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Study of the Distribution of Impurity Elements in Coals and Clay Layers of the Karaganda Coal Basin

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Abstract. *The study of the distribution of trace elements in coal has aroused great scientific interest all over the world, not only because of the harm to health and related environmental problems when using coal, but also because of the economically valuable elements contained in it. The distribution of impurity elements in coals and clay layers of the Karaganda coal basin is considered. The main objective of this work is to identify geochemical features of elements-impurities in coals, clay interlayers of the k7 formation of the Karaganda coal basin. The paper presents the latest data on the composition of coals and clay layers. 85 coal samples of clay interlayers and coal-clay interlayers contact from three mines – Saranskaya, Aktasskaya, Kuzembaeva – were analyzed. The samples were studied by the ICP-MS method at the Far Eastern Geological Institute of the Far Eastern Branch of the Russian Academy of Sciences (DVGI FEB RAS).*

Keywords: *clay substance, coal, impurity elements, Central Kazakhstan, geochemistry, clay interlayers.*

Introduction. In Kazakhstan, coal is not only the main source of energy, but also the basis of economic and social development of the country. Thus, interest in the study of coal in our country is growing widely. This work is devoted to the study of the distribution of impurity elements in the coal of the Karaganda coal basin, which is one of the most important coal basins of Kazakhstan, the third largest coal reserves in the world after the Donbass and Kuzbass and makes up the coal base of the country.

Geochemistry of trace element in coals is an important part of coal science. Scientific assessments of trace element concentrations in coal provide a solid basis for assessing the environmental impact of harmful elements and the use of valuable elements in industry [1, 2].

Altered volcanic ash in coal-bearing strata usually occurs as thin (usually < 10 cm) but stable in extent layers, which are usually found worldwide in every coal-forming geological period [3, 4]. They are defined as tonstein, bentonite, and K-bentonite based on kaolinite, smectite, and mixed illite/smectite content > 50%, respectively [3].

The study of altered volcanic ash in coal seams has both practical and scientific significance [4]. In practice, their characteristic appearance, characterized by lighter thin seams with lateral alignment, can be used as chronostratigraphic markers to correlate coal seams during the exploration and production phase [4, 5]. Some altered volcanic ashes (e.g., alkaline tonsteins) may have highly elevated concentrations of critical elements such as Ga, Nb, Zr, Ti and rare earth elements, as well as Y (REY), which can be an economically viable source of metal recovery [4]. In addition, mineralogical and geochemical characteristics of altered volcanic ash also contain useful information about the conditions of deposition, the nature of the original magma, and regional tectonic evolution [1, 3, 4, 5].

Deposit characteristics. From the early Devonian to the late Paleozoic, a characteristic series of formations from effusive-terrigenous (Devonian), carbonate (Famennian) to terrigenous carbonaceous and red salt formations (Carboniferous-Permian) were formed in Central Kazakhstan (Degtyarev K.E., Kuzhieisov N.B., 1996). The transgression of the sea from the southeast and the accumulation of sandy-pebble sediments in the coastal-marine conditions belong to this time. Along the northern edge of the basin there is an underwater outpouring of lavas. Volcanic outpourings increase in intensity, and by the mid-Devonian they cover the entire basin area.

Coal-bearing sediments (of the Karaganda Basin) accumulated mainly in the east, when the region of the marginal trough began to experience a steady sinking, which lasted until the late Paleozoic against the background of the beginning of the general uplift of the territory of Central Kazakhstan.

Coal-bearing sediments of the Karaganda Basin belong to the Carboniferous and Jurassic ages. Their foundations are marine Upper Devonian sediments, as well as metamorphosed effusive and sedimentary rocks of Middle and Lower Devonian and Silurian ages, coming out at the margins of the basin, where they form its natural boundary. In the central part of the basin are the Carboniferous sediments, overlain in the eastern part by Jurassic sediments. The coal-bearing sequence with a thickness of 4,500-5,000 m begins with deposits of the upper Tournaisian. The lower part of this stratum contains marine fauna and flora, and according to the degree of coal formation and lithological composition in this stratum the Akuduk, Ashlyarik, Karaganda, nadkaraganda, Dolina, Tentek (naddolina) and Shakhan formations are distinguished.

