form in the coals (Y_{org}), as well as the probable mineral form of antigens phosphates (Y_{phos}). In addition, the mineral yttrium (Y_{min}) can be present in clastogenic ash, in the composition of accessor minerals and clay matter. However, it should be noted that during the thermal metamorphism and/or hypergenic oxidation of coals, the yttrium deportment can change, which leads to its migration, ingress or removal from the coals.

Using the SEM-EDS method, in the coal samples (Fig. 8a), on the contacts (Fig. 8b), as well as in host rocks (Fig. 8c) of Karaganda coal basin trace ineral inclusions of different sizes, mainly of YPO (*xenotime?)* composition were found. According to previously published results (R. Finkelman,1980) that were obtained using the combined SEM + EDS method, substantial amounts of yttrium in many coals were found in the form of abundant xenotime particles. According to (D. Swain,1990), this gives a good basis for the statement that fine-grained xenotime is the major deportment of Y in many coals.

Conclusion

This is the first comprehensive mineralogical and geochemical research of clayey interlayers and coals of the Karaganda coal basin. The research showed that increased REE contents relate to the clayey interlayers and contact zones of the coal-clay interlayer. In terms of REE content in coal, the increase is seen in the REE content from the bottom towards the top of the stratum. The lanthanum-ytterbium (La/Yb) ratio in coal that was normalized to UCC and the La/Yb ratio in coal normalized to chondrite, indicated the presence of mixed types of REE distribution in coals, which supposes various forms of REE migration and different mobility of heavy and light lanthanides within the hypergenesis zone. La/Yb ratio in this case also grows from coals to clayey interlayers, which indicates a predominantly clastogene mechanism of REE input to the coals. An increase was established in REE content from the west (at Saranskaya mine) to the northeast (at T. Kuzembayev mine), with the minimum REE content found at the Aktasskaya mine. To establish such a distribution, additional research is required for these sites of the mines.

Calculated Eu - and Ce - anomalies in the coals and clays, which are normalized by chondrite and UCC, showed negative europium and cerium anomalies, which are characteristic of clayey interlayers formed with the participation of ash material of acidic composition. Analysis of REE distribution showed increased total concentrations of light and medium lanthanides in the Karaganda coal basin. A high total content of Se, Y, Nd and La was noted in all three mines. Correlation analyses of Y and Ce showed positive correlations with light and medium lanthanides.

To define trace mineral deportments of REE in the coals of the Karaganda coal basin, researches were performed using the highly local method of analytical scanning electron microscopy along with energy-dispersive X-ray spectroscopy (SEM-EDS), automated search for mineral phases with the set characteristics was performed using the AZtecFeature program modules. Using this method, it was found that the predominant mineral form of REE was light lanthanide phosphates. Sparry crystals with CeLaNdPO composition were found in the coal and clayey interlayer samples. Y inclusions in the form of abundant xenotime particles in the coal and clayey interlayer samples, as well as in samples taken at the contact of coal and clayey interlayers were revealed for the first time.

Conflict of interest. On behalf of all the authors, the correspondent author declares that there is no conflict of interest.

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ҚАРАҒАНДЫ КӨМІР БАССЕЙНІНІҢ САЗДЫ ҚАБАТТАРЫ МЕН КӨМІРЛЕРІНДЕ СИРЕК ЖЕР ЭЛЕМЕНТТЕРІНІҢ (СЖЭ) ЖИНАҚТАЛУ ТАБИҒАТЫ

