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Research Article

GEOCHEMICAL SPECIALIZATION ON RARE-EARTH ELEMENTS OF MESOZOIC AND CENOZOIC SEDIMENTS OF KULJUKTAU-AUMINZATAU REGION OF CENTRAL KYZYLKUM

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ABSTRACT
The results of field study and laboratory-analytical studies on Meso-Cenozoic sediments of Kuldjuktau-Auminzatau region are summarized in this article. The distribution of rare-earth and other chemical elements in the Jurassic, Cretaceous, Paleogene, Neogene and Quaternary sediments of the region was studied in detail. It was established that the largest concentrations of rare-earth elements are associated with Formation, the sediments of which were formed under certain geological conditions.

Keywords: *Rare-Earth Elements, Meso-Cenozoic Sediments*

INTRODUCTION
Rare-earth elements are widely used in various fields: nuclear power engineering, radio electronics, aviation and rocket engineering, machine and instrument engineering, chemical industry, etc. The leading countries having explored reserves of rare earth elements are: China, USA, Southeast Asian countries, Russia and others. In the countries of the Central Asian region (i.e., Kazakhstan) in recent years, there have been accelerated trend of exploration of the mineral-raw-material base of rare-earth elements (Kembayev, 2015).
Recently, due to strong need for raw materials, both endogenous, exogenous and metamorphogenic sources of rare-earth elements are of utmost importance.
In Uzbekistan, the geologists of the State Enterprise «Institute of Mineral Resources» study rare earth mineralization associated with the Mesozoic sediments of the Central Kyzylkum (Krikunova *et al.,* 2016), who noted that the Lower Cretaceous sediments of the southern frame of the Kuljuktau ridge in the Shuruk, Ayak-Gujumli, Jamanyar areas are characterized by higher concentrations of La, Ce, Nd, Y, and other chemical elements.

MATERIALS AND METHODS
To identify the stratigraphic levels of concentration of these rare elements by the geologists of the Stratigraphic Group of the State Enterprise under the "Regional Geological Survey Expedition" (State Committee on Geology, Uzbekistan) exploration was carried out in the Jurassic, Cretaceous, Paleogene, Neogene and Lower Quaternary sediments in the foothills of the eastern Auminzatau (Sarbatir site), southern Kuldjuktau (Jamanyarsai, Ayak-Gujumli, Shuruk, Tashkuduk), in Okuzkak (Shontybai, Uchyuzkak , Chevremboy, Ayukazgan), in Karakata (Balakarak, Karakata) and in Agitma (Yuzbol well) flexures. The stratigraphic sequence of the distinguished Formations and sub-Formations was established, their comparison with the units of the International Stratigraphic Scale was made. Various lithological varieties of rocks (clays, marls, siltstones, sand, sandstones, ferruginous-concretions) of the separated subdivisions were tested by the authors and analyzed 61 chemical elements using the ICP-MS analysis at the State Central Laboratory.

RESULTS AND DISCUSSION
The results of the investigations made it possible to reveal geochemical specialization for rare-earth and other elements of a series of Formations formed in different physical and topographical conditions.

Jurassic sediments in the region are distinguished in the Kuduk-Sarbatir Formation, composed of variegated gravels, sandstones, clays with interlayers of black coal formed in the lake-marsh conditions. It contains large-sized plant residues, typical for the Middle and Upper Jurassic. The thickness is 70 m. In the rocks of the Formation, there is an increased content of some rare-earth elements from heavy lanthanide series of the dysprosium and ytterbium sub-groups (Table No. 1).

Cretaceous sediments are represented by the lower and upper series. In the lower series there are Tuzkoy, Kalaatin, Jamanjary, Uzunkuduk, Shuruk Formations; in the upper - Donguztau, Djerantuy, Kendyktube, Kynyr and Karakatina Formations.

