ORIGINAL ARTICLE

DOI: https://doi.org/10.18599/grs.2023.3.10 Russian Original 2023. Vol. 25. Is. 3. Pp. 163–174

Pseudorutile-leucoxene-quartz ores of Timan – a new genetic type of titanium raw materials: prospects for industrial development

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Abstract. The two largest deposits of Russia – Yaregskoye and Pizhemskoye belong to the same genetic type; hydrothermal-metamorphic indigenous deposits. They are located in the same Timan structure at a distance of no more than 230 km from each other. According to the total approved reserves and forecast resources of titanium dioxide, they are approaching 60% of the all-Russian and will form the basis of industrial titanium raw materials used in Russia in the near future. In the interests of technological mineralogy, morphological features, internal structure, chemical composition of grains of the two main titanium mineral phases – leucoxene and pseudorutile, TiO_2 polymorphs, as well as the composition of mineral microinclusions in these phases have been studied in detail. The compositions of all mineral phases in polished preparations of leucoxene and pseudorutile were analyzed by SEM-EDS method at the Institute of Geology and Geochronology of the Precambrian of the RAS, 147 chemical analyses were obtained at the point (3 μk) and many images of polished grains of anatase, leucoxene and pseudorutile were scanned over the area (20×20 μk). In the leucoxene grains themselves, 12 mineral phases were diagnosed and characterized in the form of inclusions: pseudorutile, rutile, anatase, quartz, hydromuscovite-illite, kaolinite, siderite, zircon, xenotime, pyrite, florencite, monazite and kularite. TiO_2 polymorphs are verified by Raman spectroscopy and X-ray diffraction analysis. New evidence has been obtained that the transformation of ilmenite into leucoxene occurs hydrothermally through intermediate phases – Fe-rutile and pseudorutile; the enlargement of rutile crystals in the leucoxene grain itself is shown; the presence of secondary crystals of siderite, florencite and others inside the studied grains.

Keywords: Pizhemskoye deposit, Yaregskoye deposit, hydrothermal metamorphogenic genesis, leucoxene, pseudorutile, rutile, anatase

Recommended citation: Makeyev A.B., Skublov S.G., Galankina O.L., Vasiliev E.A., Krasotkina A.O. (2023). Pseudorutile-leucoxene-quartz ores of Timan – a new genetic type of titanium raw materials, prospects for industrial development. *Georesursy = Georesources*, 25(3), pp. 163–174. https://doi.org/10.18599/grs.2023.3.10

Introduction

In the structure of the all-Russian reserves, the share of two Timan titanium deposits – the Yarega oil titanium (South Timan) and Pizhemskoye titanium-zirconium (Middle Timan) is approaching 70%. The reserves of 66.8 million tons of TiO_2 in categories A+B+C have been approved in the Yarega deposit of the State Commission on Mineral Reserves (GKZ), and the reserves of the Pizhemskoye deposit on 10% of its area are 12.8 million tons of TiO_2 in categories C_1+C_2. The forecast resources of the titanium ores of the Pizhemskoye deposit are estimated at category P_1 – 2,5 billion tons (on the license area of 35 km^2 of RUSTITAN JSC) and at category P_2 – 7 billion tons of the entire deposit, the area of which is 90 km^2 (Makeyev, 2021). The Yarega deposit can be worked out by a mine method, and the Pizhemskoye deposit can be worked out by an open–pit mine. The Yarega and Pizhemskoye titanium deposits are located in a single Timan structure (Fig. 1) at a distance of no more than 230 km from each other, have a similar geological structure (Pervushin et al., 2012; Makeyev, 2016, 2021; Skublov et al., 2022a): they lie on the Riphean clay shales of the foundation and are overlain by volcanogenic sedimentary the thickness of the middle-

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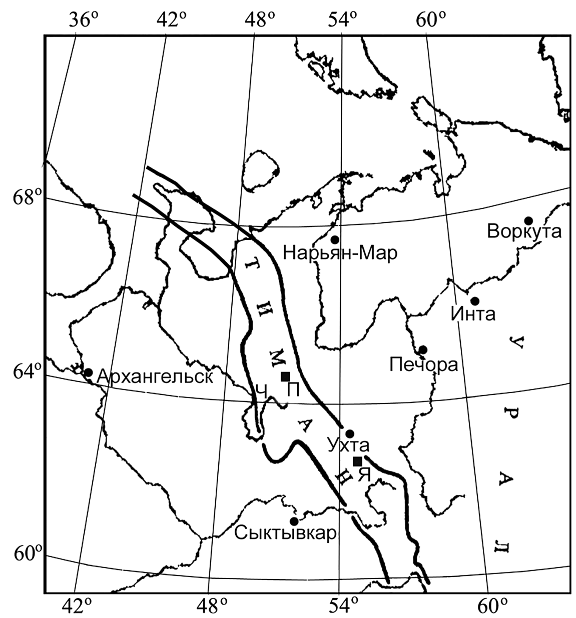

Fig. 1. Geographic scheme of the North-Eastern part of European Russia with the location within the Timan of the two largest titanium deposits: P – Pizhemskoye, Ya – Yarega

upper Devonian (D_{2-3}). These new data, which appeared after 2020, namely the approval of the GKZ reserves of the Pizhemskoye deposit, complement and update the analysis of the availability of titanium raw materials to the Russian industry (Bykhovsky, Remizova, 2021). The recent complete solution of technological issues of processing pseudorutile-leucoxene-quartz ores at Baykov Institute of Metallurgy and Materials Science of the RAS (IMET RAS) (Method for processing..., 2022) with the production of commodity products (porous rutile, pseudorutile and wollastonite), as well as the expected solution of logistical issues (approval by the government of the Russian Federation of the Sosnogorsk – Indiga railway construction project, which will take place in the immediate vicinity of Pizhemskoye deposits) shift the focus of attention to the Timan region.

The institutes of the Russian Academy of Sciences (Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM), Institute of Geology and Geochronology of the Precambrian (IGGP), Geological Institute (GIN), IMET and others have actively joined in the execution of the instructions of the President of Russia (06.28.2022 No. Pr-1130, item 3 a)-b) "to determine the priorities of the development of the mineral resource base of solid minerals in conjunction with the forecast of scientific and technological development of the Russian Federation in order to create promising high-tech products and materials for the long term".

The development of these two Timan deposits in the near future is an urgent task, the solution of which will relieve tension in the search for raw materials for hundreds of years and will cover all the needs of Russia in titanium metal, white and colored pigments based on TiO_2, there is also a special industrial interest in the above overburden rocks − quartz sandstones of glass quality (with 97–99 SiO_2 and 0.01–0.30 wt. % FeO). The Pizhemskoye deposit differs from the Yarega by a more complex polymineral composition (Makeyev, 2016, 2021), the main titanium phases in the Pizhemskoye deposit are pseudorutile and leucoxene, and in the Yarega – only leucoxene.

Leucoxene is a composite phase of $2TiO_2 \cdot SiO_2$ consisting of a sagenite lattice of rutile (anatase) with quartz embedded in it (15–40%). Pseudorutile is also a composite phase consisting of the mineral pseudorutile $(Fe^{3+}{}_xFe^{2+}{}_yMn^{2+}{}_z)_2Ti_3O_9$, also with a large number of quartz microinclusions (10–22%).

According to the Fedorovsky All-Russian Research Institute of Mineral Raw Materials classification (Tigunov et al., 2005), metamorphogenic titanium deposits with leucoxene (one of which is the Yarega oil-titanium, and the second – Pizhemskoye titanium-zirconium) belong to leucoxene-quartz (according to the main mineral forms) indigenous deposits. The Pizhemskoye deposit is unique in reserves and mineral composition of ores: the main titanium phases are pseudorutile and leucoxene (Makeyev, 2016). There are no more similar deposits in Russia and the world. We offer in the classification of titanium ore deposits among metamorphogenic deposits should include a new genetic subtype – pseudorutile-leucoxene-quartz (Makeyev, 2021; Sadykhov et al., 2021).