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ТҮЙІНДЕМЕ
Орталық Қазақстанның Қарағанды көмір бассейнінің көмірінде алғаш рет сирек жер элементтеріне (СЖЭ) (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) кешенді минералдық-геохимиялық зерттеу жасалды. Жұмыста Қарағанды көмір бассейнінің Саран, Т.Күзембаев, Ақтас шахта кенжарларында 85 көмір сынамасында және к7 сазды қабаттарында СЖЭ (лантаннан лютецийге дейін және Y) таралуын зерттеу нәтижелері ұсынылған. Саз қабаттары мен көмірлер сынамаларының элементтік құрамы индуктивті байланысқан плазмалық атомдық эмиссиялық спектрометрия және индуктивті байланысқан плазмалық масс-спектрометрия (ICP-OES және ICP-MS) әдістерімен зерттелді. СЖЭ элементтерінің жиынтық концентрациясының латералдық және тік өзгергіштігін зерттеу көмірде СЖЭ таралуының аралас түрлерінің болатынын көрсетті, бұл СЖЭ жылжуының әртүрлі формаларын және гипергенез аймағында ауыр және жеңіл лантаноидтардың әртүрлі қозғалғыштығын білдіреді. UCC-ге нормаланған және La/Yb<1-ге тең көмірдегі лантан-итерби (La / Yb) қатынасы СЖЭ таралуының H типі бар көмірге, сондай-ақ хондритпен нормаланған La/Yb>1-ге тең, СЖЭ таралуының L типі бар көмірге жатады, яғни бұл Қарағанды көмір бассейнінің шөгінділерінде тәуелсіз көздердің және СЖЭ жинақталуының әртүрлі тетіктерінің болуы туралы қорытынды жасауға мүмкіндік береді. Сондай-ақ, La/Yb қатынасы көмірден сазды қабаттарға дейін жоғарылайтыны анықталды, бұл көмірде СЖЭ таралуының негізінен кластогендік механизмін көрсетеді. Жыныстардағы сирек жер элементтерінің микроминералды формаларын анықтау үшін көмірдің негізгі жыныстармен жанасу аймағынан алынған көмірдің, сазды қабаттардың 13 сынамасы зерттелді және рентгендік спектрометр көмегімен құрамның дисперсиялық спектрлері алынды. Қарағанды көмір бассейнінің көмір үлгілері мен сазды қабаттарындағы СЖЭ-нің басым минералды түрі жеңіл лантаноидты фосфаттар болады. Көмір және саз қабаттарының үлгілерінде CeLaNdPO құрамының бағаналы кристалдары табылды. Көптеген көмірде Y негізінен ксенотим түрінде болатыны анықталды.

Түйін сөздер: көмір, сазды қабаттар, Орталық Қазақстан, Қарағанды көмір бассейні, сирек жер элементтері, орташа құрамы.

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ПРИРОДА НАКОПЛЕНИЯ РЗЭ В ГЛИНИСТЫХ ПРОСЛОЯХ И УГЛЯХ В КАРАГАНДИНСКОМ УГОЛЬНОМ БАССЕЙНЕ

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АННОТАЦИЯ
Впервые выполнено комплексное минералого-геохимическое исследование РЗЭ (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) в углях Карагандинского угольного бассейна Центрального Казахстана. В работе представлены результаты по изучению распределения РЗЭ (от лантана до лютеция и Y) в 85 пробах угля и глинистых прослоях пласта к7 Карагандинского угольного бассейна на забоях шахт – Саранская, им. Т. Кузембаева, Актасская. Элементный состав проб глинистых прослоев и углей проводился методами атомно-эмиссионной спектрометрии с индуктивно-связанной плазмой и масс-спектрометрии с индуктивно-связанной плазмой (ICP-OES и ICP-MS).
Исследование латеральной и вертикальной изменчивости суммарной концентрации элементов РЗЭ показало на присутствие смешанных типов распределения РЗЭ в углях, что подразумевает различные формы миграции РЗЭ и различную подвижность тяжелых и легких лантаноидов в зоне гипергенеза. Установленное лантан-итербиевое (La/Yb) отношение в угле, которое нормированно к UCC и равное La/Yb<1, относится к углям с H-типом распределения РЗЭ, а также равное La/Yb>1, нормированное по хондриту, относится к углям с L-типом распределения РЗЭ, что позволяет сделать выводы о существовании независимых источников и различных механизмов накопления РЗЭ в отложениях Карагандинского угольного бассейна. Так же установлено, что La/Yb отношение возрастает от углей до глинистых прослоев, указывая на преимущественно кластогенный механизм поступления РЗЭ в угли. Для определения микроминеральных форм нахождения РЗЭ в породах исследованы 13 проб угля, глинистых прослоев и проб, отобранных на контакте угля с вмещающими породами и получены дисперсионные спектры состава с использованием рентгеноспектрометра. Преобладающей минеральной формой РЗЭ в образцах углей и глинистых прослоях Карагандинского угольного бассейна являются фосфаты легких лантаноидов. Обнаружены шестоватые кристаллы CeLaNdPO состава в образцах угля и глинистых прослоев. Установлено, что ксенотим является главной формой нахождения Y во многих углях.

Ключевые слова: уголь, глинистые прослои, Центральный Казахстан, Карагандинский угольный бассейн, редкоземельные элементы, среднее содержание

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