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Unique titanium Deposits of Timan: genesis and age issues

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Abstract. The article critically analysesthe hypotheses about the formation, age, and sources of material of large Timan titanium deposits, which were previously considered ancient buried placers formed along the weathering crusts of the Riphean shales. We discuss an alternative hydrothermal-metamorphic hypothesis about the formation of these deposits and the source of ore material. It is established that the incoming zircon of different ages (570-3200 Ma), as well as two other geochronometers, rutile and monazite, underwent a thermal effect common for all varieties as a result of a hydrothermal process about 600 Ma ago. According to modern concepts, the closing temperature of the U-Pb system in rutile exceeds 500 °C, which suggests high-temperature conditions for the hydrothermal processing of rutile during the formation of the considered deposits in the Riphean.

Keywords: Pizhemskoye and Yarega deposits; formation hypotheses; placer and hydrothermal-metamorphic formation hypotheses; sources of material; Riphean shales; lamprophyres

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Introduction. The share of two Timan titanium deposits, Yarega oil-titanium (Southern Timan) and Pizhemskoye titanium-zirconium (Middle Timan), approaches 80 % in the Russian reserves. The FBU GKZ approved reserves of 65 Mt of TiO_2 in the Yarega deposit in categories A + B + C, and the Pizhemskoye deposit reserves on 1/9 of its area are 12.8 Mt of TiO_2 in categories $C_1 + C_2$. Inferred resources of titanium ores in the Pizhemskoye deposit are estimated in category P_1 at 2.5 Bt (on a license block of 35 km^2 of RUSTITAN JSC) and P_2 at 7 Bt of the entire deposit [1]. The Yarega deposit can be mined by shaft method, while the Pizhemskoye deposit can be mined by open pit method. The deposits are in a single Timan structure at a distance of no more than 230 km from each other, have a similar geological structure [1, 2]: they lie on the Riphean shales of the basement and are overlain by volcanogenic sedimentary strata of the Middle-Upper Devonian.

The development of these deposits is relevant, as it will relieve tension in the search for raw materials for hundreds of years and cover all the needs of Russia in metallic titanium, white and coloured pigments based on TiO_2. The overlying quartz sandstones of glassy quality are of particular commercial interest as well. The Pizhemskoye deposit is distinguished by a more complex polymineral composition [3] and the main titanium phases (in the Pizhemskoye deposit, pseudorutile and leucoxene, and in the Yarega deposit – leucoxene). The Yarega oil-titanium deposit was discovered more than 80 years ago. V.A.Kalyuzhny was recognized as its discoverer in 1973.

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More than 60 years ago, titanium mineralization was noted in the banks of the Umba and Pizhma rivers, and the Ukhta geological exploration expedition conducted prospecting work at their. In 2010-20ies, geological exploration was conducted at the Pizhemskoye deposit of RUSTITAN JSC with mineralogical and technological studies and the calculation of ore reserves approved by the State Reserves Committee in 2020. In 2021, Rosnedra recognized RUSTITAN JSC as the pioneer.

Until now, it has been impossible to involve large reserves of Timan non-standard titanium ores in mining due to the lack of an effective industrial technology for their enrichment and processing. However, in recent years, laboratory research has been successful. The experimental work of chemists and technologists at IMET RAS with Timan leucoxene ores gives hope for the successful involvement of deposits in commercial mining using a single environmentally friendly technology by reducing firing of concentrates to separate leucoxene from quartz [4] and autoclave desiliconization of titanium phases using lime milk [5]. Technological studies revealed new criteria for understanding the nature and conditions of quartz-leucoxene deposit formation.

In the 1950-60 ies, V.A.Kalyuzhny put forward a hypothesis [6-9]: the source of titanium accumulations in the discovered Yarega deposit of Timan could be the strata of the metamorphosed Riphean shale containing ilmenite and leucoxene, along which weathering crusts were formed. Destruction, rewashing, and redeposition of weathering crust material along shales led to the formation of the Yarega commercial titanium placer. The hypothesis was picked up by other Timan researchers [10-14] and became generally accepted.