It is known that relic ilmenite and modified ilmenite and pseudorutile (hydrothermal-metamorphogenic mineral), are present in small amounts (up to 6% of the sum of titanium phases) in the deep horizons of the Yarega deposit in water-saturated grades of ore sandstones (Shvetsova, 1975). According to this study, rutile-leucoxene has become the most widespread in the Pizhemskoye deposit. Note only that when studying under binoculars on the surface of flat grains of yellow leucoxene, secondary secretions of small crystals of blue anatase, up to several microns in size, in the form of peculiar corollas, are often observed on their surface. We have not detected anatase in polished preparations by Raman spectroscopy.

The first study on the diagnosis of TiO_2 polymorphs (rutile, anatase and brookite) in shales and ore bodies of the Yarega deposit was carried out by I.V. Shvetsova (1975). According to morphological features in polished preparations and X-ray diffraction analysis, it was found that in the large fraction (0.52–0.32 mm) of Yarega leukoxene, the rutile component prevails (~ 80%), in the middle fraction the proportion of rutile-analyte leukoxene increases, and in the small fraction (0.08–0.03 mm) anatase-leukoxene predominates (~ 60%). In the same direction, the content of SiO_2 in leucoxene decreases and the proportion of TiO_2 increases. The average ratio of TiO_2 polymorphs in ore leucoxene samples is rutile (70%): rutile-anatase (20%): anatase (10%). Previously, there was an opinion (Shvetsova, 1975) that polymorphic transformations of TiO_2 occur under hypergenic conditions, namely, metastable anatase turns into rutile. This assumption is refuted by modern experimental data that indicate high-temperature conditions of the polymorphic transition of anatase → rutile at temperatures of the order of 850–920 °C (Belaya et al., 2018).

An urgent task remains to establish and prove the hypothesis of the indigenous hydrothermal-metamorphogenic genesis of titanium deposits proper in connection with the establishment of practical search signs for the discovery of new similar deposits both on Timan and in other regions of Russia (Makeev, Bryanchaninova, Krasotkina, 2022).

The purpose of this work is to examine in detail the morphology, chemical composition of leucoxene and pseudorutile, all minerals included in their composition in the form of inclusions, the ratio of polymorphic modifications of rutile and anatase, to identify and discuss new arguments in favor of the hydrothermal-metamorphogenic hypothesis of the genesis of the Timan titanium deposits.

The object of the study

For a comparative study of the composition of leucoxene, five ore concentrates of two deposits were selected: from Yarega – the MYR sample (flotation concentrate), from Pizhemsky three samples of leucoxene – MPL-1, MPL-2, PZh-45: differing in the method of separation – flotation, gravity (concentration table), separation in heavy liquids and magnetic concentrate – the sample pseudorutile MPI-2. Representative samples of titanium concentrate grains of all five samples were pressed into one washer (a polished preparation with five tracks), on which microprobe and RS (Raman spectroscopy) studies were carried out. The study of the distribution, relationships and composition of polymorphic varieties of titanium dioxide (rutile and anatase) in the Yarega deposit was carried out on two leucoxene fractions (differing in dimension) obtained from one large technological sample: 1) fine- and medium-grained leucoxene fraction (0.25–1.0 mm) from the flotation concentrate of a large technological sample; 2) micrograin (< 0.1 mm) fraction, which was washed in a bromoform, thereby obtaining a mineral concentrate with a density of > 4.0 g/cm^3. Grains of accessory ore minerals were previously isolated from this fraction and their composition and isotopic age were studied: monazite (Makeyev et al., 2020), rutile (Skublov et al., 2022a), zircon (Krasotkina et al., 2020; Skublov et al., 2022b). Figure 2 shows the characteristic newly formed

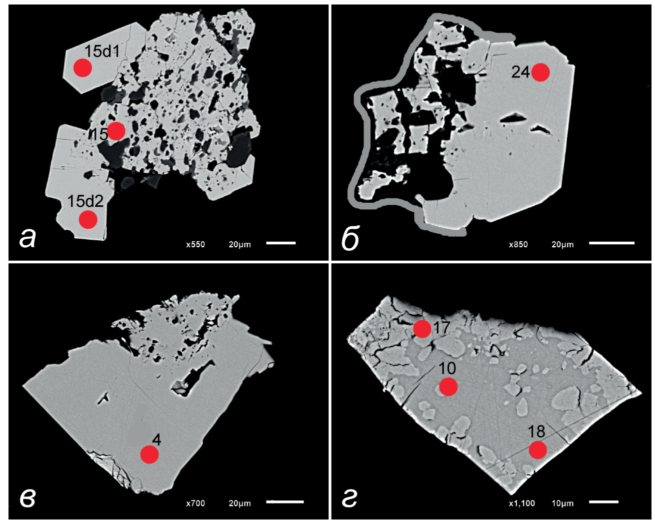

Fig. 2. Images (BSE mode) of typical small anatase crystals from the Yarega deposit: a, b – accretion of newly formed anatase crystals on anatase leucoxene grains (15 and 24), black inclusions – quartz; c – a separate anatase crystal (4); d – a fragment of the aggregate (17) of rutile and anatase (white). Red dots – location of the Raman spectroscopy probe and numbers of spectra

dipyramidal anatase crystals and the coalescence of rutile and anatase grains from the micrograin fraction. Chemical X-ray fluorescence analysis of all five ore concentrates for major oxides and micro-components (Table 1, 2) revealed the main differences in the composition of the studied titanium concentrates. X-ray diffraction analysis made it possible to establish the phase mineral composition of titanium concentrates (Fig. 3, Table 3). Diagnostics of TiO_2 anatase and rutile polymorphs of the small fraction of the Yarega deposit was carried out using RS (Raman spectroscopy) (Fig. 4). As it turned out, most of the small (40–80 μk) grains and crystals of TiO_2 are represented by anatase. The larger grains of Yarega leucoxene (0.2–0.5 mm), as well as all Pizhemsky grains, according to Raman spectroscopy data, are composed mainly of rutile (Fig. 5). The X-ray diffraction analysis made it possible to clarify that all concentrates of the sandy (psammite) fraction contain a minimum amount of anatase from 0.8% to 5%, the maximum amount of anatase turned out to be in the Yarega concentrate, the minimum – in the pseudorutile.

Materials and methods

A complete chemical analysis of all five ore titanium concentrates was carried out using a MagiXPRO ("Philips Analytical B.V.", Netherlands) wave X-ray fluorescence spectrometer at IGEM RAS (analyst A.I. Yakushev). The main oxides were determined in tablets fused with lithium tetraborate, losses after calcination (IFR) were determined separately, micro-components were analyzed in pressed tablets (Table 1) according to the NSAM methodology No. 439-RS.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O
MYR	28.30	64.35	3.46	1.86	0.009	0.08	0.19	0.79	0.08
MPL -1	21.68	69.71	2.95	1.84	0.056	0.17	0.18	0.98	0.06
MPL -2	21.95	68.87	3.12	2.11	0.062	0.19	0.19	0.97	0.06
Pzh -45	33.18	61.89	2.00	1.26	0.010	0.01	0.16	0.95	0.05
MPI -2	13.96	56.18	2.35	22.88	1.242	0.06	0.14	0.74	0.05

