ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫ

Satbayev University

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН Satbayev University

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NAS RK is pleased to announce that News of NAS RK. Series of geology and technical sciences scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of geology and technical sciences in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of geology and engineering sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы «ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы» ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Webof Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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THE NATURE OF RARE EARTH ELEMENTS ACCUMULATION IN CLAY LAYERS AND COALS OF THE SHUBARKOL DEPOSIT

Abstract. This paper presents data of mineralogical-geochemical studies of clay layers of the Western section of the Shubarkol deposit, which can shed light to the origin of these specific formations. A comprehensive analysis of possible sources of accumulation of the clay layers matter has been carried out, and the main patterns of distribution and conditions for the REE accumulation in coals and coal-bearing rocks have been studied. The analysis of the carried out studies indicates the existence of a number of independent sources and various mechanisms of REE accumulation in the sediments of the Shubarkol deposit. The REE accumulation in coal seams and clay layers at the deposit is caused by the peculiarities of the composition of the feeding area of the ancient peat accumulation basin, manifestation of epigenetic processes, and the peculiarities of the hydrogeochemistry of the region. In this regard, the increased contents of REE and impurity elements in coals are confined to contacts with enclosing rocks and clay layers, as well as to zones of hypergene oxidation. Forms of presence of valuable elements in coals are various. Most of the impurity elements are associated with mineral phases. The enrichment of coals with a wide range of impurity elements is expressed in a variety of micromineral forms including specific ones. At the same time, individual micromineral phases tend to contacts with clay layers and zones of hypergene oxidation.

Key words: coal, clay layers, tonsteins, geochemistry, Shubarkol, rare earth elements, coal seams, formation conditions.

А.Н. Копобаева*, Г.Г. Блялова, А. Бакыт, В.С. Портнов, А. Амангелдікызы

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ПРИРОДА НАКОПЛЕНИЯ РЗЭ В ГЛИНИСТЫХ ПРОСЛОЯХ И УГЛЯХ МЕСТОРОЖДЕНИЯ ШУБАРКОЛЬ

Аннотация. В настоящей работе приведены новые данные минералогогеохимических исследований глинистых прослоев Западного разреза месторождения Шубарколь, способные пролить свет на происхождение этих специфических образований. Проведен комплексный анализ возможных источников накопления вещества глинистых прослоев, изучены основные закономерности распределения и условия накопления РЗЭ в углях и углевмещающих породах. В данной работе представлены результаты по изучению глинистого прослоя в угольном пласте 2В Западного участка, мощностью 2-5 см. В ходе проведения исследований установлено, что La-Yb отношение >1, что позволяет сделать вывод о том, что Шубаркольские угли относятся к углям Н-типа распределения РЗЭ. Анализ проведенных исследований свидетельствует о существовании ряда независимых источников и различных механизмов накопления РЗЭ в отложениях месторождения Шубарколь. Накопление РЗЭ в угольных пластах и глинистых прослоях на месторождение обусловлено особенностями состава области питания древнего бассейна торфонакопления, проявлением эпигенетических процессов и особенностями гидрогеохимии региона. В связи с этим повышенные содержания РЗЭ и элементов-примесей в углях приурочены к контактам с вмещающими породами и глинистыми прослоями, а также к зонам гипергенного окисления. Формы нахождения ценных элементов в углях разнообразны. Большая часть элементовпримесей связана с минеральными фазами. Обогащенность углей большим спектром элементов-примесей выразилась в многообразии микроминеральных форм, в том числе специфических (циркон, бадделеит и т.д.). При этом отдельные микроминеральные фазы тяготеют к контактам с глинистыми прослоями и зонам гипергенного окисления.

Ключевые слова: уголь, аргиллит, глинистые прослои, тонштейны, геохимия, Шубарколь, редкоземельные элементы, угольные пласты, условия образования.

