

Specific Features of the Geochemistry of Eocene–Miocene Rocks in the Perovskii Gulf, Northern Aral Region

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Abstract—The major and trace element distribution was studied in the Eocene–Miocene stratotype section of the northern Aral region, northern coast of the Perovskii Gulf. The geochemical specific of ore-bearing rocks is shown. Qualitative trends in the distribution of element in genetically diverse rocks are established.

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The geological structure of the northern Aral region has attracted the attention of researchers over more than half century (Vyalov, 1934; Yanshin, 1953; Formozova, 1959; Voznesenskii, 1978; Popov et al., 1993; Kholodov et al., 1995). Oligocene–Miocene rocks are most interesting, because they represent the facies transition zone from a typical continental setting in the eastern Turgai trough to marine sediments of the Ustyurt region. They contain specific oolitic iron ores formed in a continental setting. The main attention in previous works was given to the stratigraphy, lithology, mineralogy, facies affiliation, and paleogeography of rocks mentioned above, and genesis of iron ores. However, the geochemistry of rocks and ores was only briefly characterized. In this work, we report the distribution of major elements in the section of the northern Aral region and their associations with trace elements. The results obtained represent a new stage of our works devoted to the study of geochemical specifics of the formation of oolitic iron ores (Golubovskaya, 2001, 2003, 2005).

We studied Eocene–Miocene rocks on the northern coast of the Perovskii Gulf (northern Aral region), which are considered regional stratotype section (Ovechkin, 1962).

The base of the section consists of gray sandy jarosite clays with lenses of light gray glauconite–quartz sands of the Middle Eocene Saksaul Formation with the apparent thickness up to 15 m (Fig. 1).

They are conformably overlain by rocks of the Upper Eocene–Lower Oligocene Chegan Formation (Akhmet'ev and Zaporozhets, 1992). They are composed of gray jarosite–gypsum clays grading into sandy clays with marly nodules in the upper part. The nodules contain remains of marine fauna (Ovechkin, 1962). Clay minerals are represented by smectite (peaks at 11.8–11.9 Å in natural species, 17.8–18.0 Å in glycerin-saturated clays, and 9.83–9.94 Å at heating up to

550°C), kaolinite, and hydromica. The thickness of sequence is 60–70 m.

The Chegan clays are disconformably overlain by rocks of the Oligocene Turgai Group (Vyalov, 1934; Yanshin, 1953), which consists of diverse continental and coastal-marine rocks. The base of the Turgai Group is made up of the Lower Oligocene Kutambulak Formation. The main part of its section consists of fine-grained light gray (almost white) cross-bedded, occasionally horizontally bedded sands and silts with thin clay intercalations. The rocks fill ancient erosion depressions at the surface of the Chegan clays. The maximal thickness (up to 50 m) is observed in the western part of the gulf near the town of Kum-bulak. In the Ak-choko, Kara-sandyk, and Rudnyi Mys mountain area, the upper section of the Kutambulak Formation includes lenses of oolitic iron ores intercalated with ferruginous sandstones, clays, and siderite interbeds. Interore clays contain thin layers of travertine-type carbonate rocks. The ore thickness is maximal at the Karasandyk deposit near Mt. Rudnyi Mys, where the ore-bearing bed is up to 17.5 m thick with ores accounting for more than 14 m. The ore lens at this deposit has an asymmetric structure. In the western part, the ores overlie the eroded surface of sandy-clayey rocks. They grade westward into ferruginous sandstones and the clay beds become thicker. The transition zone contains abundant remains of coalified flora, marine and brackish-water mollusks typical of the Solenovian time, teeth of sharks and land mammals, and phosphoritic nodules up to 10 cm across. The eroded surface of ore lens is overlain by a 5-m-thick bed of conglomerate ores. In ore-barren sectors, the top of the Kutambulak Formation includes a horizon of ferruginous cross-bedded sandstones up to 30 cm thick. Clays of the barren part contain the following assemblage: finely dispersed smectite (peaks at 13.7 Å in the natural clay, 19.3 Å in the glycerin-saturated state, and 9.94 Å at heating up to