The Tuzkoi Formation is represented by heterogeneous grained sandstones and gravel-stone formed in shallow coastal waters, inhabited by numerous bivalve and gastropod mollusks of the Middle and Late *Apta Exogyra ex gr. falco Coq., Paraglauconia dimorpha Djal*. The thickness is up to 6m.

The Kalaatin Formation is composed of dark gray, almost black clays enriched with fine charred vegetable detritus with interlayers of siltstones, sandstones, coals and ferruginous-concretions with bivalves and ammonites. The thickness ranges from 5 to 60m. The rocks are characterized by foraminiferas: *Trochammina tutakensis Suleym., Verneuilina vinokurovae Zhuk; bivalve mollusks: Grammotodon carinatus Sow., Linotrigonia gissarensis Vinok; ammonites: Hypacanthoplites ex gr. jacobi Col.,* characteristic of the late Aptian. The Formation was formed in shallow coastal waters. The rocks contain rare-earth elements with a high content of the Ytterbium subgroup (Yb) (Table No. 1).

The Jamanyar Formation consists of clays of aleurite, dark- and greenish-gray, interlayers of siltstones and sandstones, containing in the base small ferruginous concretions and rounded cores of bivalves and ammonites. The thickness ranges from 17 to 90m. The Formation was formed in the marine basin on coastal shallow water and faunistically characterized by foraminifers: *Gaudryinopsis gissarensis Zhuk., G. oblongus Zasp. and plant residues: Tempskya jatsenko-khymelevskii Shilk.et Chudajb., Cycadocorticites sp., Piceoxylon aff. benstedii (Stopes) et Krausel.,* known from early and middle Albian. In the rocks of the Formation, there is an increased content of heavy lanthanide series of the dysprosium and ytterbium sub-groups (Table No. 1).

The Uzunkuduk Formation is represented by clays of aleurite, gray, greenish-gray, motley-colored, gray siltstones with layers of concretions of ferruginous sandstones, gravelstone and conglomerates. Throughout the section of the Formation in the clays there are numerous, mainly elongated, concretions ranging in size from 0.5 to 7 cm with Fe_2O_3-73.46% content and numerous black fragments of ferruginous sandstones with Fe_2O_3-73.35-81.61%. The thickness is 4-46 m. The Formation was formed on the low plain, the coastal-marine periodically flooded by the sea. In clays, there are many silicified and ferruginated shells of foraminifera: *Ammobaculoides ex gr. subcretaceus Cushm. et Aleks., Am. aff. explanatus Mam.,* typical of the late Albian. The rocks of the Formation are characterized by a high content of ytterbium (Yb) (Table No. 1).

Shuruk Formation is composed of siltstones, clays, gray to greenish-gray sandstones, gravel, dark brown, ferruginous (Fe_2O_3-32-58%.). The thickness is 6-35 m. The formation was sedimented on the lowland, coastal-marine, periodically flooded by the sea. The rocks of the Formation contain numerous cores of gastropods: *Nerineoptyxis amudariensis Pcel., Bivalve molluscs: Lima paralella Sow., Liostrea pseudodelletrei I.Abd.,* and others; clay layers - silicified and ferruginized small foraminifera shells: *Haplophragmoides umbilicatulus Dain., Trochammina aff. planoconvexa Mam., Gumbelitria sp., Hedbergella sp.,* known from the late Albian. The rocks of the Formation are characterized by a high content of ytterbium (Yb) (Table No. 1).

The Donguztau Formation is represented by sandstones of fine-grained, brick-red, gray; clays aleurite, siltstones clayey, gray, greenish-gray, bluish - and light gray; in the base - sandstones, gravelstones, conglomerates gray. Thickness is up to 144m. Sediments are typical of coastal shallow water, the shelf of the interior. The Formation is characterized by foraminiferas: *Haplophragmoides sibiricus Zasp., Gaudryinopsis asiaticus (N.Byk.), Paragaudryina inornata Suleym.;* bivalve molluscs: *Lopha dichotoma*

Bayle, Exogyra trigeri Coq., Chlamys elongatus Orb., Amphidonte lubrica Vinok., Korobkovitrigonia ferganensis (Arkh.), common in the lower and middle Cenomanian.

