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Study of rare earth elements in the coals of the Shubarkol deposit

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ABSTRACT

The work studies mineralogical and geochemical features of the Jurassic coals of the Shubarkol deposit. The samples were examined using the method of scanning electron microscopy (SEM-EDX) Hitachi S-3400N, which was carried out at the Uranium Geology Research and Development Center at the Department of Geoecology and Geochemistry of TPU. Coal geochemistry was studied by instrumental neutron activation analysis (INAA) at the nuclear geochemical laboratory of the Department of Geoecology and Geochemistry of National Research Tomsk Polytechnic University (TPU). The choice of this object of study was determined by the tasks of research including the study of the patterns of accumulation of abnormal concentrations of REE, the effect of various factors of the geological environment on the levels of their accumulation in coals, as well as the conditions of its concentration and forms of occurrence in coals to expand the mineral resource base of Kazakhstan for rare earth elements. According to the results of scanning microscopic analysis, aluminosilicates, sulfides and sulfates with inclusions of microparticles of rare and rare earth elements were found in the composition of the Shubarkol deposit coals. According to the INNA results, abnormal concentrations of Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce and REE were found. Weathering processes led mainly to the loss and redistribution of REE in the coal seams of the Shubarkol deposit, which in turn led to increasing the content of rare earth elements from the bottom up the section. As a result of the action of multiple processes, increased concentrations of rare earth metals, mainly of the yttrium group, were formed. The absence of negative europium anomaly was determined, which confirms the original rocks composition peculiarity. The maximum contents of rare-earth metals are confined to weathered coals; for the medium-heavy group (Nd, PM, Sm, Eu), they are almost a hundredfold higher than the clarke in the upper continental crust. The tenfold excess of the clarke for elements from Gd to Lu was found in clayey sandstones and siltstones; for the rest of the rocks of the deposit the excess over the clarke is significantly lower. It was found that the coals of the deposit belong to the H-type and L-type of REE distribution. During the formation of oxidized H-type coals, clayey matter of terrigenous ash predominated as a carrier of REE, while unoxidized L-type coals were formed with the introduction of REE into the coal accumulation basin mainly in the composition of clay minerals and LREE-phosphates. Here the main source of REE was apparently the weathering crust over acidic rocks.

Keywords: coal, Shubarkol, rare earth elements, mineralogy, geochemistry.

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Introduction

Explored coal reserves in Kazakhstan (according to the BP Review of the World Energy statistics, June 2020) amount to 34 billion tons, which is 4% of the total world reserves. Despite declining the share of coal in the global energy balance, the demand for this type of fuel in the world market will remain stable for a long time to come. In this regard, it is planned to introduce a number of innovative projects in the coal industry. In order to develop the coal industry, to take systemic measures to support the industry, as well as to implement new projects, the Roadmap of developing the coal industry of the Republic of Kazakhstan for 2019-2021 was developed and approved. According to it, it is necessary to pay special attention to coals containing industrial concentrations of rare and trace elements such as germanium, gallium, yttrium, tungsten, and others. Some of them are toxic - mercury, arsenic, antimony, beryllium and others. Some of them are toxic, such as mercury, arsenic, antimony, beryllium and others. Comprehensive use of coal and associated minerals increases profitability of developing coal deposits and contributes to solving a number of environmental problems. At present, reliable estimate of the average content of rare earth elements in coals for most of the coal basins and deposits of Kazakhstan needs to be clarified using up-to-date research methods. In the countries with developed economies (USA, Europe, Australia, China), the rare metal composition in organic matter has been partially estimated and published in numerous editions, where it has been shown that waste of the coal use can also contain high, in some cases industrially significant concentrations of impurity elements (Zharov, 2004; Seredin, 2006; Yudovich, 2006, Dai et al, 2010, 2011, 2019 and others).