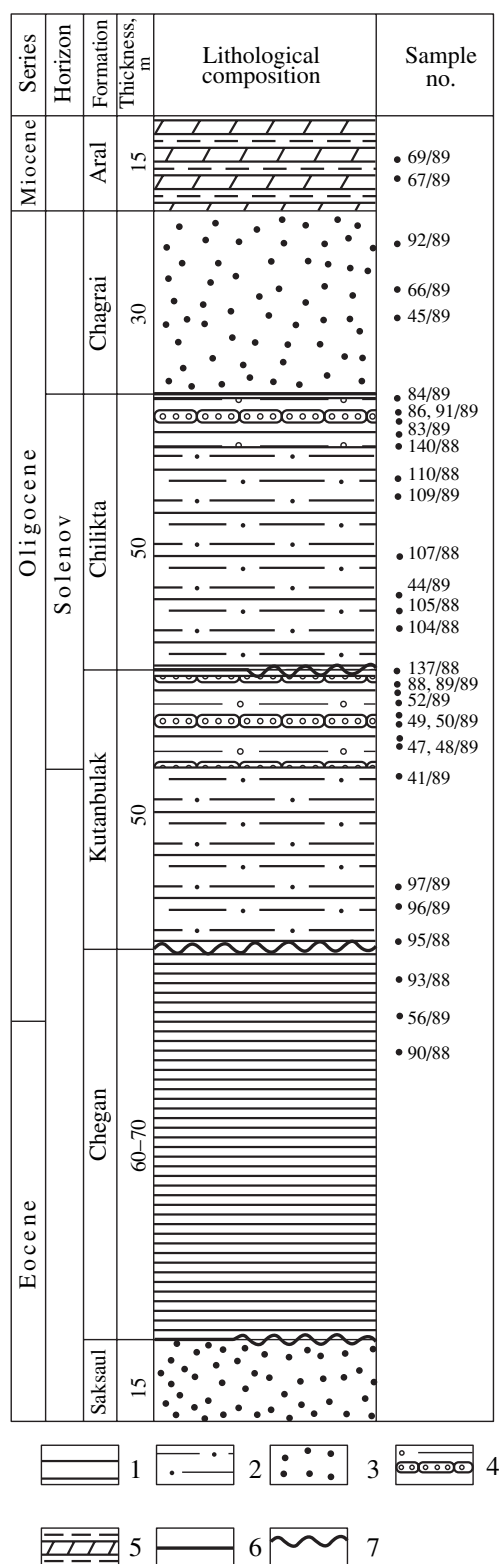


Fig. 1. Schematic section across Eocene–Miocene rocks on the northern coast of the Perovskii Gulf, northern Aral region. (1) Clay; (2) alternation of fine-grained sand, silt, and clay; (3) sand; (4) alternation of oolitic iron ore, ferruginous sandstone, sand, and clay; (5) alternation of limestone, marl, and carbonate clay; (6) sharp boundary; (7) erosion.

550°C), kaolinite, and hydromica. Interore clays are composed of a similar mineral assemblage: poorly crystallized Fe-smectite (peaks at 14.03 Å in the natural clay, 19.8 Å in the glycerin-saturated state, and 9.94 Å at 550°C heating). Judging from the attitude, composition, and structure of rocks of the Kutanbulak Formation at cliffs on the northern coast of the Perovskii Gulf, they were formed in lacustrine basins, whereas ore lens of the Kara-sandyk deposit was formed in a lagoon setting (Formozova, 1959).

The Kutanbulak section is overlain with insignificant erosion by Lower Oligocene rocks of the Chiliktka Formation (alternation of horizontal thin-bedded chocolate-lilac clays and silts with horizontal bedded, occasionally cross-bedded fine-grained sands and silts. In some places, individual beds 2–5 m thick are separated by interbeds of ferruginous sandstones, which often contain shells *Ergenika cimlanika* Zhizh, and shark teeth, while clays often contain coalified flora remains. The total thickness of the formation is as much as 50 m. In the Mt. Kara-sandyk area, the upper part of the Chiliktka Formation contains a bed of oolitic and conglomerate iron ores up to 5 m thick. On the eastern side, the top of this formation includes a horizon of ferruginous sandstones and low-grade oolitic iron ores with brackish-water mollusks. The clay mineral assemblage is as follows: smectite (peaks at 13.8–14.3 Å in the natural phases, 18.8–19.0 Å in the glycerin-saturated state, and 9.93–10.0 Å at heating up to 550°C), kaolinite, and hydromica with chlorite admixture.

