

Mineralogical and Technological Features of the Titanium-Bearing Sandstones of the Pizhenskoye Deposit

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Abstract—The material composition of pseudorutile-leucoxene sandstones of the Pizhenskoye deposit is investigated. It is shown that the formation of minerals of this deposit occurred as a result of metamorphism of primary ilmenite under oxidative hydrothermal conditions with the participation of carbon dioxide, which proceeded with the removal of iron in the form of iron bicarbonate, followed by its transformation into siderite. The main titanium-containing phases formed during the weathering of ilmenite are pseudorutile ($(\text{Fe}^{2+}, \text{Fe}^{3+})_{2-n}\text{Ti}_3\text{O}_9$ (modified ilmenite) and leucoxene. As the iron was removed, the voids formed in the ore grains of ilmenite were filled with ultrafine quartz, which crystallized from the silica brought by hydrothermal solutions. The products of ilmenite alteration (siderite and iron oxides), as well as clay minerals, could be filtered by meteoric waters through quartz sand (or sandstone) into the lower layers, as a result of which the Pizhenskoye deposit acquired a layered structure. The upper layer is represented by gray-colored sandstones, characterized by a low content of ferrous minerals. The lower layer is red-colored ferruginous sandstones, and the intermediate layer is red-colored siltstones with a high content of clay and ferruginous minerals. Siderite, crystallizing from hydrothermal solutions in the form of a cementing bond, densely filled all the space and pores between the grains of mineral phases, as a result of which it is very difficult to open the ore phases even with fine grinding (<0.2 mm) of sandstones. In addition, siderite has magnetic properties. Therefore, its presence in the form of inclusions or growths on the surface of mineral phase grains affects their magnetic susceptibility and other physical properties. The combination of these factors complicates the application of physical methods for the enrichment of pseudorutile-leucoxene sandstones of the Pizhenskoye deposit.

Keywords: Pizhenskoye deposit, ilmenite-leucoxene sandstones, pseudorutile, leucoxene, quartz, siderite, hematite, zircon, wet disintegration, sludge

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INTRODUCTION

In November 2020, the Federal Agency for Subsoil Use approved the protocol of the State Commission on Mineral Reserves (FBU “GKZ”) on the discovery of the largest deposit of titanium ores and quartz sandstones of glasses quality in Russia by the user of the subsoil of JSC “Russian Titanium Resources” (JSC “RUSTITAN”). GKZ approved reserves in the amount of 300.4 million tons of titanium ores ($C_1 + C_2$), 345 million tons of quartz sandstones of glasses quality (C_2) on an area of 10.2 km². The estimated resources ($P_1 + P_2$) within the remaining area of 22.4 km² of the license amount to 1012.5 million tons of titanium ores. RUSTITAN company plans to start developing this

field in 2026. The field development project is included in the Development Strategy of the Arctic Zone of the Russian Federation until 2035 [1].

The Pizhenskoye deposit of pseudorutile-leucoxene-quartz sandstones is located on the Middle Timan in the Ust-Tsilemsky district of the Komi Republic, 80 km southwest of the district center. The geology and mineralogy of the deposit were previously studied in detail [2–7]. Ore deposits have a layered structure. The upper layer is represented by gray-colored sandstones, and the lower one is red-colored. Between them there is a transition layer of red-colored siltstones with a thickness of 60 to 100 cm. Layers and lenses of siltstones and mudstones are also part of the lower deposit of red-colored sandstones. Sandstones

Table 1. The yield of fractions during wet crushing of the core of different types of ores of the Pizhenskoye deposit

Type of sandstone	Average fraction yield, %, mm				
	>3	1–3	0.63–1	0.05–0.63	<0.05 (slime)
Gray-colored	15.35	8.65	3.04	57.25	15.71
Red-colored	11.76	6.98	3.42	55.62	22.22
Red-colored siltstones	4.15	7.74	4.28	59.47	24.36

have a complex polymineral composition. The main rock-forming mineral of sandstones is clastogenic sharp-angled quartz. The sandstones contain a significant amount of clay minerals—potassium mica hydromuscovite-sericite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) and kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). The content of TiO_2 in sandstones ranges from 2 to 13%, and in red-colored siltstones and mudstones 1–2%. The main titanium-containing phases are ilmenite FeTiO_3 proper (found only in gray-colored sandstones in the amount of 5–7% of the heavy fraction of titanium phases), modified metamorphosed ilmenite-pseudorutile $(\text{Fe}^{2+}, \text{Fe}^{3+})_{2-n}\text{Ti}_3\text{O}_9$, leucoxene $\text{TiO}_2 \cdot \text{SiO}_2$ and needle-shaped secondary rutile TiO_2 [3], which were formed as a result of changes in primary ilmenite under hydrothermal conditions. Secondary products of the hydrothermal process are siderite FeCO_3 , goethite FeOOH and hematite Fe_2O_3 . Zircon and rare-earth minerals monazite-kuralite, xenotime and florencite are present in small amounts in sandstones as associated useful components [3].

The purpose of this report is to characterize the features of the mineral and material composition of the pseudorutile-leucoxene sandstones of the Pizhenskoye deposit, which are very important for creating an effective technology for processing the ore of this deposit with the production of high-quality titanium raw materials and with the associated extraction of other valuable components.

EXPERIMENTAL

Sixty-eight ore core samples from 27 exploration wells were selected for research. 23 samples of gray-colored sandstones from the middle pack, 36 samples of red-colored sandstones from the lower pack and 9 samples of red-colored siltstones from the lower pack were studied. Taking into account the fact that the hardness of leucoxene and pseudorutile (3–4 on the Mohs scale) is significantly less than the hardness of quartz (7), to avoid over-grinding of their brittle grains, the disintegration of core samples was carried out by wet crushing under a press. All samples after crushing were separated from the sludge, dried at

100°C and classified to determine the yield of large (>0.63 mm) and small (0.05–0.63 mm) fractions.

In addition, crushed samples of gray-colored and red-colored sandstones presented by the customer of the work were used for technological research. It should be noted that the names “gray-colored” and “red-colored” refer to two layers of the deposit and are to some extent conditional. So, in samples of gray flowers, there are samples with pink and red spots, and in red-colored samples—with gray ones.

To study the material composition of the presented sandstone samples and their enrichment products, chemical X-ray diffraction (X-ray fluorescence wave research spectrometer “MagiX PRO PANalytical,” IGEM RAS) and microprobe (Jeol JSM-6480LV, MSU) X-ray phase analysis, as well as morphological (microscopic, electron microscopic) research methods were used.