Sample	P_2O_5	ZrO_2	IFR	Total	Cr	Sr	Th	Y	Nb
MYR	0.12	0.159	0.36	99.76	100	103	44	120	530
MPL -1	0.32	0.283	1.40	99.63	160	568	48	90	620
MPL -2	0.37	0.449	1.19	99.53	220	630	50	160	710
Pzh -45	0.11	0.070	0.14	99.83	14	179	34	76	184
MPI -2	0.23	0.041	1.78	99.65	440	587	66	120	450

Table 1. Chemical composition (wt. %) of titanium concentrates from Yarega and Pizhemskoye deposits (rare elements – ppm), analyst – A.I. Yakushev

Sample	*Qzt*	*Ilt*	*Kln*	*Sid*	*Chl*	*Apt*	*Zrn*	*Lec*	*PsRt*	Total
MYR	23.67	7.18	1.44	0.00	0.90	0.14	0.237	66.43	0.00	100.00
MPL -1	15.34	8.91	0.00	2.22	0.86	0.30	0.422	71.96	0.00	100.00
MPL -2	16.49	8.82	0.00	1.69	0.90	0.33	0.670	71.09	0.00	100.00
Pzh - 45	2.87	8.64	0.00	0.00	0.76	0.02	0.104	87.62	0.00	100.01
MPI -2	1.30	6.73	0.00	3.48	0.67	0.11	0.061	15.59	72.14	100.06

Table 2. Normative recalculation of chemical analyses of concentrates on mineral composition (%). Note. Sample MYR – flotation concentrate from Yarega deposit; three leucoxene samples MPL-1, MPL-2, PZh-45 from Pizhemskoye deposit – flotation, gravity (concentration table) and separation in heavy fluids; sample MPI-2 – magnetic pseudorutile concentrate. Qzt – quartz, Ilt – illite, Kln – kaolinite, Sid – siderite, Chl – chlorite, Apt – apatite, Zrn – zircon, Lec – leucoxene, Rt – rutile, PsRt – pseudorutile, Ant – anatase, Ilm – ilmenite. Quartz is calculated as a free mineral, unlike SiO_2, which is a part of silicates and as inclusions in titanium phases leucoxene and pseudorutile

The chemical composition of leucoxene grains and mineral inclusions at the level of the main elements was determined by the SEM-EDS method at the IGGP RAS (analyst O.L. Galankina) on a scanning electron microscope JSM-6510LA (JEOL, Japan) with an energy dispersive spectrometer JED-2200 (JEOL, Japan). Washers with leucoxene grains and TiO_2 polymorphs were sprayed with carbon. The analysis was carried out at a point of 2–3 microns in size, and scanning over the area of a square with a side of about 20 microns with an accelerating voltage of 20 kV and a current of 1 nA. The accumulation time of each spectrum was 35 s, natural minerals, pure oxides and metals were used as standards. The ZAF algorithm was used to correct matrix effects. The image of the objects was taken in SE and BSE modes at different magnifications.

Raman spectroscopy (RS) was used to diagnose polymorphs of TiO_2 and other minerals, measurements were carried out at SPbSU using the Renishaw Invia (International Renishaw Company) spectrometer (analyst E.A. Vasiliev), the Inspector R532 (EnSpectr, Russia) spectrometer (analyst A.S. Novikova) was used at GIN RAS, the probe width is 20 microns.

X-ray diffraction analysis of powder preparations was carried out in the Laboratory of Crystal Chemistry of minerals named after N.V. Belov (IGEM RAS) using an X-ray diffractometer Proto AXRD (Proto, Canada). Operating mode – 30 kV, 20 mA, cobalt radiation, measuring range – 5–80° 2θ, scanning angle step 0.02° 2θ, exposure 15 seconds, fixed focusing slit system, silicon spot detector SPD-A (Proto, Canada). Diagnostics of the mineral composition was carried out by comparing experimental and reference spectra from the PDF-2 database in the Jade 6.5 software package of MDI (Gates-Rector, Blanton, 2019). Quantitative mineral analysis of the concentrate was carried out by the method of full-profile processing of X-ray images from undirected preparations using the Rietveld method (Rietveld, 1969).

Results and their discussion

Morphological features of the leucoxene grains of the Yarega and Pizhemskoye deposits do not differ significantly (Fig. 5–7). Leucoxene grains have the form of flattened and elongated volumetric ellipsoids ranging in size from 0,1 to 1 mm (along the long axis) in the Pizhemskoye deposit and from 0,1 to 3–5 mm in the Yarega deposit, the modal size of ellipsoids is 0,3 mm. There are envelope-like pseudomorphoses of leucoxene according to ilmenite. In the Pizhemskoye deposit, along with leucoxene, another titanium phase, pseudorutile, is widely distributed in ore concentrates,

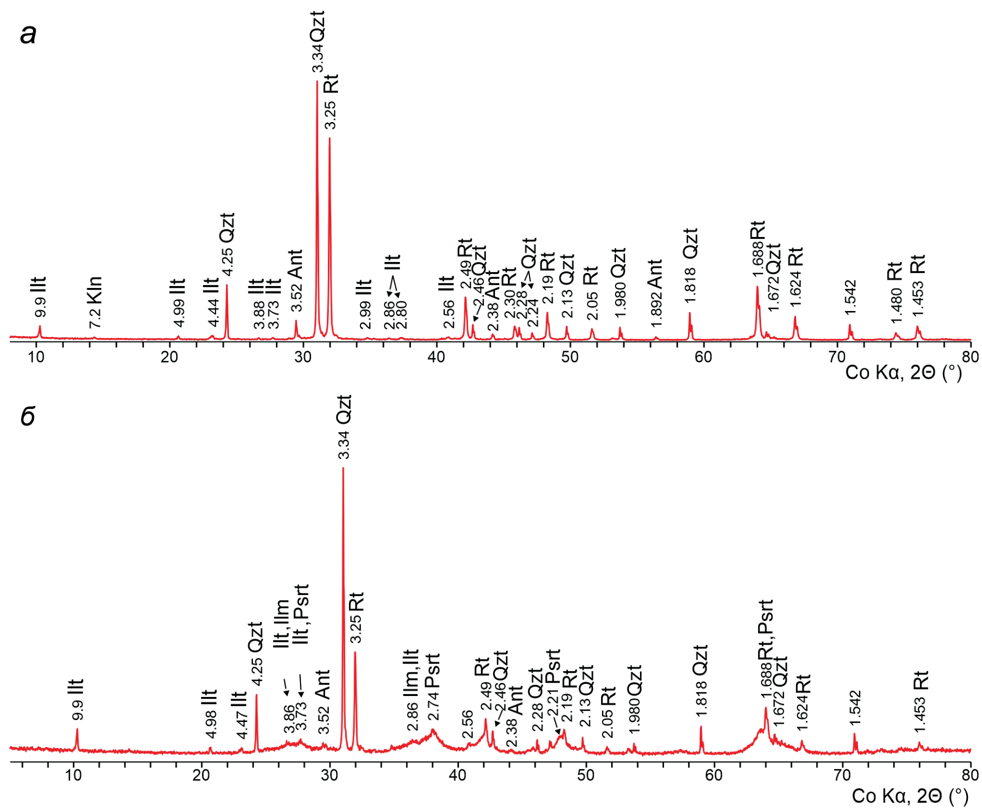

Fig. 3. X-ray diffraction patterns of the samples: a – MPL-2, Pizhemsky leucoxene concentrate, b – MPI-2, Pizhemsky pseudorutile concentrate

Sample	*Qzt*	*Ilt*	*Kln*	*Rt*	*PsRt*	*Ilm*	*Ant*	*Rt/Ant*
MYR	60.2	–	–	34.7	–	–	5.1	6.80/1
MPL -1	32.6	8.8	1.1	52.7	1.3	–	3.5	15.06/1
MPL -2	36.4	9.0	2.1	49.5	–	–	3.0	16.50/1
Pzh -45	22.1	10.6	1.5	56.7	7.5	–	1.6	35.44/1
MPI -2	17.1	5.8	–	9.1	56.3	10.9	0.8	11.37/1

