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Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
Қазақстан Республикасының Ғылым Академиясының
Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

NEWS

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OF THE REPUBLIC OF KAZAKHSTAN
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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. Web of 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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**MINERALOGICAL AND GEOCHEMICAL FEATURES
OF SATPAEV Ti-Zr PLACER DEPOSIT, EAST KAZAKHSTAN**

Abstract. The data of mineralogical and geochemical studies of Ti-Zr mineral sands and heavy fraction of the mineral concentrate of Placer No. 1 of the Satpaev deposit (East Kazakhstan) are obtained. The mineralogical composition of the mineral sands: quartz, albite, ilmenite, and feldspar; micro-sized crystals of barite, zircon, monazite, a mineral of pyrochlore composition, were identified by electron microprobe. Crystal morphology of ore minerals: ilmenite and zircon and chemical composition of ilmenite were determined. The development of leucogenization in microcracks and edges of ilmenite crystals have also been revealed.

Geochemical features of productive horizons include the apparent enrichment of light rare-earth elements (LREE) in comparison with heavy rare-earth elements (HREE), and pronounced negative Eu anomaly that indicate high degree of fractionation of source rocks. Granitoids of the Preobrazhensk intrusion are the likely source of the Satpaev placer deposit.

Results of petrological and geochemical research indicate that localization of ore minerals took place during chemical weathering, which enabled release of ore minerals of titanium and zirconium with their further redeposition in local continental coastal settings in warm and humid climate.

Keywords: Satpaev Ti-Zr placer deposit, Preobrazhensk intrusion, rare-earth elements, East Kazakhstan.

1. Introduction. Titanium is widely used in the production of pigmentary titanium dioxide, titanium sponge, titanium ferroalloys, and various compounds used in metallurgy. The main minerals of titanium ores include ilmenite, rutile, anatase and brookite, leucoxene, loparite, titanite, perovskite and titanomagnetite. In complex titanium deposits the accompanying elements of economic value include: Fe, V, Zr, Sc, P, Nb, Ta, Th and rare-earth elements (REE) [1, 2].

Titanium deposits are divided into three main groups: magmatogenic (25.3% of all reserves of titanium dioxide), metamorphogenic (19.5%), and exogenetic (55.2%) [3]. In the world mineral base of titanium, exogenetic deposits occupy the leading position in terms of reserves (52.3%), production (65-70%) and their economic value (67-73% of produced titanium dioxide in concentrates) [4].

The Kazakhstani producer of titanium is JSC “Ust-Kamenogorsk Titanium Magnesium Plant” (JSC “UK TMP”) that manufactures a wide range of titanium products; the main ones include titanium sponge, pigmentary titanium dioxide and metallic titanium. Mineral resources of titanium production in Kazakhstan are represented by three geological-economic deposits types: coastal (Obukhovsk, Shokash, Kumkol', Zayach'e, Tobol'sk and other placer deposits), alluvial-proluvial (Satpaev deposit) and proluvial-alluvial (Karaotkel deposit) [5].

At present JSC “UK TMP” receives ilmenite concentrates from the nearby located Satpaev titanium-zirconium placer deposit [6]. The Satpaev deposit is located in the northwestern part of the Zaysan depression, 220 km to the south of Ust-Kamenogorsk city (the regional center of the East Kazakhstan

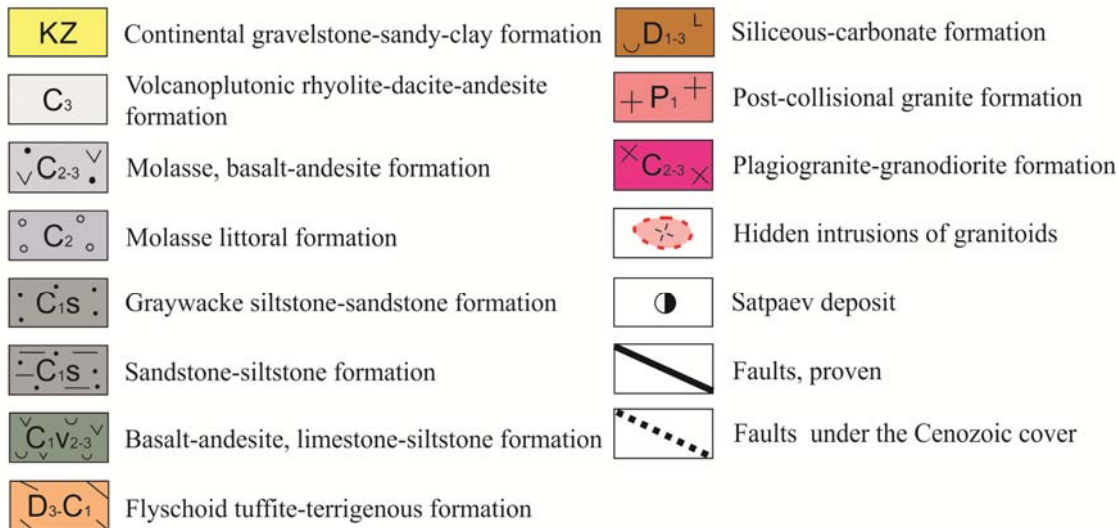
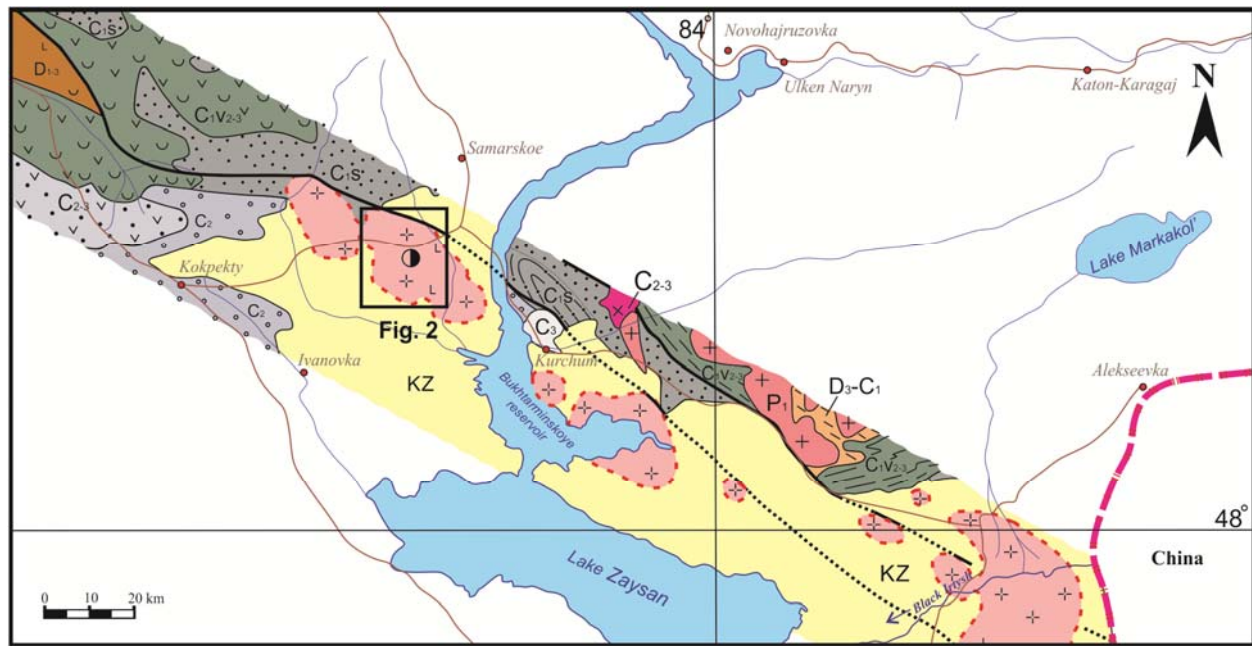


Figure 1 – Overview location map of the Satpaev Ti-Zr placer deposit

region) and 40 km to the east of the Kokpekty village (figure 1). Placers are localized within the Preobrazhensk multiphase intrusion and are composed mainly of gabbro and gabbro-norites with subordinated role of granitoids and subalkaline rocks (monzonite, diorites, quartz diorites, syenites), that collectively comprise the Maksut Late Permian – Lower Triassic gabbro-granitoid complex [7].