Rocks of the Chiliktka Formation presumably formed in the lacustrine and swampy settings, but the presence of horizons with brackish-water fauna suggests a periodical link with the World Ocean (Formozova, 1959; Voznesenskii, 1978).

The Kutanbulak and Chiliktka formations are age analogues of the Ashcheiryk Formation, Solenov Horizon, and partially, Baigubek Formation of the Ustyurt region (Akhmet'ev and Zaporozhets, 1992). In the studied section, the oolitic iron ores are developed in the Solenov Horizon, at in the top of the Kutanbulak Formation, and in the upper part of the Chiliktka Formation. This distribution is also typical of other sections in the northern Aral region (Formozova, 1959; Akhmet'ev and Zaporozhets, 1992; Kochenov and Stolyarov, 1996).

The top of the Turgai Group is composed of Upper Oligocene rocks of the Chagrai Formation. They are represented by white fine-grained, more rarely medium- to coarse-grained mica-rich quartz sands (up to 30 m thick) deposited in a coastal brackish basin (Formozova, 1950). The clay fraction consists of smectite (peak at 13.94 Å in the natural phase, 18.5 Å in the glycerin-saturated variety, and 9.83 Å at heating up to 550°C), hydromica, and kaolinite with subordinate chlorite.

Table 1. Chemical composition (%) of oolitic ores and barren rocks

Ord. no.	Sample no.	Fe	Mn	Ti	P	CO ₂	C
1	90/88	6	0.04	0.6	0.06	0.85	0.47
2	56/89	5.2	0.05	0.71	0.11	0.5	–
3	93/88	4.09	0.12	0.6	0.07	–	–
4	95/88	14.44	0.05	n.a.	–	–	–
5	96/88	2.51	0.08	0.54	0.03	–	–
6	97/88	1.18	0.02	0.49	0.02	–	–
7	41/89	10.24	0.24	0.32	0.43	14.25	–
8	47/89	3.81	0.04	0.4	0.07	34.35	–
9	48/83	34.85	0.17	0.33	0.37	1.1	–
10	49/89	20.19	0.34	0.21	0.45	–	–
11	50/89	7.46	0.08	0.42	0.16	0.55	0.6
12	52/89	4.67	0.12	0.31	6	2.3	0.4
13	88/89	32.94	0.69	0.22	0.57	0.5	–
14	89/89	13.77	0.21	0.28	0.24	0.45	0.4
15	137/88	35.06	1.02	0.21	0.55	1.35	–
16	104/88	2.57	0.06	0.52	0.06	–	–
17	105/88	1.83	0.04	0.46	0.04	–	–
18	44/89	15.36	0.24	0.4	0.26	1.35	–
19	107/88	2.55	0.18	0.8	0.04	–	0.87
20	109/88	1.22	0.04	0.57	0.02	–	–
21	110/88	3.62	0.04	0.68	0.06	–	0.64
22	140/88	36.91	0.27	0.22	0.9	2.65	–
23	83/89	18.92	0.08	0.37	0.17	0.75	–
24	86/89	40.83	0.29	0.21	1	–	–
25	91/89	2.43	0.02	0.63	0.03	–	–
26	84/89	18.19	0.03	0.38	0.15	0.8	–
27	45/89	1.74	0.01	0.34	0.02	–	–
28	66/89	2.53	0.01	0.85	0.02	0.3	0.64
29	92/89	0.49	0.01	0.31	0.06	–	–
30	67/89	3.57	0.1	0.32	0.13	11.45	–
31	69/89	0.28	0.06	0.14	0.03	35.25	–

Note: (1–3) Chegan Formation; (4–15) Kutanbulak Formation; (16–26) Chilikta Formation; (27–29) Chagrai formation; (30, 31) Aral Formation; (1–3, 5, 11, 16, 19, 21, 25, 28, 30) clay and clayey silt; (6, 17, 20, 27, 29) sand; (4, 7, 10, 14, 18, 23, 26) iron sandstone and sandy iron ore; (9, 13, 15, 22, 24) iron ore; (8) travertine; (12) phosphorite; (31) limestone. (–) Below detection limit; (n.a.) not analyzed.

