

Article

A Comprehensive Study of the Spatial Variations in the Distribution of Rare Earth Elements (REE) and Their Potential in the Coals of the Shubarkol Deposit, Kazakhstan

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Abstract: Due to the gradual depletion of traditional metallic mineral resources, the search for new potential sources is an important issue. One such source is coal deposits. The extraction of metals from coal is a way to produce clean energy. This study presents the results of detailed research on geochemical features and mineralogy to understand the processes of microelement enrichment in the coal-bearing deposit of Shubarkol, in Central Kazakhstan. Modern analytical techniques were used to obtain information about the conditions and processes of trace element accumulation in coal, as well as the modes of occurrence of these elements. Geochemical data were analyzed using multidimensional statistical methods, including correlation, clustering, and factor analysis, which allowed us to draw several scientific conclusions. Numerous factors indicate that the enrichment of trace elements in sediments is controlled by clastic terrigenous material and low-temperature hydrothermal solutions circulating in the coal basin. The main sources of removal of trace elements from coal are ancient igneous rock complexes located within deposits that were directly involved in coal enrichment through secondary geological processes. According to estimates, the degree of enrichment of Jurassic coals at Shubarkol was close to the average value for world coals ($0.5 < CC < 2$), and coal seams were enriched with lithophilic and chalcophilic elements such as Ba, U, Yb, Co, La, Nb, Hf, Sc, V, Sr, Cu, and Zn. A correlation analysis of coal deposits revealed a significant correlation between main oxides and rare earth elements (REEs). The strongest correlation was between Zr, Hf, Th/Ta, and REEs. The positive correlations between Zr and Al_2O_3 , Nb and Al_2O_3 indicate that these elements (Zr, Hf, Nb, Ta, and REY) are probably related to Al. The results obtained make it possible to consider coal as a potential mineral resource for the production of rare metals and serve as a guide for the industrial processing of the most important elements found in coal.

Keywords: geochemistry; REE; coal; Shubarkol deposit; mineralogy; geostatistical analysis; Kazakhstan



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1. Introduction

At present, with the increasing risk of crisis phenomena in the global economy and the need for the structural reorganization of industrial production, many countries face the acute challenge of maintaining industrial production with alternative energy resources. In this context, increased attention is being paid to coal as a natural energy source due to its significant global reserves and its greater availability compared to other combustible mineral fuels.

The increasing demand for rare earth elements (REE), due to their economic significance and supply risks, has led to the exploration of alternative secondary sources for these elements. Coal and coal combustion by-products have been identified as potential raw materials for REE extraction. This research aimed to investigate the distribution of REEs and the mechanisms behind their accumulation within coal deposits.

In recent years, questions have been raised about the nature of the accumulation of impurity elements in coal deposits in different parts of the Earth's crust and the development of mineralization, particularly in regard to environmental problems. Thus far, the main sources and factors associated with the formation of abnormal concentrations of various elements and components in coals have been considered [1]. These include rocks in the feeding area of the coal accumulation basin; the volcanogenic–clastogenic entry of pyroclastic material into the paleotorph; the hydrothermal introduction of impurity elements into the paleotorph or coal seam; and hydrological factors. REEs [2] are considered strategic resources, as they play a crucial role in key sectors of the economy, such as defense, renewable energy, electronics, and the chemical industry [3,4]. Natural deposits of REEs are unevenly distributed worldwide, with China accounting for nearly 38% of the global reserves and dominating this area of production since the late 1980s [5]. Currently, rare earth element (REE) supplies to Europe are predominantly derived from China, accounting for 98% [6]. The growing demand for REEs (3.7%–8.6% annually) and the risks associated with their supply have led to the classification of these elements as a “critical” raw material, prompting the search for alternative sources [7,8]. Coal has been identified as a potential source of REEs, and numerous studies have been conducted on the content, forms, and extraction potential of these elements in coal [9–14].

The analysis of the forms and concentrations of elements in coal, along with the determination of their geochemical speciation, contributes to the organization of prospecting operations within coal-bearing areas and in framing structures. This allows us to solve the following important theoretical and practical issues associated with certain elements [15–17]:

- (1) The reconstruction of paleogeographic conditions in coal-bearing formations, enabling conclusions about the process of coal formation and the origins of the mineral phases within coal;
- (2) The potential extraction of valuable elements from coal and its combustion by-products (REEs, Ge, Ga, U, etc.);
- (3) The elimination of the technical problems associated with the extraction, processing, and disposal of coal;
- (4) The occurrence of anomalies of toxic elements in coal (for example, As, Hg, Se) with a reduction in their impacts on the environment and human health;
- (5) The performance of an environmental safety assessment of coal mining and processing.

The method of determining trace elements in coal is significant from both a scientific and environmental perspective, as the behavior of these elements during the use of coal is dependent not only on their concentrations but also on their chemical states or forms.

This work was the final result of research conducted during the implementation of a scientific project. Numerous geochemical and mineralogical data collected over several years studying the Shubarkol deposit were processed using both direct and indirect methods. Statistical methods were used for the first time, including correlation coefficients between elements, as well as cluster analysis and factor analysis. These methods are some of the most common indirect approaches to interpreting modes of element occurrence, and the results obtained by them were significantly new for coal geochemistry at Shubarkol. However, considering the limitations of using statistical methods [18,19], their results are not accurate data but serve only as confirmation of previous studies on geological factors in-

fluencing trace element introduction into coal deposits. Studies of the content, distribution, and mineralization of critical elements in coal provide not only important references for potential discovery of such deposits but also substantial geochemical and mineralogical evidence to identify the geological genesis of coal seams. This research also helps to correlate the formation of coal seams with post-sedimentary modification of coal basins and regional geological evolution, which has important implications for the economic development of the coal industry and the protection of the environment in coal use, as well as ensuring the safety of metal resources [20]. Statistical methods are some of the most frequently used indirect approaches for the interpretation of elements' modes of occurrence. These methods include the coefficient of correlation between the elements, as well as cluster and factor analysis. In this work, using data obtained from 120 samples from the Shubarkol deposit, it is demonstrated that statistical analysis with slightly different sets of elements can lead to significantly different conclusions regarding the elements' modes of occurrence. Here, it is assumed that statistical methods can provide useful information about the modes of occurrence of trace elements for a limited set of samples. This is supported by previously obtained data on the accumulation of trace elements in coal, which may be a potential method for extracting metals from coal deposits and dumps. This approach is relevant to industrial and commercial applications because it reduces disposal costs and minimizes harmful environmental impact.

The present study aimed to investigate the geochemistry of the Shubarkol coal deposit, located in Central Kazakhstan, in the western part of the Central Asian orogenic belt (Figure 1). These coal deposits have low ash and sulfur content, making them a valuable fuel. In addition, coals contain a variety of impurities. Coal mining at this deposit is accompanied by the constant geochemical analysis of the coals and coal-bearing rocks in order to assess the potential for the extraction of certain elements that reach industrial concentrations.

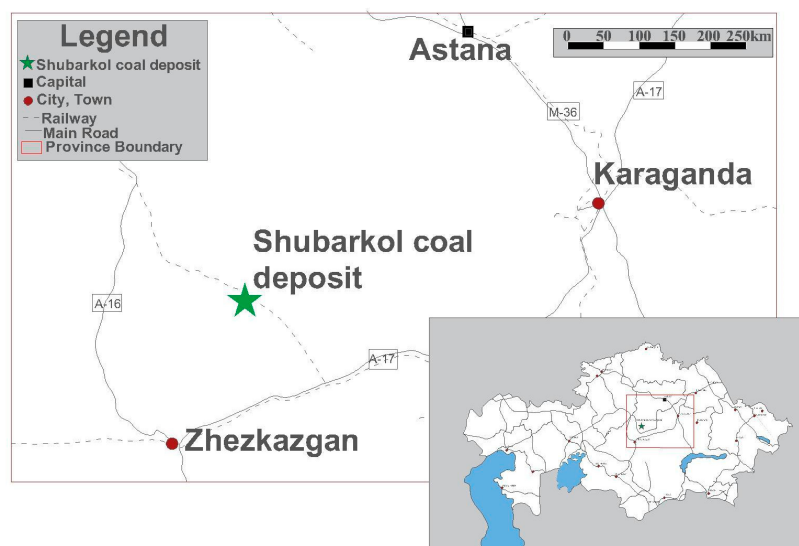


Figure 1. Location of the Shubarkol deposit.

Geological Settings

Despite the large number of coal deposits in Kazakhstan, the Shubarkol deposit meets most of the country's domestic demand for solid fuel. Additionally, a significant proportion of the coal produced from the deposit is exported to markets in Northwestern Europe and the Commonwealth of Independent States (CIS).

The Shubarkol deposit was formed in an inherited depression on ancient sedimentary complexes in the Caledonian accretion-folded regions of the central Sarysu–Teniz uplift [21].

Deep faults had a significant impact on this area, which led to a variety of ore formations and complex transformations.

The host rocks are terrigenous-carbonate sediments from the Upper Devonian and Lower Carboniferous periods, as well as terrigenous rocks from the Middle and Upper Carboniferous periods [22]. The Jurassic sediments of the Shubarkol syncline (Figure 2) are carbon-bearing. The Lower Jurassic coal-bearing sediments, with a thickness of up to 330 m, form a sub-latitudinal thrust (7.16 km) with gentle western and eastern wings ($5\text{--}10^\circ$ and $5\text{--}15^\circ$, respectively) and steeper southern and northern wings ($20\text{--}48^\circ$ and $40\text{--}90^\circ$, respectively). In the inner part of the deposit, the angles of inclination of the rocks do not exceed $3\text{--}5^\circ$. In the central part of the syncline, there is a gentle transversal uplift in the coal-bearing layers that fades to the north of the long axis of the feature. This uplift divides the fold into the western and eastern sections. The deposit consists of three sections: western, central, and eastern (see Figure 2). Industrial coal mining takes place in the lower part of the Jurassic sedimentary section, where three coal seams are distinguished: the upper, middle, and lower seams. The upper seam, which is currently being mined using an open-pit method, is considered to be the most promising for future development.

The composition of the Shubarkol deposit's coals is varied, and they enriched trace elements such as Ba, Sr, Th, Rb, Co, Ce, Zn, and Sc [23]. The influence of the source rocks on the geochemical composition of coal is emphasized by the accumulation of certain elements. Plutonic rocks, such as granodiorites, quartz diorites, and granites, are common in the southern part of the studied coal deposit and may be considered a source of these lithophilic rare metals. The coals also contain elevated levels of Hf, Ta, and Nb, as well as Sr, which are characteristic of alkaline rocks and granitoids. The enrichment of Zn, Ba, and Pb in the rocks is consistent with the occurrence of hydrothermal barium–lead–zinc deposits, similar to those found in the Atasu area [24].