RESULTS

A characteristic feature of all ore samples is that when they are pre-wetted with water, samples of all types of ores are relatively easily crushed to form a loose material in the form of sand with a grain size of 0.05–0.63 mm. At the same time, the clay sludge is easily separated from the sand during deslamation. During wet disintegration of ore core samples, regardless of the type of ore, the yield of fractions varies widely. The average yield of different fractions during core crushing is shown in Table 1. Thus, the yield of the fine fraction (0.05–0.63 mm) on average for gray-colored sandstones is 57.25%, for red-colored sandstones—55.62%, and for red-colored siltstones—59.47%. The yield of sludge from gray-colored sandstones is at the level of 15.7%, from red-colored sandstones—22.2%, and from red-colored siltstones—24.4%. The yield of a large fraction (>0.63 mm) from gray-colored sandstones is 27%, red-colored sandstones—22%, and red-colored siltstones—16%.

Thus, during the wet disintegration of sandstones, the yield of the fine fraction (0.05–0.63 mm) is on average 55–60%, 15–25% falls on the share of the large fraction (>0.63 mm) and the same amount on the share of the sludge with a fineness of <0.05 mm.

Table 2. Average chemical compositions of slurries obtained by wet crushing of different types of sandstones of the Pizhemskeye deposit

Sludge samples	Content of components, wt %									
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	K ₂ O	Zr	Nb	Y	Ce
SH-GS	57.66	3.31	19.95	6.10	0.071	3.79	0.032	0.004	0.008	0.016
SH-RS	54.01	2.87	19.97	8.69	0.043	4.25	0.032	0.003	0.009	0.020
SH-RSil	53.83	2.64	19.59	9.62	0.031	4.13	0.032	0.003	0.010	0.019

The chemical compositions of the sludge are shown in Table 2. The main components of sludge are oxides of silicon, aluminum, iron and potassium. According to X-ray phase analysis, the mineral composition of the sludge is represented by clay minerals (kaolinite and hydromuscovite), as well as goethite, hematite and siderite. Titanium oxides are present in significant quantities (on average about 3%), and in small quantities Zr, Nb, REE in the form of zircon, columbite, monazite, xenotim [4].

The general appearance of small fractions (0.05–0.63 mm) obtained by wet crushing of sandstones is shown in Fig. 1. Small fractions of gray-colored sandstones consist mainly of free quartz grains (Figs. 1a, 1b). Quartz has different color shades: colorless transparent, yellowish, pink and reddish. The fractions contain pseudorutile grains of dark gray or black color and leucoxene of gray or yellowish color.

The grains of leucoxene and pseudorutile have a porous structure, and consist of a sagenite lattice of rutile filled with fine quartz (Fig. 2). Leucoxene contains 55–70% TiO₂ and 25–40% SiO₂, and pseudorutile—50–55% TiO₂ and 15–20% SiO₂.

Unlike the gray-colored ones, the fine fractions from the samples of red-colored sandstones have a more complex mineral composition. In addition to quartz and titanium minerals, they contain a large number of loose, but relatively strong brick-red agglomerates (Figs. 1c, 1d). They are formations of fine fractions, and with weak manual crushing they turn into powder. According to the XRD analysis, these agglomerates consist of an almost homogeneous mixture of fine quartz, hematite and clay minerals (kaolinite and hydromuscovite). The chemical composition of such agglomerates is as follows (wt %): 52 SiO₂, 0.9 TiO₂, 19.8 Fe₂O₃, 14.1 Al₂O₃, 3.3 K₂O and 8.3 LOI. In chemical composition, these loose formations are close to sludge, but with a higher content of iron oxides. They have magnetic properties and during magnetic separation, together with pseudorutile and

other iron-containing minerals of titanium [3, 4], they are separated into a magnetic fraction. This circumstance requires the use of additional operations to purify the magnetic fraction from these formations to obtain a pseudorutile concentrate.

In the fine fraction of red-colored sandstones, almost all granular quartz is colored pink-red, probably due to the presence of impurities of iron oxide compounds (siderite, goethite and hematite). In this fraction, minerals are present mainly in the form of aggregates.

During the wet disintegration of red-colored siltstones, the resulting fractions are very similar in general appearance to the fractions from red-colored sandstones (Figs. 1d, 1f). But in siltstones there is much less fraction with a grain size of >3 mm and more sludge.

Large pieces are characterized by a higher hardness, which can create certain difficulties in preparing the ore for further enrichment.

Morphological analysis of large fractions (>0.63 mm) of all types of sandstones showed that these fractions are represented by grains of free quartz and agglomerates of different shapes and sizes. Quartz grains are either transparent or have a yellow color, their size reaches 3–10 mm. For clarity, shows images (Fig. 3) of several samples of the largest fractions (>3 mm).

The microstructures of agglomerates from large fractions of gray-colored sandstones were studied using optical microscopy (Fig. 4). It is clear that in the agglomerates, quartz grains (gray) and titanium minerals with high reflectivity are tightly cemented together by a binding component (siderite), which has a light gray color in the photos. Clay minerals (dark color) cement agglomerates of quartz grains and ore minerals. The chemical composition of mineral phases in agglomerates was determined using microprobe analysis. Three samples from gray-colored sandstones were analyzed. The microstructures of these samples with the location of the analyzed points

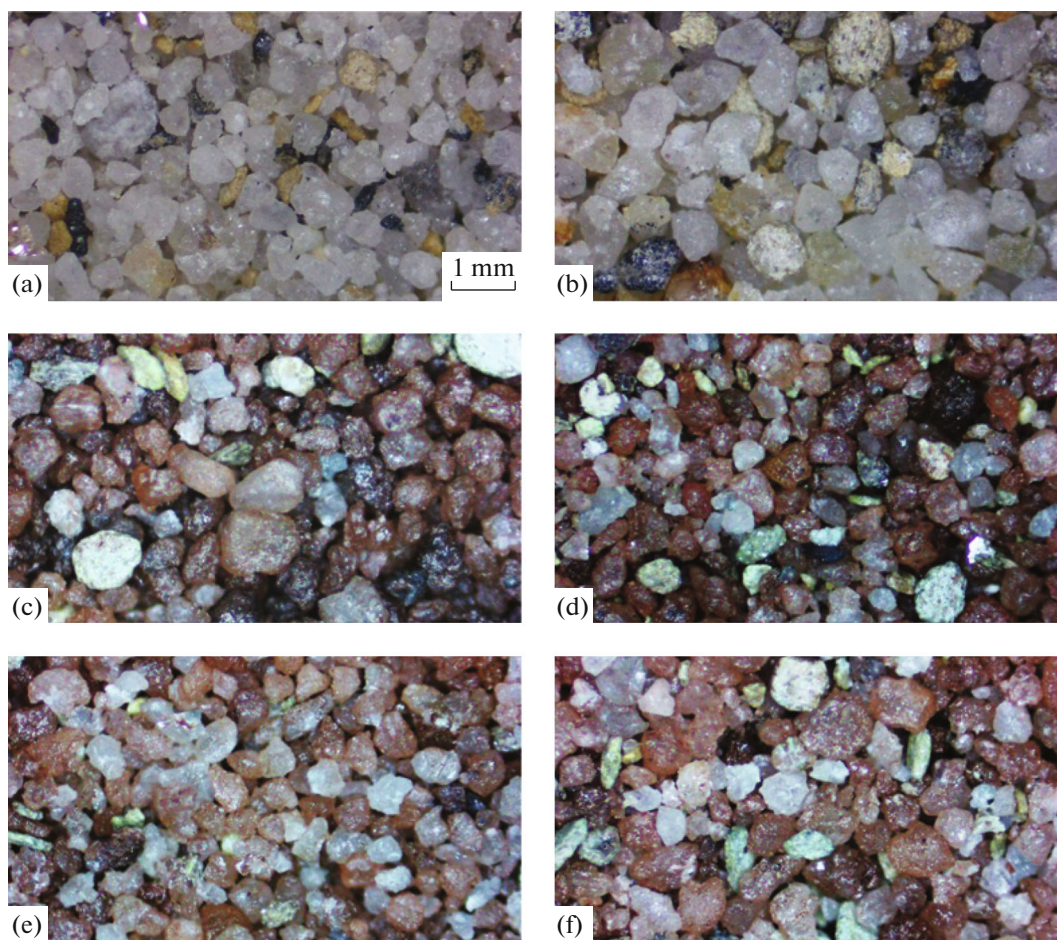
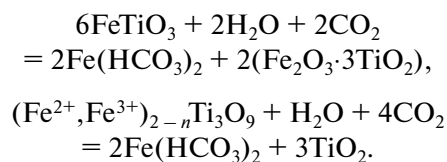