Table 2. Trace element contents (ppm) in ores and barren rocks

Ord. no.	Sample no.	Nb	Zr	Y	Rb	Sr	Ba
1	90/88	13	150	27	130	68	410
2	56/89	14	170	38	120	78	480
3	93/88	14	170	37	120	47	390
4	95/88	5.1	270	8.2	29	180	360
5	96/88	12	270	23	72	120	640
6	97/88	11	330	14	61	140	750
7	41/89	6	400	24	31	280	230
8	47/89	1.7	34	9.4	7	2250	70
9	48/89	3.5	81	57	25	68	590
10	49/89	3.6	61	25	8.5	46	100
11	50/89	9.4	190	23	47	94	430
12	52/89	6.8	170	27	31	1300	670
13	88/89	2.7	78	69	28	47	150
14	89/89	9.3	170	77	36	110	120
15	137/88	1.8	85	31	13	73	70
16	104/88	14	270	37	85	100	480
17	105/88	11	450	24	58	160	350
18	44/89	8.3	430	23	34	200	300
19	107/88	16	320	31	64	120	250
20	109/88	11	420	18	62	140	200
21	110/88	15	240	27	80	100	230
22	140/88	1.8	100	27	4.8	2350	90
23	83/89	6	250	12	34	67	280
24	86/89	–	51	43	–	4600	440
25	91/89	14	280	17	85	120	490
26	84/89	7.2	470	9.5	33	76	290
27	45/89	14	140	8.3	130	160	860
28	66/89	19	200	39	110	100	730
29	92/89	5.8	160	9.1	35	80	370
30	67/89	9	110	19	110	440	590
31	69/89	1.7	72	2.3	6.5	840	190

Note: See Table 1.

The Turgai Group is overlain with erosion by marine clayey–carbonate rocks of the Lower Miocene Aral Formation (green carbonate clays intercalated with marls and limestones). The apparent thickness of the formation exposed along the Perovskii Gulf is up to

15 m. The smectite-free clay mineral assemblage is composed of hydromica with admixture of kaolinite and chlorite.

The major terrigenous minerals of Upper Eocene–Miocene rocks are quartz and feldspars, including both

Table 3. Trace element distribution (ppm) in ores and barren rocks

Ord. no.	Sample no.	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Zn	Sn	Ag	B
1	90/88	185	67	440	30	24	23	21	1.2	–	110	4.7	–	100
2	56/89	155	60	395	20	22	15	26	1	1.8	110	4.5	0.13	85
3	93/88	190	75	425	20	35	11	24	1.4	2.5	120	4	0.09	80
4	95/88	75	16	70	15	17	15	5	1	–	70	6.5	–	15
5	96/88	170	55	200	25	27	20	18	1.2	–	70	3	0.09	54
6	97/88	85	23	55	15	12	18	8	–	0.8	–	2	0.1	38
7	41/89	72	18	138	10	10	10	5	1	–	–	4.5	0.1	23
8	47/89	20	22	23	5	11	5	–	1	–	n.a.	1	–	9
9	48/89	60	75	88	10	46	18	6	–	–	620	7.5	0.33	24
10	49/89	135	60	320	15	35	18	5	–	–	135	5.5	0.2	18
11	50/89	110	90	195	15	53	20	12	1	–	95	5	0.08	40
12	52/89	90	65	65	10	38	18	7	1	–	55	4	–	43
13	88/89	70	140	235	10	125	20	5	–	–	210	8.5	0.3	18
14	89/89	320	115	>1000	25	115	50	11	–	–	220	7.5	–	33
15	137/88	140	175	455	10	100	20	6	–	–	270	8	0.35	17
16	104/88	165	50	230	25	25	22	19	1.2	1.3	80	4.5	0.08	65
17	105/88	120	33	90	15	21	21	10	–	1	65	3	0.1	48
18	44/89	90	49	125	10	44	19	5	–	–	80	8.5	0.17	30
19	107/88	220	82	290	35	60	26	24	1.4	1.9	138	4	0.13	85
20	109/88	130	33	98	20	18	18	10	1	0.9	50	3	0.1	45
21	110/88	160	55	220	40	23	23	25	1.1	1.5	90	4.7	0.1	65
22	140/88	158	135	420	10	80	11	7	–	–	320	10	0.47	13
23	83/89	95	75	250	20	65	17	7	–	–	190	7	0.22	27
24	86/89	158	115	415	15	73	22	6	–	–	270	8	0.38	33
25	91/89	160	53	250	20	17	21	18	1.2	–	65	4	0.1	73
26	84/89	120	62	315	20	32	25	7	1	n.a.	165	7.5	0.25	27
27	45/89	63	22	45	15	8	20	16	1	0.8	–	5	0.17	37
28	66/89	170	46	270	110	16	14	35	2.2	n.a.	–	6	0.13	110
29	92/89	55	5	20	5	7	11	4	1	0.9	–	1	0.13	29
30	67/89	80	40	100	15	14	20	10	1	0.8	65	4	0.13	75
31	69/89	20	5	10	5	3	5	–	1	–	n.a.	1	–	6