Table 3. Mineral composition of titanium concentrates of Yarega and Pizhemskoye deposits (%) according to the X-ray diffraction analysis, analyst – V.V. Krupskaya. Note. Quartz was determined by X-ray diffraction analysis as a total free mineral, as well as in the form of microinclusions in titanium phases leucoxene and pseudorutile

it is easily separated from leucoxene into a magnetic fraction. The internal structure of the grains is a sagenite lattice of rutile microliths (2–5) × (10–15) microns in size, fused at angles of 60° and 120°. Diagnostics of titanium dioxide polymorphs in leucoxene grains of both deposits was carried out using Raman spectroscopy in two laboratories. 19 Raman spectra of a fine fraction of the Yarega concentrate with a dimension of less than 0,1 mm were obtained at the SPbSU (Fig. 2, 4). This fine fraction (Fig. 2) consists of recrystallized dipyramidal crystals of anatase, anatase-leucoxene and rare aggregates of anatase and rutile. At the GIN RAS, 50 spectra were taken on 22 grains of polished leucoxene preparations from the Pizhemskoye and Yarega deposits (with a dimension of more than 0.1 mm), only rutile was found everywhere (Fig. 4).

The pore space in the sagenite rutile lattice is filled with quartz secretions in the bulk, shapeless or rounded, very rarely faceted. The volume of quartz inclusions varies from 10% to 42%. In addition to quartz, microinclusions were found and diagnosed by chemical composition: pseudorutile, hydromuscovite-illite, siderite, kaolinite, zircon, xenotim, pyrite, florencite. As inclusions, illite is most often found, which is reflected in the chemical composition of leucoxene, in which there are noticeable amounts of aluminum and potassium oxides. The size of inclusions of quartz, illite, siderite reaches 10–30 microns; xenotime, pyrite, zircon, florencite up to 3–10 microns. Inside the leucoxene grains of both Yarega and Pizhemsky, evidence of past hydrothermal recrystallization processes was found: significant enlargement of rutile crystallites up to 10–20 microns in width and up to 150 microns in length (Fig. 6, a, b, e; 7, a, b, e); the presence of secondary minerals siderite, florencite, metamict yttrium zircon.

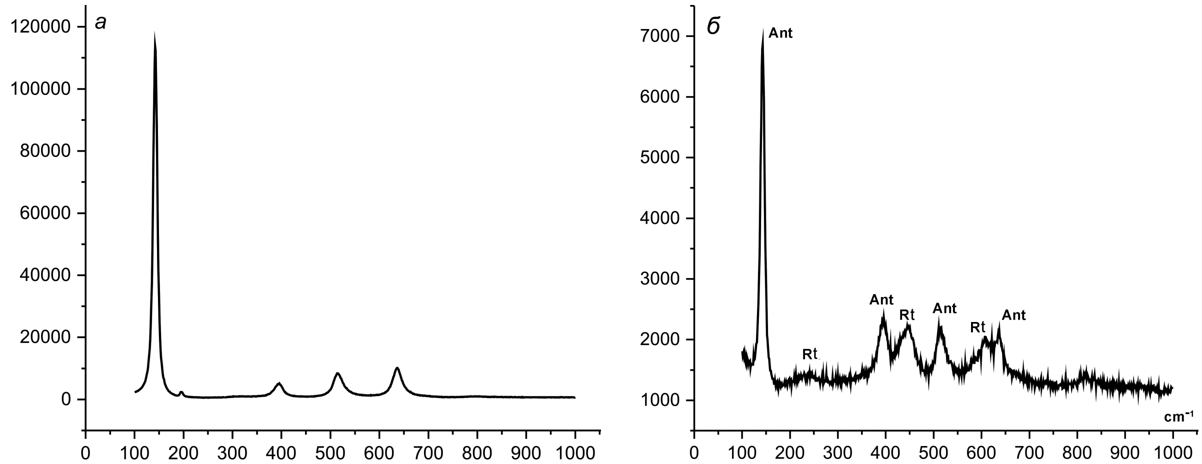

Fig. 4. Raman spectrum: a – anatase crystal (15d1) from the Yarega deposit with characteristic peaks: 145, 195, 395, 520, 635 cm^{-1}; b – of a mixture of rutile (Rt) and anatase (Ant) extractions in grain No. 17 from the Yarega deposit (Fig. 1) with characteristic peaks: anatase – 145, 395, 520, 635 cm^{-1}, rutile – 240, 450, 610 cm^{-1}

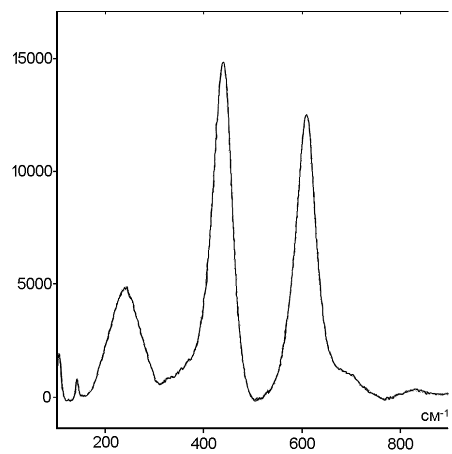

Fig. 5. Typical Raman spectrum of rutile. Recrystallized rutile crystals 50–150 microns in size, from Pizhemsky leucoxene grain with peaks – 240, 450, 610 cm^{-1}

The grains of the magnetic fraction (MPI-2 sample) of titanium minerals (Fig. 8) of the Pizhemskoye deposit, according to the data of the Messbaurov spectroscopy, consist of pseudorutile, Fe-rutile and ilmenite in a ratio of 10:3:2 (Makeyev, Lyutoev, 2015). In polished preparations of pseudorutile grains (Fig. 8), there is a regular replacement of the pseudorutile grains themselves with the leucoxene phase, the released iron passes into siderite. This is a direct proof of the hydrothermal reaction of the conversion of ilmenite to leucoxene through the intermediate phases of Fe-rutile and pseudorutile according to the scheme (Makeyev, 2016):

$FeTiO_3$ (ilmenite) + H_2O+CO_2 → Fe–TiO_2(Fe-rules) → $(Fe^{3+}, Fe^{2+})_2Ti_3O_9$ (pseudorutile) → $(2TiO_2)\cdot SiO_2$ (leucoxene) + TiO_2 (rutile) + $FeCO_3$ (siderite) → Fe_2O_3 (hematite).

Residual, not fully reacted ilmenite in the amount of 10.9% (Table 3) in the magnetic fraction of the ore concentrate of gray-colored sandstones (MPI-2 sample), together with rutile and pseudorutile, it was also recorded by X-ray diffraction.

The material and mineralogical composition of all five concentrates was well studied thanks to chemical X-ray fluorescence analysis (Table 1), its conversion according to the methodology developed by us (Makeyev, 2016) to the mineral composition (Table 2) and evaluation of mineralogical composition based on X-ray diffraction analysis (Table 3, Fig. 3). These two types of analysis complement each other, allowing you to reliably imagine the gross mineral composition of concentrates. It was possible to quantify the ratio of ore phases of leucoxene and pseudorutile, rutile and anatase, to assess the presence of the primary mineral ilmenite in pseudorutile concentrate (both minerals are black and cannot be evaluated by optical method). A consistent decrease in the content of anatase in concentrates from Yarega leucoxene to Pizhemsky and then to pseudorutile has been shown. It became possible to estimate the amount of free quartz in concentrates and the content of quartz, illite, kaolinite and chlorite in the form of inclusions in titanium phases. The features of the micro-component composition of the concentrates of the two deposits are determined (in general, there are fewer rare elements in the Yarega leucoxene than in the Pizhemsky) and the inheritance of the composition of Mn, Cr, Nb in pseudorutile from primary ilmenite.