Due to poor quality of ilmenite concentrates from the Satpaev placer, JSC “UK TMP” is forced to import additional high-quality ilmenite concentrates to be able use the technology of a combined thermal melting to obtain titanium slags of required composition.

Major mineralogical factors that define technological properties of placers include: granulometric composition of sands and morphological features of ore minerals, the content of economic elements, impurity elements in ore minerals, presence of deleterious elements for this type of mineral resources, and physical (technological) features of minerals.

The quality of ilmenite sands is characterized by the content of TiO₂ and by the mineral form of titanium, as well as by the content of zircon, furthermore by mineral-carriers of elements that worsen the quality of sands; first of all, these include chromium, phosphorus and clay content of sands [9]. Technological properties of Ti-Zr placers vary depending on conditions of formation, mineral size, isomorphic

substitutions, and presence of impurity elements. The most harmful impurities influencing technological processing of Ti-Zr placers are phosphorus and chrome that are often represented by own mineral phases.

Complete replacement of imported high-quality ilmenite concentrates by domestic supply is an urgent and relevant problem for the titanium industry of East Kazakhstan. One possibility includes improving the technological parameters of mineral sand processing. In addition, studies of accompanying economic components are important for the integrated development of the Satpaev deposit, which can contribute to increased profitability of exploration.

The purpose of this research is to study mineralogical-geochemical features of mineral sands of the Satpaev deposit and to determine paleogeographic conditions of accumulation of mineral sands. This paper provides geological characteristics of the wider study region, including mineral sands of the Satpayev deposit, as well as the results of mineralogical-geochemical research of mineral sands and ilmenite concentrate as their end product.

2. Exploration history of the Satpaev Ti-Zr placer deposit. The main regional data on stratigraphy, tectonics, magmatism and metallogeny of the region of the northwest of the Zaysan depression, prospecting criteria for Ti-Zr placers, and state of knowledge and prospects of discovery of new deposits have been summarized in works of V.P. Nekhoroshev, V.S. Erofejev, B.A. Borisov, A.K. Kayupov, P.V. Yermolov, V.S. Kuzebny, G.N. Shcherby, A.M. Mysnik, Y.M. Sapargaliyev, M.M. Kravchenko, B.A. Dyachkov and many others [10–19].

G.I. Sokratov and A.P. Nikolsky carried out the first geological mapping of the region, of 1:200 000 scale in 1952. Later in 1961 N.N. Popova, V.E. Popov and others conducted the geological survey of 1:200 000 scale that allowed the definition of the stratigraphic scheme of sedimentary sequences and intrusive magmatism of the region [20].

In 1980-82 the exploration crew of nonmetallic raw material division of the Altai geologic-geophysical expedition, represented by M.M. Kravchenko and others carried out prospecting and evaluation works of 1:10 000 scales and conducted preliminary investigation of the Karaotkel ilmenite-zircon placer deposit [6, 8].

During 1988-92, the advanced geophysical and geochemical surveys of 1:50 000 scale have been carried out in the area of northwest Zaysan that led to the discovery of the Bektemir deposit in 1989 (=Satpaev) [21].

In the period of 1990-95 the prospecting and prospecting-evaluation works carried out by N.M. Pakharukov and others led to the discovery of the Placer No. 1. Subsequently, the scientific and technical Council of "Vostkaznedra" approved C₂ reserves of the Placer No. 1.

In 1997-99 LLP "Geoincentre" has investigated Placer No.1, calculated reserves and conducted the feasibility study. The deposit was renamed into the Satpaev deposit. Having considered materials of this work, the State Commission of Mineral Reserves of the Republic of Kazakhstan has approved evaluating criteria and approved the following C₂ reserves: mineral sands of 9 269.66 thous. m³, ilmenite of 1 634.1 thous. tons with the average content of ilmenite of 176.29 kg/m³.

During 2000-2003 exploration works at the Satpaev deposit were continued by LLP "Geoincentre" jointly with the Japanese company "MINDECO" to evaluate the following Ti-Zr placers: Placer No. 1, Placer No. 3, Southern Bektemir, Northern Site, and Eastern Bektemir. As a result, there were identified zones with ilmenite mineralization localized in the negative relief forms of Paleozoic basement.

The deposit has been in operation since 2002 [22]. Nowadays, extraction of sands has been conducted by LLP "Satpaev Gornoobogatitelnoye Predpriyatiye", which delivers mineral concentrates to JSC "UK TMP".

The main data about state of knowledge, geological and economic evaluation and the prospects of development of the Satpaev deposit in the near future have been published in the monograph on "Mineral resources of the titanium industry of Kazakhstan and modelling of the development of its mineral base until 2030" [3].

3. Geological characteristics of the Satpaev deposit. The Satpaev deposit is situated in the southwestern part of the Maityube syncline at the border between the West Kalba and the Zharma-Saur metallogenic zones of the Greater Altai that is part of the Central Asian Orogenic Belt (CAOB) [6]. Three structural levels comprise the geological architecture of the area: (1) rocks of Paleozoic basement represented by terrigenous and volcanogenic sedimentary rocks, intermediate-mafic lavas with the subvolcanic

intrusions, which cut through; (2) lateral weathering crust formed as a result of intense reworking of Paleozoic rocks; and (3) Cenozoic depositions represented by sedimentary rocks of the Neogene-Quaternary age, including clays with various sand content, and gravel-pebble sediments [23].

Paleozoic sediments in the region of the Satpaev deposit are represented by the Bukon (C₂bk) and Maityuba (C₂₋₃mt) Formations. These sediments are intruded by the Preobrazhensk and the Karaotkel intrusive bodies. At the southeastern and southwestern flanks of the Preobrazhensk intrusion there are located five placers with increased ilmenite content, collectively forming the Satpaev (Bektemir) ore field.

Intrusive formations within the Preobrazhensk and Karaotkel massifs are represented by the following three independent complexes of different age: 1) Maksut P₂-T₁ (andesite porphyrite), 2) Saykan T₂₋₃ (diorites, syenites, syenites-diorites and granosyenites), and 3) Delbegetey J₁₋₂ (alkaline granites, granosyenites). Subvolcanic formations and intrusions of dike series represented by granite-porphyrries, alkaline granite-porphyrries, granodiorites and syenites are also widespread within the area. Studies of interaction between gabbroid and granitoid magmas during formation of the Preobrazhensk intrusion (S.V. Khromykh, G.N. Burmakina, A.A. Tsygankov and others; [25]) established that rocks of four intrusive phases participated in the structure of the massif as follows: 1) medium and coarse-grained monzonite and quartz monzonite; 2) medium-grained gabbro-norite; 3) medium-grained biotite to biotite-amphibole granite with the facies of leucogranite and leucogranosyenite; 4) monzodiorite (gabbro- monzodiorite) [25].

The Preobrazhensk granitoids are considered to be the source of the Satpaev Ti-Zr placer deposit. The structural position of the Satpaev deposit is controlled by the Preobrazhensk intrusion (figure 2) as reflected also by its occurrence along the frame of the intrusion.

Geotectonic epochs of the Zaysan depression include 6 stages: Permian (255-265 and 275-290 million years); Triassic (210-230 million years); Jurassic (135-145 and 160-200 million years); Cretaceous (65-85 and 125-135 million years); Oligocene (23-33 million years) and Neogene - Quaternary (1.2-7.6 million years ago) [26].

The basic structural elements of the Satpaev deposit include the Northern Terektinsk and Southern Terektinsk dislocations of the northwest extension and the perpendicularly oriented Bektemir Fault with series of sub-parallel branches. They occupy a crosscut position and displace sediments of the Bukon and Maityuba Formations. They are manifested by zones of brecciation, intensive fracturing, linear distribution of weathering crusts and occurrence of concordant dikes of intermediate and acidic composition. These faults may have been favorable pathways for the formation of channels for ancient rivers and for fluvial transfer of ore material.