Coals are considered the main sources of Ge (the Pavlovskoye deposit, the Spetsugli site is the largest one in Russia). In China, germanium and lithium are extracted on an industrial scale from coal. Attempts are being made to extract individual chemical elements (U, Au, Al, Ga, Sc) from coals and their wastes. However, the efficiency of recovery techniques is not high. One of the main reasons for this is the lack of information on the forms of finding elements in coals and their combustion products. Nevertheless, it has been proven that in a number of cases individual coal seams or even deposits can be considered as a potential complex source of rare, rare-earth and noble metals (Seredin, 2003, Arbuzov S.I., 2008, etc.). But at present, there is still no sufficient geological information of the accumulation of rare earth metals in coal seams, of the forms of their occurrence and the mechanisms of concentration of these elements in the coals of Kazakhstan. In this regard, this work is very relevant, since here there arepresented the results of studying the content of chemical elements, their mineral form in the coals of the Shubarkol deposit.

Previous studies [1, 2] have shown that the deposit contains significant contents of Ba, Zr, Sr, U, Rb, Th, Co, Fe, Zn, Ce and Sc. Studying the distribution of REEs and the form of their occurrence can provide important information for understanding in what environment of coal formation they appeared, as well as with what diagenetic and epigenetic processes they are associated. Minerals in coals are usually formed due to the influx of the terrigenous material, ground and sea water, fallout of volcanic ash, intrusion of volcanic rocks [3-6]. As some researchers point out [3, 6, 7], igneous rocks are one of the main geological factors that can cause ncreasing the content of REE and satellite elements in coals.

Experimental part

Within the framework of studying coals and enclosing rocks of the Shubarkol deposit for the content of satellite elements and REE, studies were carried out using instrumental neutron activation analysis (INAA) at National Research Tomsk Polytechnic University (TPU) and inductively coupled plasma at the Institute of Mineralogy, Geochemistry and Crystal Chemistry of Rare elements (IMGRE-Moscow), the total number of samples was 45. The samples of the Central and Western sections of the field were taken by the bulk method, the sampling interval was kept within 15-35 m. The rocks of the western wing of the Central section were sampled by the point method. The rocks of the Western section were sampled by the core method, the sampling interval was kept within 5-20 m. Using the primary samples, briquettes of 2cm*3cm were made for scanning electron microscopy. The forms of occurrence of minerals in coal samples were stuudied using SEM-EDX at the IISEC "Uranium Geology". The chemical content of coal was determined by the INAA method at the nuclear-geochemical laboratory of the Department of Geoecology and Geochemistry (TPU) (analyst A.F. Sudyko).

Discussing the results

Based on the results of scanning microscopic analysis, various micro-mineral impurities were found in the composition of the Shubarkol deposit coals. These are mainly aluminosilicates, sulfides and sulfates with inclusions of microparticles of rare and rare-earth elements, and according to the results of INAA, abnormal concentrations of Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce and REE were found.

The specific features of the analytics of lanthanides by the INAA method have identified a group of studied elements in detail: La, Ce, Sm, Eu, Tb, Yb, Lu. Their average contents in the Shubarkol deposit coals were estimated based on 45 samples.

The average content of lanthanides in run-of-mine coals of the deposit are lower (approximately 2 times) than the clarke ones. The analysis of the distribution maps in the Western and Central areas of the field of a group of studied elements in detail havw shown that the elements have a different degree of concentration over the area. Attention is drawn to the spatial discrepancy in the concentrations of the elements. The maximum concentrations within the lower clarke contents of La, Ce and Sm are found in the coals of both areas, mainly in the Western area: Tb, Yb, Lu and Nd mainly in the Central area. This fact can indicate both the difference in the sources of input and different mechanisms of the concentration of lanthanides in coals.

Above the “coal clarke” (ytterbium is somewhat lower) are their contents, as well as the number of the above-considered elements, in oxidized coals. Moreover, the La-Yb ratio is noticeably higher than in ordinary coals. This is explained by the peculiarities of the geochemical specialization of the framing rocks, the conditions of peat accumulation and coal formation. It was found that the average La-Yb ratio for the coals of the deposit is higher than for the post-Archean Australian shales (PAAS) and corresponds to that for sandstones according to [8].