The Uchkuduk Formation is composed of the lower part of the sandstones by fine-grained, greenish-gray, brown; different size of grains, gray gravelites; in the upper - clays aleuritic, greenish-gray, sandstones fine-grained, gray, greenish-gray with interlayers of gravel. The thickness is 10-34 m. The Formation was formed on the lowland, coastal-marine, periodically flooded by the sea. The rocks contain foraminifera: *Haplophragmoides semiinvolutus Zasp .; Gaudryinopsis asiaticus (N.Byk.), Paragaudryina inornata Suleym .;* bivalve mollusks: *Korobkovitrigonia darwaseana (Rom.),* characteristic of the late Cenomanian. In the sandy rocks of the Formation, an increased content of ytterbium (Yb) is observed (Table No. 1).

The Jeirantuy Formation is represented by clays of aleuritic, greenish-gray with interlayers of yellowish, greenish-gray siltstones, gray and pink sandstones. The thickness is 40-101 m. Sediments are typical of coastal shallow water, the shelf of the interior. The Formation contains foraminifers: *Haplophragmoides turonicus (Zhuk.), Reophax kysylcumensis Suleym., Gaudryinopsis akrabatensis Zhuk.,* Bivalve mollusks: *Inoceramus labiatus Schloth.,* establishing the Inoceramus labiatus zone of the lower Turonian. The clay interlayers of the Formation are characterized by a rich ytterbium content (Yb) (Table No. 1).

The Kendyktjuba Formation consists of sands, fine-grained quartz-mica sandstones, yellowish-green, brick-red, with charred vegetable detritus; clays aleuritic, variegated, greenish-gray with interlayers of clayey, yellow siltstones. The thickness is 14-63 m. Svita in the foothills of Auminzatau was formed on the lowland, coastal sea, periodically flooded by the sea, in Kuldzhukau - on the shallow coastal waters. The Middle-Uron age is based on foraminifera *Gaudryinopsis asiaticus (N.Byk.), Paragaudryina inornata media Suleym., P. inornata inornata Suleym .; bivalve Liostrea jaxartensis (Sim.) Zapr., Megatrigonia khoresmensis Beljak.,; gastropods Caucasella cf. acanthophora (Muller).* The sandy-argillaceous rocks of the Formation are characterized by a rich ytterbium content (Yb) (Table No. 1).

Kynyr Formation is composed of sands, sandstones, ochroid siltstones, red, yellowish-green, with thin interlayers of clays and conglomerates of strongly ferruginous, formed in the plain of low-lying coastal-marine, periodically flooded by the sea. The thickness is up to 20m. The sediments are characterized by bivalve mollusks, foraminifera and vertebrate remnants, typical of the late Turonian-Santonian. The rocks of the Formation are characterized by a high content of ytterbium (Yb) (Table No. 1).

The Karakata Formation is composed of sandstones, gray-grained, light-gray, greenish-yellow, yellowish-brown with ferruginous concretions, with interbeds of gray clays and light gray sandstone limestones, fine fine-grained phosphorite pebbles and shark teeth are found in sandstones. Thickness 8-98m. In rocks of the foraminifera series: *Trochammina ex gr. senonica Belous., T. aff. uzbekistanensis Zhuk., Ammoglobigerina ex gr. tenuisa (Belous.); bivalve mollusks: Chlamys dujardini Roem., Liostrea lehmannii Rom., Liostrea acutirostris Nilsson, Amphidonta pyrenaica (Leym),* the core of the rudist, typical of the Campanian and Maastrichtian sediments. The Formation was sedimented in the marine basin on the coastal shallow water. The rocks are characterized by a high content of ytterbium (Yb) (Table No. 1).