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ШҰБАРКӨЛ КЕН ОРНЫНЫҢ САЗДЫ ҚАБАТТАРЫ МЕН КӨМІРІНДЕ СЖЭ ЖИНАҚТАЛУ ТАБИҒАТЫ

Бұл жұмыста Шұбаркөл кен орнының Батыс қимасы Аннотация. саз қабаттарының минералогиялық және геохимиялық зерттеулерінің жана деректері келтірілген, олар осы саз қабаттарының түзілуін жаңаша айшықтай түседі. Саз қабаттары құрамының жинакталу көздеріне кешендік талдау жүргізіліп, көмір мен көмір сыйыстырушы жыныстарда сирекжер элементтердің (СЖЭ) негізгі таралу заңдылықтары мен жинақталу жағдайлары зерттелді. Жұмыста кен орнының Батыс бөлігі 2В көмір қабатындағы қалыңдығы 2-5 см болатын саз қабаттарының зерттеу нәтижелері берілген. Зерттеу барысында La-Yb қатынасы >1 болатыны анықталды, бұл Шұбаркөлкөмірі СЖЭ таралуының Н-типті көміріне жатады деген қорытынды жасауға мүмкіндік береді. Жүргізілген зерттеулердің нәтижесі Шұбаркөл кен орнының шөгінділерінде СЖЭ жинақталуының бірқатар тәуелсіз көздерінің және әртүрлі механизмдерінің бар екендігін көрсетеді. Кен орнындағы көмір қабаттары мен сазды қабаттарда СЖЭ жиналуы ежелгі шымтезек жинақталған бассейнінің қоректену аймағы құрамының ерекшеліктеріне, эпигенетикалық үрдістердің көрінісіне гидрогеохимиясының ерекшеліктеріне аймактын Осыған орай көмірдегі СЖЭ және қоспа-элементтерінің жоғары құрамы негізгі жыныстар байланысымен және саз аралық қабаттармен, сондайақ гипергендік тотығу аймақтарымен тығыз қатынаста. Көмірдегі құнды элементтердің табылу пішіндері әртүрлі. Қоспа элементтерінің көп бөлігі минералды фазалармен байланысты. Көмірдің қоспа-элементтерінің үлкен спектрімен байытылуы микроминералды пішіндердің алуан турлілігінде, соның ішінде спецификалық (циркон, бадделеит және т.б.) көрініс тапты. Бұл жағдайда жеке микроминералды фазалар сазды қабаттар байланыстарымен және гипергенді тотығу аймақтарымен қатынасқа бейім болып келеді.

Түйін сөздер: көмір, аргиллит, сазды қабаттар, тонштейндер, геохимия, Шұбаркөл, сирек жер элементтері, көмір қабаттары, түзілу шарттары.

Introduction. Rare earth elements (REE) play an important role in the economy of the XXI century, especially in rapidly developing innovative industries. The main sources of REE are the weathering crusts of granites, carbonatite deposits, and coastal-marine placers. In addition to traditional raw material sources of lanthanides,

metal-bearing coals are also considered as potentially promising (Spears D.A., 2012; Arbuzov S.I., 2007; Dai S., 2012; Seredin V.V., 2013; Dai Sh., 2015; Finkelman R.B., 2019). The colossal resources and huge volumes of coal consumption, alongside with the presence of anomalous REE concentrations in a number of coal deposits, make it possible to consider this potential raw material source of rare metals in more detail, and require large-scale prospecting to identify metal-bearing coals. At present, the content of lanthanides in the coals of the United States, China, and a number of other countries has been estimated, and the average content of all individual rare earth elements in the coals of the world has been calculated (Ketris M.P., 2009; Li J., 2016; Dai S., 2016). Comprehensive geochemical studies have been carried out at a number of deposits.

At the same time, despite significant progress in studying the geochemistry of lanthanides, a number of issues related to the conditions of accumulation, migration, and fractionation of lanthanides in coals, their occurrence forms, and factors controlling the formation of rare-earth metal-bearing coals have not been resolved (Spears D.A., 2012; Dai Sh., 2015 and others).