The chemical composition of the minerals composing leucoxene was studied by the SEM-EDS method at the IGGP RAS, 147 analyses were obtained, both point and area scanning. When analyzing an object with a square with a side of about 20 microns, more than one mineral fell into the analysis area, therefore, components uncharacteristic of the host mineral were recorded in the analysis results (Tables 4–7). The compositions of rutile microcrystals were studied in the most detail (Table 4, n = 30); the composition of leucoxene proper was also determined in detail by scanning the area (Table 5, n = 56); the composition of pseudorutile was characterized both by scanning by area and by point

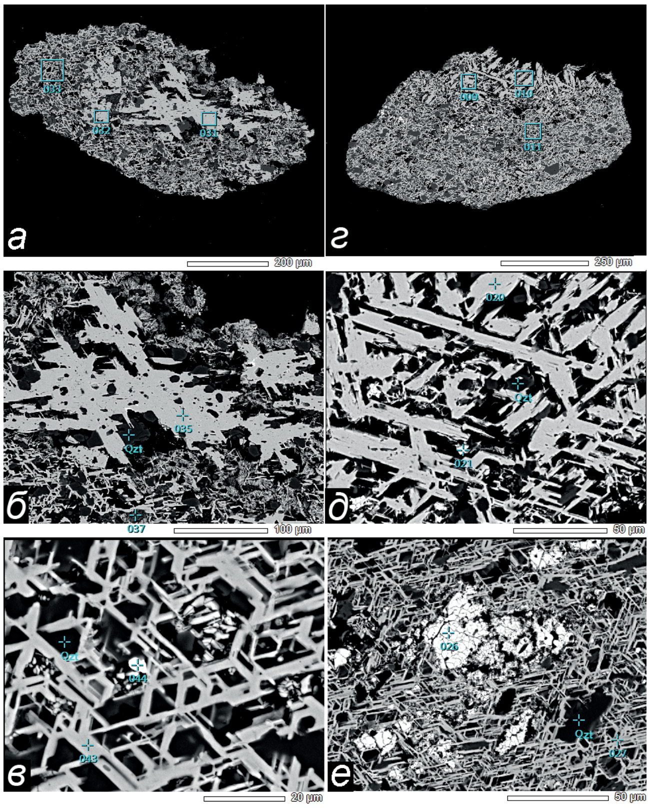

Fig. 6. Images (BSE mode) of leucoxene grains (a – MYR sample, Yarega deposit; d – sample MPL-1, Pizhemskoye deposit) and their enlarged fragments (b, c, g, e). Frames – places of area scanning analyses and location of the Raman spectroscopy probe, cross – point analyses and their numbers. White large spots – pseudorutile, Qzt – qualitative determinations of quartz by EMF spectrum. The numbers of the analyses coincide with the numbers in the tables of chemical analyses

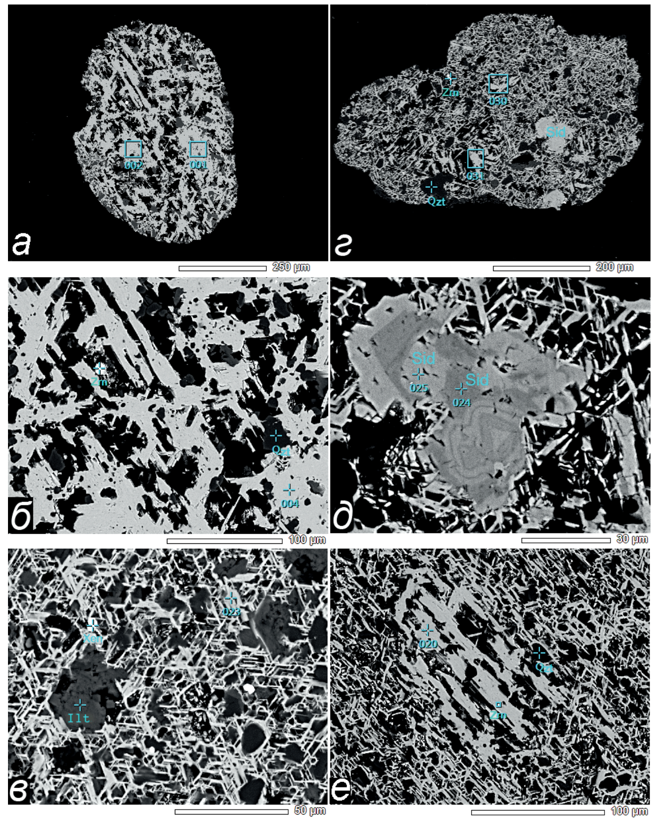

Fig. 7. Images (BSE mode) of rutile-leucoxene grains. a – sample MPL-2, d – sample PZh-45 (Pizhemskoye deposit) and their enlarged fragments (b, c and g, e), e – inclusions of zonal siderite crystals and their analysis numbers. Frames – places of area scanning analyses and location of the Raman spectroscopy probe, cross – point analyses and their numbers by EMF spectra: Qzt – quartz, Zrn – zircon, Ilt – illite, Sid – siderite, Xen – xenotime

analyses (Table 6, n = 17), in analyses by scanning by area of pseudorutile there is a different amount of SiO_2 in the form of inclusions of quartz and clay minerals; for the first time the composition of inclusions of a clay mineral – illite was characterized (Table 7, n = 11); several analyses of siderite, zircon, xenotime and florencite were obtained. All these minerals are present in the Yarega and Pizhemsky leucoxene. The results of analyses (n = 23) of anatase and rutile from the micrograin fraction of the leucoxene concentrate of the Yarega deposit were published by us earlier (Skublov et al., 2022a).

The main isomorphic admixture of micron rutile crystallites in leucoxene is iron, the FeO content varies from 0.03 to 1.84 wt. %, the average is 0.57 wt. % (Table 4). The maximum amount of iron remains in the rutile from the accretions of the grains of the leucoxene phase with the pseudorutile of the Pizhemskoye deposit (MPI-2 sample). In terms of iron content, rutile from the Yarega and Pizhemsky leucoxene almost does not differ. This residual iron in rutile microlites in leucoxene was later used by IMET RAS technologists to concentrate

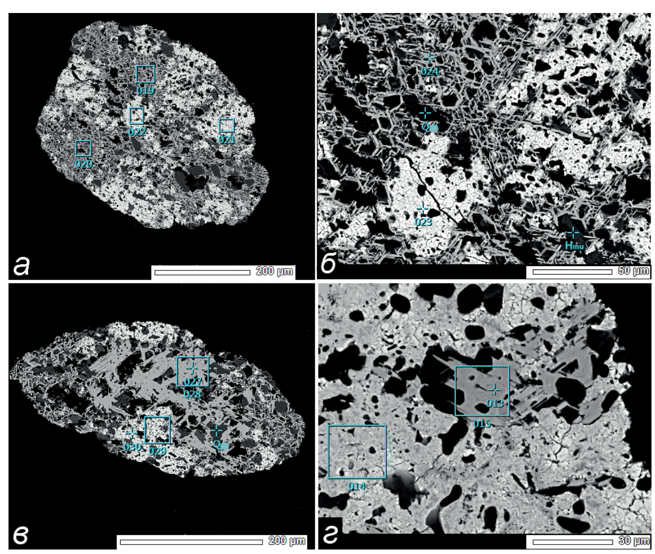

Fig. 8. Images (BSE mode) of two grains (a, c) of rutile leucoxene in coalescence with pseudorutile fragments (white) of sample MPI-2 and their enlarged fragments (b, d), Pizhemskoye deposit. Frames – locations of microprobe analyses by area scanning, crosses – point analyses and their numbers