Paleogene sediments are represented by terrigenous-carbonate rocks (clays, sands, sandstones, limestones, shellrock) formed in coastal shallow waters. In them, according to faunal remains, foraminifera, bivalves and gastropods, Paleocene, Eocene, and Oligocene formations have been identified. We have taken samples of the Middle Eocene rocks in the volume of the Kulttaban and lower Oligocene parts of the Sarbatyr Formation for mass spectrometric analysis.

The Kultaban Formation is composed of clay light gray, green, horizontally layered with sand nests, siltstones greenish-gray, sandy, with thin interlayers of sandstones and bentonite clays. The thickness is up to 50 m. The Formation is characterized by foraminifera: *Globogerina turkmenica Chal., Haplophragmoides orfaensis Rod., etc.,* of Bartonian age. The rocks of the Formation are characterized by an high content of thulium and ytterbium (Yb) (Table No. 1).

The Sarbatir Formation refers to the Upper Paleogene-Lower Neogene. According to its lithological features, it is divided into two parts: the lower Oligocene - clayey with rare interbeds of sandstones and the sandy Upper Early Miocene.

The lower parts of the Oligocene part of the Formation are composed of red-motley clays with a lithological benchmark (two closely spaced layers of red-colored ferruginous clays), those age is characterized by foraminifers *Hyperammina caucasica Bogd., Haplophragmoides stavropolensis Ter-Grig., Cyclammina constrictimargo R. Stew. et K. Stew., Cibicidoides tschagalaensis (Korov).*, as an early Oligocene, ryupel.

Clay rose pink with interbeds of yellow sands and sandstones and siltstones pink, gray with a pinkish tinge with rare shells, the foraminifera *californica uruchensis Bogd, Quinquiloculina akneriana rotunda (Orb.),* characterizing this part of the Formation as a late Oligocene.

The upper part of the Sarbatyr Formation is composed of sands and sandstones gray with interbeds of siltstones and brown clays, at the base with shells. In the roof of the Miocene part of the Formation there is a paleontological benchmark with balanomorphs, characterized by foraminifers. *Cibicidoides stavropolensis (Bogd.), Porosononion dendriticus (Chal.), And ostracods. Cytheridea pernota Oertli et Keij., Carinovalva mediocrisa (Roz.),* characterizing the age of this part of the Formation as the early Miocene (Aquitaine-Burdigalian age).

The Sarbatir Formation was sedimented on the shallow coastal waters at a salinity of 30.5-34 ‰ and a depth of 200 m; In the Hutt time the salinity changed periodically. In the early Miocene time, it was a marine littoral with a muddy bottom with a slight salinity.

In the Upper Oligocene (Hutt) sandstones and sands, less often in sandstone siltstones and clays, a high ytterbium content of up to 3.25 ppm is noted, as well as contained gold and silver.

Neogene sediments. The Agitmina Formation is composed of siltstones, clay brick red, brown, light brown, often brown with a cherry or pink hue, sometimes with a layer of light gray clays, with subordinate sands and sandstones. Clays and siltstones are massive, not laminated with a large-spheroidal texture. The rocks contained sometimes epigenetic gypsum, but mostly syngenetic gypsum of few thickness. The thickness is 50-115m. The rocks contain foraminifera *Quinqueloculina akneriana (Orb.), Ostracods Eusypris aggeratus Gr., Mediocypris ordinata Schn., Hemicyprideis villandrautensis (Moyes), and Harnichara sarmatica Masl. Char. Algae* characteristic of the Early Middle Miocene (Burdigalian - Seravil age). The Formation lies with erosion on the Sarbatyr Formation or its base is not exposed.

The Agitmina Formation was deposited in the shallow coastal waters of the eastern margin of the vast East Paratethys with salinity over 17 ‰ and due to its existence, its transgressions and apparently, the slow descent of the Turan plate, its upper part - in the shallow coastal waters of the more desalinated basin.