The Karaganda Basin is a synclinorium of latitudinal direction with a gentle north wing and a steep northward tipping south wing. From the west, it is bounded by a large disjunctive disturbance of meridional direction – the Tentek surge with an amplitude of about 400 m. Along the southern boundary runs a large Jartas, or Jalanr, thrust with a steep (up to overturned) bedding of rocks and numerous disturbances. In the basin, there are three large mulds (from east to west): Verkhne-Sokurskaya, Karagandinskaya and Cherubay-Nurinskaya.

According to data (Lushchikhin G.M., 1961, Rengarten N.V., 1957) studied the coal seams Karaganda formation, established a high saturation of their tosteins, among which prevail coarse and crystalline varieties, whose thickness varies from fractions of millimeters to 2 cm. He also found that formation k_1 in the Gorbachev Mine has up to 20 interlayers of tonsteins, and formation k_7 – 6 horizons of tonsteins.

Gopetsky Y.K. and Petrovskaya A.N. were among the first to study tonsteins of the Karaganda coal basin (in the late 30s), they distinguished among tonsteins crystalline and microbeobic varieties. According to these researchers, the formation of these interlayers occurred chemogenic. This theory of tonstein origin was also shared by other researchers (Krylova N.M., G.K. Khrustaleva).

Research Methodology. The research was conducted by sampling clay interlayers (hereinafter referred to as «CI»), as well as coals (C) and their contacts at the face of formation k_7 in the mines Saranskaya, Aktasskaya, Kuzembaeva.

During the study, samples of coal and clay interlayers were taken by the furrow method across the strike of coal seams in the direction from the roof to the ground, weighing 1200-1500 g. At a distance of 50-80 cm at three mines in the basin, a total of 85 samples.

Preparation of samples for analytical studies in all cases was carried out according to standard methods – drying in vivo, crushing, quarting and abrasion.

The set of studies was chosen based on the objectives to determine the content of impurity elements in samples of coal and rock interlayers. Composite samples weighing 200 g were made from primary furrow samples in Azimut Geology LLP, Karaganda. Prepared samples were mixed, quarted, divided into equal 4 parts of 200 g. To determine the chemical composition of the samples were studied by ICP-MS method in FEB RAS RF.