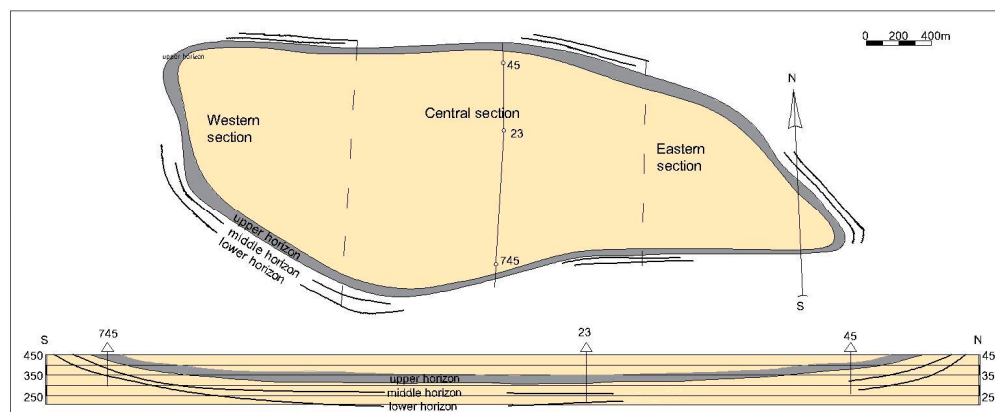


Figure 2. Cont.

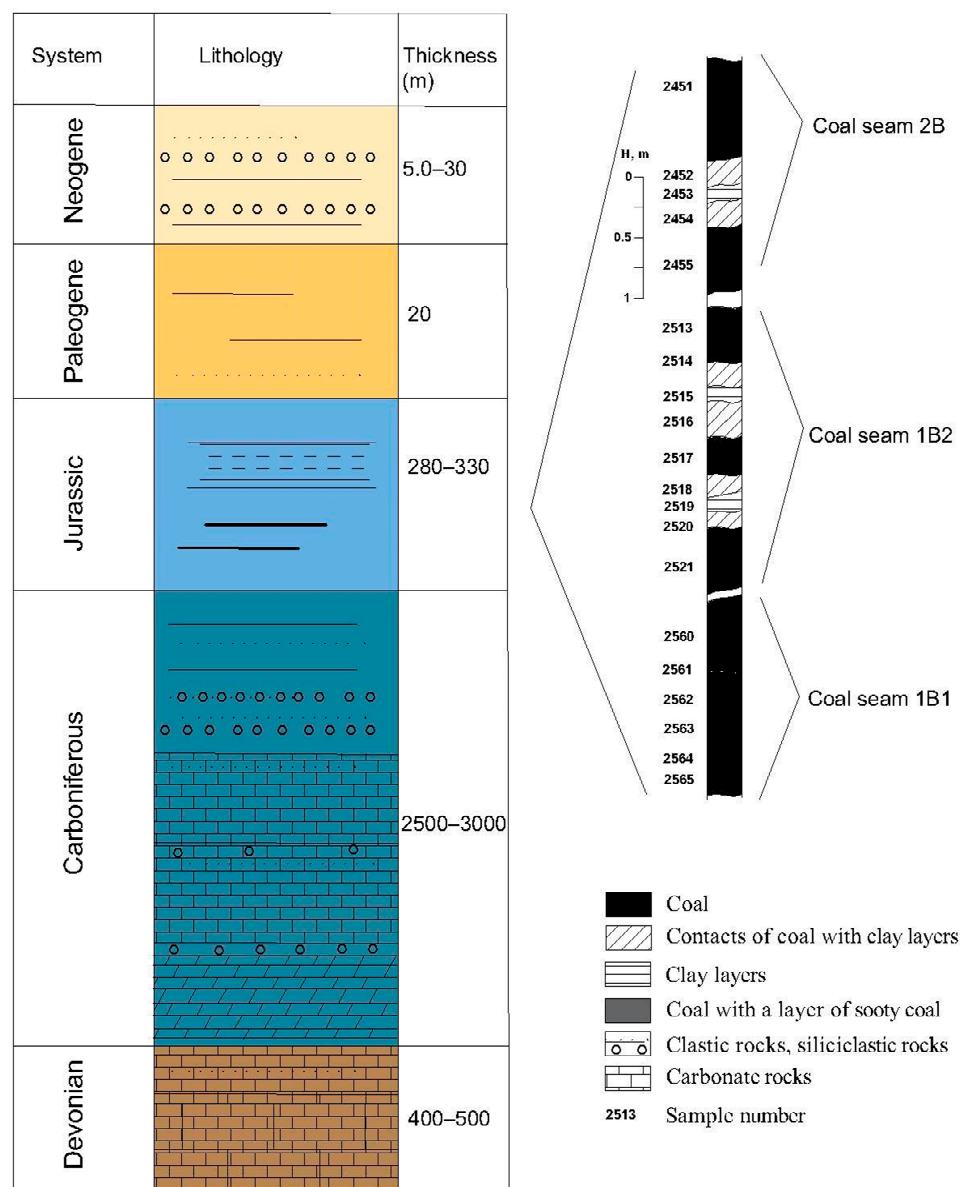


Figure 2. Geological positions of coal seams at the Shubarkol deposit.

2. Materials and Methods

2.1. Sample Collection and Preparation

Furrow samples of coals and mudstones weighing 1.2–1.5 kg each were collected for the geochemical analysis. Sample preparation, involving reductions in initial samples weighing 1.5–2 kg and their abrasion to 250 g, was conducted in the laboratory of Azimuth Geology LLP, Karaganda. A total of 120 samples were collected, at a distance of 30–50 cm from each other, from the upper coal horizons of the central and western sections (layers 2B, 1B, and 1B2). Sample preparation for the analytical studies was carried out according to the standard method: drying in natural conditions, crushing, quartering, and abrasion.

2.2. Experimental Analytical Methods

2.2.1. ICP-OES and ICP-MS Analysis

The determination of the elemental content of the samples was conducted via inductively coupled plasma–atomic emission spectroscopy (ICP-OES) using the iCAP 7600 Duo (Thermo Scientific, Waltham, MA, USA)) and inductively coupled plasma spectroscopy (ICP-MS) using an Agilent 7500 spectrometer (Agilent Technologies, Santa Clara, CA, USA).

These methods were performed in an accredited, leading laboratory at 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) (Vladivostok, Russia) (analyst: N.V. Zarubina). The ICP-OES method was used to determine the contents of Ti, Al, Fe, Mn, Mg, Ca, Na, K, and P in terms of oxides; the ICP-MS method was used to determine the contents of Li, Be, S, Al, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Sn, Sb, Te, Y, Mo, Ag, Zr, Cd, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Tl, Pb, Bi, Th, and U. To assess the accuracy of the research results, standard samples of the CLB-1 and SARM 19 coals from the US Geological Survey were analyzed with each batch of samples.

2.2.2. Electron Microscopic Analysis

The visualization and qualitative elemental analysis of the powder, lumpy material, and coal and clay layer samples were conducted using analytical scanning electron microscopy in combination with energy-dispersive X-ray spectroscopy (SEM-EDS), and the clay samples were studied using X-ray Energy-Dispersive Spectroscopy (XEDS). Electron microscopic analysis of the samples was performed in the laboratory for micro- and nano-research using a Tescan Lyra 3 XMH (Brno—Kohoutovice, Czech Republic) two-beam scanning electron microscope and Aztec X-Max 80 Standard EDS (Abingdon, Oxfordshire, UK). Using the highly localized method of analytical scanning electron microscopy (SEM-EDS), the morphometric characteristics of the solid-phase components in the samples were analyzed, and the elemental compositions of these components were determined. An automated search for the mineral phases was conducted with the set characteristics using the AZtecFeature 3.1 software modules, including the electronic documentation of images captured in various modes under the scanning electron microscope and the definition of the compositions of the obtained X-ray-dispersive spectra.

2.3. Statistical Analysis

The statistical analysis was performed for 58 components, consisting of 49 elements and 9 petrogenic oxides, based on the ICP-OES and ICP-MS results. The main (basic) statistical indicators were assessed, and diagrams and correlation relationships were constructed using Excel spreadsheets.

When studying complex geological systems, methods of multidimensional mathematical statistics are used, such as cluster and factor analysis. Cluster analysis identifies classes (or clusters) of parameters based on a set of variables that characterize geological objects. Objects belonging to the same class exhibit greater similarity to each other than objects belonging to different classes. The most common method of cluster analysis used in scientific research, which was also adopted in this study, is the unification method (tree clustering). This method involves creating a hierarchical tree that can be used to detect and interpret clusters (branches).

Factor analysis is a statistical technique used to identify hidden patterns or factors that can explain the variability in a set of related variables. It allows us to understand the internal factors that contribute to the specific characteristics of a phenomenon. Using factor analysis, a measure of the relationship between the parameters is determined, and generalized factors that underlie the changes in the characteristics are identified. The aim of this analysis is to represent a large number of parameters in terms of a smaller number of more comprehensive internal characteristics of a phenomenon (reducing the data using the principal component method); at the same time, these are the most significant and determinant factors. The main findings of such an analysis are presented in the form of factor loadings and factor scores. The STATISTICA 10 software was used to conduct the multivariate statistical analysis in this study.

3. Results and Discussion

During the course of the laboratory and analytical research, 120 coal samples were analyzed. The interpretation of the data made it possible to identify trace elements, whose average concentrations in the coals and the surrounding clay layers are presented in the subsequent diagrams (Figure 3). The average concentrations of most impurity elements in the Jurassic coals and mudstones from the Shubarkol deposit were lower than the average values for these elements in hard coal [25] and the average concentrations in sedimentary rocks. The high contrast in the anomalies of impurity elements allows for the prediction of coal seams containing industrially significant concentrations of Ce, V, Yb, U, Sc, Sr, and Zr.