In the Agitmina Formation, there is an rich content of gold, silver, selenium, tantalum (9.29 ppm), as well as rare-earth elements of the cerium group (La-Ce-Yb)

Quaternary sediments. The Tashakyr Formation is represented by light gray sands, sandstones and marly clays with a conglomerate-breccia horizon at the base with pebbles to boulder with a "cerebral" texture of cracking or round spherical. The thickness is 2-47 m. The rocks contain *ostracods Bacunella dorcoarcunata (Zalanyi), Paracyprideis naphtatscholana (Liv.), Characteristic of the late Eopleistocene*. Precipitation of the Formation formed on the shallow coastal waters of the eastern margin of the decaying Apsheron basin.

In the rocks of the Formation, an increased content of ytterbium (up to 1.18 ppm) and gold (up to 0.28 ppm) is noted.

Most of the samples taken from the Mesozoic and Cenozoic sediments are characterized by high ytterbium concentrations (from 1.0 to 10.0 ppm), half of which are subabnormal in character, exceeding the Clark value by more than 5 times.

As a result, high concentrations of chemical elements of the rare-earth group in the Mesozoic (Jurassic-Cretaceous) and Cenozoic (Paleogene-Neogene-Quaternary) sediments were found: La (up to 50.6 ppm),

Table No.1: The mean contents of rare-earth elements in the Mesozoic-Cenozoic Kuldjuktau-Auminzatau sediments by mass spectrometric analysis (ICP-MS)

№	Formation	number of samples	Some rare-earth elements													
			cerium group (light lanthanides)							yttrium group (heavy lanthanides)						
			lanthanum subgroup			neodymium subgroup				dysprosium subgroup			ytterbium subgroup			
			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
			Clark of chemical elements													
			29	70	9	37	8	1.3	8	4.3	5	1.7	3.3	0.3	0.3	0.8
			The average content of chemical elements by mass-spectrometric analysis (ICP-MS), ppm													
1	Tashakyr – $Q_{E_{II}}$ tš	15	12.4	20.1	2.8	10.5	2.1	0.4	2.0	0.3	1.5	0.3	0.8	0.1	0.7	0.1
2	Agitmin - Ni^{1-2} *ag*	4	30.9	132.4	6.8	26.0	5.0	1.4	4.6	0.6	3.6	0.9	2.0	0.3	1.9	0.3
3	Sarbatyr Formation – P_3 – N_1^1	44	21.1	42.9	4.9	19	3.7	0.9	3.5	0.5	3	0.5	1.5	0.2	1.5	0.2
4	Kultaba – P_2^2b *klt*	3	23.1	45.1	5.7	22.0	4.6	1.1	4.7	0.7	4.5	0.9	2.5	0.4	2.5	0.4
5	Karakata K_2km-m *kr*	9	11.6	24.8	2.9	11.6	2.3		2.3	0.3	2.2	0.4	1.1	0.2	1.1	0.2
6	Kynyr - K_2t_3-st *κn*	18	12.9	24.3	3.3	12.7	2.6		2.4	0.4	2.3	0.5	1.3	0.2	1.3	0.2
7	Kendyktuba - K_2t_2 *κn*	4	15.4	34.5	3.9	16.2	3.5		3.3	0.5	3.2	0.6	1.8	0.3	1.9	0.3
8	Jeyrantuy - K_2t_1 *dž*	12	19.5	44.0	6.2	24.1	5.4	1.3	5.1	0.7	4.6	0.8	2.2	0.3	2.1	0.3
9	Uchkuduk - K_2S_3 *uc*	2	15.3	27.9	3.1	12.6	2.3		1.9	0.3	1.7	0.3	1.0	0.2	1.2	0.2
10	Shuruk – K_1al_3 *šr*	24	21.1	38.7	5.2	20.0	4.2	0.9	3.9	0.6	3.5	0.7	1.9	0.3	1.8	0.3
11	Uzunkuduk - K_1al_3 *uz*	17	23.0	49.6	5.6	21.1	4.3	1.0	4.0	0.6	3.6	0.7	1.9	0.3	1.7	0.2
12	Jamanyar - K_1al_3 *dž*	4	26.3	54.5	7.3	28.9	6.4	1.3	6.5	1.0	6.5	1.3	3.8	0.6	3.9	0.6
13	Kalaata – K_1a_3 *kl*	14	17.0	36.8	4.1	15.3	3.2	0.7	3.0	0.4	2.7	0.5	1.4	0.2	1.5	0.2
14	Kuduk-Sarbatir - J_{2-3} *ks*	2	22.0	50.5	6.3	27.0	6.5		7.0	1.0	6.0	1.1	3.3	0.5	3.0	0.4