Over the entire area of the deposit, the Paleozoic rocks developed a weathering crust with a thickness of 10-20 m. In the profile of weathering crusts, the following zones (from top to bottom) are distinguished:

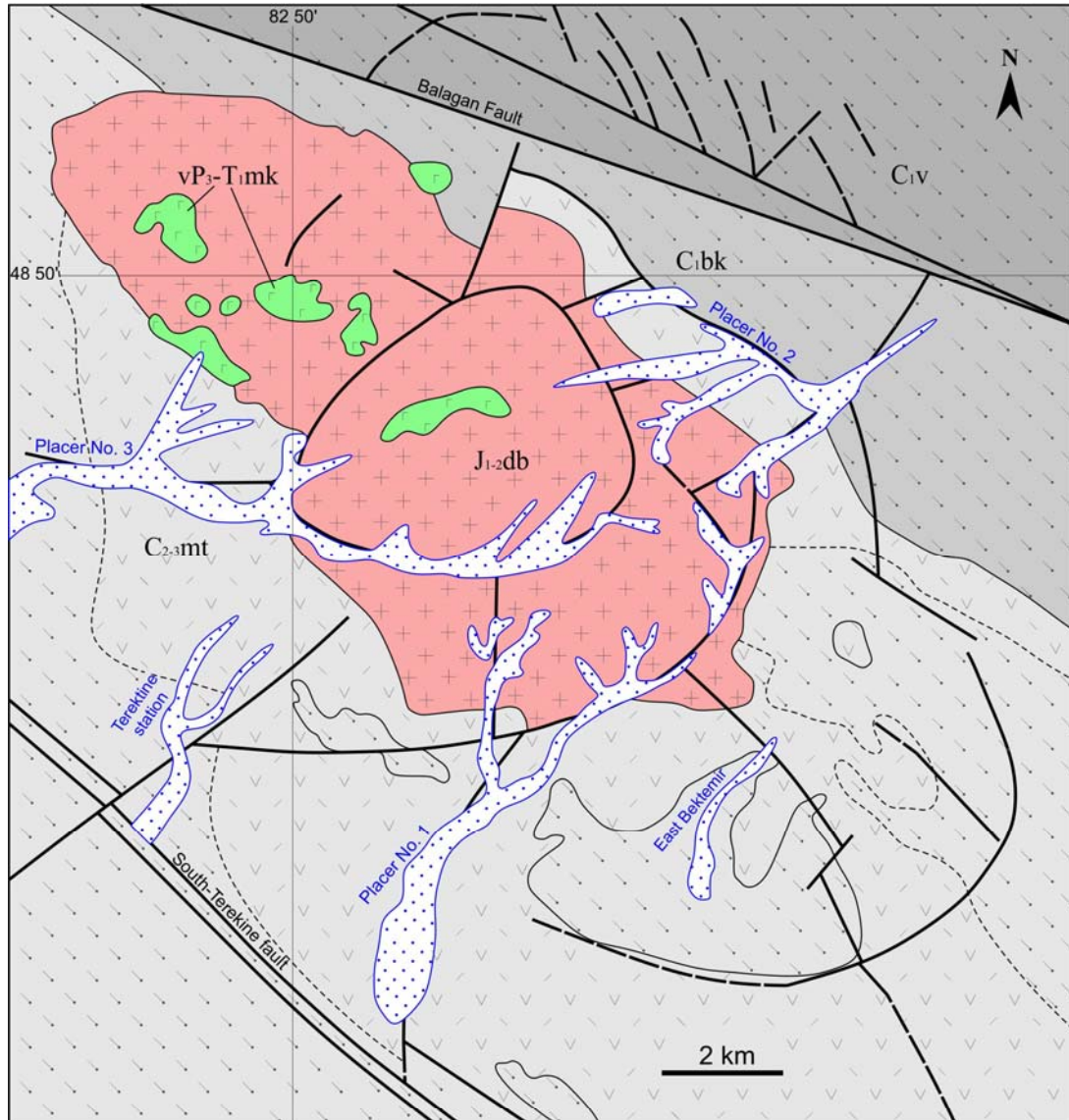
- a) zone of kaolin clays, representing bleached clay eluvium; the structure of parent rocks is completely lost;
- b) zone of hydromica - clay structural eluvium, composed of clay products of chemical decomposition, retaining the structure of parent rocks;
- c) zone of disintegration - zone of structural eluvium, consisting of weathered, strongly fractured bleached rocks; bleaching is caused by partial removal of alkalis and hydration of mica.

The Satpaev deposit includes 5 sites: Placer No. 1, Placer No. 2, Placer No. 3, East Bektemir and Terektinsk. The lower horizon of the Aral Formation (N₁¹⁻²ar) is also of economic importance as it contains Ti-Zr placers. These deposits overlie with angular unconformity the eroded surface of the Paleozoic basement and, in some cases, the weathering crusts. The Aral Formation is overlaid by Quaternary sediments.

Geomorphologically the area is comprised of the following relief forms:

- a) alluvial - the relief forms created by the channel accumulation are represented by gravel-pebble deposits, sand, loam, silt; the forms of alluvial plains are represented by loams with crushed rock;
- b) accumulative-denudational - form weakly inclined surfaces created by a complex of slope processes and lithologically represented by loess-like loams with clays in the basement;
- c) structurally denudational - form slopes of elevations, predetermined by destructive preparation of the marginal parts of the intrusion.

Generally, Ti-Zr mineralization in the continental deposits of the Cenozoic in the northwest of the Zaysan depression is distinguished by nature of their sources. In the Paleogene and Neogene, they are



- C_{2-3mt} Maityuba suite: volcanomictic sandstone of lavas and tuff of andesite porphyte
- C_{1bk} Bukon suite: interbedding of clayey, argillaceous clayey aleurolite
- C_{1v} Visean suite: polymictic calcareous sandstone, siltstone, siliceous and argillaceous shale, covers of lavas and tuff of andesite and dacite porphyrite
- J_{1-db} Delbegetei complex: alkaline granite, granosyenite, syenite
- vP_{3-T1mk} Maksut complex: gabbro-norite, gabbro-diorite, diorite, monzonite
- / / / Siltstone, sandstone, shale
- ∇ / ∇ Lava, tuff of andesite porphyrite
- a) / b) Deep faults (regional): a) established; c) proposed
- ⊂ Ti-Zr placers

Figure 2 – Geological-tectonic scheme of the Satpaev deposit of Ti-Zr placers.
(Note: Cenozoic cover is removed) [24]

associated with redeposition of the chemical weathering crust. In the Quaternary period - with redeposition of older sediments enriched with quartz psammites and dilution of polymictic detrital material.

The lithological-formation analysis determines the time for the formation of weathering crusts and the accumulation of quartz psammites in the Paleogene and Neogene deposits, which coincides with early Alpine geotectonic movements [15, 23, 27, 28]. The total mass of the accumulated precipitates in the sediments, variations in their lithologic-petrographic and granulometric compositions depend on the degree of maturity of the weathering crust, the duration of formation and altitude position of the peneplain over the basis of erosion, the material composition and geochemistry of the original rocks, climatic data, the dynamics of geotectonic movements, the participation of organic matter in decomposition of the parent rocks and many other factors.

Figure 3 shows lithological and paleographic conditions of the Zaysan depression: during periods of the formation of the Preobrazhensk intrusion (Permian, Triassic, Jurassic); during periods of weathering crust formation and Ti-Zr placers.