The maximum concentrations of elements found in private coal samples are 205 ppm for La, 644 ppm for Ce, 227 ppm for Sm, 79 ppm for Eu, and 97 ppm for Tb, for Yb 358 ppm, for Lu 59 ppm. In coal ash, the content of the total of rare earth elements in some samples can reach 2-3% with the sharp predominance of light lanthanides.

Coal oxidation processes affecting the distribution of REE are manifested in the Western area of the deposit in the near-roof part of the oxidized coal seam.

Oxidation of coal is accompanied by the formation of regenerated humic acids that interact with elements and contribute to their redistribution. It was found that redistribution of lanthanides over the site in the section is uneven. There is a general tendency expressed in increasing the content of rare earth elements from the bottom upward along the section.

It has been established that weathering processes within the Shubarkol deposit have mainly led to the loss and redistribution of REE in coal seams. They are most significant for heavy lanthanides that are relatively mobile under hypergene conditions. The maximum accumulation took place under the mudstone screen, i.e. in the upper part of the section, the coals underwent a "cerium" phase of weathering: the relative contents of lanthanum and cerium decreased, in turn, the contents of yttrium and "heavy" REE increased. As a result of the multiple processes action, increased concentrations of rare earth elements, mainly of the yttrium group, were formed.

The combined concentration and separation of lanthanides in coals are most clearly manifested in the normalized distribution curves (Figure 1).

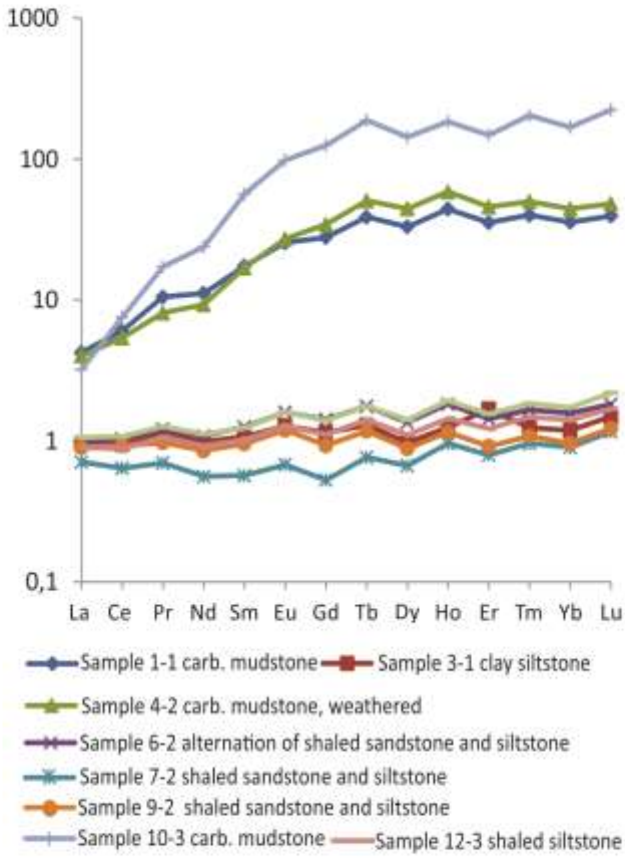

Figure 1 – Pattern of REE distribution in enclosing rocks

The nature of the REE distribution curves in the coals of the Shubarkol deposit normalized to chondrite according to [8], shows that the negative europium anomaly characteristic of most sedimentary rocks is not pronounced. The nature of the distribution curve for coals (Figure 2) is similar to that for the coal-bearing rocks (Figure 1) of the deposit.