Sample	Photo	SiO_2	TiO_2	Al_2O_3	FeO	Total
1-1-2	008	–	98.98	–	0.48	99.46
1-2-2	014	–	99.65	–	0.35	100.00
1-3-2	021	–	99.48	–	0.52	100.00
1-4-2	026	–	99.92	–	0.08	100.00
1-5-2	035	0.22	98.76	0.25	0.77	100.00
1-5-1	031	3.94	94.68	0.73	0.66	100.00
1-6-2	043	–	99.22	–	0.03	99.25
1-7-2	049	0.94	98.22	0.52	0.32	100.00
2-1-1	002	–	99.76	–	0.24	100.00
2-2-1	005	2.36	97.23	–	0.41	100.00
2-3-2	016	0.40	99.33	–	0.27	100.00
2-3-3	020	–	99.20	–	0.80	100.00
2-4-2	027	–	99.30	–	0.42	99.72
2-2-5	031	0.72	98.61	0.22	0.45	100.00
3-1-2	004	–	99.51	–	0.62	100.10
3-2-2	009	–	98.68	–	1.18	99.86
3-3-2	014	–	99.77	–	0.11	99.88
3-4-2	023	0.92	98.98	–	0.10	100.00
3-5-1	026	2.30	96.40	0.66	0.65	100.00
3-5-2	029	–	99.36	–	0.43	99.79
3-1-2	005	–	99.79	–	0.21	100.00
3-2-2	011	1.29	98.52	–	0.19	100.00
3-3-2	017	–	99.03	–	0.92	99.95
3-4-2	020	–	99.11	–	0.70	99.81
3-5-3	034	0.31	98.76	0.14	0.78	99.99
5-2-2	006	0.70	97.70	–	1.60	100.00
5-2-2	010	1.52	96.38	0.32	1.84	100.10
5-2-3	013	0.67	97.76	–	1.58	100.00
5-3-2	018	0.38	98.99	0.48	0.15	100.00
5-5-1	027	–	99.73	–	0.27	100.00
Average. n=30		**0.56**	**98.69**	**0.11**	**0.57**	**99.93**

Table 4. Chemical composition of rutile, wt. %, analyst – O.L. Galankina. Note. The first digit in the first column shows the serial number of the lane in a polished preparation and sample number (1 – MYR, 2 – MPL-1, 3 – MRL-2, 4 – PSR-45, 5 – MPI-2), the second digit shows the number of grains, the third – the serial number of images. In the second column, the numbers of analyses on the BSE-images

leucoxene and separate it from free quartz. A method of reducing firing was used, while isomorphic iron in rutile is reduced to metallic iron, then leucoxene with microinclusions of native iron is separated from the bulk of quartz by magnitoseparation (Method for processing..., 2022; Sadykhov et al., 2021).

The variable chemical composition of leucoxene grains consists of a variable amount of three minerals in its composition – rutile, quartz and illite. Also, to a large extent, the result of a single chemical analysis of the leucoxene grain will depend on the specific location of the square when scanning by area. As a result of the conducted studies, it was found out that the Yarega leucoxene contains slightly more quartz than the Pizhemsky, the average ferruginicity of leucoxene is at the same level as the rutile composing it (average 0.59 wt. % FeO); the content of Al_2O_3 and K_2O in leucoxene depends entirely on the number of inclusions of hydromuscovite-illite and, to a lesser extent, kaolinite in it. It has been established that the amount of clay minerals in the Yarega leucoxene is somewhat greater than in the Pizhemsky (Table 5). In leucoxene from coalescing with pseudorutile there is a minimum amount of clay minerals. The results obtained by us in the course of this study explain the revealed patterns in the course of technological experiments on autoclave desiliconization of leucoxene. A noticeable amount of aluminum and potassium oxides remains in the desalinated product – porous rutile, due to residual clay minerals that cannot be removed from leucoxene, as this happens with quartz, which binds in reaction with CaO, resulting in the formation of an additional commodity product wollastonite – $CaSiO_3$ (Zablotskaya et al., 2011).

The composition of pseudorutile was determined using point analyses and scanning by area (Table 6). Pizhemsky pseudorutile contains on average (wt. %): 62.85 TiO_2; 31.27 Fe_2O_3; 2.55 MnO. In addition, pseudorutile contains (wt. %): 2.48 SiO_2, 0.57 Al_2O_3, 0.11 K_2O, the presence of which is due to inclusions of quartz and clay minerals. Manganese in pseudorutile (as well as V, Nb, Cr, Ni) is inherited from primary ilmenite (Makeyev, 2016). Using Mossbauer spectroscopy, it was found (Lyutoev, Makeyev, 2019) that the composition of pseudorutile includes both divalent and trivalent iron $(Fe^{3+}_{1,66}Fe^{2+}_{0,11}Mn^{2+}_{0,11})_2Ti_{3.12}O_9$. In its composition, Pizhemsky pseudorutile is very similar to arizonite from the Volnogorsky deposit (Ukraine), the latter has long been the main raw material for the production of titanium metal at the Russian enterprise PJSC VSMPO-AVISMA Corporation.

Small inclusions of muscovite and clay minerals were analyzed, which in most cases are close in composition to illite (Table 7). A small admixture of titanium in it can be attributed to the influence on the analysis of the rutile matrix or inheritance of the composition of titanium biotite, according to which, most likely, this mineral was formed. In one case, we analyzed a small inclusion of kaolinite corresponding to the standard aluminosilicate composition.

For the first time, zonal siderite crystals containing isomorphic impurities (wt. %) were detected and analyzed in leucoxene grains from the concentrate of the PG-45 sample (Fig. 7, d, e): in the dark zone (analysis 024) – 48.63 FeO, 4.59 MnO and 4.22 MgO; in the light zone (analysis 025) – 56,91 FeO, 1.57 MnO and 0.05 MgO. This finding confirms our assumption (Sadikhov et al., 2021) that the reaction of the hydrothermal transformation of ilmenite into leucoxene takes place with the participation of a carbon dioxide fluid with the removal of iron and the formation of siderite.

Often in the leucoxene grains of both Yarega and Pizhemsky, there are small secretions of the secondary mineral rare earth-strontium-aluminophosphate – florencite, two of them have been analyzed. Yarega florencite (analysis 028) contains (by wt. %): 36.18 Al_2O_3, 32.33 P_2O_5, 2.01 FeO, 5.96 SrO, 12.27 La_2O_3, 7.68 Ce_2O_3, 1.55 Nd_2O_3, 0.22 Sm_2O_3. Pizhemsky florencite (analysis 001) contains (wt. %): 39.51 Al_2O_3, 35.36 P_2O_5, 1.68 FeO, 1.87 SrO, 4.37 La_2O_3, 8.86 Ce_2O_3, 3.90 Nd_2O_3. As can be seen, the compositions of florencite from the two deposits are radically different, Yaregsky is more enriched with strontium and rare earths. Florencite is a secondary mineral formed by kularite. We have directly observed similar inclusions of florencite in the form of inclusions in the grains of Pizhemsky kularite (Makeyev et al., 2020), as well as in the form of shells on the grains of monazite occurrence of Ichetyu (Makeyev, Makeyev, 2011).