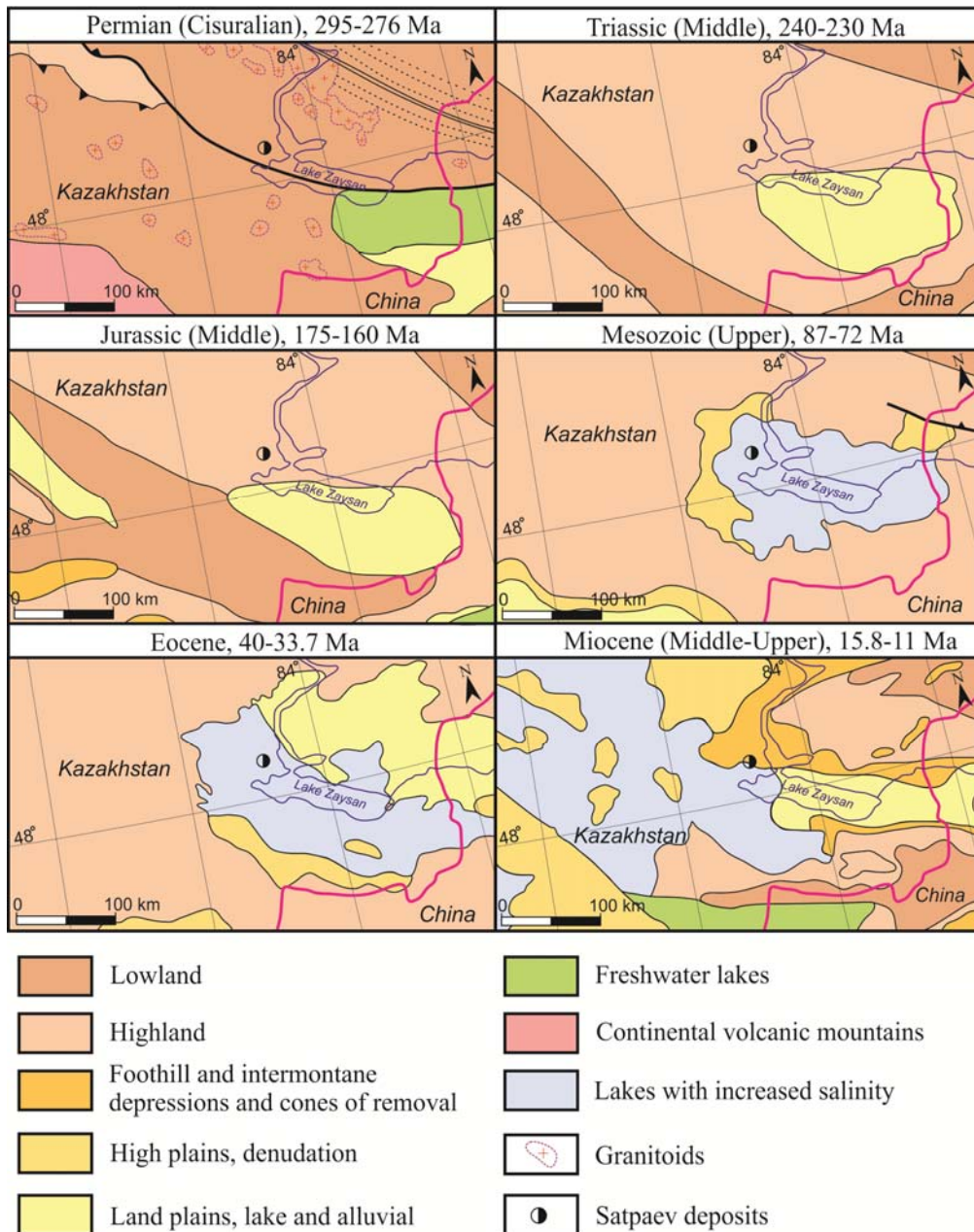


Figure 3 – Lithologic-paleographic maps of the Zaysan depression, *modified after Fedorenko et al., 2002* [29]

4. Features of the geological structure of productive deposits. The combination of favorable geological and geomorphological conditions is facilitated by the formation of productive Ti-Zr placer deposits in certain epochs of the geologic history of the region, i.e. presence of the bedrock source of metal-bearing crystalline rocks, shallow occurrence of primary sources, and widespread development of predominantly chemical weathering processes - reaching to a considerable depth. The lithologic-stratigraphic column of the Satpaev deposit is shown in figure 4.

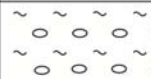
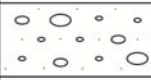
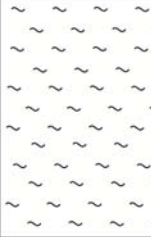
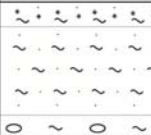

Stratigraphic index	Horizon number	Lithologic description of rocks	Layer thickness, m	Geological section
Q ₁	1	Gravel and pebble deposits	3.4	
	2	Boulder-gravel-pebble deposits	4.4	
N ₁₋₂ ^{ar}	3	Clays: dense, viscous, plastic, with oolites of limonite and with hematite flakes, with rare dust-like impregnation of ilmenite up to 1%. Gradual increase of the sand portion to 15%, ilmenite content 1-2%	15.4	
	4	Ore horizon: sandy iron-rich clays with fragments of quartz	7.8	
K _{ma}	5	Weathering crust developed over gray to greenish-gray, fine-grained sandstones, less often over yellowish-gray iron-rich sandstones	8.0	

Figure 4 – Lithological stratigraphic column of the region of the Satpaev deposit [24]

In the vertical section, clays are characterized by varying degrees of sand content, and inequigranular quartz-feldspar sand, more rarely by sand and sand-gravel material with small pebbles. Further down the column are sandy-clay deposits, which, according to the formation conditions, are alluvial and located on the weathering crusts of the Paleozoic basement.

In very rare cases, alluvial deposits forming placers are underlined by clays or feather out in clays. The thickness of productive deposits ranges from 2.4 to 15.6 m, average is 7.8 m. There are two specific features of the mineralised zone that can be also observed: a) almost everywhere the boundaries of this zone begin with sand; b) due to presence of ilmenite, the productive strata are distinguished by a darker color.

Ilmenite mineralization has a very close correlation with the lower sandy part of the deposits of the Aral Formation (table 1) and ilmenite content is directly dependent on the amount of sand in the stratum. The intensity of ilmenite mineralization is even greater close to the bedrock. The gradual increase in the content of ilmenite with depth is visible in the vertical zoning, which is the most important feature of the internal structure of the placer deposits. Clays overlaying the sands of the ore-bearing horizon contain only a rare impregnation of very thin ilmenite. According to the mineral analysis it is in the order of 0.1-1 kg/t. Closer to the boundary of the ore-bearing horizon there are small lenses enriched in quartz-feldspar sand and ilmenite.

Table 1 – Average chemical composition of ore-bearing rocks of the Aral Formation of the Satpaev deposit and calculated petrological parameters

#	Component	The Aral Formation	
		Lower horizon 4	Upper horizon 3
1. Average chemical composition [24]:			
1	SiO ₂	59.81	50.11
2	TiO ₂	1.39	1.18
3	Al ₂ O ₃	17.25	14.46
4	Fe ₂ O ₃	7.69	6.35
5	FeO	0.14	0.16
6	MnO	0.02	0.09
7	MgO	2.11	2.06
8	CaO	3.44	7.39
9	Na ₂ O	0.10	0.10
10	K ₂ O	1.98	1.74
11	P ₂ O ₅	0.06	0.09
12	Σ	93.99	83.73
2. Petrological parameters:			
13	(Al ₂ O ₃ +TiO ₂ +Fe ₂ O ₃ +FeO)/SiO ₂	0.44	0.44
14	Al ₂ O ₃ /SiO ₂	0.29	0.29
15	TiO ₂ /Al ₂ O ₃	0.08	0.08
16	Na ₂ O+K ₂ O/Al ₂ O ₃	0.12	0.13
17	FeO+ Fe ₂ O ₃ +MnO/Al ₂ O ₃ +TiO ₂	0.42	0.42

Sandy-argillaceous deposits are characterized by zonal coloration. In the lower part of the sequence, they have a darker gray color with a greenish, less often bluish, shade. Higher in the section, clays gradually change the color to a lighter yellowish-gray and light gray shades with a weak greenish tinge. Clays in the southern part of the placer are often marked by beans of the hydroxides of manganese, iron and the inclusion of marls.

Sands are represented by clastic material of different granularity. They are of quartz-feldspar composition containing ilmenite. Feldspar grains have a light color and can be clearly distinguished on the common gray background. Feldspar is completely decomposed to clay. Only 15% of feldspars remain in the light fraction of the concentrates and 85% is quartz. Generally, productive deposits have the appearance of sand and contain 30-65% of clays due to decomposed grains of feldspars.

Clays stand out in sands as lenticular nests and thin interlayers, whereas sandy clays are composed of greenish-gray clay with lenses and nests of quartz-feldspar sand.