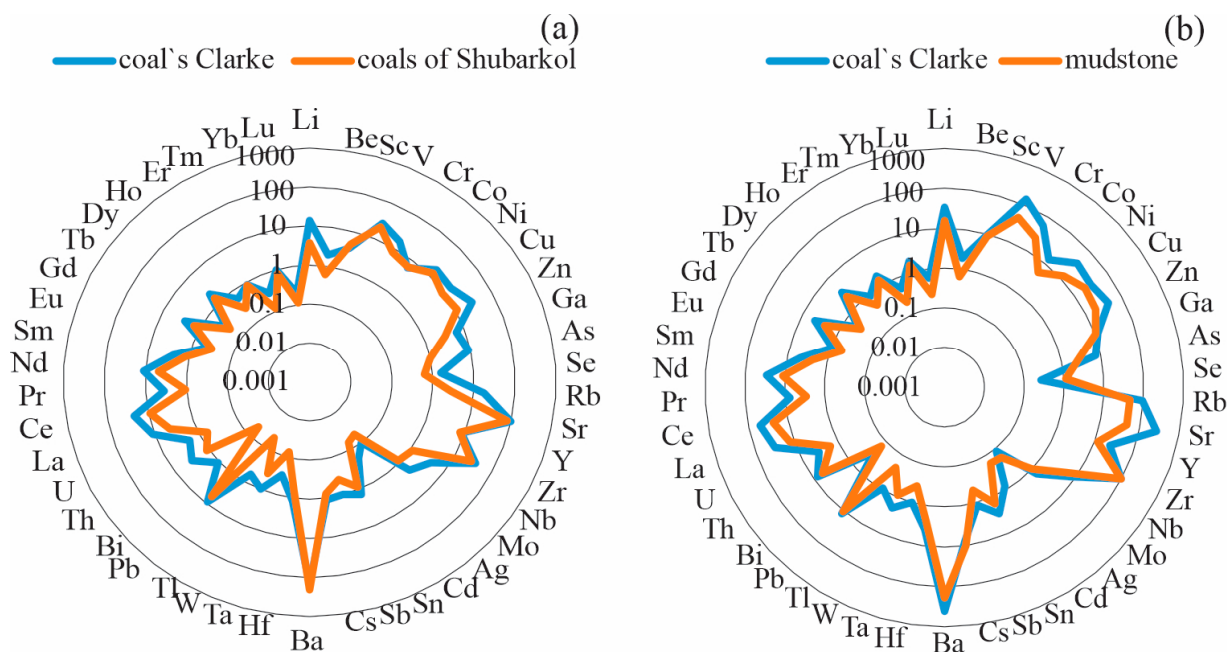


Figure 3. Comparison of the average content of trace elements with Clarke's estimates for (a) coals and (b) mudstones from the Shubarkol deposit.

The average REE content in the coals from the Shubarkol deposit (layers 2B, 1B2, and 1B1) in comparison to that in hard coals around the world and in the upper continental crust (UCC) is shown in Table 1. The analysis of these data indicated that the rare earth element (REE) content in the Shubarkol coals was low when compared to hard coals [25] and significantly lower (two–three times) relative to the upper continental crust (UCC) [26].

Table 1. The average REE content in the coals, ppm.

Coals	Rare Earth Elements, ppm															
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Ho	Er	Tm	Yb	Lu	ΣREE
Shubarkol	8.06	17.5	2.11	9	1.97	0.4	2	0.31	1.79	10.1	0.38	1.13	0.17	1.19	0.18	56.4
UCC [26]	30.0	64.0	7.1	26	4.50	0.9	3.8	0.64	3.50	22.0	0.80	2.30	0.33	2.20	0.32	168.4
Hard coals, from [25]	11.0	23.0	3.4	11	2.40	0.4	2.7	0.31	2.10	8.20	0.57	1.00	0.30	1.00	0.20	67.6

According to the results of the analysis in [24], the distribution of REEs according to the concentration coefficients [27] in Jurassic coal indicated that LREE: La–Nd was slightly depleted; the MREEs consisted of Sm–Dy; and it was slightly enriched in HREEs such as Ho–Lu. Since the ion radius of the REEs decreases according to the La→Lu sequence, the

alkalinity of these elements gradually decreases. According to [28], the ability of REEs to complex increases in the La→Lu sequence, and the HREEs' ability to complex is greater than that of the LREEs, so the migration ability of the latter is higher. Thus, it is speculated that the sources of the heavy REEs in the coals of Central Kazakhstan included a decrease in the pH values of terrigenous materials when entering a peat bog and an increase in the absorption capacity of the REEs from La to Lu, which led to their accumulation in peat [24].

The concentrations of the trace elements in the Shubarkol deposit were close to the average values for worldwide coals ($0.5 < CC < 2$), according to [29]. Large ionic lithophilic elements (Ba, Sr, Sc, Zr, and V) had the highest concentrations, while the remaining REEs exhibited average values. This confirms that the coals from the Shubarkol deposit are characterized by a lithophilic–chalcophilic type of speciation, and the coals are specialized in Va, U, Au, Yb, Cd, La, Nb, Hg, Se, Sc, Sr, and Zn [24].

Based on the geochemical characteristics of the elements and the application of direct analytical methods, it has been established that there are numerous mineral inclusions of Ba and Zn (barite and sphalerite) in coal, due to their high content in coal deposits. This is due to the migration of mobile and organometallic forms during diagenesis, which leads to the presence of nanoparticles with an aluminosilicate composition, such as Si–Zr–Al and Ti–Si–Al. These are autigenic epigenetic mineral formations that were transported to peat bogs as mechanical impurities by surface water and wind. Studies of oxidized coals have shown that the concentrators of impurity elements consist mainly of calcium and strontium sulfides. Hypergenic oxidation is caused by sulfurous acid water.

During our electron microscopic studies, well-faceted crystals of zircon, native silicon, and baddeleyite were found in the mudstones in the Shubarkol deposit [24]. At the same time, some zircons contained an admixture of scandium, titanium, and yttrium or other heavy REEs. A rarer baddeleyite was found in some clay and coal in contact with zircons. This association may indicate a calm mode of transport associated with zircon minerals or different modes of REE migration in the coal and host rocks [30].

In order to identify trends in the distribution of the chemical elements in the coal, the correlation coefficients (r) between the elements were calculated. The coefficients obtained for the coal samples are shown in Table 2. Several geochemical associations are evident in these correlation coefficients.

Table 2. Paired correlation coefficients between chemical elements in Shubarkol coals. Top-down coefficients for (a) petrogenic components, (b) trace elements, and (c) REEs (51 sub-samples from each sample).

(a)								
TiO ₂								
0.932	Al ₂ O ₃							
0.290	0.219	Fe ₂ O ₃						
0.530	0.459	0.411	MnO					
0.580	0.677	0.095	0.152	MgO				
−0.291	−0.284	−0.079	−0.018	−0.185	CaO			
0.154	0.115	−0.094	0.054	0.484	0.155	Na ₂ O		
0.604	0.734	0.163	0.167	0.937	−0.219	0.225	K ₂ O	
0.183	0.159	0.033	0.314	−0.092	0.518	−0.021	−0.081	P ₂ O ₅

Table 2. Cont.

(b)														
Sc														
0.683	Cr													
0.243	0.41	Rb												
0.221	0.132	0.072	Sr											
0.783	0.730	0.523	0.022	Zr										
0.707	0.562	0.642	0.126	0.900	Nb									
0.652	0.790	0.010	0.186	0.387	0.156	Sb								
0.173	0.348	0.972	0.018	0.436	0.580	0.040	Cs							
0.210	0.124	0.063	0.997	0.007	0.108	0.170	0.009	Ba						
0.776	0.718	0.538	0.020	0.997	0.910	0.368	0.446	0.005	Hf					
0.519	0.399	0.667	0.148	0.795	0.939	0.080	0.619	0.127	0.808	Ta				
0.263	0.219	0.627	0.102	0.521	0.696	0.159	0.614	0.078	0.532	0.715	Tl			
0.351	0.241	0.277	0.033	0.411	0.494	0.094	0.172	0.034	0.426	0.427	0.403	Pb		
0.662	0.528	0.633	0.136	0.910	0.972	0.078	0.564	0.115	0.919	0.936	0.686	0.469	Th	
0.643	0.544	0.320	0.189	0.800	0.818	0.195	0.241	0.161	0.796	0.751	0.600	0.505	0.837	U
(c)														
Y														
0.055	La													
0.100	0.967	Ce												
0.182	0.930	0.983	Pr											
0.332	0.806	0.912	0.965	Nd										
0.674	0.506	0.676	0.771	0.892	Sm									
0.618	0.579	0.713	0.807	0.905	0.969	Eu								
0.847	0.293	0.476	0.572	0.721	0.941	0.910	Gd							
0.935	0.074	0.247	0.350	0.512	0.824	0.790	0.958	Tb						
0.968	0.024	0.129	0.226	0.379	0.724	0.690	0.891	0.980	Dy					
0.974	0.061	0.074	0.160	0.298	0.647	0.614	0.829	0.942	0.987	Ho				
0.944	0.029	0.076	0.149	0.256	0.579	0.552	0.752	0.877	0.946	0.982	Er			
0.896	0.040	0.037	0.096	0.177	0.484	0.454	0.648	0.790	0.884	0.940	0.984	Tm		
0.851	0.022	0.039	0.089	0.150	0.438	0.407	0.590	0.736	0.839	0.902	0.963	0.992	Yb	
0.827	0.002	0.049	0.096	0.148	0.420	0.393	0.559	0.703	0.810	0.880	0.950	0.985	0.995	Lu

Trace elements in coal can form parts of minerals, bind to organic matter, and dissolve in pore water. Minerals are the main carriers of trace elements in coal. Correlation analysis is an indirect statistical method for the study of the elements that occur in coal. After obtaining a correlation coefficient, it is possible to determine the degree of similarity between them in order to measure the genetic relationships between various trace elements in coal.

From the analysis of the correlation matrix for the petrogenic elements (Table 2a), it can be concluded that there are no correlations between iron and the other components, which suggests the independence of their formation in coal. This may occur via introduction from surrounding plutons and volcanites, as well as their formation during coal accumulation or in subsequent periods. The titanium oxide in the coal is positively correlated with

Al_2O_3 ($r = 0.93$), which may indicate the entry of titanium into the composition of clay minerals [31]. The ICP-MS results showed that some kaolinite contained Ti, most likely in the form of submicron oxides.

A positive and significant correlation was established between Zr, Hf, Th, and Ta, which indicates the accumulation of these elements in heavy accessory minerals [32]. The correlation analysis (Table 2b) indicated that there was a significant and positive relationship between hafnium coals and Zr, Ta, Nb, Cs, and Th and other lithophilic rare metals. This suggests the accumulation of a significant proportion of hafnium, which was not due to clastogenic substances but resulted from its sorption concentration from aqueous solutions and, possibly, biogenic accumulation. Hf and Zr have very similar chemical properties. Hf does not have its own minerals, but it accompanies Zr in all its mineral forms, as their ionic radii are similar ($Zr = 0.74$, $Hf = 0.75$).