This work is dealing with the original data of the geochemistry and mineralogy of coals and coal-bearing rocks of the Shubarkol deposit obtained by the authors in the course of complex geochemical studies of this object. At the moment, there are a large number of works that indicate industrially significant concentrations of various chemical elements in coals. All this indicates a growing interest in coals as a source of ore elements.

Layers of essentially kaolinite clays, tonsteins, are extremely characteristic formations in coal seams and coal basins of the world, they are a source of rare metals (Spears D.A., 2012; Erkoyuna H., 2019). The main purpose of studying clay layers is to obtain valuable metals from coals. To implement this, it is necessary to have clear understanding of where and under what conditions coals enriched with valuable elements are formed, in order to identify such coals and to develop methods of their processing. The relevance of the work is caused by the need to search for new sources of valuable elements that determine the development of the present day innovative economy. Coals are considered as their promising source. Studying the geochemical features of coals and the forms of chemical elements occurrence coals is necessary for assessing the metal content of coal deposits, developing criteria for identifying metal-bearing coals and methods of extracting valuable elements.

Characteristics of the deposit. The study was carried out at the coal deposit of Central Kazakhstan, Shubarkol, by testing the open and accessible for studying coal seams. Jurassic deposits of the Shubarkol trough are coal-bearing. The Lower Jurassic coal-bearing deposits, up to 330 m thick, form a sublatitudinal trough (7x16 km) with gentle western and eastern (5-10 and 5-15°) and steeper southern (20-48°) and northern (40-90°) wings. In the inner part of the trough, the slope angles of rocks do not exceed 3-5°. In the central part of the trough, a gently sloping transverse uplift of the coal-bearing stratum is noted, which fades

north of the long axis of the structure. It divides the trough into western and eastern parts. In the first part, the roof of the Upper coal level has a maximum subsidence from the daylight surface of 127 m, and in the eastern one 90 m. The deposit consists of three sections: Western, Central and Eastern. This paper presents the results for the Western section.

At the turn of the century, studying the rare metal content of coals from the Shubarkol deposit was suspended for almost a thirty-year period. A new surge of research in this aspect has occurred only in recent decades.

The maximum contents of rare earth metals are associated with weathered coals; for the medium-heavy groups, they are almost a hundred times higher than the clarke in the upper continental crust. It has been established that the contents of Ce, Ba, Sr, Sc, Zn in individual coal samples are higher than the Clarke. The maximum contents of Sm, Ce, U, Cr, Yb, Ba, Sr, Nd, As, Sc, Zn, Eu, La exceeding the clarke values for sedimentary rocks are established in the composition of mudstone and clay layers (hereinafter referred to as CL).

Research materials and methods. In order to elucidate the origin of the clay layers of the Shubarkol deposit, the clay layers themselves and the coals containing them were tested and studied. In the Western section, a 2-5 cm thick clay layer was studied that was located in seam 2B. In eight vertical sections along seam 2B in two sections, which were 1000 m apart, 23 furrow samples of coal, clay layers and coal-CL contact zone were taken. The sampling interval at the sites was kept within 30-35 m. Composite samples weighing 200 g were made using primary samples. In total, the group composition of 23 samples taken from the Western section of the deposit was studied. The samples were studied by instrumental neutron activation analysis (INAA) to determine the average contents of 28 elements in the nuclear geochemical laboratory of the Department of Geoecology and Geochemistry of National Research Tomsk Polytechnic University (TPU) (analyst A.F. Sudyko). Irradiation of the samples with a neutron flux was carried out at the IRT-T research nuclear reactor of the TPU Physical-Technical Institute. X-ray structural analysis was performed in the laboratory of the Department of Technology of Silicates and Nanomaterials of TPU using a DRON-3M setup. Mineral forms were studied by the method of scanning electron microscopy (SEM-EDX) on the basis of the Institute of Science and Technology "Uranium Geology" of the Engineering School of Natural Resources of TPU. The samples were examined on a Hitachi S-3400N microscope with a Bruker X@Flash 5010 energy-dispersive spectrometer for X-ray spectral analysis.