Table 1 shows petrological parameters of ore-bearing deposits of the Aral Formation that indicate the following:

- the hydrolysis parameter $((Al_2O_3+TiO_2+Fe_2O_3+FeO)/SiO_2-0.44)$ [31] shows that deposits are characterized by average level of maturity, which indicates their formation as a result of predominantly mechanical destruction of parental rocks with subordinate role of chemical weathering;

- according to the values of the aluminosilicate parameter $(Al_2O_3/SiO_2= 0.17)$ [32], the deposits belong to the class 0.22-0.35, that is typical for clay rocks;

- the increased value of the titanium parameter $(TiO_2/Al_2O_3=0.8)$ [33] is characteristic for sedimentary rocks that accumulate in continental coastal conditions, in humid climate;

- the iron parameter $(FeO+Fe_2O_3+MnO/Al_2O_3+TiO_2=0.42)$ and the total alkalinity $(Na_2O+K_2O/Al_2O_3=0.12, 0.13)$ characterize deposits as hypo-alkaline and normally-ferruginous.

5. Sampling and methods of research. Sample B-1 (ilmenite concentrate) was selected to study mineral and chemical composition of a mineral concentrate of Placer No. 1 of the Satpaev deposit. A representative stream sample B-2 from the mine site of Placer No. 1 was selected to study mineralogical and geochemical features of the Ti-Zr placers of the Satpaev deposit. Sampling has been carried out through the full thickness of the mineral sands sequence.

Sample B-2 is a sandy-clay material (clay - 46% approx., sandy material - 54% approx.), has a grayish-white color with a red tint, impregnated with iron hydroxides. It contains about 20 minerals, main ones include quartz, ilmenite, potassium feldspar and kaolinite.

The mineral processing scheme consists of the following stages:

- 1) filtration of the clay fraction, removal of gravel and pulping of light mineral fraction;
- 2) concentration to grey sand stage to preserve minerals with low density (zircon, monazite, cassiterite, ilmenite, etc.) and to obtain more complete information about mineral composition;
- 3) weighing of the concentrate and collection of a representative sample.

Study of mineral and chemical compositions of samples has been carried out in the mineralogical laboratory of the K. I. Satpaev Institute of Geological Sciences in Almaty. X-ray diffractometric analysis of samples has been carried out using an automated diffractometer Dron-3 with $Ci_{K\alpha}$ radiation, β – filter. Conditions of obtaining the diffractograms are: $U=35$ kV; $I=20$ mA; shooting ENU 2-ENU; detector 2 deg/min. X-ray semi-quantitative phase analysis has been performed on diffractograms of powdered samples using the method of “equal lots and artificial mixtures”. Quantitative relations of crystal phases have been determined. Interpretation of diffraction patterns was carried out using the ICDD data of base powder diffractometric PDF2 (Powder Diffraction File) data and diffraction patterns of pure (from impurities) minerals.

Chemical composition of micron-sized minerals has been studied by electron microprobe analysis, using JCSA 733 with the use of energy dispersive spectrometer INCA ENERGY at accelerating voltage 15 kV, probe current of 25 na, using a focused (1-2 μ m diameter) probe. For a comparison purposes the following samples were used: albite (Na), MgO (Mg); Al_2O_3 (Al); SiO_2 (Si); adular (K), $CaSiO_3$ (Ca); TiO_2 (Ti); $Fe_2O_3 \cdot MnO$ (Fe, Mn), a metal (Zn); metal Zn, V, Nb, TA, Sn, U, Co (Zn, V, Nb, TA, Sn, U, Co); ThO_2 (Th); SrF_2 (Sr); ZrO_2 (Zr); CaF_2 (F), $BaSO_4$ (Ba), $x(PO_4)$ (x - REE).

The elemental chemical analysis of the sample B-2 was carried out in the laboratory of "Metal analysis" CPHMA at the Kazakh National University named after Al-Farabi in Almaty. Tracer and rare earth elements have been determined by mass spectrometry with inductively coupled plasma (ICP-MS Agilent 7500a, Japan). For calibration of the mass spectrometer and to obtain calibration parameters there were used standard solutions for ICP-MS. Calibrating solutions were prepared by successive dilution of standard solutions of 2.5% HNO_3 . The error of construction of the calibration plots does not exceed 1-3%.

6. Results of mineralogical and geochemical studies. The Satpaev deposit of Ti-Zr mineral sands has been the main object of mineralogical study [34]. The bulk chemical composition of deslimed mineral sands (sample B-2) has been investigated by electron microprobe analysis and results are shown in table 2.

Table 2 – Bulk chemical composition (wt. %) of deslimed mineral sands (sample B-2)

Analysis #	Element oxide, wt. %									
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	MnO	Na_2O	K_2O	Σ
1	52.01	12.83	6.95	12.02	0.36	0.76	0.87	1.30	1.43	88.53
2	46.57	14.53	8.45	13.44	0.22	1.12	0.66	1.93	1.83	88.74
3	52.03	11.56	7.46	11.45	0.27	0.91	0.83	1.75	1.78	88.04
Average	50.19	12.98	7.61	12.30	0.28	0.92	0.79	1.67	1.69	88.43

According to the semi-quantitative X-ray phase analysis the following mineral content in deslimed mineral sands (%) was identified: quartz – 62.9, albite – 17.2, ilmenite – 11.3, feldspar – 8.5. Crystal morphology of minerals and their composition have been studied using electron microprobe analysis in SEI and BEI modes (figure 5). The chemical composition of ilmenite from deslimed mineral sands is presented in table 3. The morphology of crystals is shown in figure 5 (a-c).