The correlation analysis of Nb and Ta in the coals from the Shubarkol deposit showed that there was a significant correlation between these elements ($r = 0.94$). Considering that Zr and Nb are generally considered to have an inorganic affinity in high-grade coals (bituminous or anthracite) [20], the positive correlation coefficients between Zr and Al_2O_3 and Nb and Al_2O_3 (see Figure 4) may indicate their presence in coal as kaolinite.

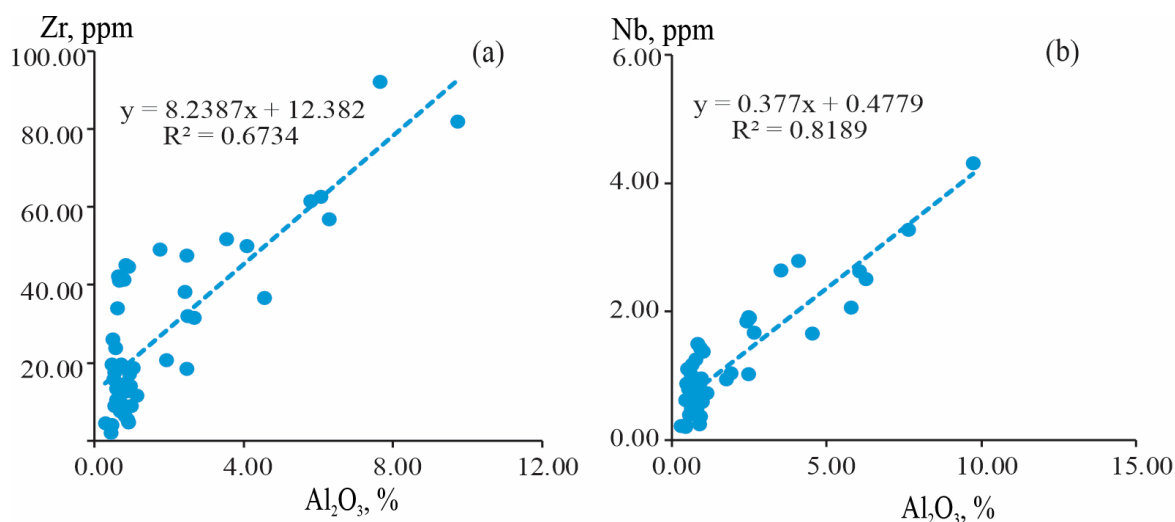


Figure 4. Graphs of correlations among Al_2O_3 and (a) Zr and (b) Nb.

Tantalum was positively and significantly associated with Th and Hf, mainly with hydrolysis elements. As shown by S. Palmer and R. Philby, who studied Ohio coal (Powhatan), although the Ta content in coal correlates with the amount of clay substances, it is contained in the micromineral phase of the pelitic dimension—rutile [33].

Thus, the conducted studies [32,34] and the literature analysis show that the concentration of tantalum and niobium in coal is due to both their accumulation in the clastogenic substance and their concentration in the organic mass of the coal. Anomalous concentrations are of a chemogenic sorption nature. Tantalum and niobium, concentrated in organic matter, can be found in both sorbed form and in the form of finely dispersed mineral phases [32].

A strong, positive correlation was established between Cs and Rb ($r = 0.97$), which indicates the attraction of Cs towards clay matter and closely related autogenic mineralization [18]. It is assumed that, if Rb is mostly sorbed by clay particles, Cs will also be concentrated in organic matter.

Strontium had a positive correlation with barium ($r > 0.90$). According to [33], carbonates and sulfates (for example, micromineral autogenic Sr-barite) are the most likely

carriers of Sr. The results showed that Ba and Sr were mainly associated with carbonate and phosphate minerals. They were mainly found in strontium sulfate (presumably celestine) and iron oxide (Figure 5), and it is possible that the increased concentrations of Sr and Ba in Shubarkol are associated with apatite mineralization, resulting from the weathering of basement rocks in sediment source areas.

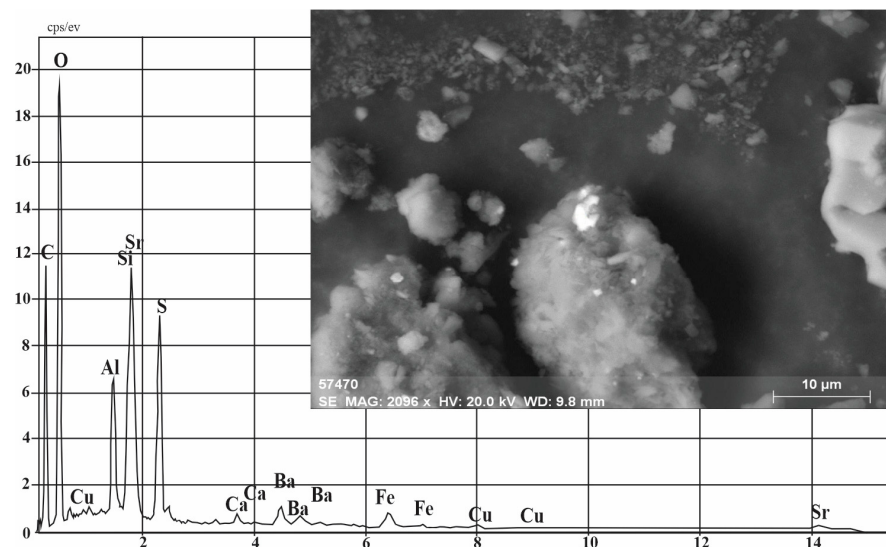


Figure 5. Celestine SrSO_4 with Ba inclusions.

The study of the correlations between the REEs showed that heavy REEs had positive and significant correlations with each other (Table 2c). La and Ce, as well as Nd and Pr, were correlated, but, according to [33], the predominant form of a rare earth element (organic matter or mineral substance) cannot be determined. The positive correlations between La and Ce and between Nd and Pr may also indicate that the micromineral monazite is a common host mineral.

The association among heavy REEs (Yb, Tb, Lu), which exhibited very strong correlations, likely indicates that there is one source of these elements and one accumulation mechanism among them.

According to Eskenazi [35–37], in low-ash coals, lanthanides are largely included in the sorption ash, whereas, in ash coals, the virtual fraction of REEclast dominates. In this case, heavy lanthanides predominantly accumulate in the composition of REEsorp, while light lanthanides accumulate in terrigenous ash, which is consistent with their differential mobility in the underground waters of the hypergenesis zone. In general, heavy lanthanides are more carbonophilic than light ones.

A joint analysis of the petrogenic components and microelements allowed us to identify five clusters (see Figure 6): “phosphate”, “rare earth”, “hydrothermal”, “micaceous”, and “clayey” (“argillite”).

The interpretation of the resulting clusters was carried out while taking into account the joint association of chemical components and associated minerals, rocks, or geological processes.

Thus, the “phosphate” cluster included the association of CaO , P_2O_5 , Sr, and Ba, typical of apatite and phosphorites; this included a group of light rare earth elements (Ce, La, Nd, Pr) as the most important impurities in phosphate minerals. At the same time, the ratios (Figure 7) between Sr and Ba with CaO and P_2O_5 , as well as the data obtained from the microprobe analysis (Figure 8), suggest that Sr, Ba, and light REEs were concentrated in phosphorus-containing minerals (apatite, monazite) or rocks (phosphorites).

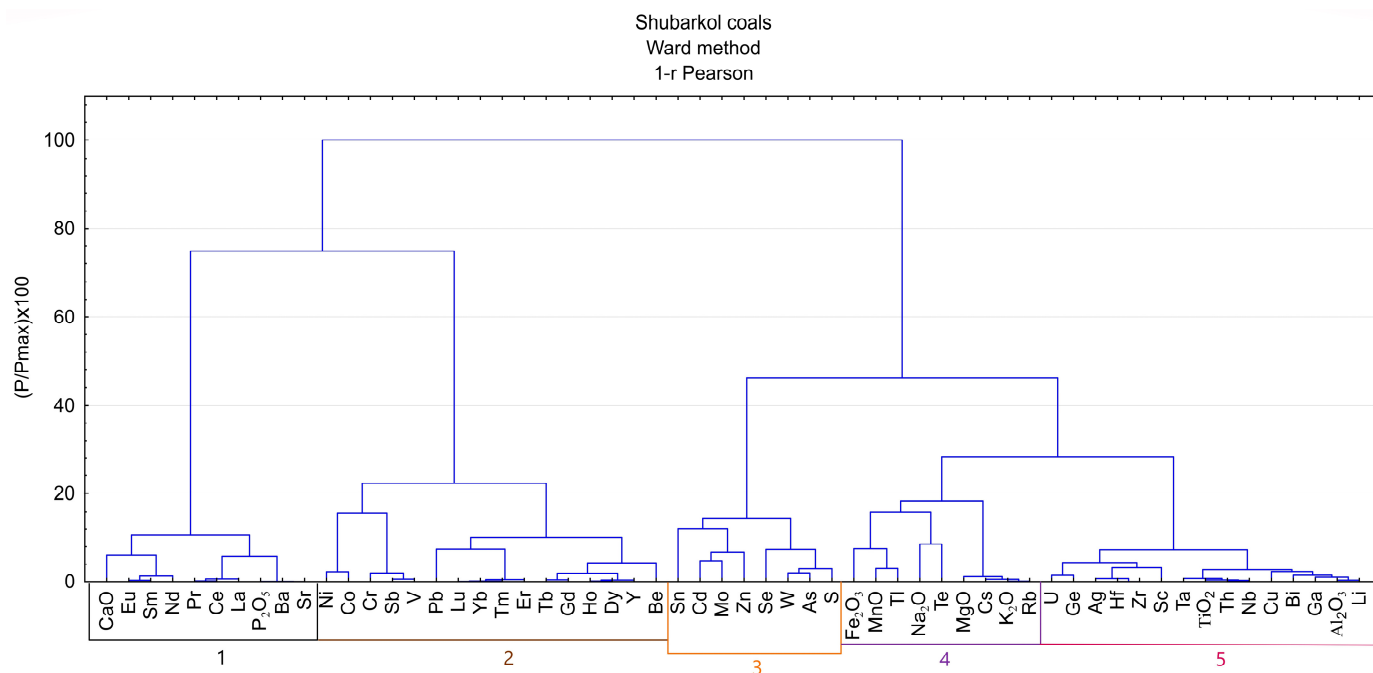


Figure 6. Cluster dendrogram for samples from the Shubarkol deposit, with 1–5 clusters: 1—“phosphate”; 2—“rare earth”; 3—“hydrothermal”; 4—“micaceous”; 5—“clay” (“argillite”).