Discussing the results. There have been studied 23 samples of coal, clay layers and the coal-GP contact zone of the Western section, the content of which is presented in Table 1.

The content of rare earth elements in the samples has been normalized according to UCC, Figure 1. The distribution of lanthanides is relatively uniform in the CL and at CL-coal contacts.

Table 1 – Results of INNA of the element contents of the Shubarkol deposit Western section

		20	1.11	15.8	0.18	0.11	0.39	0.71	6.85	0.79	0.001	0.38	44.8	15.9	6.15	0.38	0.34	2.15	92.0	0.23	3.82	4.92	0.12	7.47	0.02	13.5	0.03	0.36	3.54	0.30
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			08.0	15.0	0.18	0.07	0.18	0.53	3.26	0.54	1 0.001	0.20	48.5	14.9	5.52	0.36	0.36	2.83	0.52	0.15	1.06	2.89	0.16	5.81	0.04	5.69	0.05	0.20	3.59	0.07
		15	1.11	20.4	0.10	0.09	0.30	0.18	1.80	0.64	0.001	0.05	9.06	58.1	6.91	86.0	0.34	98.0	0.1	0.18	1.38	2.20	0.10	3.32	0.00	89.9	0.03	0.33	6.29	90.0
	Coal	Ξ	0.26	3.15	0.08	0.04	0.11	0.12	2.01	0.33	0.001	0.04	13.2	20.9	0.84	0.85	0.31	0.40	0.14	0.07	0.81	2.28	0.08	42.9	0.01	8.11	0.04	0.09	0.55	0.02
_		10	0.35	5.92	0.13	60.0	1.69	0.99	17.1	0.67	0.004	0.33	16.3	26.3	1.26	3.86	0.29	0.51	0.58	0.12	2.19	0.30	0.19	2.97	0.02	7.49	0.02	0.15	0.67	0.40
deposit western section		9	0.59	6.82	0.10	80.0	0.55	0.39	7.80	0.67	0.003	0.14	26.7	22.3	1.90	0.57	0.38	0.51	0.08	0.11	1.69	2.60	0.05	8.69	0.01	3.80	0.03	0.17	0.77	0.09
) 		1	0.82	5.36	0.11	90.0	0.28	0.27	3.50	51	060.0	0.10	16.9	28.6	2.18	98.0	0.35	0.37	08.0	60.0	1.02	2.8	0.04	7.71	0.01	2.70	0.04	0.14	69.0	90.0
csre		25	1.89 0	13.3 5	0.15 0	0.13 0	0.34 0	0.48 0	7.48	0.93 0.	0.04 0.0	0.23 0		36.5 2		0.39 0	0.30 0	1.05 0	0.19 0	0.30 0.	3.07	2.56 2	0.07 0	6.26 7		15.5 2	0.04 0	0.42 0	2.40 0	0.29 0
N 115		2					_						6 47.1		6 5.44										1 0.01					-
cho		21	0.92	16.3	0.11	0.08	0.10	0.21	2.44	09.0	0.001	0.08	22.6	38.0	5.26	0.24	0.25	2.02	0.05	0.17	1.12	2	0.06	3.95	0.01	86.8	0.03	0.26	2.95	0.05
Sildualkul		18	3.26	65.0	1.04	0.44	2.18	11.3	42.2	2.86	0.001	4.93	186.9	39.1	21.3	2.31	0.21	1.74	15.0	0.74	11.4	101.3	1.32	22.0	0.77	2.55	0.11	1.07	29.5	0.50
	Clay layer-coal contact	41	0.48	68.9	0.23	0.11	0.91	1.79	13.9	0.75	0.001	0.73	28.5	33.7	3.24	1.58	0.19	0.42	2.99	0.13	1.99	9.36	0.33	24.7	0.08	12.6	0.03	0.16	2.04	0.17