Fig. 1. General view of small fractions (size 0.05–0.63 mm) obtained by wet crushing of pseudorutile-leucoxene sandstones: (a, b) gray-colored; (c, d) red-colored; (e, f) red-colored siltstones. Dark gray and black grain—pseudorutile; gray or light matte—leucoxene.

and areas are shown in Fig. 5, and the chemical compositions of the mineral phases with the indication of the analysis point are shown in Table 3. According to the data obtained, a dense cementing mass (gray) between the grains of the mineral phases consists of siderite. Siderite has a variable chemical composition. Pure siderite in the photos has a light gray color, and siderite with a higher content of isomorphous impurities of magnesium and manganese looks darker. The content of MgO in siderite varies in the range of 0.3–6.3%, and MnO—0.2–4.1 wt %.

Siderite tightly fills all the space and pores between hard grains in agglomerates. The grains of pseudobrutite and leucoxene in most cases do not have clear boundaries and are very strongly impregnated with siderite ligament. The areas in agglomerates where siderite is absent are filled with loose clay minerals (hydromuscovite and kaolinite), as well as hematite. The siderite cementing bond makes the agglomerates more durable and therefore, during the wet disintegration of sandstones, they retain their structure.

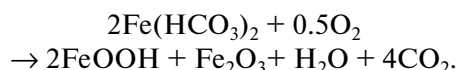
Based on the study of the mineral and material composition of sandstones, it was found that the metamorphic change of ilmenite occurred under hydrothermal conditions with the participation of carbon dioxide with the removal of iron in the form of water-soluble iron bicarbonate by reactions:



$\text{Fe}(\text{HCO}_3)_2$ is a poorly soluble and unstable compound, and when the pressure decreases, CO_2 easily decomposes to form orange-red siderite:



In the presence of oxygen, $\text{Fe}(\text{HCO}_3)_2$ is oxidized to form goethite and hematite:



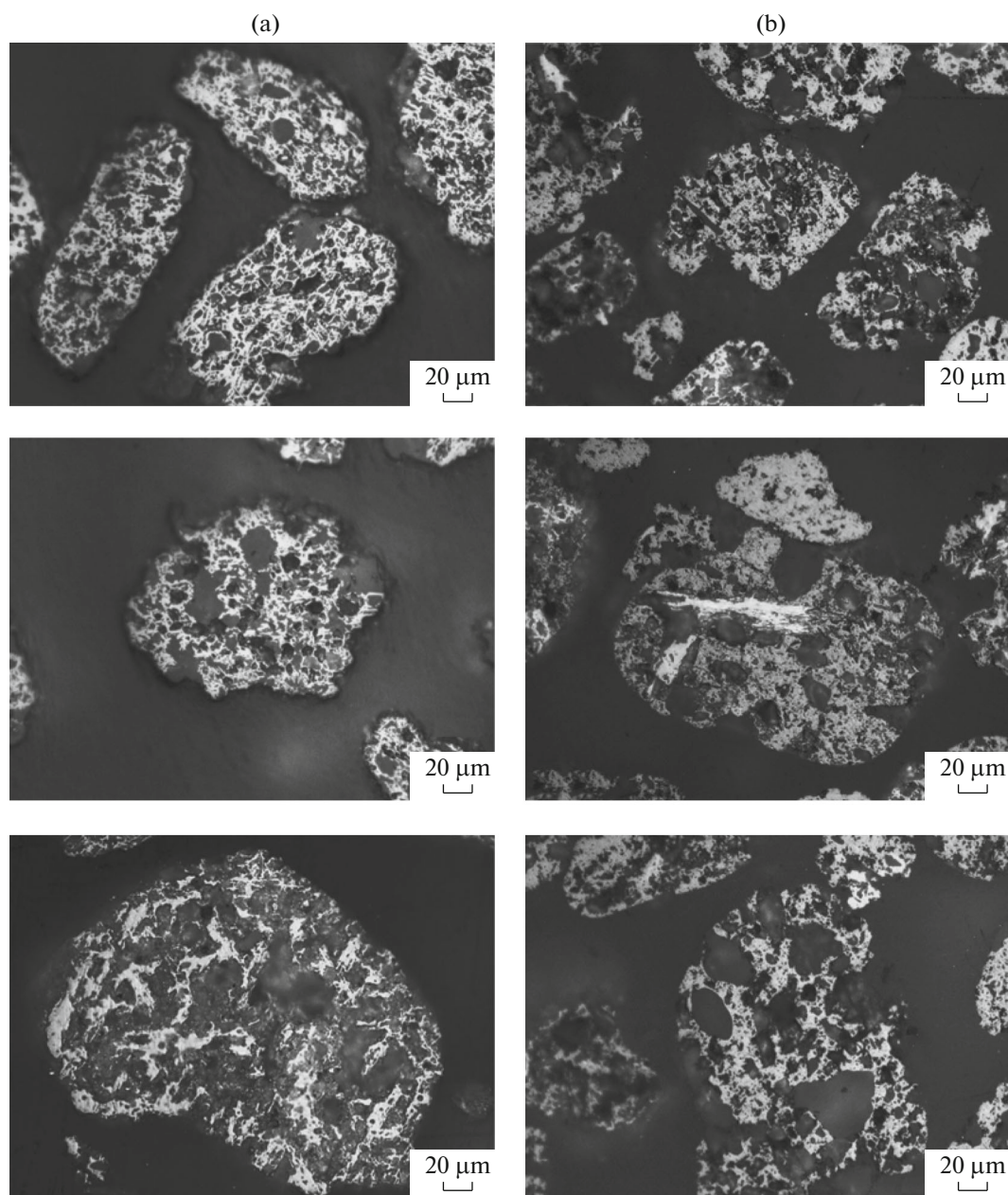


Fig. 2. Microstructures of leucoxene (a) and pseudorutile (b) grains: light—rutile and pseudorutile; dark gray inclusions—quartz.