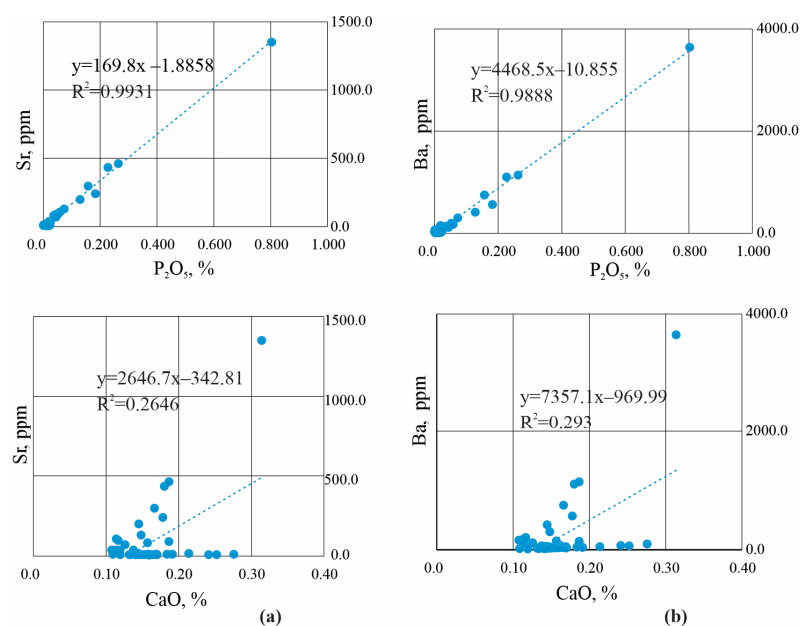


Figure 7. Correlations of (a) Sr with P_2O_5 and CaO and (b) Ba with P_2O_5 and CaO.

The established modes of occurrence of the rare earth elements in the coals of the Shubarkol deposit—in the form of aggregates of plate-like, foliated, columnar crystals or fragments of prismatic crystals (see Figure 8)—indicate the authigenic nature of their formation [32].

The “rare earth” cluster united all heavy REEs (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) and yttrium. It can be assumed that the concentrating mineral in these elements is gadolinite ($Y_2FeBe_2Si_2O_{10}$) from normal or alkaline granites. Despite the unlimited isomorphism among REEs, under certain geological conditions, separate concentrations of elements from the light (cerium) and heavy (yttrium) subgroups are possible. With alkaline volcanic rocks and the associated post-magmatic products, the cerium subgroup is predominantly

developed; meanwhile, with the post-magmatic products of granitoids with increased alkalinity, the yttrium subgroup is predominantly developed.

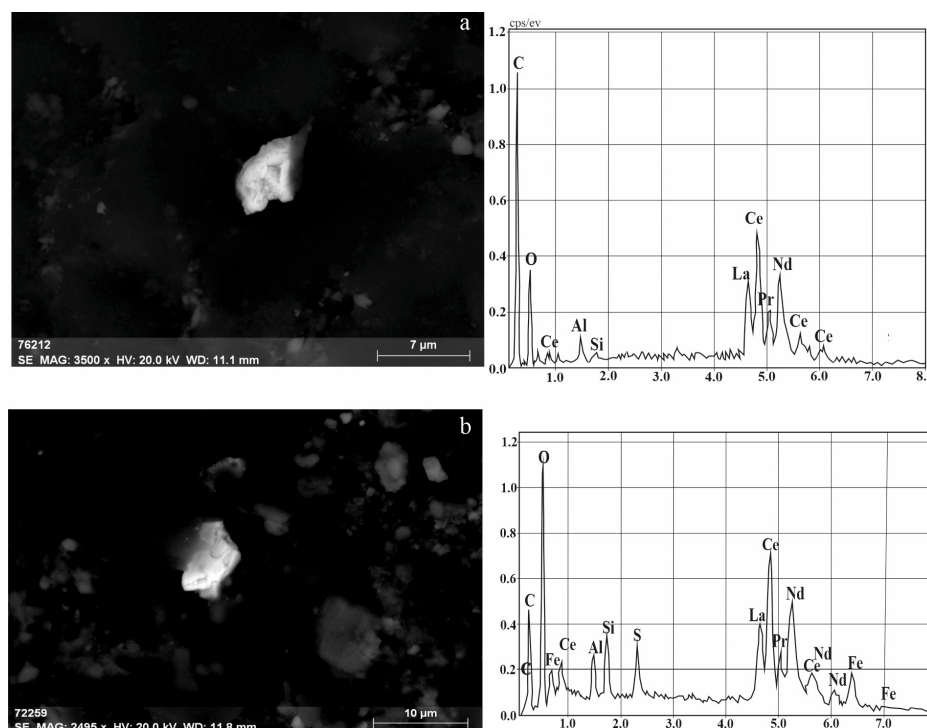


Figure 8. Mineral secretions with REEs: (a) prismatic crystal; (b) leafy crystal.

Thus, it is worth emphasizing the igneous rocks located within the studied deposit, which could have directly participated in the introduction of useful substances into the coals through secondary geological processes.

The frame structures of the Shubarkol deposit include Early and Middle Caledonian igneous complexes—mainly granites, leucogranites, granodiorites, diorites, and monzodiorites. Thus, in the west, there are large outcrops of Precambrian massifs such as Ulytau and Sarysu-Tenizsky (Kireisky ledge), consisting of granodiorite and albite alkali-feldspar complexes. To the east of the Shubarkol deposit, there is the western part of the Central Kazakhstan volcanic–plutonic belt, consisting mainly of granites, andesites, and trachyte, as well as rocks from the alkaline series: syenogabbro, monzonite, granosierite, and syenogranite. Thus, secondary geological processes such as the destruction and transformation of ancient magmatic complexes likely contributed to the formation of geochemical associations in the sedimentary rocks in the Shubarkol coal basin.

Rocks from the Archean and Proterozoic groups participated in the formation of the deposit—namely crystalline shales and gneiss and Middle Caledonian granites—which also played an important role in introducing minerals during the post-magmatic period.

The processes of tectonic–magmatic activation had a certain influence on the metallogenic and geochemical appearance of this region. The Zhailma–Karaoba zone of tectonic–magmatic activation in the Hercynian tectogenesis is located within the area of the Shubarkol deposit (Figure 9). The processes of conjugate activation in the territory of Central Kazakhstan were powerful and widespread, accompanied by ore formations, which were associated with rare metal deposits and occurrences [38,39]. They could have served as a source of rare earth elements that entered nearby coal deposits.

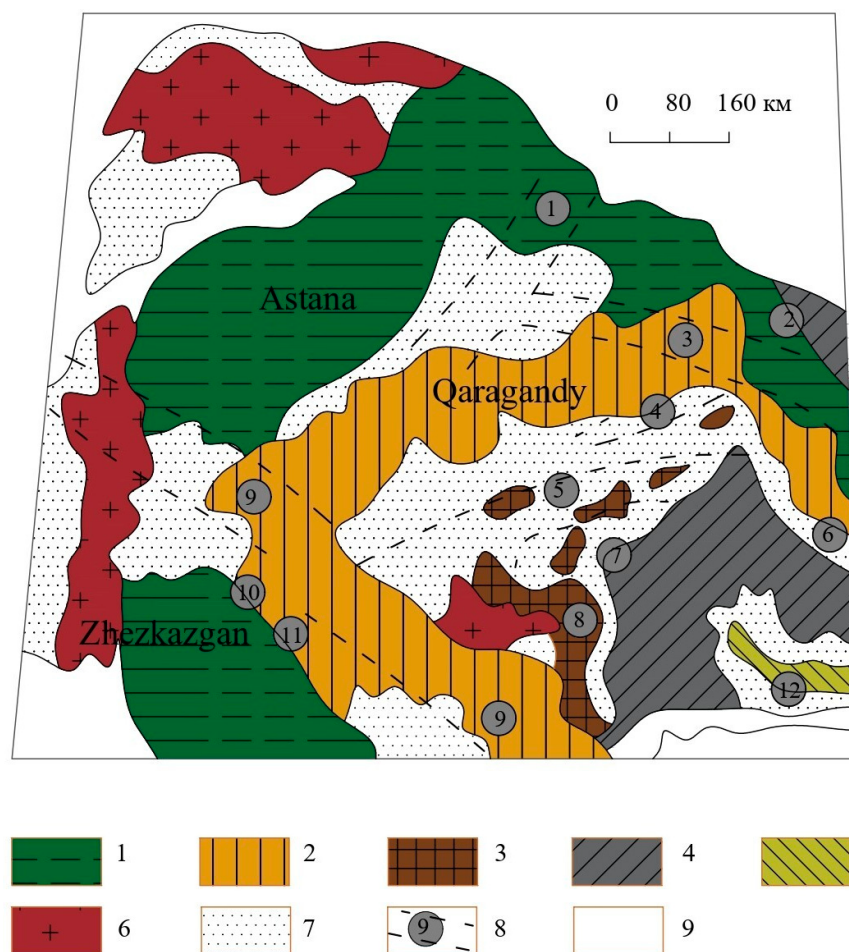


Figure 9. Main volcanic–plutonic belts of Kazakhstan mineral allocations with REEs. 1–5 orogenic volcanic–plutonic belts: 1—Early Caledonian, including the overlapping occurrence beneath the Teniz and Zhezkazgan depressions (O_2 – D_2); 2—Middle Caledonian (“Devonian”, “Central Kazakhstan”, D_1 – D_3); 3—Late Caledonian (D_2 – D_3 or C_1 ?); 4—Early Hercynian (C_1 – P_1); 5—Late Hercynian (C_2 – P_2); 6—outcrops of the Proterozoic basement; 7—Phanerozoic sedimentary basins; 8—Hercynian zones of tectonic–magmatic activation (zone numbers in circles): 1—Koytas-s, 2—Tleumbet, 3—Bayanaul, 4—Spassk, 5—Uspen, 6—Yuzhnochingiz, 7—East Zhamansarysu, 8—Akbastau–Akzhal, 9—Zhailma–Karaoba, 10—Uytas–Zhezkazgan, 11—Kenzhebai–Zhamanaibat, 12—Susyzkara.

The general processes and factors that influenced the accumulation of rare earth elements in the coal seams of this deposit have been described in [21].

The “hydrothermal” cluster included sulfur and elements associated with hydrothermal processes: Mo, Zn, As, W, Sn, etc. (see Figure 6). The accumulation of Mo and As was likely due to epigenetic hydrothermal sulfide mineralization. The forms of mineral inclusions were quite diverse. Numerous sphalerite inclusions were found (Figure 10a), as well as cadmium sulfides, zincite, and brass, albeit less often (Figure 10b,c). Zincite was mainly represented by earthy masses on the surface of the coal (Figure 10b).