		12	0.64	9.18	0.31	0.14	1.51	2.65	22.2	1.00	0.001	1.13	42.0	34.6	3.53	4.24	0.3	0.53	3.47	0.10	2.86	14.2	0.30	18.3	0.11	9.03	0.04	0.21	3.15	0.23
or me	ay laye	6	0.59	8.71	0.29	0.14	1.98	2.58	24.1	96.0	0.003	1.18	39.2	35.3	1.14	8.00	0.28	0.40	3.67	0.11	3.03	17.5	0.58	8.33	60.0	10.5	0.04	0.20	2.62	0.40
SHES	C	7	98.0	12.4	0.39	0.17	1.62	2.65	19.5	.27	0.011	1.21	51.4	35.1	4.37	2.97	0.24	95.0	3.37	0.24	3.21	15.5	0.25	20.7	0.11	13.4	0.05	0.26	3.75	0.25
element contents		4	0.58 0	8.32 1	0.25 (0.13 (1.72	1.48	19.6	0.93	0.001	0.11	30.7 \$	34.3 3	4.62 4	4.61 2	0.36	0.63	2.59 3	0.13 0	2.67 3	9.00	0.77 0	16.1	0.09	26.4	0.04 0	0.23 0	2.11 3	0.35 (
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iieiii		2	0.57	8.11	0.17	0.15	1.89	1.77	18.3	1.0	0.021	0.67	36.4	34.2	3.08	5.31	0.29	0.82	1.48	0.19	3.10	4.10	0.84	15.	0.01	59.4	0.13	0.25	2.46	0.37
		34	2.65	21.8	0.43	0.26	1.81	5.41	48.9	1.64	0.002	3.50	148.7	34.1	11.6	1.43	0.3	1.86	6.30	0.47	14.2	41.5	0.43	108.	0.419	12.3	0.07	0.73	10.6	1.41
NINA OI UIE		29	3.12	30.6	0.43	0.23	1.37	4.13	30.0	1.48	0.001	2.38	7.76	33.6	14.2	0.57	0.34	0.30	4.98	0.40	8.19	33.7	0.42	14.9	0.296	17.4	0.05	0.85	12.1	0.72
	er	26	1.80	20.8	0.16	0.10	0.29	0.65	4.49	0.81	0.003	0.28	35.5	20.5	8.01	1.14	0.38	1.25	0.67	0.22	1.19	2.42	0.11	6.92	0.01	9.83	0.05	0.37	4.84	60.0
S OI	Clay layer	17	4.05	6.79	0.85	0.45	2.32	10.18	37.3	2.82			326.2	39.5	23.8	1.45		2.40	13.7	69.0	12.5	9.78	1.35	20.9	0.709	5.85	0.10	1.18	31.3	0.49
- Results of II)	13	0.87	10.5	0.51	0.19	2.52		_		_	_	61.3	33.8	3.66	7.41	0.4	0.58	59.5	0.21	3.96	24.4	0.56	13.0	0.32	14.5	90.0	0.32	4.68	_
년 		∞	0.85	12.2	0.46	0.19	2.24	3.80	30.0	1.38	0.01		55.5	32.4	6.83	6.84	0.35	69.0	4.98	0.21	3.76	23.9	0.55	9.91	0.19	17.1	0.08	0.24	4.06	0.29
lane i		ς,	0.90	12.1	0.45	0.18	2.47	3.43	26.2 3	1.37	0.01	1.33	49.6	30.2	4.72 6	7.30 6	0.45 0	0.79	4.52 4	0.19	3.5 3	19.7	1.04	21.7	0.15	32.8	0.08	0.27	3.61 4	0.40 0
Ial	Elem- ent	Sam- ple No.	Sm 0	Ce 1		Lu			Cr 2	Yb 1	Au 0		Ba 4		Nd 4	As 7	$Ag \mid 0$		Cs 4		Sc	Rb 1	Fe 1		Ta 0		Na 0	Eu 0	La 3	
l	щ	3 1																												

Note. The content of iron, sodium and calcium is in %, the rest is in g/t.