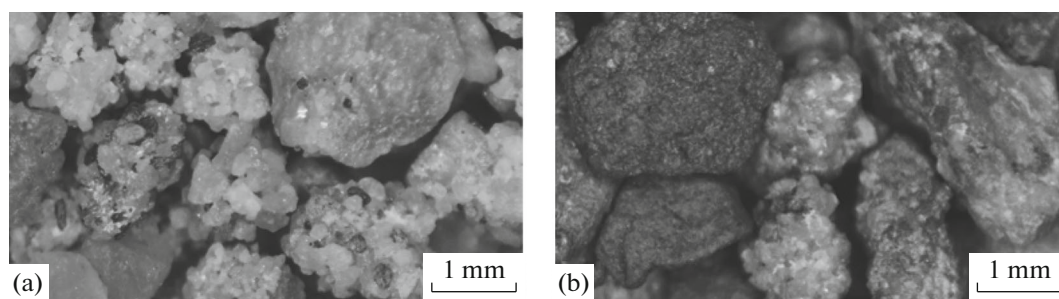


Fig. 3. General view of agglomerates in large fractions (>1 mm) of gray-colored (a) and red-colored (b) sandstones.

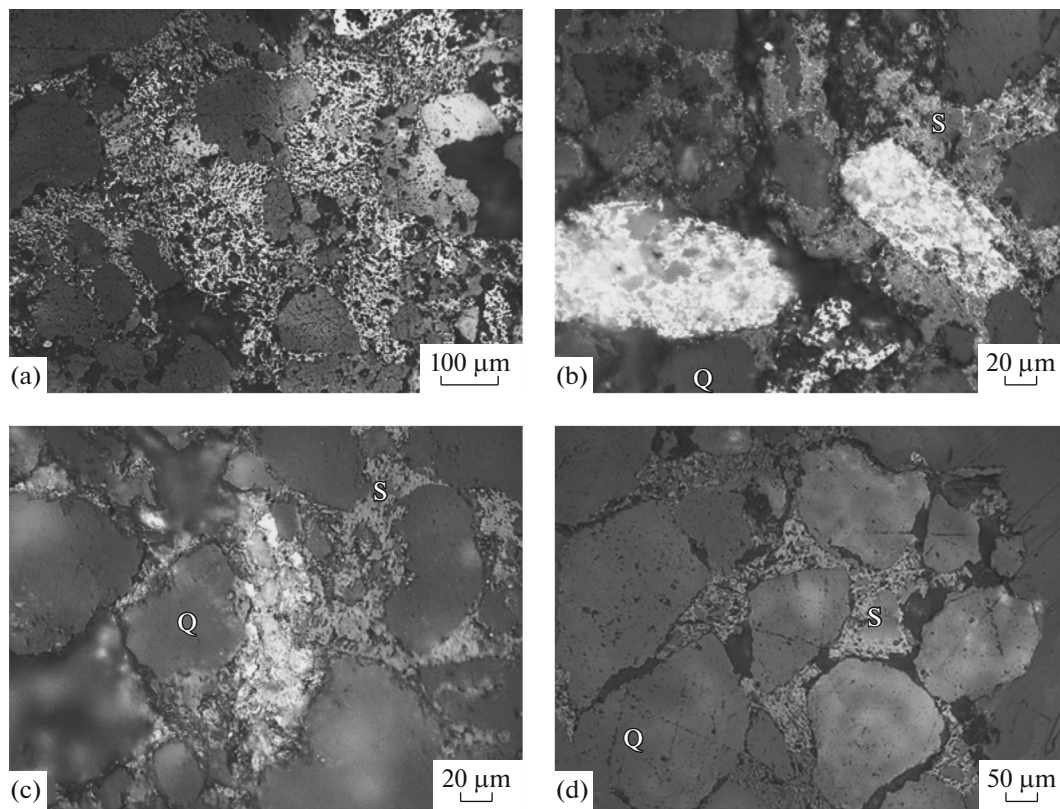


Fig. 4. The structure of aggregates in large fractions obtained by wet disintegration of gray-colored sandstones. Light gray cementing bond between quartz grains (Q), siderite (S); white—leucoxene, black between grains—clay minerals.

At the same time, along with the removal of iron, the voids formed in the ilmenite grains were filled with ultrafine quartz formed from dissolved silica brought by hydrothermal solutions (Fig. 2). Such metasomatic pseudomorphic substitution occurs without changing the volume, but with the preservation of the morphology (in the form of envelopes) of the primary ilmenite mineral.

As a result of the decomposition of ilmenite, the resulting iron bicarbonate in the form of an aqueous solution is filtered through quartz sand (sandstone) and accumulates in the lower layers and, decomposing, turns into siderite. Subsequently, iron hydroxides and partially clay minerals formed as reaction products are washed away from the upper layers of sandstones by meteoric water, which leads to a significant

Table 3. Results of microprobe analysis of agglomerates from large fractions of gray-colored sandstones

Samples	Analysis point	Phases	Component content, wt %								
			TiO ₂	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	K ₂ O	MnO	MgO	CaO
1	1	Siderite	<0.01	59.16	—	0.04	0.02	—	0.21	—	0.45
	2	Siderite	—	68.21	—	0.51	0.21	0.08	0.57	0.30	0.78
	3	Muscovite	0.55	3.74	—	52.67	32.90	10.34	0.04	1.40	0.07
	4	Siderite	—	49.36	—	—	—	—	3.96	6.28	0.21
2	1	Pseudorutile	59.32	—	37.70	0.24	0.07	—	2.71	—	—
	2	Siderite	1.60	52.26	—	—	—	—	4.14	3.87	0.27
	3	Rutile	97.97	—	0.36	0.71	0.28	—	—	—	—
3	1	Goethite	—	—	88.84	0.60	—	—	0.95	0.62	0.66
	2	Siderite	—	59.28	—	—	—	—	0.93	0.12	0.28
	3	Rutile	98.92	—	0.90	0.38	—	—	—	—	0.04