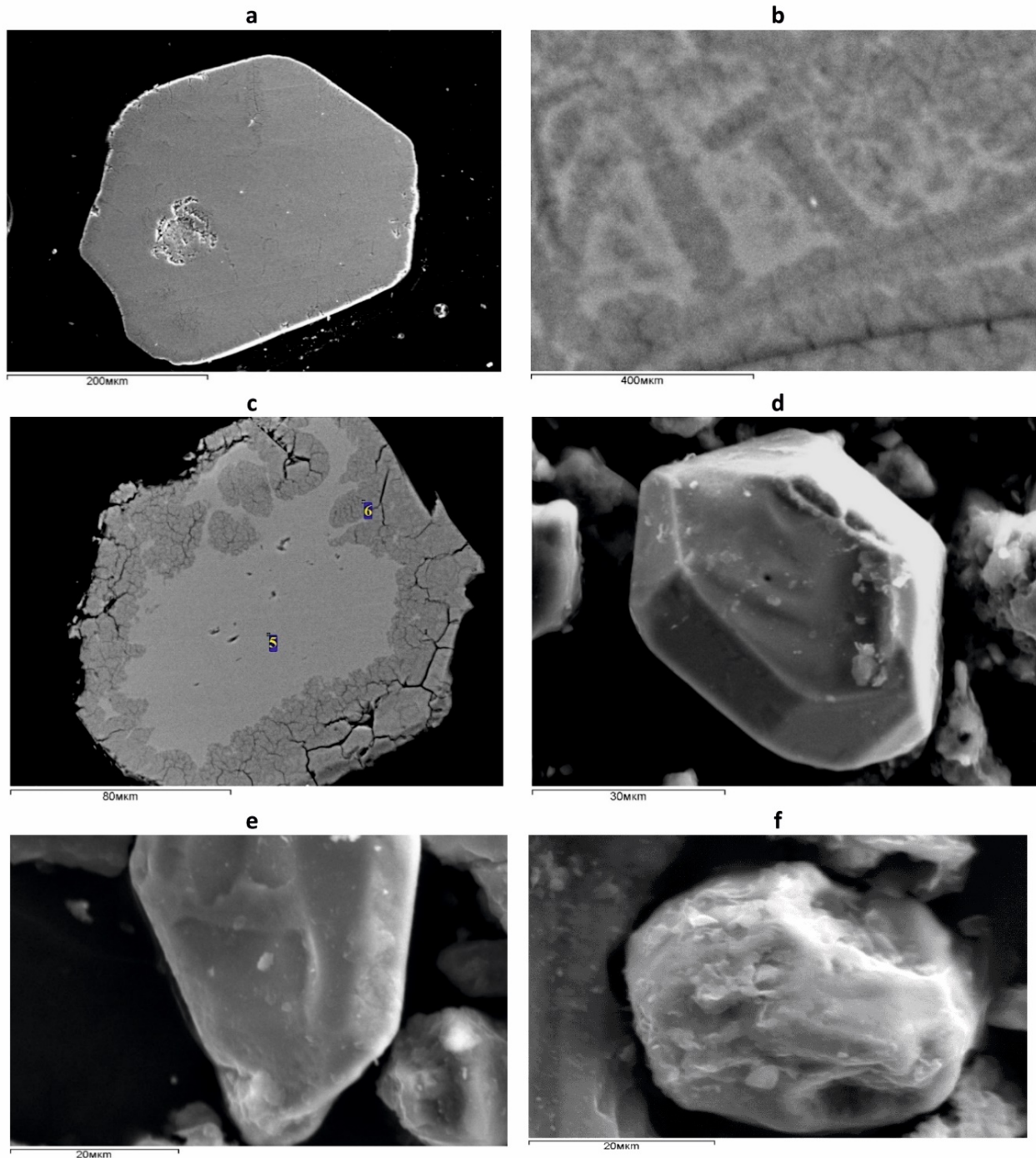


Figure 5 – Crystal morphology of minerals shown by electron microprobe analysis in SEI/BEI modes:

a – ilmenite crystal in the form of a slightly rounded hexagon (table 3, analysis 1), SEI;

b – section of ilmenite crystal. Iron content in light areas is higher than in dark areas, where as titanium content is dark areas is higher than in light areas (table 3, analyses 3-4). BEI;

c – replacement of ilmenite by leucoxene is along cracks and weak zones at the edges of the crystal (table 3, analyses 5 and 6), BEI;

d – microsized slightly rounded zircon crystal, SEI;

e – rounded shape of the elongated zircon crystal head with diverse composition: Zr, Si, Al and Fe (table 4, analysis 2), SEI;

f – microsized monazite grain (in the center), SEI.

Table 3 – Chemical composition (wt. %) of the ilmenite sample B-2

#	Element oxide				
	TiO ₂	V ₂ O ₅	MnO	FeO	Σ
1	46.93	0.54	1.79	47.45	96.71
2	52.79	0.86	6.27	40.21	100.13
3	54.25	1.19	1.85	39.85	97.14
4	55.64	0.97	1.01	33.15	90.77
5	51.46	0.83	1.63	44.72	98.63
6	58.04	0.46	1.34	35.11	94.95

Zircon from mineral sands (sample B-2) has chemical composition free of isomorphous impurities. A large number of mineral crystals have prismatic or elongated prismatic form with pyramidal peaks (figures 5d, e).

The sample B-2 also contains micro-crystals of barite (figure 6a) with traces of aluminium and iron in its composition. It should be noted that previous researchers [34] did not describe findings of barite before.

Presence of microsized (up to 50 μm) rounded phosphate crystals (figure 5f) allowed the study of forms of occurrence of rare earth elements. The qualitative chemical composition of monazite detected in mineral sands is rather stable and contains apart from Ce, elevated concentrations of Nd and La; with Pr, Sm, Gd, Ca, Th also present.

Chemical composition of a single grain of the mineral with pyrochlore composition in deslimed mineral sands (sample B-2) is presented in table 4.

Table 4 – Chemical composition (wt. %) of different areas of the polished section of the grain of water-containing mineral with pyrochlore composition

Analyses #	Element oxide										
	WO ₃	UO ₃	Ta ₂ O ₅	Nb ₂ O ₅	SiO ₂	TiO ₂	ThO ₂	CaO	FeO	K ₂ O	Σ
1	3.53	30.03	1.11	24.35	0.38	20.06	1.32	1.66	1.73	0.33	84.50
2	2.99	27.92	1.14	24.82	3.61	21.37	1.55	1.78	1.37	0.69	87.24
3	2.28	27.45	1.68	22.93	6.01	19.58	1.33	1.22	1.23	0.69	84.41

Presence of cracks in the mineral and low total sum of elements hints on significant content of water in the mineral structure.

In figure 6b, numbers 1 and 3 indicate the points of chemical analysis of barite crystals; areas enriched with heavy elements (light gray), areas with lower content (dark gray).

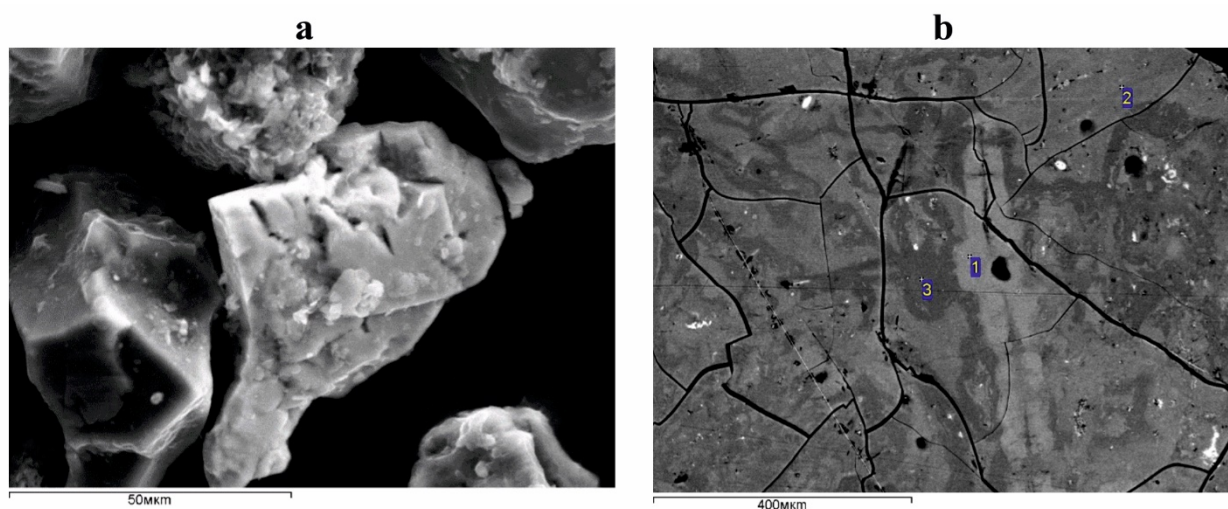


Figure 6 – The morphology of barite crystals and of mineral of pyrochlore composition:
a – microsized barite grain (center), SEI;
b – variations in water composition of the mineral with pyrochlore composition, BEI.

Results of semi-quantitative and quantitative analyses of the ICP-MS are shown in table 5.

Table 5 – Results of elemental chemical analysis of sample B-2 in comparison with the reference content of chemical elements in shale [35]

#	Sample B-2		Content of the sample / Shale clark	#	Sample B-2		Content of the sample / Shale clark
	Element	Content, g/t			Element	Content, g/t	
1	Li	5.49	0.084	33	In	0.69	8.41
2	Be	0.78	1	34	Sn	22.6	3.53
3	B	198	1.98	35	Sb	0.73	0.49
4	Na	7291	0.73	36	I	245	128.95
5	Mg	1446	0.10	37	Cs	0.37	0.06
6	Al	7486	0.10	38	Ba	333	0.50
7	K	4316	0.16	39	La	17.1	0.12
8	Ca	2815	0.13	40	Ce	43.2	0.69
9	Sc	10.7	0.82	41	Pr	4.79	0.75
10	Ti	7 440.00	1.69	42	Nd	19.8	0.73
11	V	90.7	0.70	43	Sm	3.83	0.59
12	Cr	118	1.26	44	Eu	0.93	0.85
13	Mn	5324	6.66	45	Gd	4.05	0.62
14	Fe	48244	1.09	46	Tb	0.61	0.61
15	Co	66.6	3.51	47	Dy	3.4	0.71
16	Ni	31.1	0.42	48	Ho	0.76	0.54
17	Cu	83	1.73	49	Er	2.36	0.87
18	Zn	1179	12.68	50	Tm	0.3	1.30
19	Ga	28.2	1.28	51	Yb	2.08	0.69
20	Ge	5.41	3.18	52	Lu	0.33	0.50
21	As	45.3	3.78	53	Hf	0.43	0.12
22	Se	0.93	1.60	54	W	0.16	0.11
23	Br	815	185.23	55	Ir	0.15	15
24	Rb	15.9	0.11	56	Au	11.1	3363.64
25	Sr	58.1	0.18	57	Hg	0.7	1.67
26	Y	21.7	0.72	58	Pb	44.8	2.24
27	Zr	16.1	0.09	59	Bi	0.35	3.61
28	Nb	1.5	0.08	60	U	5.8	1.57
29	Mo	6.75	2.60	Σ REE		103.54	0.39
30	Pd	7.34	7340	Σ LREE		89.65	0.37
31	Ag	2.76	38.33	Σ HREE		13.89	0.68
32	Cd	0.41	0.98	Σ LREE/ Σ HREE		6.45	