Results. 85 samples taken from the coals, clay

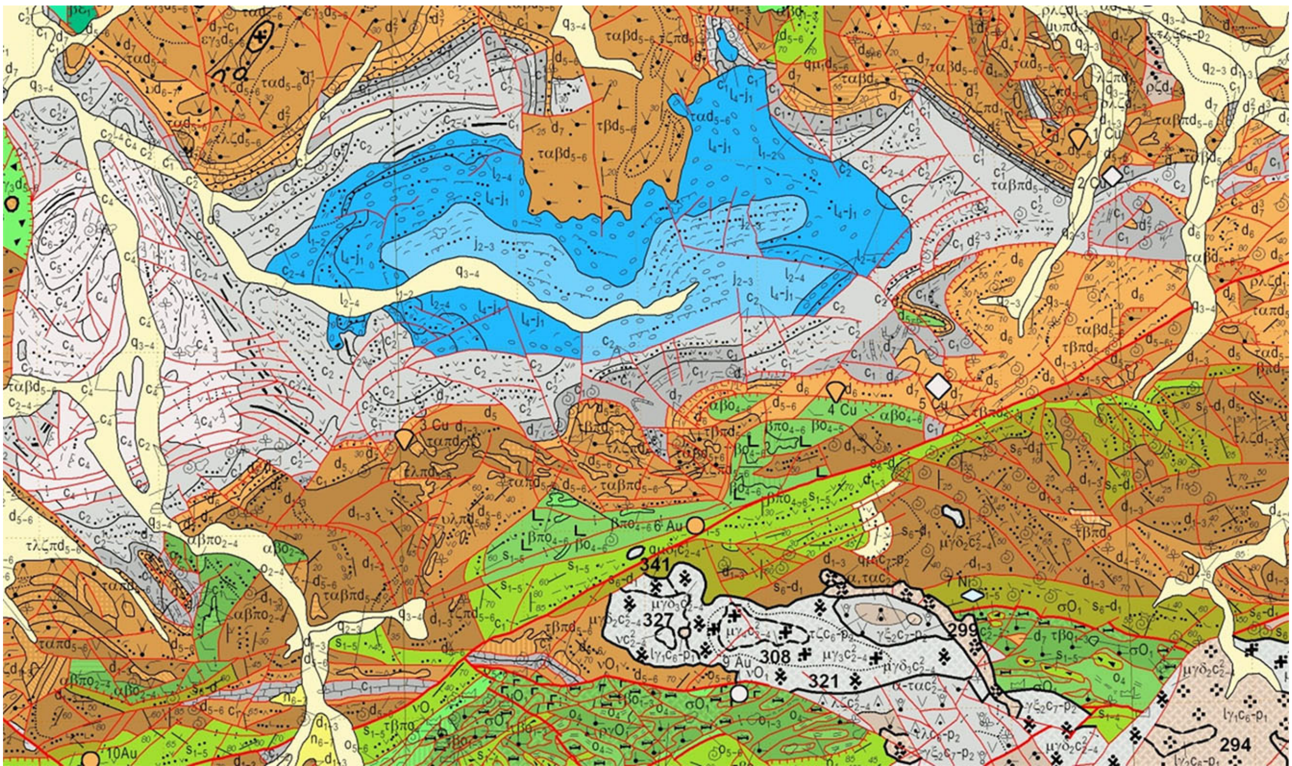

Figure 1 – Karaganda coal basin area. Fragment of the map of sheet M-43-B (Serykh, Gluhan, 2007)

interlayers and their contacts from the three mines mentioned above were studied.

According to the results of analysis by ICP-MS method, the average concentrations of impurity elements in samples taken at three KUB mines (Figure 2) have mainly near-clark values, only some elements (Li, Ba, Sc, Zr, V, Cu, Se, Y, Ag) in coals have average content above the clark one for layer k_7.

The lateral variability of impurity elements within the coal basin was assessed for layer k_7, which is accessible for sampling in many areas over 6 km. The average content of impurity elements in the coals, clay interlayers and at C-CI contacts of the three mines are given in Table. Assessment of the lateral variability of element concentrations reveals the influence of rocks of the demolition area, subsynchronous volcanism, or hypergenic oxidation on certain areas of the basin [6].

The degree of enrichment of coal with a particular element can be determined by calculating the ratio of the concentration of an element in coal to its average concentration in the Earth's crust. This ratio is defined as the enrichment factor, where the «Clark number» is a measure of the average concentration of an element in the Earth's crust. An enrichment factor of less than one (< 1) indicates depletion, and more than one (> 1) indicates that the coal is enriched in trace elements compared to its content in the earth's crust. It is quite clear that Ba, Zr, Li, Sc, V, Cu, Se, Y, Ag are markedly enriched, while a number of the following elements are conversely «depleted»: U, Th, Sn, Sb, Cs, Cd, Nb, Mo (Table).

According to the data obtained, the content of impurity elements in the clay interlayers of the three mines is characterized by an almost uniform distribution within the studied layer. However, there are also some exceedances of the clark concentrations of Li, Be, Ga, Se, Ag, Ba, Bi, Th along the lateral (Figure 3). Increased contents of Be, Ga, Bi, Th in clay interlayers is present in contrast to the contents of the same elements in the coals. Based on Figure 3, the As content at the Aktasskaya and Saranskaya mines is higher than at the Kuzembayev mine.

The increased content of many trace elements in coal can be explained by geological and geochemical processes during its formation, as well as by various epigenetic processes [1]. Analysis of the distribution of impurity elements in the formation section showed that the composition of rocks in the drift area probably plays a significant role in the accumulation of their high concentrations. Possible sources of removal of material could be granitoids of Permian-Carboniferous and Carboniferous age, as well as weathering crusts developed on them. Perhaps these weathering crusts could be a source of accumulation of Li, Ba, Sc, Zr, V, Cu, Se, Y, Ag in coals. They could be the most likely main source of barium and zirconium in the coals of the deposit. These interlayers play an important role in the accumulation of anomalous concentrations of rare impurity elements in coals.