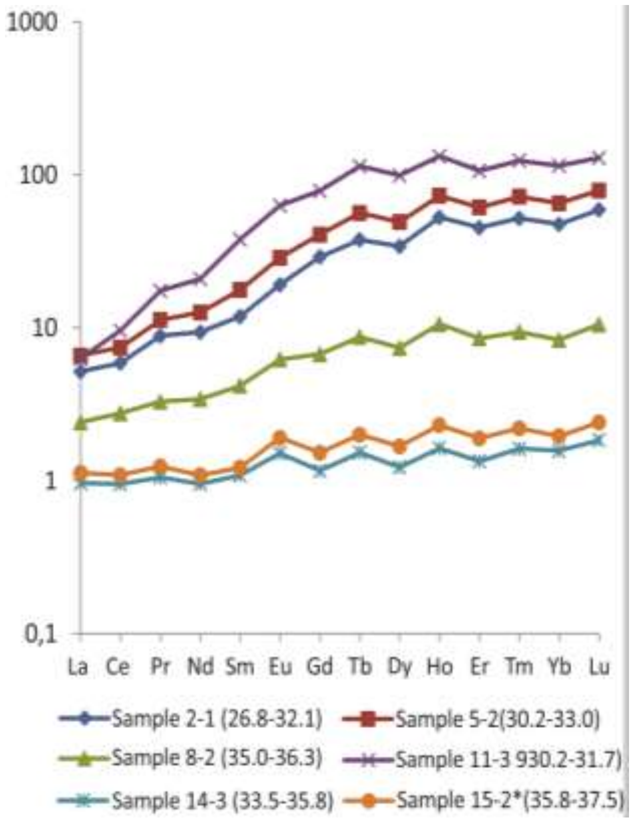

Figure 2 – Pattern of REE distribution in coals (in brackets there are the sampling intervals)

The average spectra of the lanthanides of the Shubarkol deposit normalized according to the chondrite standard [8] are in general characterized by the normal type of distribution.

The lutetium peak is clearly visible in Figure 2. Such peaks are characteristic of the Kuzbass coals and some coals of Australia and the USA.

The absence of the europium minimum can be associated with both the reducing conditions of coal accumulation and the peculiarities of the initial substrate composition. The absence of the europium minimum was noted for some coals of Canada, Far East, and Kuzbass. According to [8], the absence of a negative europium anomaly in well-mixed sedimentary deposits can be explained by only one factor: the feature of the original rocks composition.

With the general increasing the contents up the section, the nature of the distribution curves of rare earth metals with a relative depletion in lanthanum and cerium and enrichment in elements from samarium to lutetium, clearly shows the weathering processes in the upper part of the coal seam with relative enrichment in the groups of medium and heavy rare earth elements.

The maximum REE contents are confined to weathered coals; for the medium-heavy group (Nd, PM, Sm, Eu) they are almost a hundredfold higher than the clarke in the upper continental crust. The tenfold excess of clarke for elements from gadolinium to lutetium was found in clayey sandstones and siltstones; for other varieties of rocks of the deposit, the excess over clarke is significantly lower (Figure 3).

Analyzing the obtained graphs of the average content of rare earth elements in coals normalization to the average content in coals of the world and according to the method of V.V. Seredin [9], the oxidized Shubarkol coals can be classified as H-type coals of the REE distribution.

The formation of H-type coals of the Shubarkol deposit with near-clarke REE contents was dominated by the clayey matter of terrigenous ash as the carrier of REE, while the formation of metalliferous coals with record levels of REE accumulation took place upon prolonged discharge of carbonic water into the peat bog with elevated contents of heavy lanthanides with the following organic REE binding by the peat matter.

Lateral variability of the types of REE distribution and the level of their concentrations occur within the Shubarkol deposit. This indicates significant spatial variations in the nature of the processes that determine the REE geochemistry in coals. In unoxidized coals, normalized La/Yb>1 and therefore, the type of REE distribution differs significantly from oxidized weathered coals and belongs to the L-type that differs in relative enrichment with light lanthanides. Association of light REEs with clay matter and the presence of micromineral REE-containing phosphates (monazite, goyacite, gorseixite) in coals make it possible to associate the L-type formation with the input of REE into the coal accumulation basin mainly in the composition of clay minerals and LREE-phosphates. The main source of REEs was apparently the weathering crust over acidic rocks.

Based on the literature data, phosphates concentrating light lanthanides are considered to be the predominant mineral form of REE in coals [10]. Phosphates and carbonates enriched with yttrium and heavy lanthanides are much less common, despite their high contents in coals. However, according to [9, 10], this form is not primary, since a transformation from the organic to the phosphate form occurred in diagenesis.