Since the discovery of titanium mineralization (1959) in the Pizhma River basin, the age of the titaniferous strata located in the northern periclinal closure of the Volsk-Vym ridge of the Middle Timan was conditionally taken as Middle Devonian – Eifelian [13]. The stratum became known as the Malorucheiskaya Fm. (D_2mr). The absence of any fossil flora and fauna in the titaniferous sandy-argillaceous strata does not allow us to consider this assumption as final. Over lying are monomineral quartz sandstones inter bedded with banded clays of the Pizhemskaya Fm. (D_2pz). It is clays that contain spores and pollen from the Starooskolsky superhorizon of the Eifelian stage of the Middle Devonian; therefore, the underlying titaniferous stratum without any biota should be considered pre-Middle Devonian. The geological structure of the study region and other deposits can be found in [1, 2, 15, 16].

The analysis of the mineral composition features of the Timan placers and their bedrock, the comparison of the Yarega placer structure with the Pizhemskoye and Ichetyu placers shows their qualitative analogy [12, 17]. They are considered products of a single Devonian crust- and placer-forming process in Timan [2, 6, 7, 18]. The age of the Pizhemskoye placer is considered to be Early Devonian (Emsian), which is comparable with the age of Devonian lateritic bauxites of Timan, formed on the weathering crusts of carbonate-argillaceous rocks of the Late Proterozoic basement [12].

A placer is a place where a mineral (or several types) are concentrated in a limited space, represented by free grains of rock-forming and ore minerals, phases, or their aggregates. The mineral liberates from the parent rock during its disintegration and moved to different distances, rewashing and concentrating in water flows. The resulting ore body (placer) is, as a rule, in the secondary collector, loose sedimentary rock [19].

The purpose of the work is to consider the consistency of the standard ideas about the origin of the giant Timan titanium deposits: Yarega oil-titanium (Southern Timan), Pizhemskoye titanium-zirconium (Middle Timan), and lying over the last polymineral occurrence Ichetyu, based on modern factual data on the geology, mineralogy, and geochemistry of deposits. We want to substantiate the alternative hydrothermal-metamorphic hypothesis for the genesis of deposits, their age, and sources of material. A verified hypothesis is relevant in connection with the development of effective prospecting indicators for identifying new similar deposits both in Timan and in other regions of Russia.

Discussion. Metamorphosed (green schist facies) primary sedimentary pelitomorphic shales of Riphean age are wide spread in Timan. They outcrop in large areas within the Middle Timan (Chetlassky Kamen, Volsk-Vym ridge) and, to a lesser extent, Southern and Northern Timan and the Kanin Peninsula. Riphean shales were discovered by mine workings (wells) in the licensed squires of the Pizhemskoye and Yarega titanium deposits and are available for research. They contain accessory titanium mineralization represented by ilmenite and, to a lesser extent, titanomagnetite. TiO_2 content in shales varies from 0.6 to 1.2 and approaches 0.87 wt.% on average [20].

The studies [2, 11, 14] discovered a special typochemistry of accessory ilmenite from the Riphean shales, which consists in its lowest isomorphic content with respect to vanadium, niobium, nickel, chromium, and minimum content of magnesium. At the same time, it contains a high typomorphic admixture of manganese. Shale ilmenite has its own well-defined "chemical portrait", quite pure with respect to its usual isomorphic admixtures. Leucoxene, mainly anatase-leucoxene, and in smaller quantities, anatase-rutile, develops in shales after ilmenite during metamorphism. The same leucoxene-bearing shales contain siderite, which is not considered as a by-product of the reaction of iron removal from ilmenite. I.V.Shvetsova [14] did a great deal of work on diagnosing TiO_2 polymorphs (rutile, anatase, and brookite) in shales and ore bodies of the Yarega deposit. It was established that, according to morphological features (Fig.1) in polished thin sections and X-ray diffraction analysis, large fraction of the Yarega leucoxene (+0.52-0.32 mm) is dominated by rutile component (to 80 %). In the middle fraction the proportion of rutile-anataseleucoxene increases, and fine fraction (0.08-0.03 mm) is dominated by anatase leucoxene (to 60 %). SiO_2content in leucoxene decreases and TiO_2 proportion increases in the same direction. The average ratio of TiO_2 polymorphs in ore leucoxene samples is rutile:rutile-anatase:anatase – 70:20:10. Residual and altered ilmenite, pseudorutile is present in a small amount (to 6 % of the total titanium phases) in the deep horizons of the Yarega deposit in water-saturated grades of ore sandstones. In the Pizhemskoye deposit, rutile-leucoxene is the most widespread. When studying flat grains of yellow leucoxene in the thin sections, secondary segregations of small crystals of blue anatase up to several microns in size in the form of peculiar rims are often observed on their surface. Anatase was not found in polished sections.