In many samples, sphalerite was the most common mineral found after rock-forming minerals. An admixture of cadmium was observed in the compositions of some grains. Sphalerite was corroded, forming lamellar aggregates in the organic matter from the coal, with irregularly shaped aggregates and single grains (Figure 11).

Selenium was present in sulfide (or selenide) form or in native form as micromineral inclusions in pyrite. Solid solutions of variable composition were formed, with the predominance of sulfur (closer to galena) or selenium (closer to clausthalite) (Figure 12a). The

forms of galena and clausthalite were similar—hexagonal, flattened crystals and irregularly shaped grains. There were both single grains and clusters occupying small areas. Galena aggregates filled cracks and pores. Weathered selenides formed earthy masses, and an admixture of mercury (4%) was occasionally found in their composition. The composition of the oxidation product of clausthalite corresponded to molybdenum (Figure 12b). The oxidation products of solid solutions were not identified, but they sometimes contain up to 4% strontium. Mineral inclusions of native selenium were less common in the studied samples (Figure 12c); they formed flattened, scale-like crystals in which oxygen was present due to an oxide film.

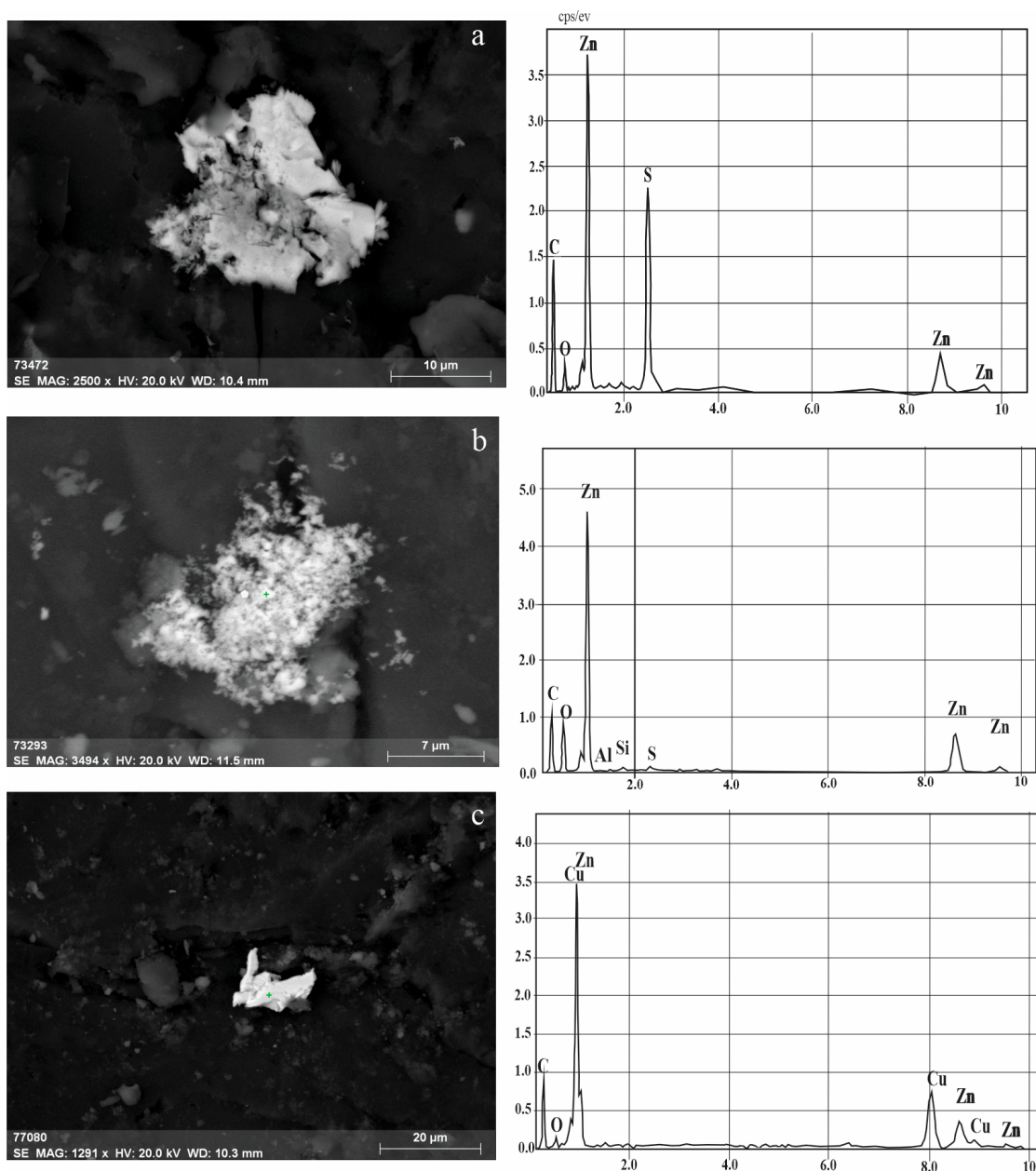


Figure 10. (a) Sphalerite, (b) zincite, and (c) brass.

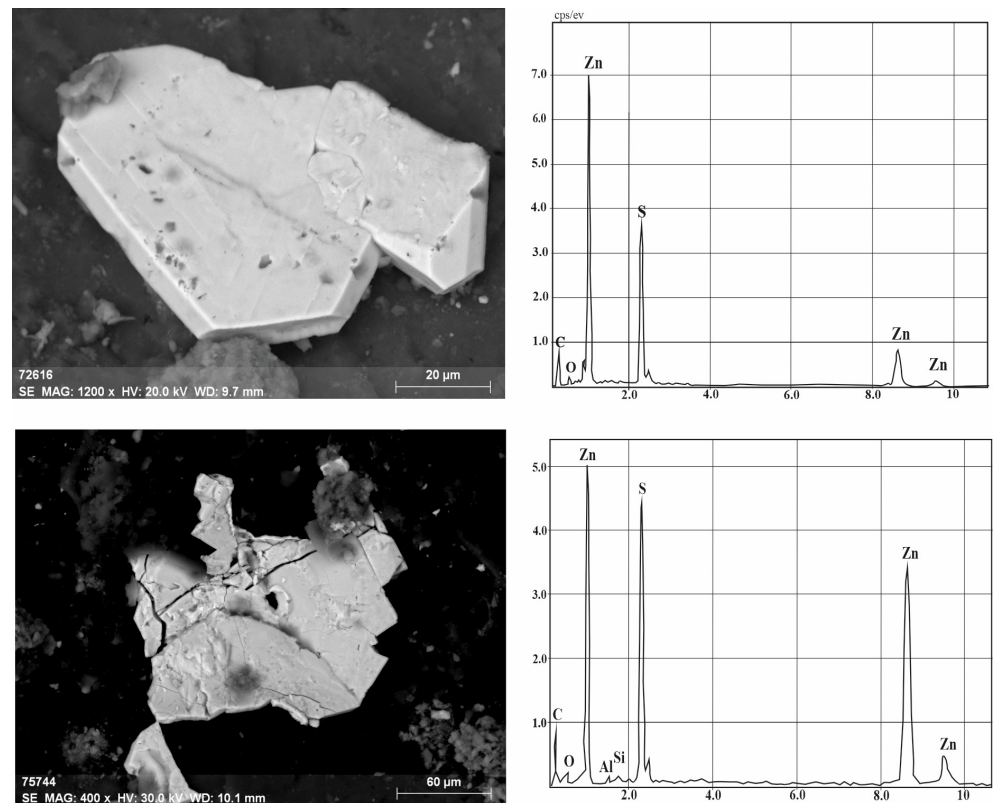


Figure 11. Sphalerite in the samples.

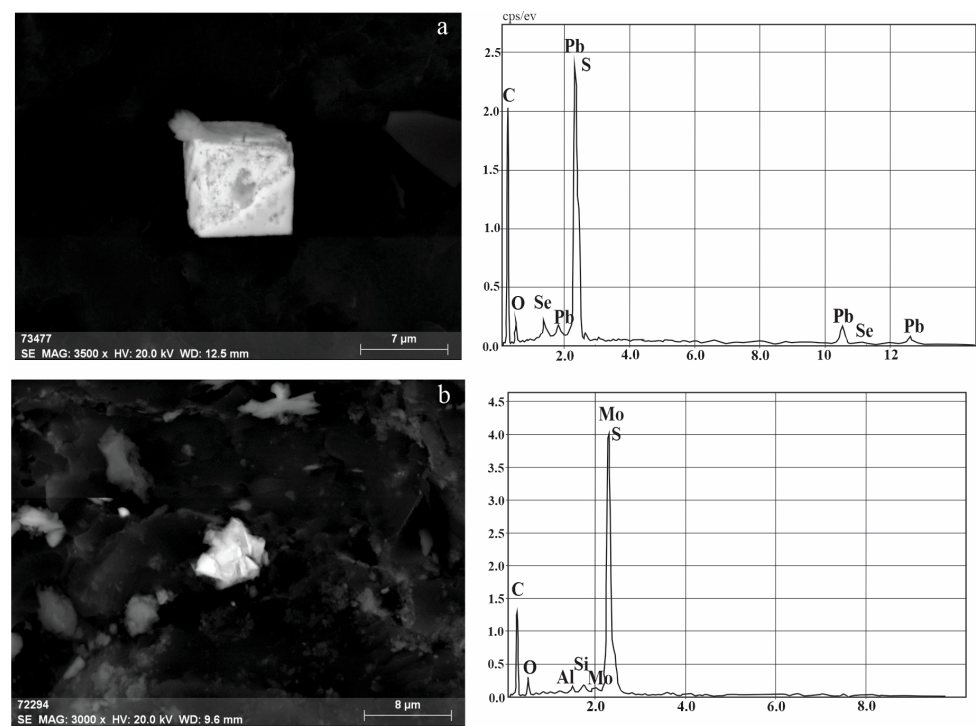


Figure 12. Cont.