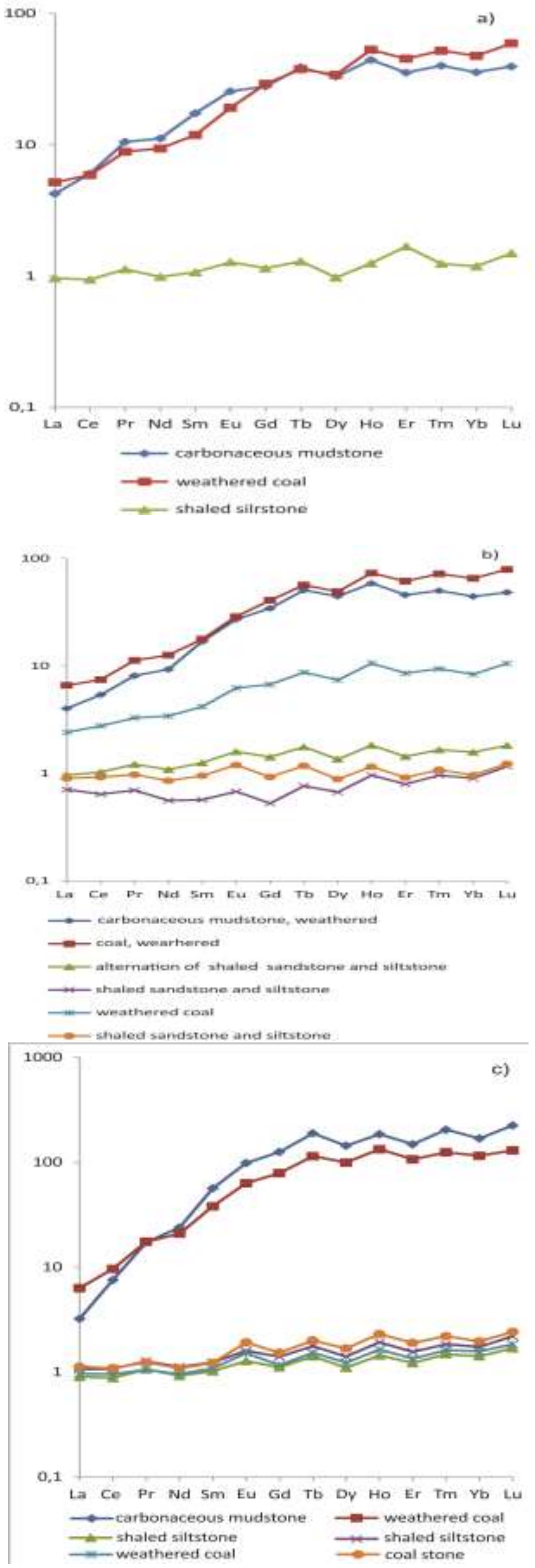

Figure 3 – REE distribution spectra in well No. 1 (a), 2(б), 3(c) normalized to chondrite (Taylor, McLenan)

High-resolution electron microscopy studies of the coals of the deposit under study revealed only a few micron-sized minerals containing REE. Kularit was identified in a sample of oxidized coal (Figure 4a). A cone-shaped particle is located in an aluminosilicate matrix. Its size is about 5 microns.

In a sample of oxidized coal there was found a differentiated micromineral phase of siderophilic Fe and individual REE-Nd in quantities not exceeding the first percent (Figure 4b).

The established extremely small REE minerals precipitates and the peculiarities of their composition allow assuming the authigenic nature of their formation. The formation of the bulk of authigenic minerals occurred in the process of maturation of brown coal and its transformation into stone. In mature coals of the Carboniferous stage, the role of mineral phases increases due to metals released during coalification caused by the loss of carboxyl, hydroxyl, and other functional groups, authigenic minerals are formed.

According to [11], some of the REEs during metamorphism remains in the composition of organometallic complexes in organic matter forming complex aluminum-sulfate-silico-phosphate compounds with different rare metal spectra.

The conditions for the accumulation of REEs in coals, like most other trace elements, are still poorly studied.