Note: See Table 1.

potassic varieties (microcline and orthoclase) and plagioclase (oligoclase). Rock fragments are represented by rounded grains of quartzites, siliceous and micaceous schists, gneisses, granites, granodiorites, and strongly altered felsic and basic volcanic rocks. Fragments of ferruginous sandstones of oolitic iron ores are also common, while the Aral Formation often contains fragments of limestones. The heavy fraction of sandy-silty rocks is composed of ilmenite, epidote, and the subordinate zircon, leucosene, and garnet. Other minerals (rutile, disthene, staurolite, magnetite, tourmaline, hornblende, titanite, andalusite, and apatite) occur as minor components or single grains. They show no distinct stratigraphic assignment (Voznesenskii, 1978).

Rocks of the studied section were analyzed for the major rock-forming and associated elements by the RFA and quantitative spectral analysis at the Analytical Center of the Geological Institute, Moscow (Tables 1–3). In order to study the distribution of individual elements in different rock types and across the section, as well as to establish correlation between elements, we plotted a series of correlation diagrams. Some diagrams are presented in Figs. 2–4.

Analysis of obtained data show that the Fe content is 4–6% in clays of the Chegan Formation, 7.5% in interore clays of the Kutambulak Formation, 2.5–3.6% in clays of the Chilikta Formation, 2.5% in the Chagrai Formation, and 3.5% in the Aral Formation. The Fe content is not more than 1–2% in barren sands throughout the entire section of the Turgai Group. It is noteworthy that the Fe content in the Chegan clay is close to its average content in clayey rocks of the Russian Plate (Ronov and Migdisov, 1996). Clayey rocks of the Chilikta, Chagrai, and Aral formations, as well as the lower subore part of the Kutambulak Formation, are depleted in Fe content. The Fe content sharply increases in interore clays of the Kutambulak Formation. The ferruginous sandstones and oolitic ores contain up to 10–20% and 30–40% Fe, respectively.

The Mn distribution in the section correlates with the Fe distribution (Fig. 2a). The Mn content in clays from the main part of the section is 0.05–0.1%, which is close to the average Mn content in clayey rocks of the Russian Plate (Ronov and Migdisov, 1996). The Mn content decreases to 0.01% in clays of the Chagrai Formation. The Mn content in the ferruginous sandstones and typical oolitic ores increases up to 0.17–0.30%, reaching maximum (1%) in the redeposited coarse-grained conglomerate ores at the roof of the Kutambulak Formation. High Mn contents in the conglomerate ores typical of the Kutambulak deposit were previously noted by Formozova (1959).

The mineralized rocks are enriched in phosphorus (0.25–0.5%, up to 1% in individual samples). The maximum P content (6%) was found in phosphorite nodules. The P content in clayey rocks of the studied section is comparable with the average P content in clayey rocks of the Russian Plate (Ronov and Migdisov, 1996).