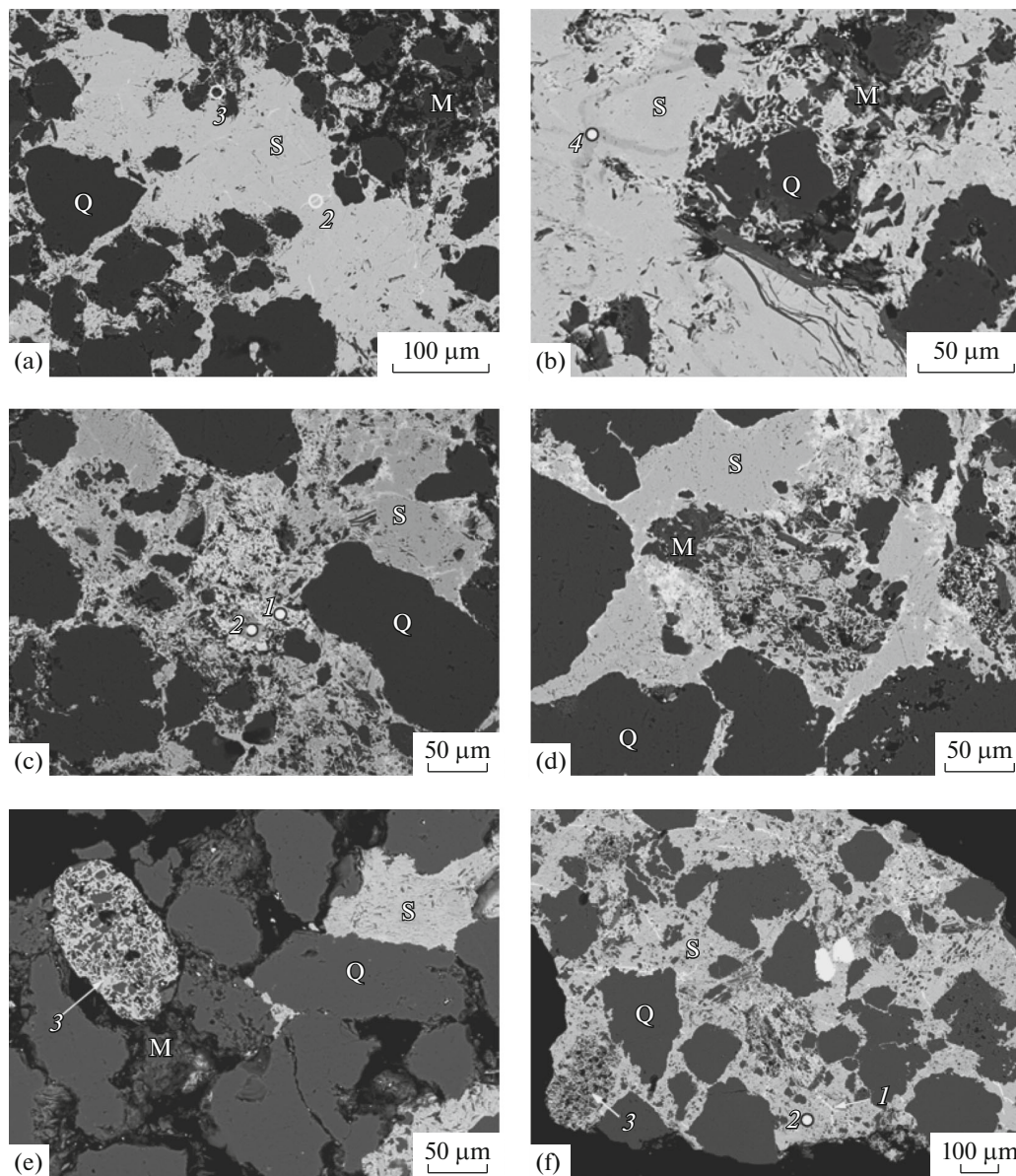


Fig. 5. The location of the analyzed points and areas on micrographs of large fractions of samples of gray-colored sandstones (1—(a, b); 2—(c–d); 3—(e)). Q—quartz, S—siderite, M—hydromuscovite.

enrichment of the upper layers with titanium. Therefore, in the upper layers of the deposit, sandstones contain a significantly lower amount of siderite and iron oxides, and with an increase in the depth of the ores (in the lower part), their content increases. As a result of these processes, the upper layers of sandstones remain gray, and the lower ones are colored red by iron-containing minerals. At the same time, as the clay minerals are filtered through the loose upper sand layer, together with iron oxides (goethite and hematite), settle in the form of silt over red-colored sandstones, or inside this thickness, they form an intermediate layer and lenses that are difficult to filter—the so-called red siltstones and mudstones. Due to the exces-

sive amount of clay minerals and iron oxides (sludge) in the intermediate layers (in siltstones), the content of titanium and quartz is lower than in the upper and lower layers of sandstones. Thus, the combination of these factors contributed to the formation of the layered structure of the pseudorutile-leucoxene sandstones of the Pizhenskoye deposit.

DISCUSSION

Metamorphogenic titanium deposits with leucoxene (the most famous of which is the Yarega oil and titanium) according to the classification of L.P. Tigunov, L.Z. Bykhovsky, L.B. Zubkov [8], they

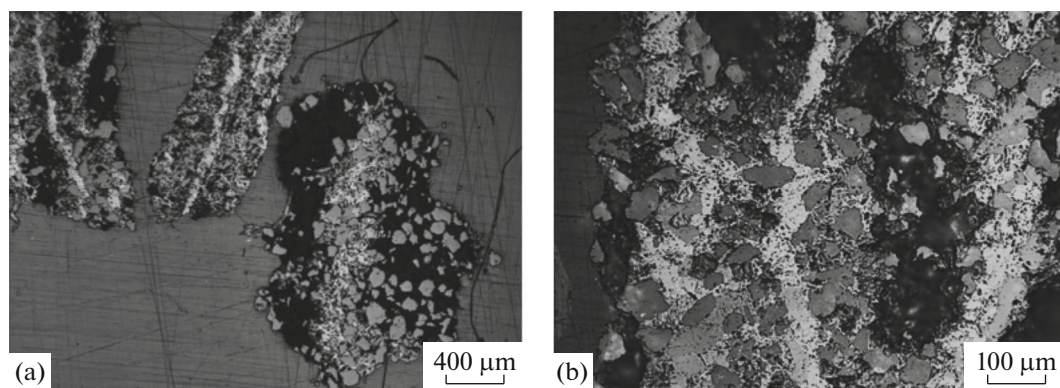


Fig. 6. Siderite bundle in the form of veins (light) in gray-colored sandstones. The black between the quartz grains is clay minerals.