A feature of leucoxene, which is not considered in the placer model, is its fragility, due to which it cannot move in water flows over long distances. It inevitably breaks down and grinds, turning into a dusty fraction. A critical analysis of the provisions of the placer hypothesis is presented in the Table.

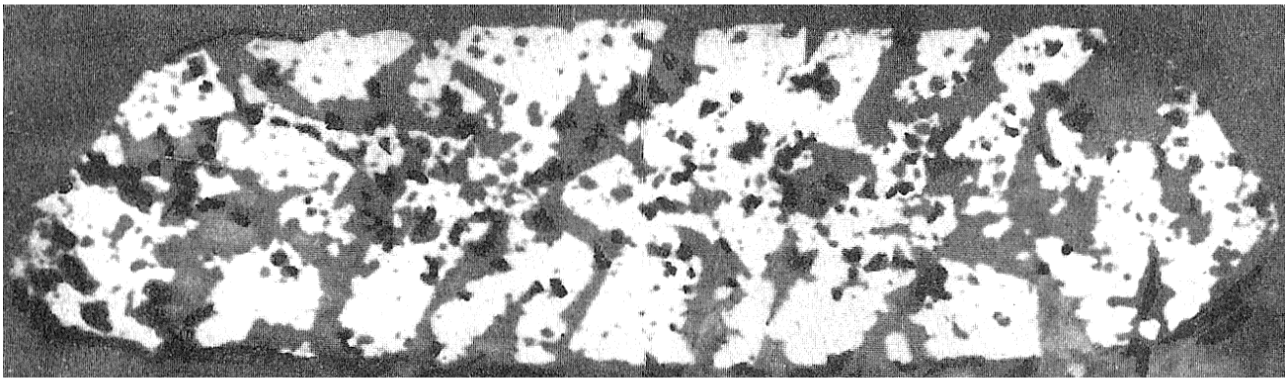

Fig.1. A flattened grain of anatase-leucoxene (about 300 μm long) from the Riphean shales of the South Timan [14] (white is anatase, gray is quartz)

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Comparison of the provisions of the placer hypothesis and actual data