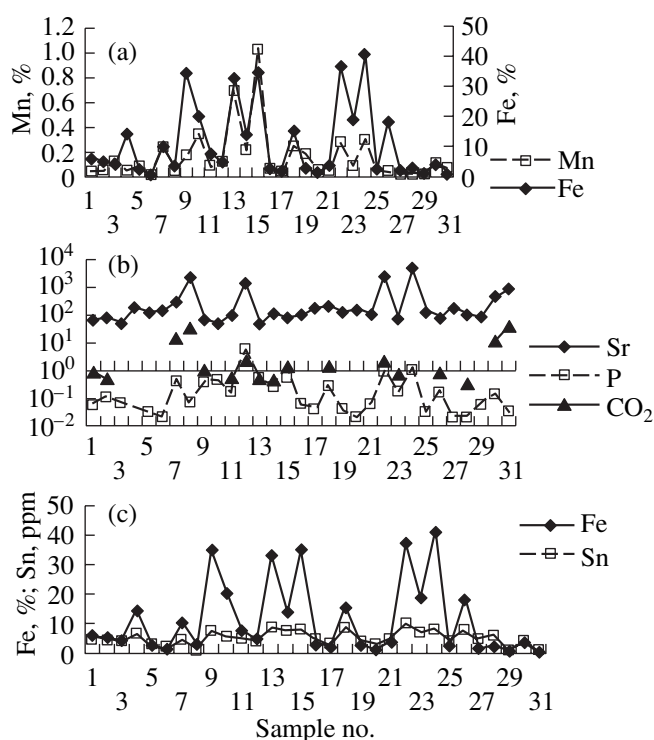


Fig. 2. Distribution of elements across the section: (a) Mn and Fe; (b) Sr, P, and CO₂; (c) Fe and Sn.

Increase in the P content is often associated with the relative increase in contents of Sr and CO₂ (Fig. 2b). These elements show similar distribution patterns across the section. The Sr clarke concentration across the entire section is less than 1 and increases to 2 only in carbonate rocks of the Aral Formation. The exceptions are carbonate and phosphate rocks of the Kutambulak Formation (Sr clarke concentration is 6.5 and 4, respectively) and iron ores with phosphate enclaves of the Chilikta Formation (Sr clarke concentration is 13.5) (Table 3).

The content of Ti incorporated in the lattice of terrigenous minerals is higher in the terrigenous, clayey, and sandy rocks, as compared to the ore and carbonate rocks (limestones of the Aral Formation and travertine-type rocks of the ore bed of the Kutambulak Formation). Steady positive correlation is observed in Ti–Zr and Ti–Y pairs.

Logarithmic-scale plots in Fig. 3 show the distribution of trace elements in rocks of similar lithology. Iron ores and ferruginous sandstones of the Kutambulak and Chilikta formations show increase in Cr, V, Ni, and Co contents upward the section. All rocks are characterized by correlation between Cr–V and Ni–Co pairs. Contents of these elements are close to clarke values (Vinogradov, 1962) in the sandy rocks, higher in the clayey and ore-bearing rocks, and minimal in the carbonate rocks (Table 2). Ores and ferruginous sandstones are enriched in Sn, relative to other rocks of the section.