Table 6 – Bulk chemical composition (wt. %) of the ilmenite concentrate (sample B-1)

Element oxide	Analysis #			Average
	1	2	3	
SiO ₂	4.21	4.39	5.22	4.60
TiO ₂	46.42	48.16	46.09	46.89
Al ₂ O ₃	0.98	1.30	0.96	1.08
Fe ₂ O ₃	39.35	40.20	38.05	39.20
V ₂ O ₃	0.34	0.24	0.59	0.38
MnO	2.57	2.35	2.79	2.57
CaO	0.25	0.08	0.14	0.15
Σ	94.12	96.72	93.83	94.87

The bulk chemical composition of the ilmenite concentrate (sample B-1) was studied by electron microprobe analysis and results are presented in table 6.

Results of semi-quantitative x-ray phase analysis showed the following elemental concentrations in the ilmenite concentrate, (%): ilmenite (FeTiO_3) - 68.0; quartz (SiO_2) - 10.0; hematite (Fe_2O_3) - 7.9; oxide Ti, V ($\text{Ti}_{0.93}\text{V}_{0.07}\text{O}_3$) - 7.7; leucoxene (pseudorutile) ($\text{Fe}_2\text{Ti}_3\text{O}_9$) - 6.4 and a minor feldspar impurity.

7. Mineralogical-geochemical features of the Satpaev Ti-Zr placer deposit. Mineralogical study of mineral sands by electron microprobe identified, apart from traditional minerals of quartz, albite, ilmenite, and feldspar, also micro-sized crystals of zircon, monazite, barite, and a mineral with pyrochlore composition. The latter two have not been detected by previous investigators.

Chemical composition of the ilmenite, the main ore mineral, varies from grain to grain, as well as within individual grains (table 3). Chemical composition of ilmenite is relatively stable and contains iron, titanium, manganese and vanadium; the ratio of titanium to iron varies. Weakened zones within ilmenite crystals exhibit substitution of titanium by iron. The substitution of ilmenite by leucoxene is observed in cracks and weakened areas at crystal edges (figures 5b, c). There can be observed progressing isomorphism of iron by titanium (or increase of Ti content).

Micro-sized slightly rounded zircon crystals have a prismatic or elongated prismatic shape with pyramidal tips (figures 5d, e), indicating the formation of zircon in more acidic environment. Chemical composition of the main part of crystals contains no indication of isomorphic impurities.

The sample of heavy fraction contains tiny grains of monazite-(Ce) (figure 5f) and of mineral with pyrochlore composition (figure 6b).

The mineral composition of ilmenite concentrate contains ilmenite, quartz, hematite, oxides of Ti, V, leucoxene (pseudorutile).

Results of elemental chemical analysis (table 5) show that mineral sands of the Satpaev deposit are characterized by a predominance of light rare-earth elements (REE) in comparison to heavy REEs. Figure 7 shows REE contents of sample B-2 from the Satpaev deposit normalized to chondrite plotted together with the Akhmirovsk and Alabaster clay deposits situated about 230 km away and localized within the same Aral Formation.

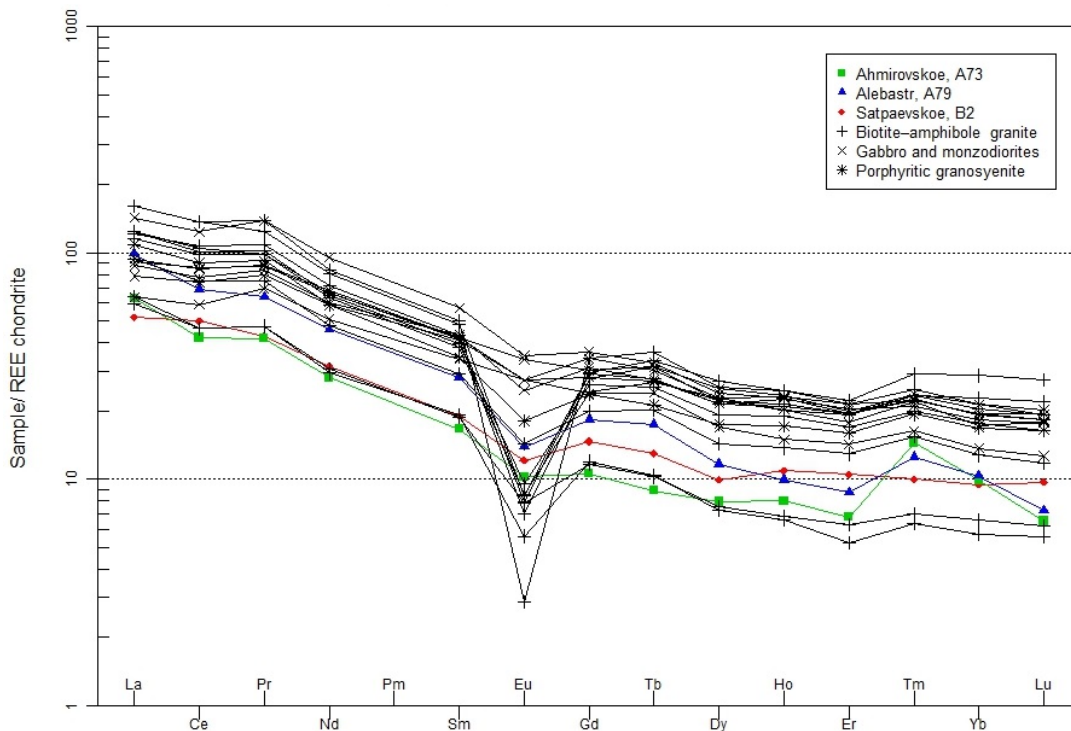


Figure 7 – Chondrite normalized REE patterns of the Satpaev Ti-Zr placer deposit (sample B-2) and two clay deposits also localized in the Aral Formation (Akhmirovsk deposit (sample A73) and Alabaster deposit (sample A79)). Potential source rocks of the Preobrazhensk intrusion (biotite-amphibole granites, gabbro and monzodiorite, porphyritic granosyenites) [25] are also plotted. Normalization values are after Nakamura (1974) [36]

REE patterns of all three deposits show negative Eu anomaly of samples and some tetrad effect, indicating relatively high degree of fractionation of their source rocks (figure 7). Samples of all three deposits are enriched in light rare-earth elements (LREE) in comparison with heavy rare-earth elements (HREE) and have similar LREE patterns compared to granitoids of the Preobrazhensk intrusion. Sample B-2 of the Satpaev deposit localized within the Aral Formation has REE patterns (both light REE and heavy REE) nearly parallel to the pattern of granitoids of the Preobrazhensk intrusion, whereas samples from the Akhmirovsk (sample A73) and Alabaster (sample A79) deposits show different behavior of heavy REEs. It can be concluded that granitoids and specifically gabbro and monzodiorites of the Preobrazhensk intrusion can be considered as source rocks of the Satpaev Ti-Zr placer but less likely of the Akhmirovsk and Alabaster deposits as behavior of heavy REE differs significantly. Therefore, distinct REE patterns exhibited by the Satpaev deposit can serve also as an exploration tool for similar deposits.

Classification diagram for sandstones (figure 8) shows that horizons of the Aral Formation have a polymictic composition that is typical for continental margins.