The analysis of studying geochemistry of the Shubarkol coal deposit allows identifying the main source of REE input into the coal-bearing deposits. This is a complex of folded framing rocks. The predominant importance of the folded framing rocks composition in the accumulation of lanthanides in coals is emphasized by all specialists involved in the coal geochemistry of REEs [12].

The role of framing is also visible in studying modern peatlands [13]. For the Shubarkol deposit, the contribution of the Kokchetav uplift in the north and northwest, the Kaptyadyr, Arganatinsk and Ulutau mountains in the west, which compose the chain of the Kokchetav-North Tien Shan fold system and the Central Kazakhstan (Devonian) volcano-eastern plutonic belt massifs of alkaline-granitoid composition are characteristic. Significant massifs of alkaline rocks in the composition of the folded framing probably caused the formation of positive europium anomalies in coals and coal-bearing rocks, which are clearly visible throughout the coal-bearing section.

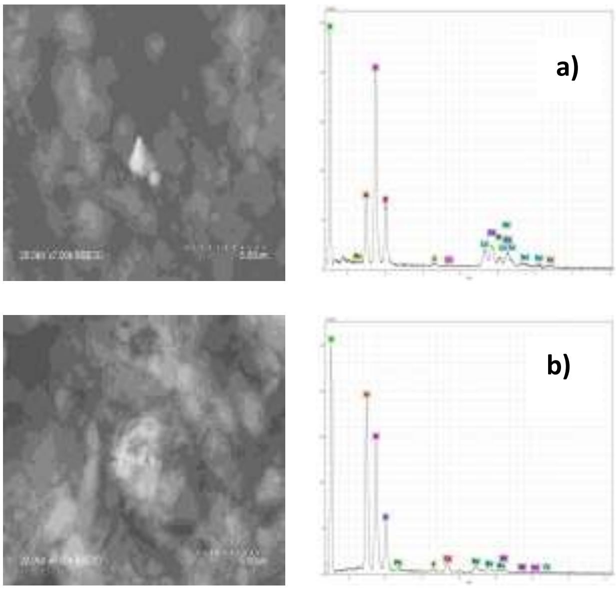

Figure 4 a – kularit, b – complex differentiated micromineral phase Fe-Nd

In this case, the mechanism of transferring the matter from the listed sources and the accumulation of rare earths in coals in the form of clastogene material ensures the accumulation of background concentrations of impurity elements in coals.

Weathering of rocks in the warm, humid Jurassic climate also caused transition of elements to the dissolved state and their transfer in aqueous solutions. Carbonate rocks in the framing structures caused the formation of carbonate and hydrocarbonate waters of varying degrees of alkalinity. The degree of saturation of terrigenous ash with REEs is in direct proportion to the chemical composition of the areas fed by the clastic material of the ancient peat bog. The sharp predominance of coals in the geochemical spectrum indicates the important role of the clastogene component in the accumulation of light lanthanides. Probably, the important role of ultramafic rocks in the framing structures ensured the enrichment of groundwater, suspended matter, and more coarse detrital material with europium. This explains the increased content of this element in the coal-bearing rocks and coals and the absence of the characteristic europium minimum on the normalized curves.

The analysis of the graphs allows concluding that the distribution of REEs formed in the process of peat accumulation, with the removal of cerium and lanthanum characteristic of atmospheric weathering processes, was superimposed on the processes of weathering the coals; increasing the content of rare earth elements in coals in the oxidation zone was caused not by the introduction of elements into the coal seam but by changing its ash content due to the loss of organic matter as a result of coal oxidation to carbon dioxide, water-soluble humic substances and other mobile compounds, which is also observed in other coal basins (Minussinsky, Kuznetsky and other deposits of Siberia).

Conclusions

Based on the results of scanning microscopic analysis, various micromineral inclusions were found in the composition of the Shubarkol deposit coals: aluminosilicates, sulfides and sulfates with inclusions of microparticles of rare and rare earth elements, and according to the results of INAA, abnormal concentrations of Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce and REE.