The total amount of REE in the CL and contact zones varies within REE = 21.8-132.2 g/t. Their total content in coal is within REE = 5.3-36.0 g/t. The analysis of the lanthanides distribution in clay layers shows that rare earth elements have a positive correlation with each other (Fig. 2). The calculated lanthanumytherbium (La/Yb) ratio for coals, equal to La/Yb>1 of the Western section, allows attributing Shubarkol coals to H-type coals of REE distribution and concluding that in the formation of H-type coals of the Shubarkol deposit with near-clarke REE contents, clay matter of terrigenous ash prevailed as a carrier of REE, while the formation of metal-bearing coals with record levels of REE accumulation occurred during long-term unloading of carbonic waters with high contents of heavy lanthanides into a peat bog followed by binding of REE by peat organic matter (Seredin V.V., 2007).

In the near-top and near-soil zones, a sharp decrease in the La/Yb ratio was noted, which indicates participation of their water-soluble forms in the accumulation of REE in coals (Arbuzov S.I., 2016). It can be seen from the graphs that pronounced REE anomalies are associated with CL overlying coals due to their sorption capacity. The analysis of the impurity elements distribution in clayey rocks of the Western area shows that large ionic lithophilic (Rb, Ba, Sr) and transit (Cr, Zn) elements have the highest concentration, and the rest (As, Ca, Fe, Sb) are relatively average.

The analysis of the vertical distribution of La and Yb along the 2B layer in three sections in the Western area of the deposit (Fig. 3) shows that the highest concentrations of all REE are characteristic of clay layers and oxidized coals. In this case, the La/Yb ratio increases up the section indicating a predominantly clastogenic mechanism of REE supply to coals (Arbuzov S.I., 2007).

It has been established that the distribution of lanthanides over the site in the section is uneven. Within the Shubarkol deposit, the weathering processes led mainly to the loss and redistribution of REE in coal seams, which led to increasing the content of rare earth elements from bottom to top in the section. The maximum accumulation occurred under the mudstone screen, i.e. in the upper part of the section, the coals underwent a "cerium" phase of weathering: the contents of lanthanum and cerium decreased, in turn, the contents of yttrium and "heavy" REE increased.

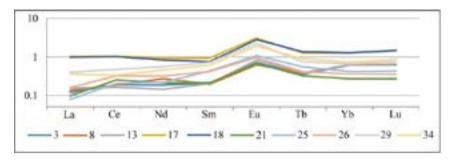


Figure 1 – Distribution of rare earth elements in mudstones, contacts of mudstones with coal of the Western section of the Shubarkol deposit (normalized according to UCC).

Note. 3, 8, 13, 17, 26, 29, 34 is the CL sample number, 18, 21, 25 is the coal and CL contact sample number.

The established absence of negative europium and positive cerium anomalies at this deposit confirms the peculiarity of the composition of the original rocks and the ways of introducing REE into the deposits. It has been found that only in some coal samples the cerium anomaly is positive, which could be affected by rocks with an insignificant admixture of "background" clastic material. Thus, the analysis of the data obtained indicates the existence of a number of independent sources and various mechanisms of REE accumulation in the sediments of the Shubarkol deposit. If to consider the mineralogical and geochemical state, then these concentrations can be caused by the action of sea water or hydrothermal action (Arbuzov S.I., 2014), which in turn could affect the appearance of the cerium minimum, which is explained by the presence of authigenic minerals (for example, clay minerals, which the cerium minimum inherits from sea water) (Ayupova N.R., 2002), rare earths also probably entered the sedimentation area as part of clastic material.

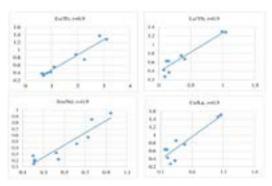


Figure 2 – Correlation plots of elements of the lanthanide group in mudstones of the Western section of the Shubarkol deposit.