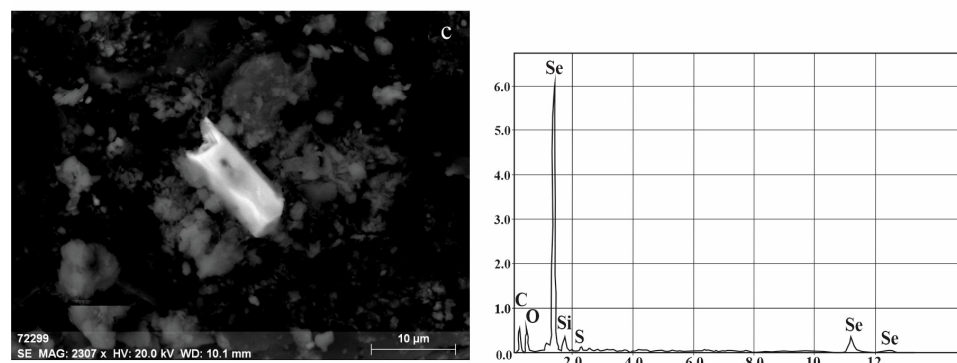


Figure 12. (a) Solid solutions of galena–clausthalite, (b) molybdenite, and (c) native selenium.

The “micaceous” factor combined elements (Fe, Mg, K, Ce) associated with micas, mainly biotite. They form in pores or cracks together with clay minerals. Iron predominated in oxide and sulfide forms. Flattened crystals of hematite or goethite were often found on the surface of the coal, as they were formed by cracks. They were often assembled into aggregates, forming millimeter-sized plates. Up to 2% manganese was present in the composition of the minerals. Hydrogetite occurred as sedimentary and earthy formations. Pyrite was found mainly in the form of framboidal and individual grains (tetrahedral, octahedral, and hexahedral forms and their combinations). Often, pyrite grains filled cracks, or plate-like aggregates formed along the cracks; a star-shaped aggregate composed of lamellar grains of pyrite (marcasite) was identified. Single grains of pyrite contained impurities of selenium and manganese. Pyrite framboids (Figure 13) were replaced by iron sulfates. Lamellar and tabular crystals, as well as irregularly shaped grains of iron sulfate, crystallized on the surfaces of the samples.

The “clay” cluster was distinguished by the presence of Al_2O_3 and elements often associated with fine-grained rocks (for example, U) in an aluminosilicate matrix. The predominant mineral form corresponding to this cluster was kaolinite. Kaolinite occurred both as earthy aggregates on the surface of organic matter and as veins. Lamellar aggregates with a spherical shape could be found on the surfaces of the coal samples. Newly formed plates of sphalerite were found on their peripheries. Concentric formations of hydrogetite could be located in the center. There were well-crystallized vermiculites of kaolinite that broke into plates. Titanium oxides can form both earthy aggregates in the voids of organic matter in coal and large aggregates composed of radiant, needle-like crystals in rock. Single grains of titanium oxide were also found in the coal. The plate aggregate Al-Ti-Zr-O (Mg, Sc, Y), with the composition $\text{ZrAl}_2\text{Ti}_{4.5}\text{O}_{18}$, was found in the coal. There were two minerals with similar sets of elements: carmeltase ($\text{ZrAl}_2\text{Ti}_1\text{O}_{11}$) and pangite (TiAlScMgZrCaO_3).

The conducted factor analysis (Table 3 and Figure 14) generally confirmed the results of the cluster analysis (see Figure 6). The “clay” factor, with a factor loading weight of 30.4%, corresponded to fine-grained and pelitic rocks, which are important for the Shubarkol deposit (Figure 3). The second and third factors, “rare earth” and “phosphate”, with weights of 20.3% and 14.5%, respectively, could be combined into a phosphate–rare earth association, corresponding to the “phosphate” and “rare earth” clusters in Figure 6. The fourth factor was associated with hydrothermal processes not related to carbon formation.

Thus, according to the cluster and factor analyses, the three most characteristic associations among the chemical elements were identified. The concentration coefficients of the trace elements in the coal deposit according to the selected three groups are shown in Figure 15. The concentrations of the trace elements are close to ($0.5 < \text{CC} < 5$) or considerably lower than the average concentrations for worldwide coals [21]. However, S had the highest concentration in the third group ($\text{CC} = 10,000$). The “clay” association (Figure 15A)

was responsible for the composition of the coal and host rocks; the “rare earth” (Figure 15B) cluster was significant for phosphate minerals, phosphorites, and REE minerals introduced into the coal basin and transformed; and the “hydrothermal” (Figure 15A) association was important for hydrothermal processes within the Shubarkol syncline. The content of the elements in hard coal was taken as 1 [25].

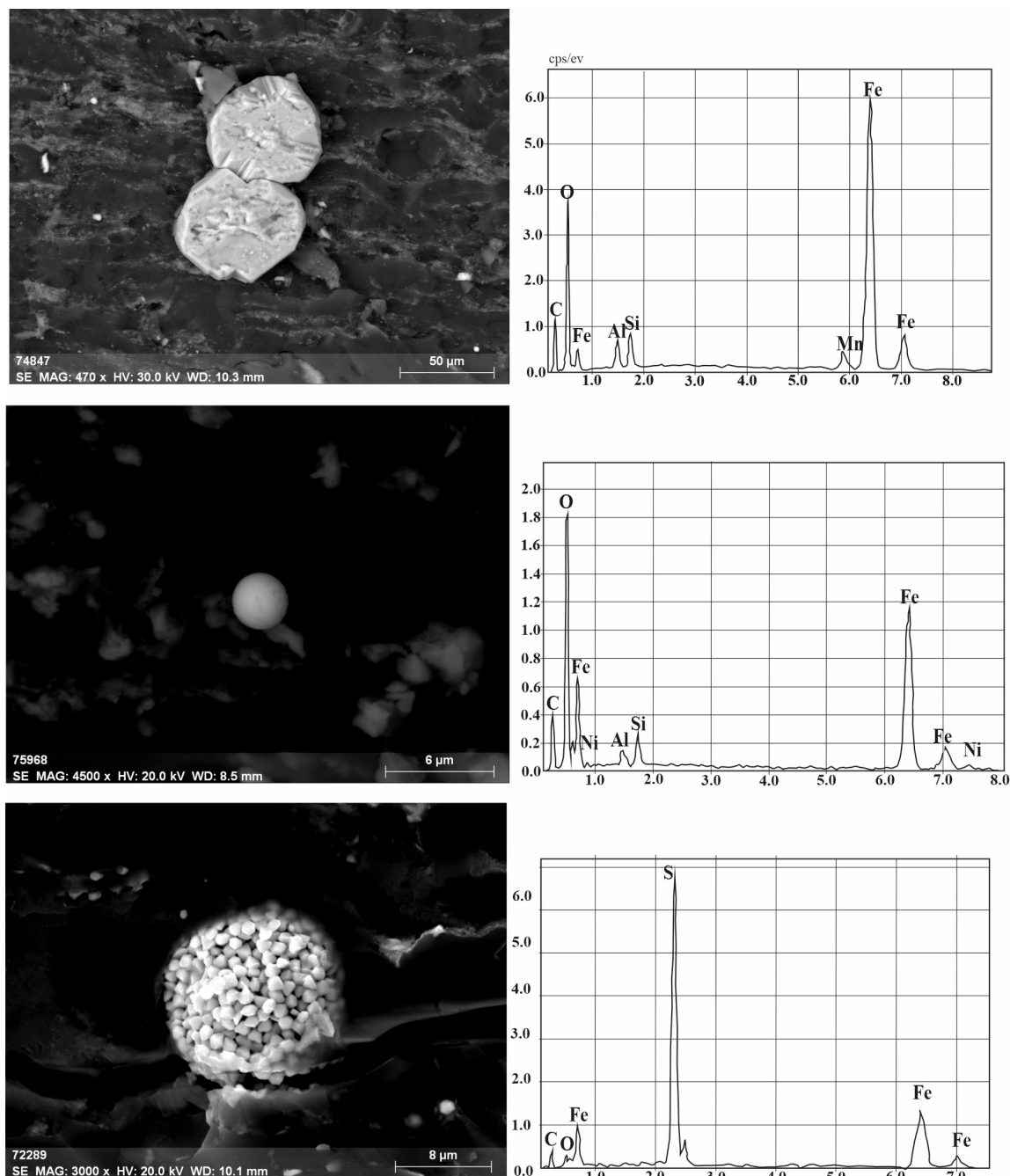


Figure 13. Iron oxides (top and middle) and framboidal pyrite (bottom).

Table 3. Factor loadings of rock samples from the Shubarkol deposit (see Figure 14).

Element, Component	Clay (Argillite) (Factor 1)	Rare Earth (Factor 2)	Phosphate (Factor 3)	Hydrothermal (Factor 4)	Micaceous (Factor 5)
Li	0.92	−0.20	0.11	−0.11	0.00
Be	−0.12	0.78	−0.33	0.24	0.20
S	0.11	−0.20	0.06	0.76	−0.28
Sc	0.71	0.33	0.01	0.02	0.54
V	0.36	0.42	−0.39	0.25	0.54
Cr	0.59	0.31	−0.41	0.27	0.28
Co	−0.50	0.60	−0.36	0.18	−0.04
Ni	−0.39	0.56	−0.12	−0.11	0.18
Cu	0.80	−0.15	0.19	−0.09	0.19
Zn	−0.03	0.09	−0.21	0.02	−0.15
Ga	0.93	−0.08	−0.08	0.02	0.17
Ge	0.74	−0.04	−0.12	0.35	0.40
As	0.31	−0.31	0.07	0.66	−0.34
Se	−0.11	−0.05	0.19	0.56	−0.42
Rb	0.65	0.03	−0.13	−0.31	−0.48
Sr	0.12	−0.01	0.90	0.05	0.21
Y	0.07	0.94	−0.12	0.02	−0.21
Zr	0.92	0.12	−0.17	−0.02	0.22
Nb	0.97	−0.02	0.01	−0.11	0.04
Mo	0.11	−0.45	−0.01	0.64	−0.16
Ag	0.95	0.03	−0.06	0.00	0.19
Cd	0.68	−0.20	−0.14	0.27	−0.20
Sn	0.01	−0.22	−0.08	0.05	−0.07
Sb	0.17	0.51	−0.42	0.30	0.52
Te	−0.03	−0.02	−0.02	−0.19	0.12
Cs	0.57	−0.03	−0.08	−0.32	−0.49
Ba	0.10	0.02	0.89	0.03	0.22
La	0.32	0.03	0.91	0.05	0.00
Ce	0.16	0.20	0.93	0.03	−0.05
Pr	0.12	0.30	0.93	0.02	−0.07
Nd	−0.02	0.46	0.87	0.00	−0.09
Sm	−0.11	0.78	0.58	0.02	−0.13
Eu	−0.03	0.75	0.64	0.04	−0.01
Gd	−0.14	0.92	0.32	0.05	−0.10
Tb	−0.07	0.98	0.06	0.07	−0.09
Dy	0.05	0.98	−0.08	0.07	−0.10
Ho	0.15	0.95	−0.15	0.05	−0.12
Er	0.31	0.90	−0.17	0.04	−0.14
Tm	0.43	0.82	−0.22	0.04	−0.18
Yb	0.49	0.77	−0.22	0.05	−0.19
Lu	0.54	0.74	−0.21	0.02	−0.18

Table 3. Cont.