Hypothesis provisions	Criticism
Mature linear and areal chemical weathering crusts develop along the Riphean shales, from which ilmenite crystals, leucoxene grains, and other accessories could be washed out	In Timan, according to exploratory drilling data, weathering crusts are known along diabases, granites, and calcareous-marl rocks (Vezhayu-Vorykva bauxite deposit), along which bauxite manifestations and deposits were formed. But no one has ever seen or described mature classical zonal chemical weathering crusts over shale. According to observations on the daylight surface of the Volsk-Vym ridge and description of the exploratory core, only the first stage of shale hard rocks destruction is known, their disintegration with the formation of shale grus. Neither published nor reported materials indicate the locations of findings in specific outcrops. There is no description of the chemical composition of weathering crusts, i.e., nothing to wash out
Concentration of titanium minerals and phases occurs by prolonged rewashing of weathering crusts on shales, their transfer by water flows with the placers formation	The dimension of quartz in shales does not correspond to the dimension of quartz particles intitaniferous strata: in shales, the dimension of grains of quartz and other minerals is less than 0.1 mm, and in sandstones and gritstones from the deposits under consideration, 0.2-2 and 3-10 mm, respectively (Fig.2, 3). The Pizhemskiye and Yarega titaniferous gritstones and sandstones are composed of clastogenic unrounded quartz (near by provenance area), by all indications, originating from the ancient Neoproterozoic quartzites. Weathering crusts on shales more than 500 m thick would be required to form giant deposits. Apart from two known deposits, there is no chain of even small titanium manifestations along the entire length of the ridges
Yarega and Pizhemskoye titanium deposits are marine beach placers	Characteristic features of marine beach placers are flat, well-rounded pebbles and broken shells (marine biota), but they are absent in both deposits. Gritstones consist of clastogenic fine grus from angular fragments of vein quartz and quartzite, and the sandy fraction of rocks, from clastogenic angular unrounded quartz without signs of long-range transport and abrasion (Fig.2, 3)
Age of the Yarega and Pizhemskoye titanium deposits is Eifelian (D_2)	Age of the Yarega deposit was erroneously taken as Middle Devonian, since the Middle Devonian pollen was found in the ore. Later it was found that the Late Devonian pollen was also present. After the formation of titaniferous sandstones of the Yarega deposit, oil migrating into them, having its own Permian-Jurassic age [21], brought the Middle-Late Devonian flora (spores and pollen) of the Devonian plants [22]. Sandy-argillaceous titaniferous rocks of the Pizhemskoye deposit do not contain leading biota. The age of the Malorucheiskay atitaniferous series of the Pizhemskoye deposit is groundlessly taken as Middle Devonian (D_2mr). The true age of these deposits is much older, Neoproterozoic (Riphean; PR_3mr), which can only be established by isotopic methods. The age of the Pizhemskoye deposit was determined by the Rb-Sr method at 685±30 Ma [23]
Ilmenite transforms into leucoxene in shales under supergene conditions	This hypothesis has not been proven. Hydrothermal conditions are required for iron removal from ilmenite and impregnation of pores in a sagenite rutile or anatase lattice with quartz with leucoxene formation: the presence of carbon dioxide in the fluid and a relatively high temperature (150-250 °C) for the transport of iron bicarbonate and silicic acid (SiO_2) in dissolved form [6]
Polymorphic transformations of TiO_2 occur under supergene conditions: metastable anatase transforms into rutile	Researchers of the Timan Riphean shales note that predominantly anatase leucoxene develops after ilmenite in them [8, 11, 14, 16]. In the Yarega and Pizhemskoye deposits, rutile-leucoxene is the most widespread. The ratio of TiO_2 polymorphs in the deposits is different. Experimental data indicate high-temperature conditions for the anatase → rutile polymorphic transition, 850-920 °C [24]
Leucoxene is formed under supergene conditions from ilmenite in titaniferous sandstones in an alkaline reducing medium [14] or is inherited as an accessory phase, being released from shales	This notion is erroneous. Leucoxene is formed during the hydrothermal alteration of ilmenite in a multi-stage sequential chemical process. The replacement of ilmenite by leucoxene proceeds with the removal of iron due to its interaction with carbon dioxide fluid and the formation of siderite ($FeCO_3$) through the phases: ferruginous rutile (nigrin), pseudorutile, then into leucoxene [3, 6]. Siderite in the lower Malorucheiskaya titaniferous series of the Pizhemskoye deposit is oxidized at high Eh to hematite. Leucoxene incorporatesmicroinclusions of quartz, monazite, xenotime, columbite, etc., which are deposited in the sagenite rutile lattice pores from hydrothermal fluid under acidic conditions. The conditions for leucoxene formation are completely different: acidic oxidizing medium and a relatively high temperature

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Hypothesis provisions	Criticism
Ilmenite from the Riphean shale strata served as a source of titanium for Timan deposits	Typomorphic features of relict ilmenite in Timan titanium deposits do not correspond to the typochemistry of shale ilmenite, which is pure and contains only the usual Mn admixture. Relic ilmenite in deposits contains significant isomorphic admixtures of Mg, Mn, V, Nb, and Cr. Such ilmenite is a typomorphic mineral of alkaline-ultramafic rocks [3, 16]

Much later, V.G.Kolokoltsev proposed an alternative hypothesis for the source of material and genesis of the Yarega deposit [25]. It suggested that the Yarega leucoxene is a product of the convective transfer of ore material from the basement rocks to the already formed sedimentary quartz sandstones as a result of hydrothermal alteration. He also considered Riphean shales enriched in ilmenite and anatase-leucoxene as a source of ore material [26]. This assumption removes the contradictions in V.A.Kalyuzhny's hypothesis – it is not necessary to transfer shale "pure" ilmenite and anatase-leucoxene from shale as initial titanium phases into sandstones. The criticism of V.G.Kolokoltsev's hypothesis lies in the fact that the Yarega deposit does not show characteristic signs of a hydrothermal process and crystals of ore minerals and vein minerals, metasomatic impact on host rocks, etc. There are no zoning, quartz and carbonate veins, large segregations and crystals of ore minerals and