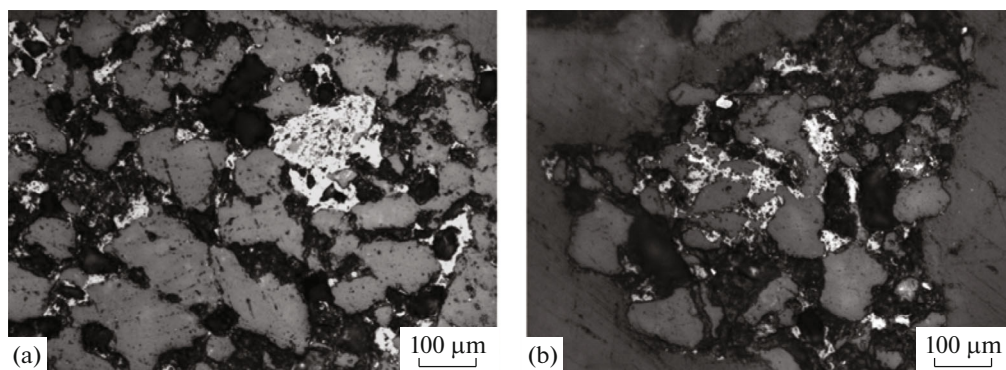


Fig. 7. A characteristic cementing bond (black) of siderite, hematite and clay minerals in red-colored sandstones.

belong to leucoxene-quartz (according to the main mineral forms) indigenous deposits. The Pizhenskoye deposit differs from the Yarega deposit in a more complex polymineral composition. In the Pizhenskoye deposit, due to the spread of titanium phases, pseudorutile and leucoxene are the main ones, there are no such deposits anywhere else in Russia and the World—it is unique in terms of reserves and mineral composition of ores.

Based on the study of core samples, it should be noted that the formation of siderite in sandstones occurred both throughout the entire volume and through a network of thin hydrothermal veins (cracks), along which carbon dioxide diffused from bottom to top. As the siderite was formed, it crystallized in the form of a volumetric cementing bond and thin (1–2 mm) veins along the cracks between the grains of minerals in the sandstones. This is clearly seen in the core samples from the upper layers of (gray-colored) sandstones (Fig. 6). In the lower layers (in siltstones and red-colored sandstones), such veins are not observed due to a significant increase in the amount of siderite. Siderite veins in the upper layers of titanium-bearing sandstones, as well as even greater concentrations of siderite, hematite and clay minerals

in the lower layers of the ore strata form a strong cementing mass (Fig. 7), which indicates a long-term hydrothermal processing of titanium-bearing strata with the participation of carbon dioxide in an oxidizing atmosphere. This is quite consistent with the results of early studies [3]. The source of the ore substance could be weathering crust along the areal vein fields of lamprophyres known on the Chetlas Ridge of the Middle Timan and assumed in the Neoproterozoic quartzite-shale thickness of rocks under the Pizhenskoye deposit. The evidence of this assumption is a completely identical set of accessory and rock-forming minerals and their indicator typomorphic features established in lamprophyres and titanium-bearing Pizhenskoye sandstones [3].

The crystallization of siderite from hydrothermal solutions has led to the fact that it is less or more present in the form of rims, growths or inclusions in all minerals in contact with it. Therefore, even in small fractions (0.05–0.63 mm) obtained during the disintegration of sandstone samples, especially red-colored ones, the necessary degree of mineral disclosure does not occur (Fig. 8).

Siderite has magnetic properties, like ilmenite and iron-containing products of its change (pseudorutile

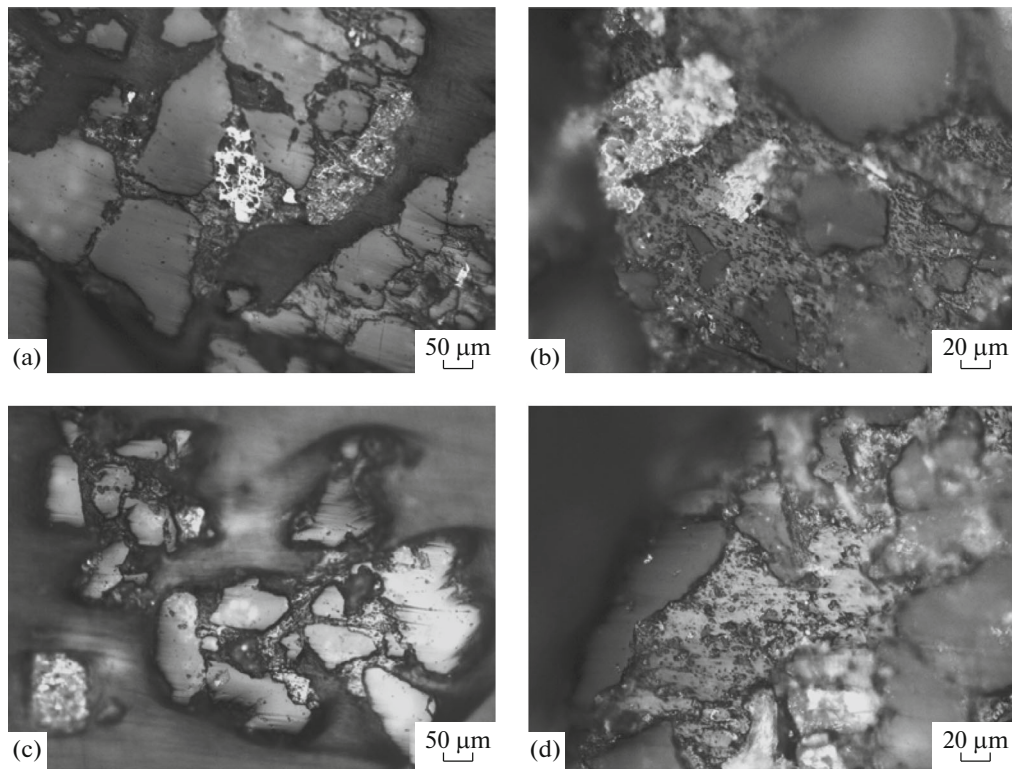


Fig. 8. Structures of aggregates in small fractions (<0.63 mm) obtained during wet disintegration of gray-colored (a, b) and red-colored (c, d) sandstones.

and other iron-containing products [3, 4]). Siderite is released into the magnetic fraction at a magnetic field intensity of ≥ 0.25 T. In the magnetic fractions of crushed sandstones, especially red-colored ones, there are practically no free pseudorutile grains, since they are in the form of aggregates with a cementing bond of siderite (Fig. 9).