It was found that redistribution of lanthanides over the site in the section is uneven. Within the Shubarkol deposit, weathering processes resulted mainly in the loss and redistribution of REE in coal seams, which led to increasing the content of rare earth elements from the bottom upward along the section. The maximum accumulation took place under the mudstone screen, i.e. in the upper part of the section; the coals underwent the "cerium" phase of weathering: relative contents of lanthanum and cerium decreased, the contents of yttrium and "heavy" rare earth metals in turn increased. As a result of the multiple processes action, increased concentrations of rare earth metals, mainly of the yttrium group, were formed. The absence of negative europium anomaly at this deposit was determined, which confirms peculiarity of the composition of the original rocks.

The maximum contents of rare-earth metals are confined to weathered coals; for the medium-heavy group (Nd, PM, Sm, Eu), they are almost a hundredfold higher than the clarke in the upper continental crust. The tenfold excess of clarke for elements from gadolinium to lutetium was found in clayey sandstones and siltstones; for other varieties of rocks of the deposit, the excess over clarke was significantly lower.

When studying the normalized average content of REE distribution in coals, it was found that the coals of the deposit belong to the H-type and L-type. During the formation of oxidized H-type coals, clayey matter of terrigenous ash predominated as the carrier of REE, while unoxidized L-type coals were formed with introducing REE into the coal accumulation basin mainly in the composition of clay minerals and LREE-phosphates. Here the main source of REE was apparently the weathering crust over acidic rocks.

An electron microscope revealed single micron-sized rare-earth minerals. Kularit was determined in a sample of oxidized coal: a cone-shaped particle with the size of about 5 microns was located in the aluminosilicate matrix. In a sample of oxidized coal in quantities not exceeding the first percent, a differentiated micromineral phase of siderophilic Fe and individual REE-Nd was found.

The established extremely small precipitates of REE minerals and the peculiarities of their composition allow assuming the authigenic nature of their formation.

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Conflict of interests. On behalf of all the authors, the corresponding author declares that thata is no conflict of interests.

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Шұбаркөл кен орнының көмірлеріндегі сирек жер элементтерін зерттеу

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Қабылданды: *13 қазан 2021*

ТҮЙІНДЕМЕ

Мақалада Шұбаркөл кен орнының юра көмірінің минералогиялық және геохимиялық ерекшеліктері зерттелген. Үлгілер ТПУ-дағы геоэкология және геохимия кафедрасына қарасты, «Уран геологиясы» ХЗҒБО-да жүргізілген Hitachi s-3400n сканерлейтін электронды микроскопия (SEM-EDX) әдісін қолдана отырып зерттелді. Көмір геохимиясы Томск ұлттық зерттеу политехникалық университетінің (ТПУ) геоэкология және геохимия кафедрасының ядролық-геохимиялық зертханасында аспаптық нейтрондық-белсендіру арқылы талдау (АНАТ) әдісімен зерттелді. Осы зерттеу объектісін таңдау геологиялық ортаның әртүрлі факторларының олардың көмірде жинақталу деңгейлеріне әсер етуінің сирек кездесетін элементтерінің аномальді шоғырлануының жинақталу заңдылықтарын, сондай-ақ оның шоғырлануы шарттарын және сирек кездесетін элементтер бойынша Қазақстанның минералдық-шикізат базасын кеңейту үшін көмірде болу нысандарын зерттеуді қамтитын зерттеу міндеттерімен айқындалды. Сканерлеуші микроскопиялық талдау нәтижелері бойынша Шұбаркөл кен орны көмірінің құрамында алюмосиликаттар, сульфидтер мен сульфаттар сирек және сирек жер элементтері микробөлшектерінің қосындыларымен табылды. АНАТ нәтижелері бойынша Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce және сирек жер элементтерінің аномалды концентрациялары анықталды. Үгілу үрдістерінің әсерінен Шұбаркөл кен орнының көмір қабаттарында сирек жер элементтерінің жоғалатыны және қайта бөлінетіні анықталды, бұл өз кезегінде кеніш бойынша төменнен жоғары қарай сирек жер элементтері құрамының ұлғаюына әкелді. Көптеген процестердің нәтижесінде сирек кездесетін металдардың, негізінен иттрий тобының жоғары концентрациясы пайда болды. Теріс еуропийлік аномалия анықталмады, бұл бастапқы тау жыныстары құрамының ерекшелігін растайды. Сирек кездесетін металдардың ең көп мөлшері үгілген көмірлермен шектелген, орташа ауыр топ үшін (Nd, PM, Sm, Eu) олар жоғарғы континентальды қыртыстағы кларктан жүз есе асады. Gd-ден Lu-ға дейінгі элементтер үшін кларктардың он есе артуы сазды құмтастар мен алевролиттерде анықталған, кларк құрамынан айтарлықтай төмен. Кен орындарының көмірі СЖЭ-нің Н-типіне және L-типіне жататыны анықталды. Тотыққан Н-типті көмірді қалыптастыру кезінде СЖЭ тасымалдаушысы ретінде терригенді күлдің сазды заты басым болды, ал L-типті қышқылданбаған көмірлер негізінен саз минералдары мен LREE фосфаттарының құрамында көмір жинау бассейніне СЖЭ енгізу арқылы пайда болды. Мұндағы СЖЭ-нің негізгі көзі қышқыл жыныстардағы үгілген қабықтары болған сияқты.