Element, Component	Clay (Argillite) (Factor 1)	Rare Earth (Factor 2)	Phosphate (Factor 3)	Hydrothermal (Factor 4)	Micaceous (Factor 5)
Hf	0.93	0.13	−0.17	−0.04	0.20
Ta	0.92	−0.14	0.08	−0.16	−0.13
W	0.25	−0.21	−0.05	0.75	−0.33
Tl	0.72	−0.28	0.13	0.05	−0.33
Pb	0.56	0.32	0.08	0.13	−0.18
Bi	0.88	−0.18	0.15	−0.09	0.12
Th	0.97	−0.06	0.02	−0.10	0.01
U	0.87	−0.19	0.04	0.32	0.19
TiO ₂	0.95	−0.15	0.12	−0.13	0.01
Al ₂ O ₃	0.94	−0.18	0.09	−0.11	−0.10
Fe ₂ O ₃	0.30	−0.01	0.02	0.10	0.10
MnO	0.46	−0.31	0.37	0.08	0.06
MgO	0.66	0.11	−0.17	−0.36	−0.40
CaO	−0.31	0.29	0.58	−0.05	0.14
Na ₂ O	0.15	0.19	−0.07	−0.40	0.03
K ₂ O	0.69	0.05	−0.14	−0.32	−0.45
P ₂ O ₅	0.13	0.02	0.89	0.06	0.24
Factor weight, %	30.4	20.3	14.5	6.5	5.9

Note: Significant factor loadings are highlighted in bold.

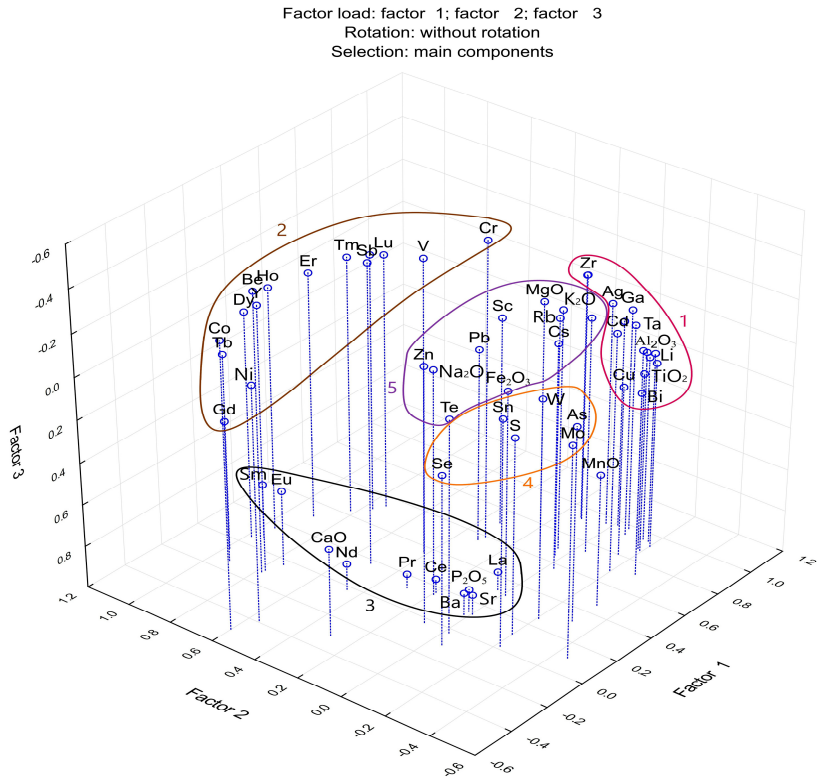


Figure 14. Factor diagram of the Shubarkol deposit (see Table 3). Factors: 1—“clay”; 2—“rare earth”; 3—“phosphate”; 4—“hydrothermal”; 5—“micaceous”.

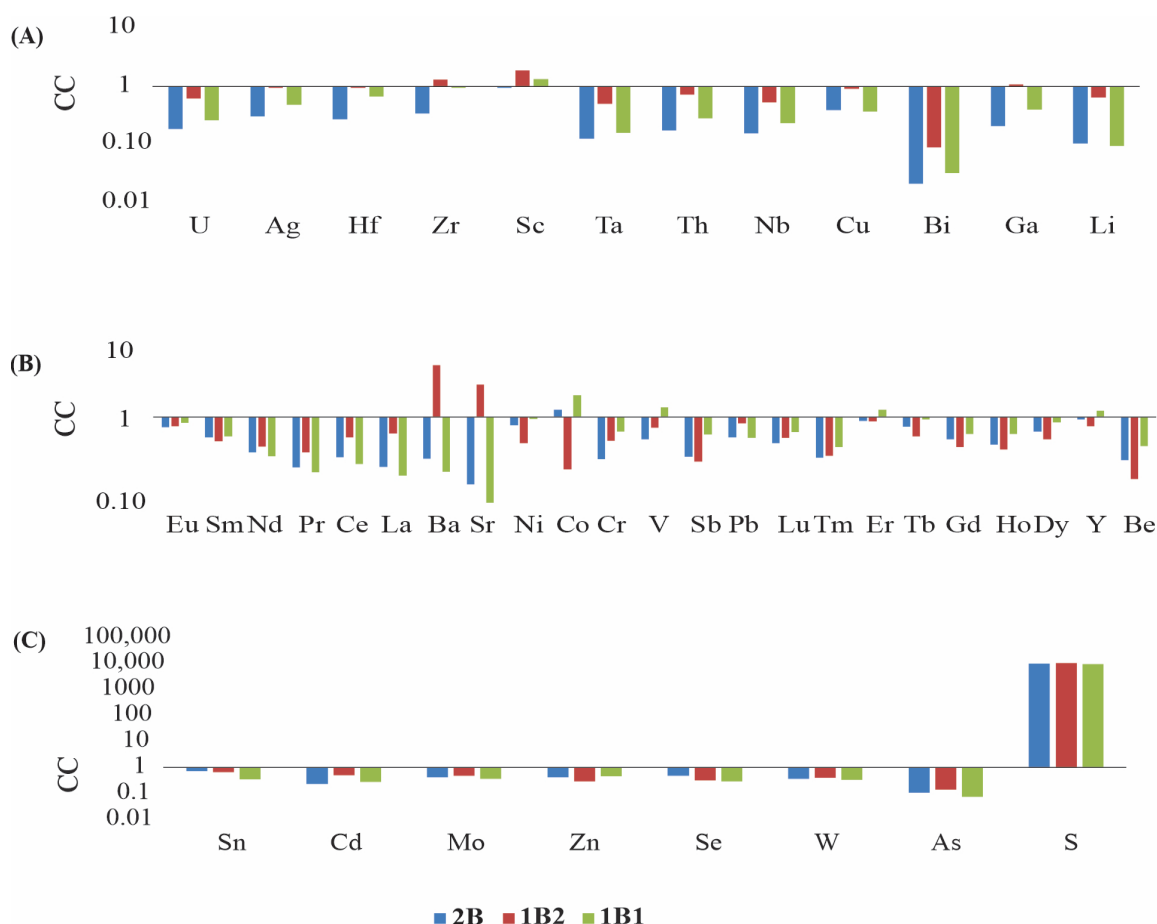


Figure 15. Concentration coefficients (CC) of microelements in coals from seams 2B, 1B2, and 1B1 in the Shubarkol deposit according to selected clusters: (A) clay cluster, (B) rare earth cluster, (C) hydrothermal cluster.

4. Conclusions

The present work considered the genesis of a coal deposit while using new approaches to the statistical processing of geochemical data. New data on the geochemical origins of the trace elements in the Shubarkol deposit were presented. Statistical processing was performed for 58 components, comprising 9 petrogenic oxides and 49 elements, based on the results of ICP-OES and ICP-MS. The composition of the coals in the Shubarkol deposit was diverse, and they contained trace elements and rare metals such as Ba, Sr, Th, Rb, Co, Ce, Zn, and Sc. Moreover, the results of the geostatistical data processing were confirmed by the mineralogical associations among the elements in the coals, as obtained via the SEM-EDS methods.

The electron microscopic studies of the argillites in the Shubarkol deposit revealed well-faceted crystals of zircon, native silicon, and baddeleyite. In general, all studied samples were characterized by the predominance of two minerals: kaolinite and quartz. The ratios between Sr and Ba with CaO and P₂O₅, as well as the data obtained from the microprobe analysis, suggest that Sr and Ba, as well as light REEs, are concentrated in phosphorus-containing minerals (apatite, monazite) or rocks (phosphorites).

The results of the analysis of the REE distribution in the Jurassic coals at the Shubarkol deposit indicated that they were enriched in heavy rare earth elements and depleted of light rare earth elements. Possible sources of heavy REEs in coal deposits include a decrease in the pH of terrigenous materials when entering a peat bog and an increase in the absorption capacity for REEs from La to Lu, leading to their accumulation in peat.

The correlation analysis indicated that there was a highly significant, positive association between Hf and Zr, Ta, Nb, Cs, and Th, as well as other lithophile rare metals, in the studied coals. This allows us to posit that a significant proportion of hafnium was accumulated, not at the expense of clastogenic substances but via its sorption from aqueous solutions and possibly through biogenic accumulation. The concentrations of tantalum and niobium in the coal were due to their accumulation in both the clastic substance and the organic mass of the coal. Abnormal concentrations were of a chemogenic-sorptive nature. The association between heavy rare earth elements (Yb, Tb, Lu), with a very strong correlation between them, likely points to a single source for these elements and a common mechanism of accumulation in coal.

Multiple indicators of origin indicate that the enrichment of impurity elements in this deposit is controlled by clastic terrigenous material and low-temperature hydrothermal solutions, which circulate within the coal basin. A large number of ancient magmatic complexes, such as granodiorites, quartz diorites, granite, leucogranite, alaskite, syenite gabbro, and monzonite, are common within the coal deposit. These participated in creating the geochemical background of the area, as well as framing the rocks and acting as the main thinners for the introduction of impurities, including REEs, into the sedimentary basin [38,39].

The overall results of the cluster and factor analyses demonstrate the complex nature of the coal structure, which is primarily associated with the emergence and further transformation of entire coal deposits. In addition, this work demonstrates the influence of the initial mineral introduction (using apatite as an example) and superimposed hydrothermal processes on general mineralization formation. Another important aspect is the assumption of element migration inside coal deposits as they evolve.

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