The behavior of siderite was studied during sequential magnetic separation, crushed to a grain size of <0.2 mm and de-cluttered samples of gray-colored sandstones, at a magnetic field intensity in the range of 0.45–1.7 T. The chemical compositions of the magnetic fractions are shown in Table 4. As can be seen from these data, the highest content of iron oxide (36–

Table 4. Results of magnetic separation of a crushed sample of gray-colored sandstones (size <0.2 mm) without slime

Intensity, T	Content of components, wt %							
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	CaO	MgO	K ₂ O
0.45	44.03	4.45	1.99	37.30	0.784	0.47	0.52	0.43
0.50	36.61	14.57	1.85	35.67	1.067	0.27	0.46	0.48
0.55	39.17	20.04	1.78	27.78	0.951	0.20	0.35	0.50
0.60	34.75	26.64	2.11	26.43	1.034	0.19	0.34	0.58
0.70	36.34	29.20	2.18	22.62	0.943	0.15	0.30	0.59
0.80	35.52	32.51	2.28	19.24	0.849	0.18	0.30	0.63
1.70	40.41	34.47	2.60	12.63	0.550	0.11	0.24	0.66

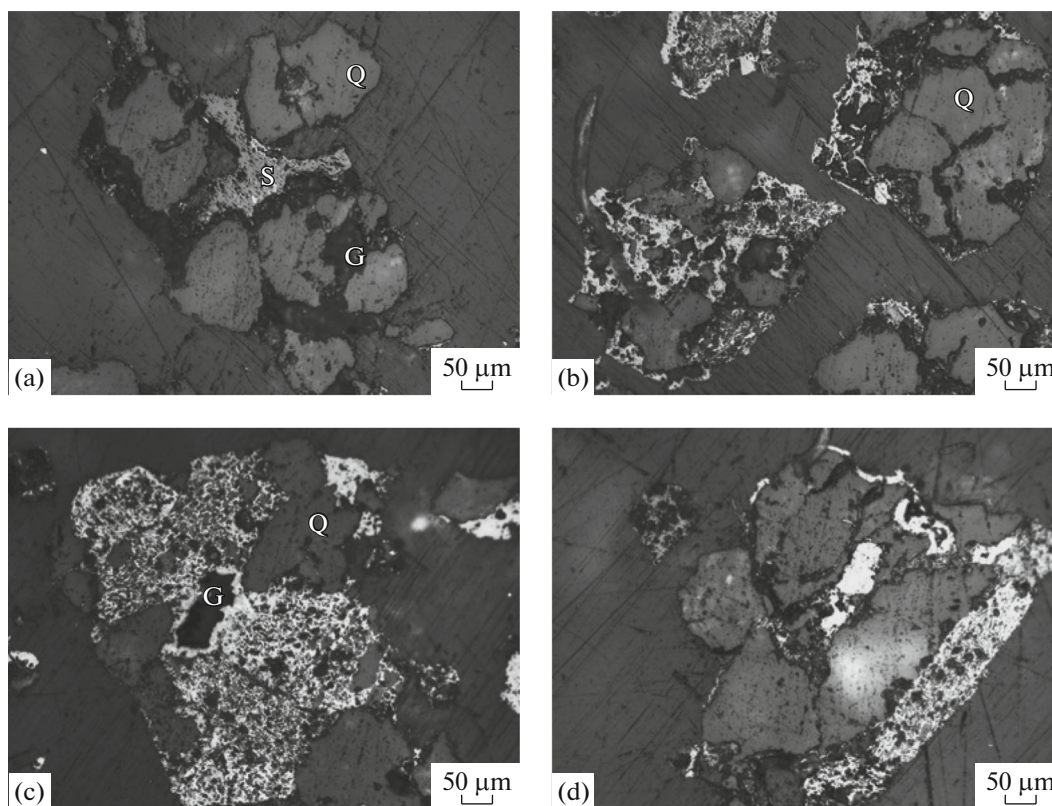


Fig. 9. Structures of aggregates in the magnetic fraction (0.05–0.63 mm) of red-colored sandstones. White mesh formations—leucoxene and pseudorutile; light—leucoxene; dense gray—quartz (Q); gray—cementing bond between grains—siderite (S), dark—hematite with clay (G).

37%) was noted in the magnetic fractions obtained at a intensity of 0.45 and 0.5 T. In these fractions, the TiO_2 content is very low and is in the range of 4.45–14.57%. With an increase in the magnetic field intensity from 0.5 to 1.7 T, the Fe_2O_3 content gradually decreases from 35.7 to 12.63, and TiO_2 increases from 14.57 to 34.47 wt %.

X-ray phase analysis showed that siderite is mainly released at a magnetic field intensity in the range of 0.45–0.60 T. In the magnetic fraction at 0.7 T, the content of siderite decreases markedly. A significant release of pseudorutile occurs at 0.6 T and above. At 0.45–0.50 T, its content in the magnetic fraction is significantly less. In all magnetic fractions, there is a lot of quartz due to the presence of accretions or films of siderite on its grains. Clay minerals and hematite are present in the splices.

Figure 10 shows micrographs of particles of magnetic fractions (<0.2 mm) obtained at 0.8 T from crushed gray- and red-colored sandstones without slime. It is clearly seen that even when crushing to a fineness of <0.2 mm, there is no full disclosure of minerals. These fractions are mainly represented by aggregates and various types of aggregates. The magnetic

fraction of red-colored sandstones in the aggregates contains a much larger amount of cementing bond, which consists of siderite, hematite and clay minerals.

On the other hand, the finer the grinding, the greater the losses of titanium with fine fractions (sludge), which significantly reduces the technical and economic indicators of sandstone enrichment. Therefore, we consider fine grinding of ore during the enrichment of siderite-leucoxene sandstones to be inappropriate. Another more effective way of destroying aggregates and getting rid of siderite ores should be found.

Thus, the presence of siderite, as well as hematite in the form of aggregates or edges on the surface of mineral grains significantly affects their magnetic susceptibility, as well as other physical properties, which greatly complicates the effective use of physical methods for enriching pseudorutile-leucoxene sandstones. Taking into account this problem, it was necessary to develop a set of new non-standard approaches to ore processing at the Pizhenskoye deposit, the largest in Russia, aimed at obtaining high-quality titanium raw materials with high recovery rates for titanium and other valuable related elements [9]. The results of