Түйін сөздер: көмір, Шұбаркөл, сирек жер элементтері, минералогия, геохимия.

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Изучение редкоземельных элементов в углях месторождения Шубарколь

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АННОТАЦИЯ

В работе изучены минералогические и геохимические особенности юрских углей месторождения Шубарколь. Образцы исследовались с использованием метода сканирующей электронной микроскопии (SEM-EDX) Hitachi S-3400N, которая проводилась в МИНОЦ «Урановая геология» при кафедре геоэкологии и геохимии ТПУ. Геохимия углей изучена методом инструментального нейтронно-активационного анализа (ИНАА) в ядерно-геохимической лаборатории кафедры геоэкологии и геохимии Национального исследовательского Томского политехнического университета (ТПУ). Выбор данного объекта изучения определялся задачами исследований, включающими изучение закономерностей накопления в них аномальных концентраций РЗЭ, влияния различных факторов геологической среды на уровни накопления их в углях, а также условий его концентрирования и форм нахождения в углях для расширения минерально-сырьевой базы Казахстана по редкоземельным элементам. По результатам сканирующего микроскопического анализа в составе углей Шубаркольского месторождения обнаружены алюмосиликаты, сульфиды и сульфаты с включениями микрочастиц редких и редкоземельных элементов. По результатам ИННА были обнаружены аномальные концентрации Sc, Ta, Nb, Hf, Zr, Ba, Sr, Ce и РЗЭ. Процессы выветривания привели преимущественно к потере и перераспределению РЗЭ в угольных пластах Шубаркольского месторождения, что привело к увеличению содержания редкоземельных элементов снизу вверх по разрезу. В результате действия множественных процессов сформировались повышенные концентрации редкоземельных металлов, преимущественно, иттриевой группы. Определено отсутствие отрицательной европиевой аномалии, что подтверждает особенность состава исходных пород. Максимальные содержания редкоземельных металлов приурочены к выветрелым углям, для средней-тяжелой группы (Nd, PM, Sm, Eu) они практически стократно превышают кларк в верхней континентальной коре. Десятикратные превышения кларков для элементов от Gd до Lu выявлены в глинизированных песчаниках и алевролитах, для остальных разностей пород месторождения превышения над кларком существенно ниже. Установлено, что угли месторождения относятся к H-типу и L-типу распределения РЗЭ. При формировании окисленных углей H-типа преобладало глинистое вещество терригенной золы как носитель РЗЭ, тогда как неокисленные угли L-типа формировались с привносом РЗЭ в бассейн угленакопления в основном в составе глинистых минералов и LREE-фосфатов. Основным источником РЗЭ, здесь по-видимому, являлись коры выветривания по кислым породам.

Ключевые слова: уголь, Шубарколь, редкоземельные элементы, минералогия, геохимия.

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