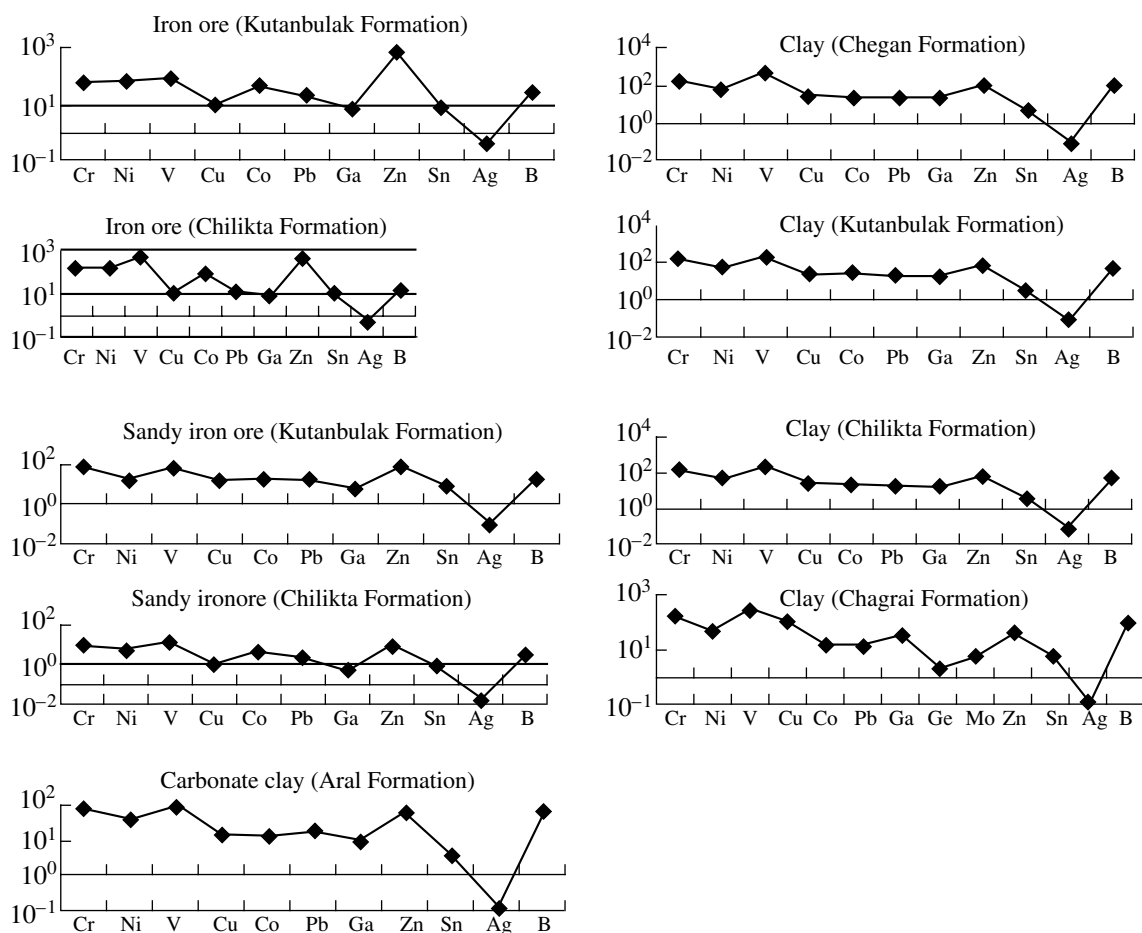


Fig. 3. Distribution of trace elements in different lithological rock types.

The distribution pattern of Sn is close to that of Fe, with a more gradual transition from the interore rocks to the ore horizons (Fig. 2c).

The Ag content shows wide variations across the section. It is below the detection limit in carbonate rocks, at the clarke level in clayey and sandy rocks, and up to five times higher than the clarke level in the Fe-rich rocks. The similar distribution is typical of Zr (average clarke concentration is 2.5). The Ga content across the entire section is below the clarke value and reaches the clarke level only in the clayey rocks. The boron distribution is very uneven. Its concentration is eight times higher than the clarke value in clayey rocks and no more than three times higher than the clarke value in ore interbeds. In all analyzed samples, the Cu content is below the clarke value, whereas the Pb content is 1.5 times higher than the clarke concentration. In the majority of samples, the Mo and Ge contents are below the detection limit in iron ores, ferruginous sandstones, sands, and carbonate rocks. They reach the clarke values only in clays and clayey silts.

Trace elements considered below were determined by the XRF method. Contents of Nb, Rb, and Ba across the section are below their clarke values, while contents

of Zr, Y, and Sr vary from below the clarke level to above the clarke value in different rocks (Table 3). Logarithmic-scale plots presented in Fig. 4 show similar distribution patterns of elements in the same rocks from different parts of the section. However, the Sr content is significant in the Aral clays. Iron ores of the Kutanbulak and Chilikta formations are characterized by different distribution patterns of elements mentioned above. The Chilikta ores are enriched in Sr and depleted in Rb and Nb relative to the Kutanbulak ores.

The lowest contents of these elements (except Sr) were recorded in the carbonate rocks, travertines of the Kutanbulak Formation, and limestones of the Aral formation. Sands and clays are enriched in Nb, while iron ores are depleted in this element. The highest contents of Zr accumulating in the terrigenous heavy fraction are typical of sandy and ferruginous rocks. The Zr content is at the clarke level in clayey rocks and two times lower than the clarke level in the oolitic iron ores. The Y distribution shows an opposite pattern. The Y content is high in iron ores, at the clarke level in clays, and low in sandy rocks. Clayey rocks from the lower part of the section (i.e., the Chegan Formation) and its upper part (Chagrai and Aral formations) are enriched in Rb. In the