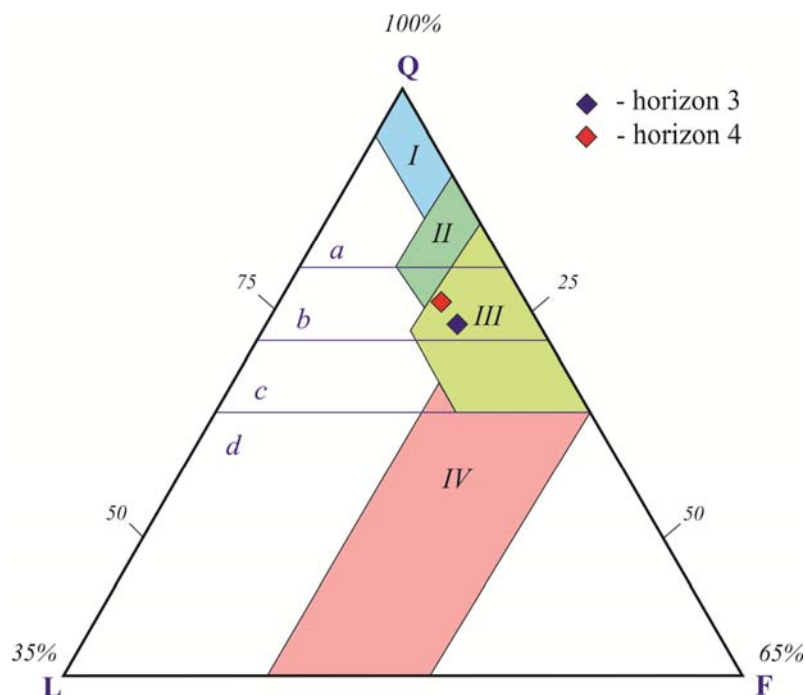


Figure 8 – Classification diagram for sandstones, after M.R. Bhatia (1983) [37]:

1. $Q = SiO_2$, $F = Al_2O_3 + CaO + Na_2O + K_2O$, $L = Fe_2O_3 + FeO + MgO + TiO_2$;
2. I-IV - sandstone fields: I - quartz, II - oligomictic, III - polymictic, IV - volcanoclastolithic [38];
3. Fields of arenaceous rocks characterizing (a) passive and (b) active continental margins, (c) marginal-oceanic and (d) intra-oceanic arcs

8. Conclusions. Mineralogical study of mineral sands from the Satpaev Ti-Zr placer deposit revealed that apart from quartz, albite, ilmenite and feldspars, also barite and a mineral of pyrochlore composition have been detected. Mineralogical investigation uncovered as additional mineralogical features the hexagonal shape of ilmenite crystals and development of leucoxenization processes along microcracks and crystal edges [39]. Microsized zircon crystals have prismatic or elongated-prismatic shape with pyramidal peaks.

Sample B-2 from the Satpaev placer is enriched in light rare earth elements (LREE) in comparison with heavy REEs. Generally, the content of REEs in sample B-2 has a similar range with the Akhmirovsk and Alabaster clay deposits that are also situated within the Aral Formation. However, their distribution patterns of heavy REEs are rather different and when compared with granitoids of the Preobrazhensk intrusion, similarities are evident only in LREE and HREEs patterns of the Satpaev Ti-Zr deposit only establishing that granitoids of the Preobrazhensk intrusion can be considered as likely source for the Satpaev placer deposit.

As a result of studying the geological framework of the Satpaev deposit the following main conclusions can be drawn:

a) geochemical features of the Satpaev deposit and the Preobrazhensk intrusion [24], which also determines structural position of the Satpaev ore field due to its location along the intrusion margin and in the areas of local tectonic faults, indicate that the Preobrazhensk intrusion can be considered as a source of the Satpaev placer deposit (figure 2);

b) REE patterns of sediments of the Aral Formation that contain mineral sands (e.g., Satpaev deposit) have a very distinctive character compared to barren sediments of the same Formation; therefore it can serve as an important exploration tool for Ti-Zr placers localized within this Formation;

c) formation and localization of ore minerals took place in the environment of chemical weathering caused by the marine transgression that began in the Meso-Cenozoic when the Zaisan depression was submerged. Sea regression began after the Oligocene, and as the result the clayey Aral Formation has been formed in the Miocene. All of these factors contributed to release of titanium-zirconium minerals, followed by their redeposition in local coastal continental conditions of warm and humid climate.

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ШЫҒЫС ҚАЗАҚСТАННЫҢ САТПАЕВ КЕНОРНЫНДАҒЫ Ti-Zr ТАУ ШАШАЛЫМДАРЫНЫҢ МИНЕРАЛОГИЯЛЫҚ-ГЕОХИМИЯЛЫҚ ЕРЕКШЕЛІКТЕРІ

Аннотация. Сәтпаев кенорнының (Шығыс Қазақстан облысы) ауыр фракциялы №1 Шашылымдар минералдық концентраты мен Ti-Zr кенді құмының минералдық-геохимиялық зерттеулеріне нақты деректер алынды. Кенді құмның минералдық құрамын зерттеу кезінде келесі минералдар белгіленді: кварц, альбит, ильменит, ҚДШ, барит, циркон, монацит және пироклорлы құрамды минерал. Минералдар электрондық микронзондтық талдауларды пайдалана отырып зерттелген. Ильменит және цирконмен ұсынылған кенді минералдардың кристалды морфологиясына минералогиялық зерттеулер барысында сипаттама берілді. Ильмениттердің минералдық химиялық құрамы зерттелді және кристалдар жиектері мен микро сызаттардағы олардың лейкоксенделуі анықталды. Өнімді горизонттардың геохимиялық ерекшеліктері ауыр сирек жерді (HREE) элементтермен және айқын теріс Eu ауытқумен салыстырғанда алғашқы жыныстардың жоғары фракциялау дәрежесін көрсететін жеңіл сирек жерді (LREE) элементтердің анық байытуын қамтиды. Преображенка интрузиясының гранитоидтары Сәтпаев шашыранды кенорнының ықтимал көзі болып табылады. Петрохимиялық зерттеулер нәтижелері кенді минералдардың окшаулануы жылы және ылғалды климатта, кейіннен қайта түзілуімен окшауланған континенттік жағалау жағдайында, титан мен циркон кенді минералдардың босап шығуына ықпал ететін химиялық мүжілу жағдайында болғанын көрсетеді.

Түйін сөздер: Сәтпаев Ti-Zr кенорны, Преображенский интрузиясы, жеңіл сирек жерлер элементтері, Шығыс Қазақстан.

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МИНЕРАЛОГО-ГЕОХИМИЧЕСКИЕ ОСОБЕННОСТИ Ti-Zr РОССЫПИ САТПАЕВСКОГО МЕСТОРОЖДЕНИЯ ВОСТОЧНОГО КАЗАХСТАНА

Аннотация. Получены фактические данные минералого-геохимических исследований Ti-Zr рудных песков и тяжелой фракции минерального концентрата Россыпи №1 Сатпаевского месторождения (Восточный Казахстан). При изучении минерального состава рудных песков установлены кварц, альбит, ильменит, КПШ; электроннозондовым микроанализом – микроразмерные кристаллы барита, циркона, монацита, мине-

рала пироклорового состава. Минералогическими исследованиями выявлена морфология кристаллов, рудных минералов ильменита и циркона, определен их химический состав и установлено развитие лейкоксенизации по микротрещинкам и краям кристаллов ильменита. Геохимические особенности продуктивных горизонтов включают явное обогащение легких редкоземельных элементов (LREE) по сравнению с тяжелыми редкоземельными элементами (HREE) и выраженную отрицательную аномалию Eu, которые указывают на высокую степень фракционирования исходных пород. Гранитоиды Преображенской интрузии являются вероятным источником Сатпаевского россыпного месторождения. Результаты петрохимических исследований указывают на то, что локализация рудных минералов происходила в условиях химического выветривания, которое способствовало высвобождению рудных минералов титана и циркона с их последующим переотложением в локальных континентальных прибрежных условиях, в обстановках теплого и влажного климата.

Ключевые слова: Сатпаевское Ti-Zr россыпное месторождение, Преображенская интрузия, легкие редкоземельные элементы, Восточный Казахстан.

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