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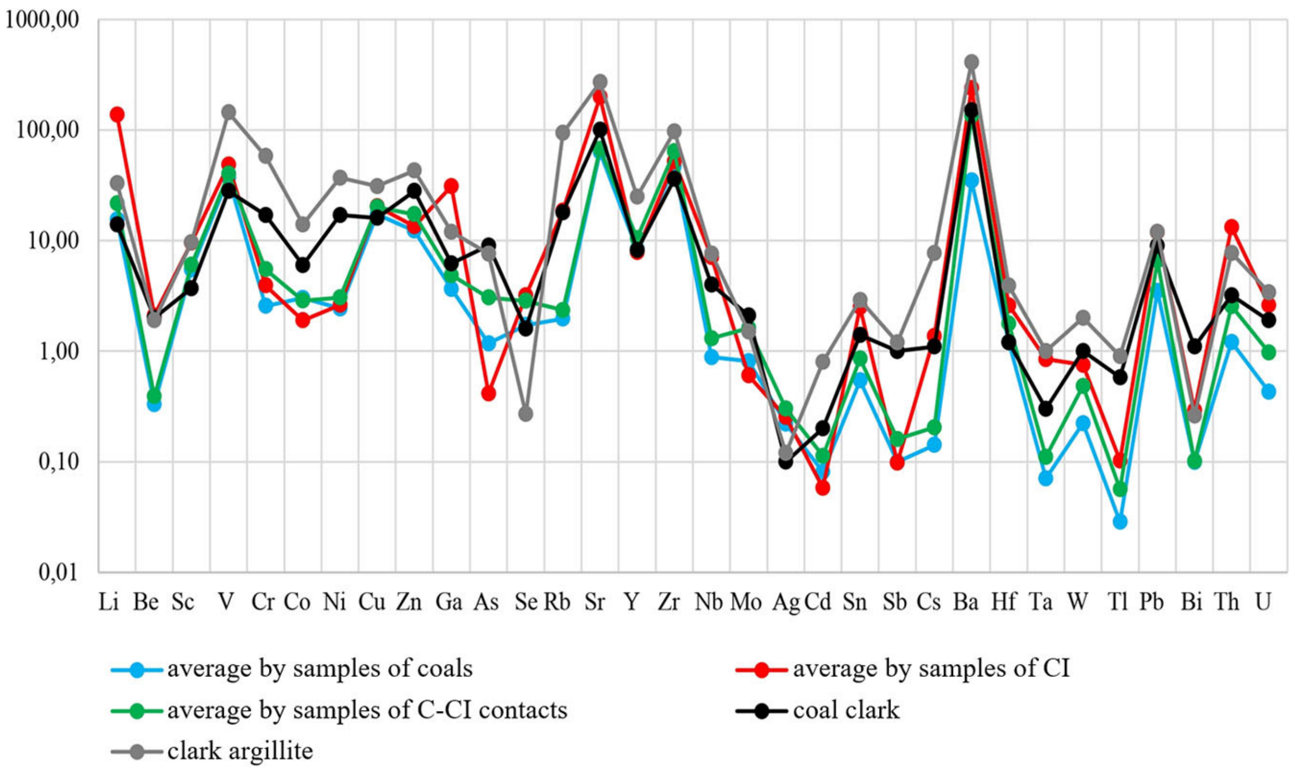

Figure 2 – Graph of the logarithmic distribution of impurity elements in coals, CI, C-CI contacts of formation k_7