In tectonic terms, multiple faults (Karakengir, Zhezkazgan-Terektinsky faults, Kainda graben, Ulzhanskaya syncline, Tantal and Shubarkul graben-synclines and horst-anticlines) and fold-block structures (Sarysu-Teniz zone of block folds) occur in the area of the deposit. Impurity elements entered the coals along the formed faults from the basement rocks due to removal and redeposition with the participation of syn- and epigenetic processes of migration of ground and underground waters (Kopobayeva A.N., 2021).

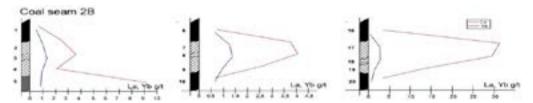


Figure 3 – Vertical distribution of La and Yb in the sections of coal seam 2B of the Western area

The analysis of studying the geochemistry of coals from the Shubarkol deposit makes it possible to identify the main source of REE entry into coal-bearing deposits. This is a complex of rocks of the folded framing of the Shubarkol deposit. The contribution of the Kokchetav uplift in the north and northwest, the Kaptyadyr, Arganata and Ulutau mountains in the west, which make up the chain of the Kokchetav-North Tien Shan fold system and the Central Kazakhstan (Devonian) volcano-plutonic belt in the east with the presence of alkaline-granitoid composition. Significant massifs of alkaline rocks in the composition of the folded frame probably determined the formation of positive europium anomalies in coals and coal-bearing rocks, which are clearly visible throughout the coal-bearing section.

The weathering of rocks under conditions of the warm, humid Jurassic climate also caused transition of elements into the dissolved state and their transport in aqueous solutions. Carbonate rocks in the framing structures determined the formation of carbonate and hydrocarbonate waters of varying degrees of alkalinity. The degree of saturation of terrigenous ash with REE is in direct proportion to the chemical composition of the areas fed by clastic material of an ancient peat bog (Arbuzov S.I., 2007). The clastogenic component also played an important role in the accumulation of light lanthanides; the rocks of ultramafic composition in the framing structures ensured the enrichment of groundwater, suspended matter, and coarser clastic material with europium. This explains the increased contents of this element in coal-bearing rocks and coals and the absence of the characteristic europium minimum on the normalized curves.

The problem of diagnosing clay layers as tonsteins arises in the case of

post-sedimentary changes in pyroclastics, when it becomes undetectable by conventional petrographic methods due to its transformation into heir minerals: smectites, zeolites, silica minerals, kaolinite, etc.

X-ray phase analysis was used as one of the diagnostic methods of studying the material composition of clay layers. It was carried out by recording diffractometric curves, which made it possible to identify the composition, to trace its changes and to obtain an approximate estimate of the ratio of the constituent components of the samples. Almost all diffractograms have reflections indicating the presence of quartz. Silicification can occur under the impact of the processes of dissolution and oxidation of the original rocks and be accompanied by the release of a part of SiO₂ which can lead to silicification of the enclosing rocks. Thus, volcanic ash is likely to be a source of authigenic silica. According to the XRD data of chemical analysis, the content of SiO₂ varies from 32.8 to 59.6%, which brings them closer to tonsteins and metatonsteins.

Based on the data obtained as a result of diffraction analysis, the diagram of the minerals distribution in the composition of the CL was constructed (average value from 6 samples) (Fig. 4).

Clay rocks are dominated by minerals: quartz, kaolinite, muscovite, while quartz occupies a leading position, only in rocks No. 1-15 sampled in section 1 of the Western section, kaolinite prevails over quartz. A distinctive feature of coalbearing and contact rocks is the low content of minerals of the feldspar group. Albite and microcline are noted among the minerals of this group. Minerals of palygorskite, barite, anatase, and siderite also appear in small amounts. The presence of palygorskite is considered as confirming the connection of tonstein with pyroclastics, but is less conclusive. The clear presence of pyroclastic material and specific mineralization is one of the conditions for the formation of palygorskite. But for the formation of palygorskite, only a suitable substrate is not sufficient; it is also necessary that it fall into a favorable environment characterized by alkaline conditions (YUdovich YA.E., 2010).