Ce (up to 364.7 ppm (up to 29.9 ppm), Nd (up to 110.0 ppm), Sm (up to 27.9 ppm), Eu (up to 3.17 ppm), Gd (28.4 ppm), Dy (24,0 ppm), But (3,69 ppm), Er (up to 10,0 ppm), Yb (up to 10 ppm) and Y (up to 110 ppm)).

There is a definite regularity associated with an increase in the average content of ytterbium from the young Quaternary sediments of the Tashakyr Formation to the older Jurassic sediments of the Kuduk-Sarbatyr Formation. In addition, an increase in the average contents of the elements of the cerium group (La, Ce) in the sediments of the Agitmina Formation, and of the yttrium group (Dy, Er, Tm, Yb) in the sediments of the Kuduk-Sarbatyrian Jamanyar Formation and (Table No. 1). Among the remaining elements, practically all the Formations, are to some extent characterized by the high Clark value concentrations of Sb, Bi, As, Mo, Ag, Te, Se, less often Sn, Cu.

In a number of samples taken from the sediments of the Tashakyr and Agitmina Formations in the eastern Auminzatau (the area of the Sarbatyr), in the Okuzkaksky (Chevrebai tract), the Karakata and Agitmin troughs, there are increased gold concentrations reaching 1.23 ppm.

Correlation analysis, among the rare-earth elements, such as La, Nd, Sm, Eu, Gd, Tb, Dy, Go, Er, Yb, Lu, Y, have established the most stable bonds. The same elements are combined into a group by factor analysis, which is also confirmed by their stable correlation relations between themselves. Among the remaining elements, positive correlation is established in pairs of the following chemical elements: Bi-Sn, Cu-Sb, Cu-Mo. Gold does not form significant correlations with any element.

Proceeding from the foregoing, it follows that the Mesozoic and Cenozoic sediments of the Kuldjuktau-Auminzatau region, at the sampling sites, have specialization for rare-earth elements, as well as increased concentrations of Sb, Bi, As, Mo, Ag, Te, Se, less often Sn, Cu and Au. The most intensively rare-earth mineralization is manifested in Okuzkak (Shontybai, Uchuekak) and Karakata (Balakarak) troughs, southern foothills of Kuljuktau (Ayak-Gujumli, Shuruk) and eastern ones - Auminzatau (Sarbatir area).

CONCLUSION

The results of the analysis show that the highest concentration of rare-earth elements in the Jurassic sediments is associated with rocks of the Kuduk-Sarbatyr Formation formed in the lake-marsh conditions. In the Early Cretaceous, the most favorable for the enrichment of sediments by rare-earth elements was the coastal shallow water, where the terrigenous material was brought down from the land from the Paleozoic uplands (Kalaata, Jamanjar, Uzunkuduk Formations).

In the Cenozoic period, as in the Mesozoic period, the concentration of rare-earth elements occurred in shallow coastal waters.

Taking into account the fact that rare-earth elements belong to strategic types of mineral raw materials and are of great importance for the State economy, it is necessary to conduct additional, more detailed and purposeful geological studies on the above-named Formations, to identify areas of their greatest concentration, with the definition of the boundaries and scale of development of this mineralization in these areas and adjacent areas.

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