Zircon microinclusions are often found in the leucoxene of both deposits (Fig. 7 b, d, e), one of them from the Yarega deposit (analysis point 027) was analyzed (wt. %): 63.84 ZrO_2; 25.12 SiO_2; 1.62 Al_2O_3; 0.72 FeO; 1.81 CaO; 4.28 Y_2O_3; 1.34 HfO_2; 1.23 UO_2. The composition of the mineral clearly indicates that it is hydrothermally altered metamict zircon, which is quite common in the Pizhemskoye deposit (from 10% to 25% of cases) among the mass of ordinary zircon from igneous rocks (Krasotkina et al., 2020; Makeyev et al., 2016; Makeyev, Skublov, 2016; Skublov et al., 2022b). It is noteworthy that such a zircon was found directly in the leucoxene of the Yarega deposit. This is proof that both deposits have the same hydrothermal-metamorphogenic genesis.

Xenotime is also often found as small inclusions in leucoxene (Fig. 6 c), its composition from the Yarega deposit (analysis 044) shows traditional enrichment with heavy rare earths (wt. %): 45.93 Y_2O_3; 38.39 P_2O_5; 3.21 Gd_2O_3; 5.13 Dy_2O_3; 4.34 Er_2O_3; 3.00 Yb_2O_3. Xenotime from the Pizhemskoye deposit is similar in composition to the Yarega deposit, but its excretions in leucoxene grains can reach 40 microns (Makeyev, 2016).

Two other minerals occurring as inclusions in leucoxene: pyrite and kularite, were characterized by us earlier (Makeyev, 2016). All this information we have obtained about the species and chemical composition of mineral inclusions in leucoxene is important for technologists and is of practical importance, since after desilinization of leucoxene to obtain porous rutile, the latter can be processed in a way already known in industry. Chlorination of porous rutile to obtain titanium tetrachloride will occur tens and hundreds of times easier and faster due to the hundreds of times larger area of its active surface. The rare and rare earth metals contained in the porous rutile (in the form of the minerals-inclusions described above) are easily extracted

Sample	Photo	SiO_2	TiO_2	Al_2O_3	FeO	K_2O	Total
1-1-1	006	37.46	59.00	2.68	0.41	0.44	99.99
1-1-2	007	20.80	76.79	1.34	0.88	0.19	100.00
1-2-1	012	22.72	74.48	2.25	0.55	–	100.00
1-2-2	013	20.03	75.96	3.27	0.50	0.25	100.01
1-3-1	018	28.91	70.20	0.43	0.46	–	100.00
1-3-2	019	42.21	55.89	0.92	0.82	0.16	100.00
1-4-1	024	36.01	63.31	0.45	0.06	0.17	100.00
1-4-2	025	25.37	73.90	0.45	0.28	–	100.00
1-5-1	032	9.55	86.85	3.07	0.47	0.24	100.18
1-5-2	033	23.69	68.86	6.41	0.37	0.51	99.84
1-6-1	040	5.63	93.23	1.10	0.04	–	100.00
1-6-2	041	11.63	86.65	1.25	0.14	0.32	99.99
1-6-3	042	17.50	80.12	1.94	0.21	0.23	100.00
1-7-1	046	16.67	77.54	4.66	0.30	0.83	100.00
1-7-2	047	11.61	81.77	4.18	0.52	0.64	98.72
1-7-3	048	18.90	74.35	5.63	0.44	0.68	100.00
Average Yarega		**21.79**	**74.93**	**2.50**	**0.40**	**0.29**	**99.93**
2-1-1	053	17.78	70.41	6.94	0.36	0.69	96.18
2-1-2	054	28.67	68.07	2.12	0.23	0.25	99.34
2-1-3	055	10.39	86.83	1.89	0.31	0.57	99.99
2-1-4	056	12.30	84.72	1.97	0.49	0.51	99.99
2-2-1	008	10.32	84.23	3.91	0.56	0.98	100.00
2-3-1	009	3.64	92.12	1.86	2.03	0.35	100.00
2-3-2	010	10.85	86.17	1.79	0.89	0.30	100.00
2-3-3	011	29.10	68.56	1.42	0.46	0.46	100.00
2-4-1	024	14.46	82.00	2.38	0.49	0.68	100.01
2-4-2	025	20.48	77.16	1.50	0.44	0.42	100.00
2-5-1	029	7.39	88.23	2.84	0.76	0.79	100.01
2-5-2	030	11.59	85.36	1.92	0.45	0.68	100.00
3-1-1	001	6.28	92.42	0.71	0.36	0.25	100.02
3-1-2	002	4.35	93.20	1.44	0.67	0.35	100.01
3-2-1	007	13.38	84.53	1.23	0.86	–	100.00
3-2-2	008	11.95	83.71	2.50	1.20	0.64	100.00
3-3-1	012	21.99	77.46	0.34	0.22	–	100.01
3-3-2	013	17.91	80.53	1.00	0.32	0.25	100.01
3-4-1	018	29.76	65.37	3.34	0.50	1.04	100.01
3-4-2	019	20.08	74.41	4.15	0.37	0.99	100.00
3-5-1	027	19.12	77.86	2.23	0.21	0.58	100.00
4-1-1	001	24.06	69.49	4.67	0.54	1.25	100.01
4-1-2	002	26.64	68.49	3.51	0.36	0.99	99.99
4-2-1	009	20.93	73.86	2.96	0.33	0.69	98.77
4-2-2	010	20.09	74.87	3.66	0.33	1.05	100.00
4-3-1	013	22.13	75.97	1.11	0.63	0.16	100.00
4-3-2	014	26.29	68.12	3.85	0.35	0.24	98.85
4-4-1	018	28.73	69.28	1.21	0.53	0.25	100.00
4-4-2	019	34.96	60.35	3.28	0.38	1.03	100.00
4-5-1	030	9.28	87.96	1.38	1.38	–	100.00
4-5-2	031	7.65	91.74	0.25	0.36	–	100.00
5-2-1	015	16.73	81.26	0.45	1.56	–	100.00
5-3-1	016	24.88	74.31	0.54	0.24	–	99.97
5-3-2	017	27.43	70.30	0.45	0.20	–	98.38
5-4-1	019	22.57	74.92	0.83	1.68	–	100.00
5-4-2	020	24.51	70.88	1.61	2.67	–	99.67
5-4-3	024	5.44	94.15	0.52	0.29	–	100.40
5-5-1	028	11.99	85.56	1.39	0.72	0.21	99.87
5-6-1	032	16.95	78.49	2.65	0.85	0.61	99.55
5-6-2	033	17.75	78.40	2.30	0.98	0.57	100.00
Average Pizhma		**17.77**	**78.79**	**2.10**	**0.66**	**0.47**	**99.81**
Average . $n = 56$		**18.92**	**77.69**	**2.22**	**0.59**	**0.42**	**99.82**

Table 5. Chemical composition of leucoxene (area scan), wt %, Analyst – O.L. Galankina

Sample	Photo	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	K_2O	Total
2-3-1	017	–	60.74	–	36.97	2.27	–	99.98
2-3-2	021	6.14	59.50	0.29	31.73	2.34	–	100.00
2-4-1	023	–	61.30	–	35.69	3.00	–	99.99
2-4-2	026	0.42	60.93	0.23	35.82	2.60	–	100.00
3-2-1	010	–	62.02	–	35.31	2.66	–	100.00
3-5-1	030	–	62.43	–	34.90	2.67	–	100.00
5-1-1	004	–	61.12	–	36.28	2.60	–	100.00
5-2-1	007	0.35	66.37	–	32.53	0.76	–	100.00
5-2-2	008	–	60.88	–	36.62	2.47	–	99.98
5-2-3	009	3.74	60.44	0.56	33.43	1.82	–	100.00
5-2-4	014	0.83	64.44	0.64	32.80	1.28	–	99.98
5-4-1	021	2.64	60.10	0.97	33.35	2.70	0.25	100.00
5-4-2	022	12.29	53.67	1.37	29.72	2.61	0.34	100.00
5-4-3	023	–	61.02	–	35.56	3.51	–	99.97
5-5-1	029	12.62	54.77	4.04	25.55	2.24	0.77	100.00
5-5-2	030	–	62.18	–	33.77	3.99	–	99.94
5-6-1	034	1.840	64.34	1.35	29.58	2.51	0.37	100.00
Average, n = 17		**2.40**	**60.96**	**0.56**	**33.51**	**2.47**	**0.10**	**99.99**