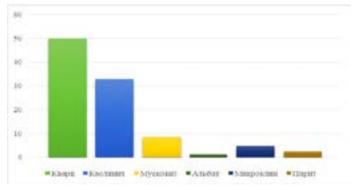


Figure 4 – Mineral distribution in the mudstone composition.

A significantly higher REE concentration is characteristic of clayey rocks rich in kaolinite and pyrite. The most convincing explanation for this is that after deposition and subsequent diagenesis, these coal and CL levels developed higher recovery conditions. Possibly later, the studied layers were affected by magmatic intrusion, during which hydrothermal activity increased the coal content and introduced some trace elements.

Detailed electron microscopic studies revealed well-faceted crystals of zircon, native silicon, and baddeleyite in the clay layers (Fig. 5).

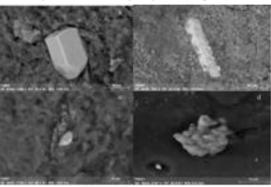


Figure 5 – Crystals of zircon (a, b), baddeleyite (c), and native silicon (d).

Individual zircon grains contain an admixture of scandium, titanium, yttrium, or other heavy rare earth elements. Baddeleyite is rarer than zircon. The mineral was found in rocks and coals on contact with them. This character of mineral excretions indicates a sparing mode of transportation of the substance and excludes its transfer by water flows. This once again points to different ways of REE migration into coals and coal-bearing rocks of the deposit.

When studying of samples of coal and coal-bearing rocks on a high-resolution electron microscope, REE carbonates were detected (Fig. 6). REE carbonates at the Shubarkol deposit occur in the form of aggregates of lamellar, foliar, columnar crystals, fragments of prismatic crystals. The extremely small size of REE mineral segregations and the peculiarities of their composition suggest the authigenic nature of their formation.

The formation of the authigenic minerals bulk occurred in the course of brown coal maturation and its transformation into hard coal. In mature coals of the coal stage, the role of mineral phases increases due to the bonds released during coalification of metals with the loss of carboxyl, hydroxyl and other functional groups, authigenic minerals are formed.

It is possible that during metamorphism some part of REE remains in the composition of organometallic complexes in organic matter forming complex aluminosulfate-silicophosphate compounds with different rare-metal spectra.

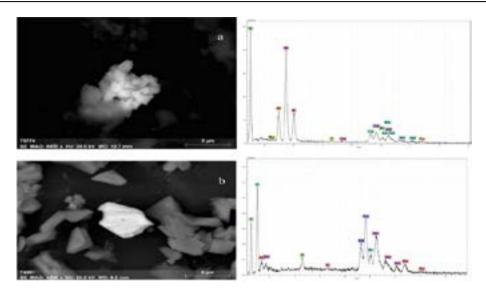


Figure 6 – REE carbonates in the form of aggregates: a – prismatic crystals, b – lamellar crystals.

Conclusion. Studying the mineralogical and geochemical features of clay layers and coals of the Shubarkol deposit shows that elevated contents of REE and impurity elements are characteristic of clay layers and oxidized coals. The nature of their accumulation and their migration paths are different: the predominantly clastogenic mechanism of REE entry into coals predominates, and there is also an impact of the original rocks composition.

The presence of mineral palygorskite in coals and clayey rocks is considered as confirming the relationship of the tonstein with pyroclastics, a possible addition from earlier volcanic rocks of the basement. The established, well-cut crystals of zircon, native silicon, baddeleyite indicate a more gentle way of transporting them to coal-bearing rocks and excludes their transfer by water flows. In addition to the clastogenic-volcanogenic source, the accumulation of REE in organic matter is also possible due to the introduction in aqueous solutions from the hypergenesis zone or hydrotherms. The extremely small size of REE mineral segregations and the peculiarities of their composition suggest the authigenic nature of their formation.

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