Average contents of impurity elements in the coal clay interlayers and at C-CI contacts of formation k_7					
Elements	**Coal Clark**	**Clark argillite**	**Average by samples of coals**	**Average for CI samples**	**Average by samples of C-CI contacts**
Li	14,00	33,00	**15,44**	**137,64**	21,72
Be	2,00	1,90	0,33	**2,10**	0,39
Sc	3,70	9,60	**5,48**	9,57	6,02
V	28,00	144,00	**36,98**	48,54	40,11
Cr	17,00	58,00	2,57	3,92	5,50
Co	6,00	14,00	3,02	1,90	2,87
Ni	17,00	37,00	2,43	2,62	3,05
Cu	16,00	31,00	**17,22**	20,39	20,03
Zn	28,00	43,00	12,30	13,46	17,27
Ga	6,20	12,00	3,65	**31,07**	4,87
As	9,00	7,60	1,18	0,41	3,06
Se	1,60	0,27	**1,72**	**3,19**	2,85
Rb	18,00	94,00	1,96	18,65	2,35
Sr	100,00	270,00	63,20	198,64	67,41
Y	8,20	25,00	**8,37**	7,87	10,49
Zr	36,00	97,00	**46,64**	52,06	63,99
Nb	4,00	7,60	0,88	7,08	1,30
Mo	2,10	1,50	0,81	0,60	1,62
Ag	0,10	0,12	**0,22**	**0,25**	**0,30**
Cd	0,20	0,80	0,08	0,06	0,11
Sn	1,40	2,90	0,54	2,49	0,86
Sb	1,00	1,20	0,10	0,10	0,16
Cs	1,10	7,70	0,14	1,37	0,20
Ba	1,10	7,7	**34,87**	**239,05**	**134,08**
Hf	1,20	3,90	1,20	2,59	1,77
Ta	0,30	1,00	0,07	0,85	0,11
W	1,00	2,00	0,22	0,75	0,48
Tl	0,58	0,90	0,03	0,10	0,06
Pb	9,00	12,00	3,48	11,87	6,58
Bi	1,10	0,26	0,10	**0,29**	0,10
Th	3,20	7,70	1,21	**13,22**	2,55
U	1,90	3,40	0,43	2,61	0,97

ably plays a significant role in the accumulation of their high concentrations. Possible sources of removal of material could be granitoids of Permian-Carboniferous and Carboniferous age, as well as weathering crusts developed on them. Perhaps these weathering crusts could be a source of accumulation of Li, Ba, Sc, Zr, V, Cu, Se, Y, Ag in coals. They could be the most likely main source of barium and zirconium in the coals of the deposit. These interlayers play an important role in the accumulation of anomalous concentrations of rare impurity elements in coals.

Conclusion. This work presents the latest geochemical data of the coal and clay interlayers of layer k_7. Studies have shown that the coals of the deposit contain significant concentrations of Li, Ba, Sc, Zn, V, Cu, Se, Y, Ag. The enrichment of coals of formation k_7 with a number of impurity elements, in which pyroclastic material as a source of these elements plays an important role, was revealed. Clay formations of formation k_7 in the Karaganda coal basin have distinctive geochemical features that allow us to consider them as transformed potentially volcanogenic pyroclastics. The question of finding the source of volcanogenic pyroclastics, from which the clay formations were formed, remains relevant. To solve it, it is necessary to investigate the mineral and petrographic