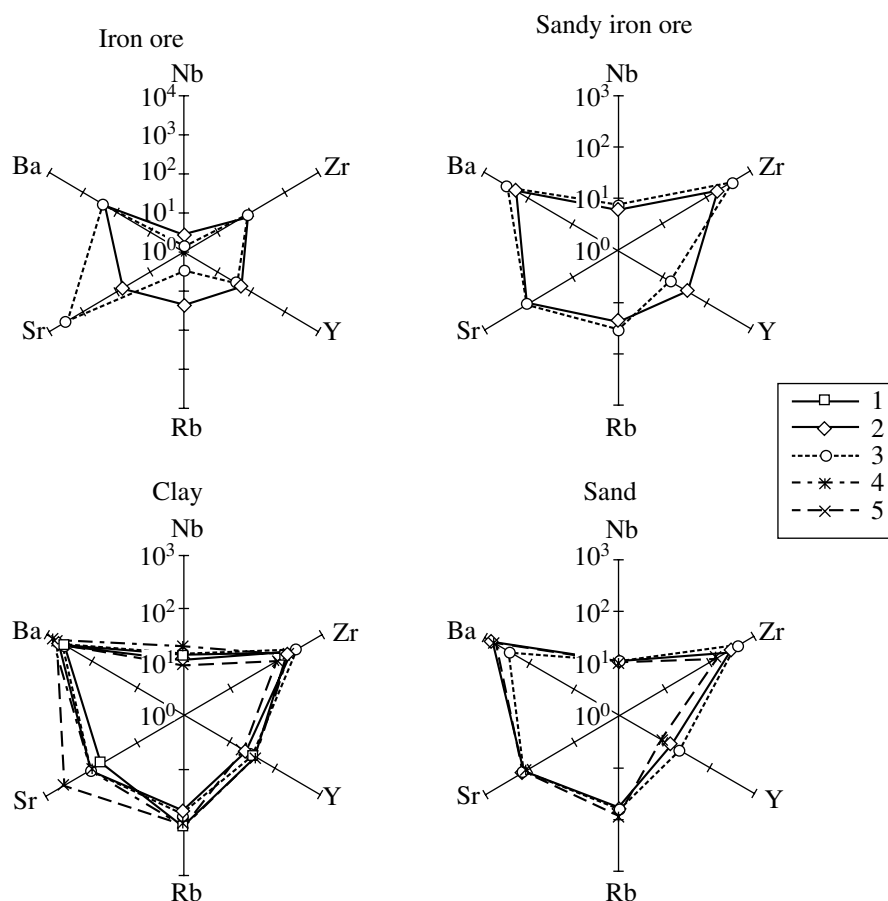


Fig. 4. Distribution of average contents of trace elements in different rock types. Formations: (1) Chegan, (2) Kutanbulak, (3) Chilika, (4) Chagrai, (5) Aral.

latter case, the Rb content is slightly below the clark level. As compared to the clark value, the Rb content is two to three times lower in barren rocks from the middle part of the section (Kutanbulak and Chilikan formations) and five times lower in iron ores.

As was mentioned above, the Sr content shows positive correlation with the P content. The highest contents (ten times higher than the clark value) were noted in the P-rich iron ores. High Sr contents were also found in carbonate rocks (three to seven times higher than the clark value). The Sr content is three to four times lower in clayey rocks and is at the clark level in the Aral clay. The iron ores are depleted in Ba (clark concentration is significantly lower than 1), whereas its content is close to the clark value in clayey and sandy rocks.

CONCLUSIONS

It should be emphasized that the trace element distribution mainly depends on the mineral composition of rocks. As compared to the barren part of the section, iron ores and ferruginous sandstones are enriched in transition elements (Cr, V), element of the Mn association (Co), as well as Ni and Y.

The ores are enriched in Ag, Zn, and Sn. Trace elements in the ores do not form individual mineral phases. They precipitated together with iron minerals or were sorbed on Fe minerals.

The iron ores are enriched in phosphorus, but we did not record steady correlation between P and Fe across the section. This is typical of iron ores of the Lisakov deposit (Golubovskaya, 1993). Irrespective of lithology, Cu and Pb show fairly even distribution across the section. The barren clayey part of the section is enriched in Mo, Ge, and B.

Contents of Ti and Zr mainly associated with the terrigenous material are decreased in ore interbeds. These elements are virtually absent in the solutions. They are transported as suspension and their concentrations in the sediment are similar to those in the initial rocks (Strakhov, 1962; Taylor and McLennan, 1985).

Carbonate rocks of the section have the lowest concentrations of trace elements, with the exception of Sr and Ba.

Thus, results reported in this paper have made it possible to establish qualitative trends in the distribution of trace elements in Eocene-Miocene rocks of the Perovskii Bay.

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