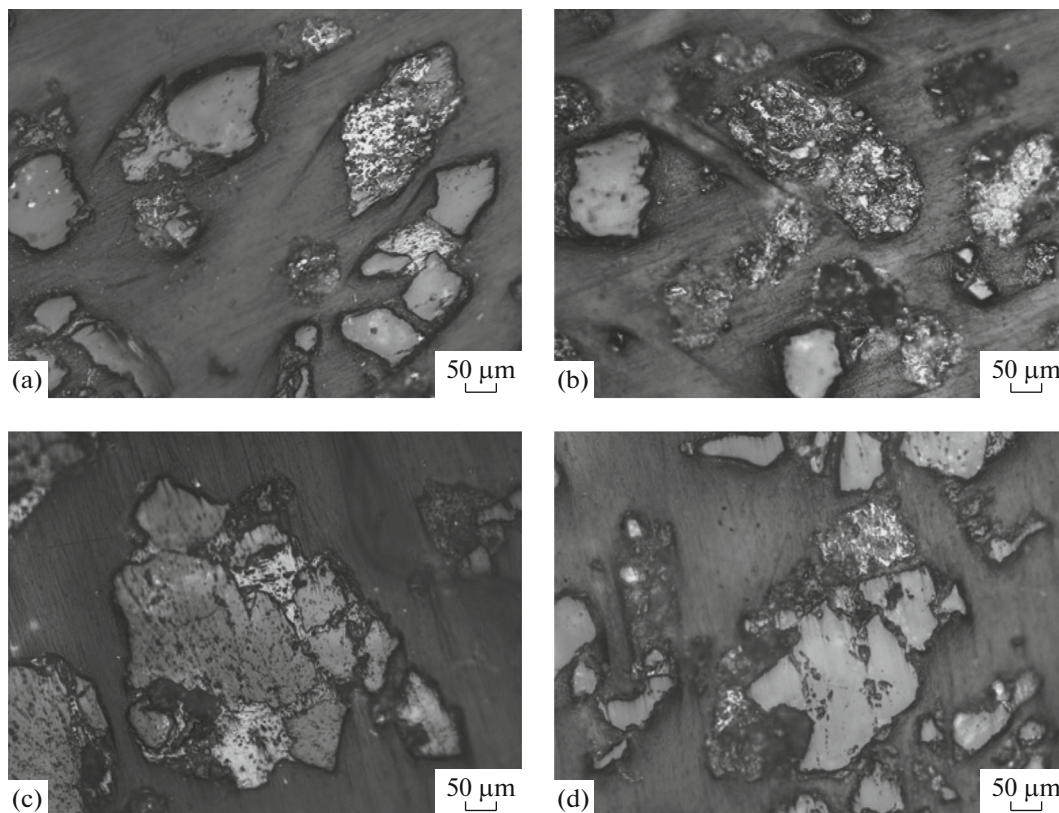


Fig. 10. Structures of particles of magnetic fractions (<0.2 mm at 0.8 T) from gray-colored (a, b) and red-colored (c, d) sandstones. Grains with white spots are pseudorutile; gray dense grains are quartz.

these studies will be reported in the following publications.

CONCLUSIONS

(1) The material composition of the sandstones of the Pizhenskoye deposit was studied and differences in the quantitative mineral composition of the upper gray-colored sandstones from the lower red-colored ones were established. The two mineral-technological types of sandstones differ in a large content of cementing ligament (clay minerals kaolinite and hydromuscovite, siderite and hematite) in the lower red-colored and a large content of quartz and useful titanium phases (rutile, ilmenite, pseudorutile, leucoxene), as well as rare-earth (monazite-kularite, xenotime) and rare-metal (zircon and ilmenorutile) in the upper gray-colored.

(2) During the formation of the deposit, the processes of ilmenite metamorphism occurred with the gradual removal of iron according to the scheme: $\text{FeTiO}_3 \rightarrow \text{pseudorutile } (\text{Fe}^{2+}, \text{Fe}^{3+})_{2-n}\text{Ti}_3\text{O}_9\cdot\text{SiO}_2 \rightarrow \text{leucoxene } \text{TiO}_2\cdot\text{SiO}_2 \rightarrow \text{TiO}_2$ under hydrothermal conditions with the participation of carbon dioxide (siderite is formed as an additional product), and the

oxidation of siderite leads to the formation of FeOOH goethite and hematite (Fe_2O_3). The removal of iron from ilmenite occurs with the formation of poorly soluble iron bicarbonate, which then, decomposing, turns into siderite FeCO_3 , which has magnetic properties.

(3) In the Pizhenskoye deposit, due to the spread of titanium phases, pseudorutile and leucoxene are the main ones, there are no such deposits anywhere else in Russia and the world—it is unique in terms of reserves and mineral composition of ores. Therefore, it should be attributed to a new genetic type—metamorphogenic indigenous deposits with their own name—pseudorutile-leucoxene-quartz.

(4) It was found that the formation of siderite occurred throughout the entire volume of the sandstone strata, as well as with the formation of a grid of thin hydrothermal veins (along cracks), along which carbon dioxide diffused from the bottom up. As the siderite was formed, it became a cementing bond of all the grains of minerals. Therefore, siderite is less or more present in the form of edges, accretions or inclusions in all minerals and phases in contact with it. The presence of siderite in the ore, firstly, significantly reduces the indicators for the disclosure of mineral

phases during the disintegration of sandstones and, secondly, affects the magnetic susceptibility and other physical properties of minerals. The combination of these factors complicates the application of physical methods of enrichment of pseudorutile-leucoxene sandstones of the Pizhenskoye deposit.

REFERENCES

1. The development of the Pizhenskoye titanium deposit, the largest in Russia, is planned from 2026, TASS. <https://tass.ru/ekonomika/10247289>. Sited December 14, 2020 [in Russian].
2. V. D. Ignatiev and I. N. Burtsev, *Leikoxen Timana: Mineralogy and Problems of Technology* (Nauka, St. Petersburg, 1997) [in Russian].
3. A. B. Makeyev, "Typomorphic features of minerals of titanium ores of the Pizhenskoye deposit," *Mineralogy*, No. 1, 24–49 (2016).
4. A. B. Makeyev and V. P. Lutoev, "Spectroscopy in technological mineralogy. The mineral composition of titanium ore concentrates Pizhenskoye deposit (Middle Timan)," *Obogaschenie rud*, No. 5, 33–41 (2015).
5. A. B. Makeyev, V. A. Dudar, G. S. Samarova, L. Z. Bykhovsky, and L. P. Tiginov, "Pizhenskoye titanium deposit (Middle Timan): aspects of the geological structure and development," *Rudnik buduschego* No. 1 (9), 16–24 (2012).
6. A. B. Makeyev, "Pizhenskoye titanium deposit, features of the geological structure and composition of ores," in *Mineral Resource Base of High-Tech Metals. Development, Reproduction, Use: Materials Scientific-Practical Conf.*, Ed. by A. B. Makeyev and G. B. Sadykhov (FSBI "VIMS", Moscow, 2020), pp. 135–140 (in Russian).
7. A. M. Plyakin, *Placers of Timan. History of Study, Deposits, Annotated Chronobibliography: Textbook. Manual* (UGTU, Ukhta, 2014) (in Russian).
8. L. P. Tiginov, "Titanium ores of Russia: state and prospects of development," in *Mineral Raw Materials, Geological and Economic Series*, Ed. by L. P. Tiginov, L. Z. Bykhovsky, and L. B. Zubkov (VIMS, Moscow, 2005), No. 17 (in Russian).
9. G. B. Sadykhov, "Fundamental problems and prospects of using titanium raw materials in Russia," *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.* **63** (3–4), 178–194 (2020).