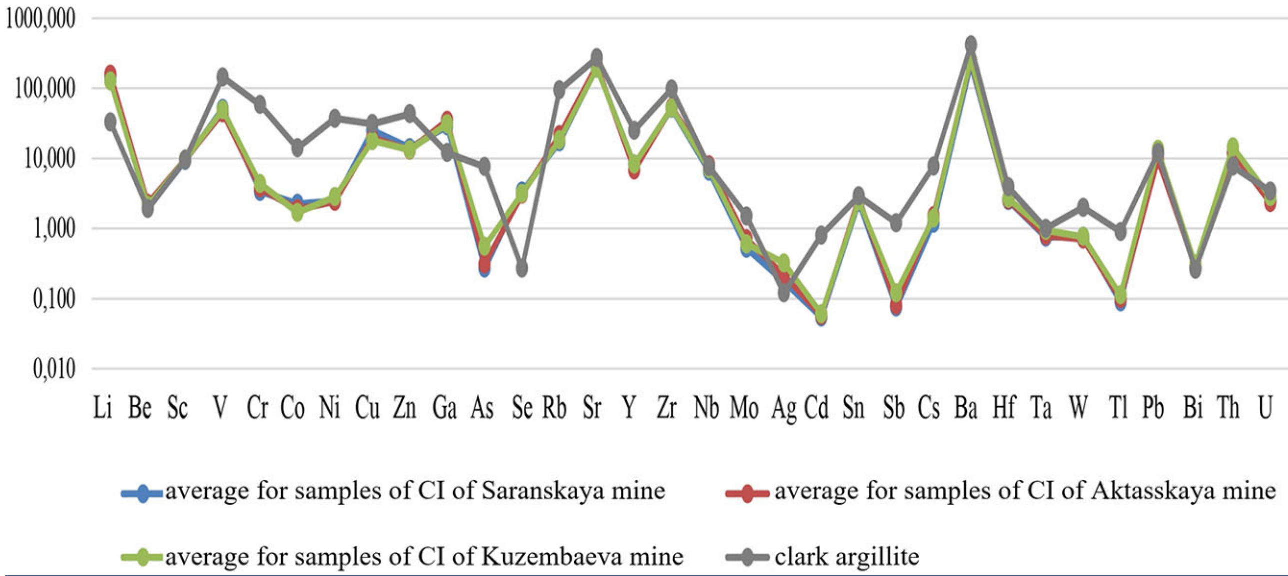

Figure 3 – Distribution graph of impurity elements in clay interlayers of layer k_7 at Saranskaya, Aktasskaya, Kuzembaeva mines

compositions, to determine the distribution patterns along the section and laterally, which will give new results in establishing their origin and allow to trace the pattern in the dynamics of changes in the composition of pyroclastics. The studying of geochemical features of coals and the presence of chemical elements in the coals is necessary to assess the metallicity of coal deposits, the development of criteria for identifying metalliferous coals and techniques for the extraction of valuable elements. Concentrations of trace elements (As, Sb) in formation k_7 are relatively low, which is beneficial for coal processing and utilization. S concentrations are relatively high compared to average clark values.

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Қарағанды көмір бассейнінің көмірі мен сазды қабаттарындағы қоспа элементтерінің таралуын зерттеу

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Аңдатпа. *Көмірдегі микроэлементтердің таралуын зерттеу көмірді пайдаланудағы денсаулыққа зияны мен онымен байланысты экологиялық мәселелерге байланысты ғана емес, сонымен қатар оның құрамындағы экономикалық құнды элементтерге де байланыстылығы бүкіл әлемде үлкен ғылыми қызығушылық тудырады. Қарағанды көмір кен орнының көмірі мен сазды қабаттарындағы қоспа элементтерінің таралуы қарастырылды. Қарағанды көмір бассейнінің көмір қабаттарының және саз қабаттарының элементтер қоспалардың геохимиялық ерекшеліктерін анықтауы осы жұмыстың негізгі міндеті болып табылады. Жұмыста көмірлер мен саз қабаттарының құрамы туралы соңғы мәліметтер келтірілген. Үш шахтадан – Саран, Ақтас, Күзембаевтан көмір және көмір саз қабаттары және олардың шекараларынан 85 сынама талданды. Сынамалар Ресей Ғылым академиясының Қиыр Шығыс бөлімінің Қиыр Шығыс геологиялық институтында ICP-MS әдісімен зерттелінді.*

Кілт сөздер: *сазды зат, көмір, қоспа элементтері, Орталық Қазақстан, геохимия, саз қабаттары.*

Изучение распределения элементов-примесей в углях и глинистых прослоях Карагандинского угольного бассейна

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Аннотация. *Изучение распределения микроэлементов в углях вызвало большой научный интерес во всем мире не только из-за вреда для здоровья и связанных с этим экологических проблем при использовании угля, но и из-за содержащихся в нем экономически ценных элементов. Рассмотрено распределение элементов-примесей в углях и глинистых прослоях Карагандинского угольного бассейна. Основной задачей данной работы является выявление геохимических особенностей элементов-примесей в углях, глинистых прослоях пласта к7 Карагандинского угольного бассейна. В работе представлены новейшие данные по составу углей и глинистых прослоев. Проанализировано 85 проб угля глинистых прослоев и контакта уголь-глинистые прослои из трех шахт – Саранская, Актасская, Кузембаева. Пробы изучались методом ICP-MS в Дальневосточном геологическом институте Дальневосточного отделения Российской академии наук (ДВГИ ДВО РАН).*

Ключевые слова: *глинистое вещество, уголь, элементы-примеси, Центральный Казахстан, геохимия, глинистые прослои.*

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