Table 6. Chemical composition of pseudorutile, wt. %, analyst – O.L. Galankina

Sample	Photo	SiO_2	TiO_2	Al_2O_3	FeO	MgO	Na_2O	K_2O	Total
1-1-3	010	48.82	1.38	33.31	1.56	0.46	0.09	8.47	94.09
1-4-1	029	50.19	1.31	33.72	1.01	1.21	0.71	9.84	97.99
1-5-1	037	49.44	1.14	33.64	1.98	1.02	0.74	7.66	95.62
1-7-1	051	50.64	1.36	34.18	0.72	1.10	0.80	8.19	96.99
2-2-1	006	51.74	1.82	33.24	1.47	1.04	0.22	8.41	97.94
2-3-1	018	49.49	1.31	32.49	1.67	1.06	0.19	9.79	96.00
2-5-1	032	47.60	1.47	33.36	1.66	0.81	0.30	10.25	95.45
3-4-1	020	47.74	1.02	31.19	1.77	1.55	0.31	11.40	94.98
4-1-1	003	49.51	0.77	31.24	1.03	1.11	–	10.53	94.19
4-3-1	015	48.09	1.28	31.72	1.75	1.50	–	10.58	94.92
5-2-1	011	47.99	1.30	34.97	1.57	0.19	0.17	10.72	96.91
Average, n = 11		**49.20**	**1.29**	**33.01**	**1.47**	**1.00**	**0.32**	**9.62**	**95.92**

Table 7. Chemical composition of illite, wt %, Analyst – O.L. Galankina

using the technology of chlorination in a fluidized bed known in industry. Thus, not only commercial products of processing of natural phases of titanium will be obtained, but also a number of rare and rare-earth metals, which can make a significant increase in value (up to 30–50%) to the main products.

Conclusion

The small and large fractions of Yarega leucoxene and Pizhemsky titanium concentrates (leucoxene and pseudorutile) were studied. Rutile turned out to be the main ore phase in all leucoxene concentrates (with a dimension of more than 0.1 mm), and only in one grain of Yarega leucoxene, a polymorphic variety (TiO_2) – anatase was detected using Raman spectroscopy. In the fine fraction of Yarega leucoxene (less than 0,1 mm), anatase is mainly present. The compositions of all mineral phases in polished preparations of leucoxene and pseudorutile were analyzed by SEM-EDS. 12 mineral phases were diagnosed in the leucoxene grains themselves: pseudorutile, rutile, anatase, quartz, illite, kaolinite, siderite, zircon, xenotime, pyrite, kularite and florencite.

The practical significance of the performed studies lies in the fact that Raman spectroscopy and microprobe analysis on representative material confirmed that Pizhemsky leucoxene and the bulk of the Yaregsky concentrate consist of only one polymorphic phase of TiO_2 – rutile. This circumstance is important for technologists, it means that they will not need to change the technology already used for the use of rutile. In addition, in the course of these studies, it was revealed that other mineral inclusions are present in small quantities in the leucoxene grains themselves: in addition to quartz, these are illite, kaolinite, florencite, xenotime, monazite and zircon with increased Y, U and HREE content, siderite, pseudorutile. Rare and rare earth metals will be extracted from rutile during its chlorination process. It becomes clear why a lot of Al_2O_3 and K_2O remain in desalinated leucoxene after autoclave leaching with lime milk (in porous rutile). Aluminum and potassium in porous scrap are in the form of mica (illite and less often kaolinite), they cannot be extracted in the autoclave process. The average chemical composition of illite, as well as the average composition of pseudorutile (without quartz inclusions) was determined. The results obtained are of great importance for technologists, which allows them to orient themselves in the composition of primary raw materials and products, as well as make the right decisions to improve technological tasks.

According to electron microscopic images of polished leucoxene preparations, it was possible to establish that inside the grains there is a recrystallization of rutile crystals from small crystallites from (2 × 15 μk) to larger ones of (20 × 150 μk). New evidence has been obtained that the transformation of ilmenite into leucoxene occurs precisely by hydrothermal means: 1) enlargement of rutile crystals in the leucoxene grain itself: 2) finding secondary crystals of siderite, zircon, florencite, pseudorutile and others inside leucoxene grains.

The effective, environmentally friendly, waste-free technology of processing pseudorutile-leucoxene-quartz ores developed at IMET RAS in collaboration with IGEM RAS will allow the Russian industry to provide raw materials from the Yarega and Pizhemkoye deposits for the production of pigment titanium dioxide, titanium metal and other marketable products for hundreds of years.

Acknowledgements

The authors are grateful to V.V. Krupskaya, A.S. Novikova, A.I. Yakushev for their assistance in conducting analytical research.

This study was carried out within the framework of the research topics of IGEM RAS (no. FMMN-2021-0005) and IGG RAS (No. FMUW-2022-0005), analytical work was supported by RFBR (grant 19-35-60001). The reported study was funded by RFBR, project number 19-35-60001.

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Manuscript received 18 November 2022;
Accepted 24 March 2023; Published 30 September 2023

IN RUSSIAN

Псевдорутил-лейкоксен-кварцевые руды Тимана – новый генетический вид титанового сырья: перспективы промышленного освоения

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Два крупнейших месторождения России – Ярегское и Пижемское – относятся к одному генетическому типу: гидротермально-метаморфические коренные месторождения. Они расположены в одной тиманской структуре на расстоянии не более 230 км друг от друга. По суммарным утвержденным запасам и прогнозным ресурсам диоксида титана ресурсы этих месторождений приближаются к 70% от общероссийских и составят в недалеком будущем основу используемого в России промышленного титанового сырья. В интересах технологической минералогии детально изучены морфологические особенности, внутреннее строение, химический состав зерен двух главных титановых минеральных фаз – лейкоксена и псевдорутила, полиморфы TiO_2, а также состав минеральных микровключений в этих фазах. В Институте геологии и геохронологии докембрия РАН методом SEM-EDS проанализированы составы всех минеральных фаз в полированных препаратах лейкоксена и псевдорутила, получено 147 химических анализов в точке (диаметр зонда – 2–3 мкм) и сканированием по площади (20×20 мкм) множество изображений полированных зерен анатаза, лейкоксена и псевдорутила. В самих зернах лейкоксена в виде включений диагностировано и охарактеризовано 12 минеральных фаз: псевдорутил, рутил, анатаз, кварц, гидромусковит-иллит, каолинит, сидерит, циркон, ксенотим, пирит, флоренсит, монацит и куларит. Полиморфы TiO_2 заверены рамановской спектроскопией и рентгенодифракционным анализом. Получены новые подтверждения того, что превращение ильменита в лейкоксен происходит гидротермальным путем через промежуточные фазы – Fe-рутил и псевдорутил; показано укрупнение кристалликов рутила в самом зерне лейкоксена; нахождение вторичных кристаллов сидерита, флоренсита и других внутри изученных зерен.

Ключевые слова: Пижемское месторождение, Ярегское месторождение, гидротермально-метаморфогенный генезис, лейкоксен, псевдорутил, рутил, анатаз

Для цитирования: Макеев А.Б., Скублов С.Г., Галанкина О.Л., Васильев Е.А., Красоткина А.О. (2023). Псевдорутил-лейкоксен-кварцевые руды Тимана – новый генетический вид титанового сырья: перспективы промышленного освоения. *Георесурсы,* 25(3), с. 163–174. https://doi.org/10.18599/grs.2023.3.10