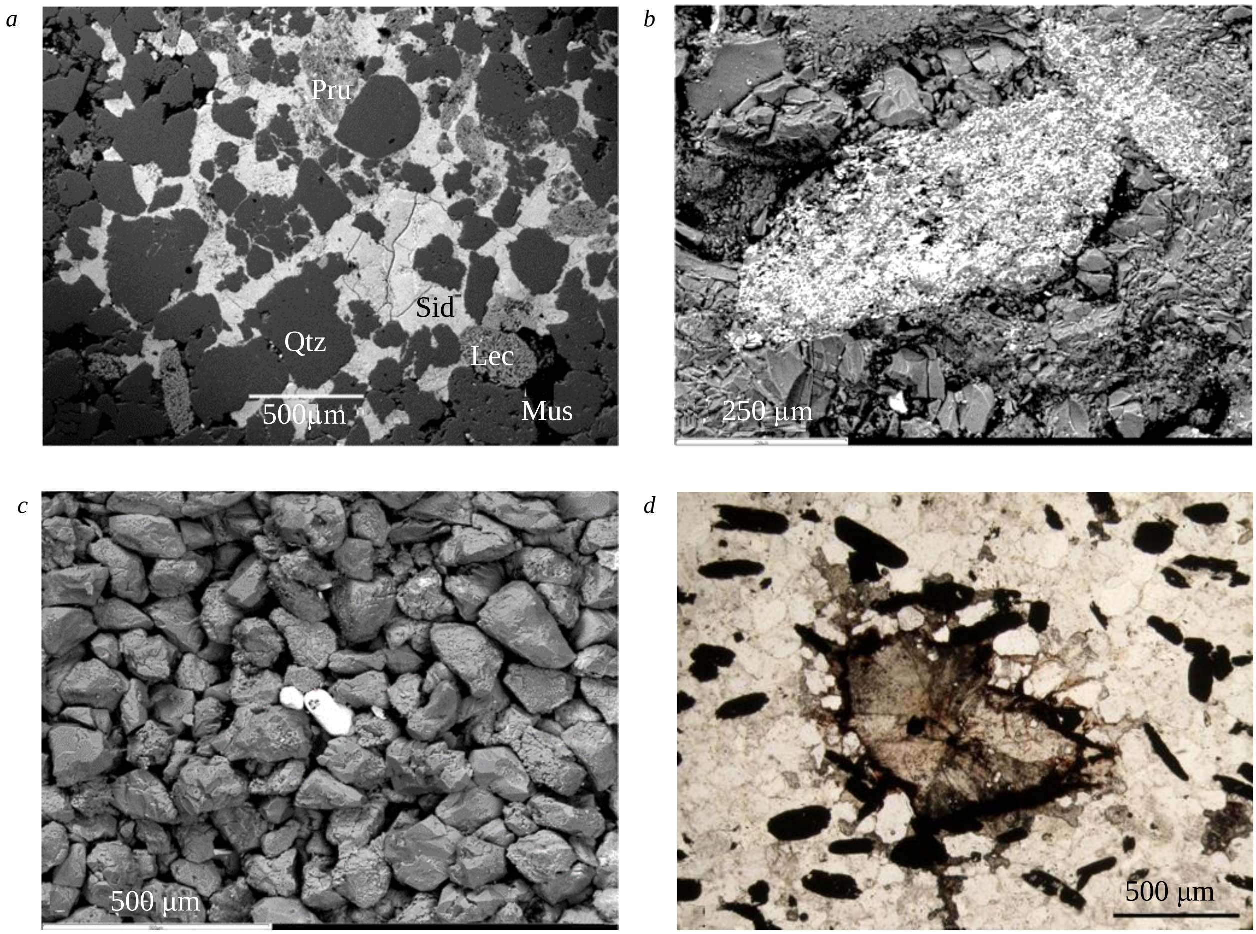

Fig.2. Electron microscopic images (BSE): *a* – clastogenic quartz (Qtz) sandstone (PR$_3$mr^2) with rutile leucoxene (Lec) and pseudorutile (Pru) in siderite (Sid) and hydromuscovite (Mus) cement; *b* – pseudomorphosis of rutile-leucoxene after ilmenite in red-coloured titanium-bearing sandstone of the lower sequence (PR$_3$mr^1); *c* – terrigenous-sedimentary quartz sandstone (D$_2$pz) of glass quality (SiO$_2$ – 96-98 wt.%), cement is absent (white – zircon grain); *d* – image of a thin section (without analyzer) of PR$_3$mr^2 titanium-bearing sandstone with numerous black grains of rutile leucoxene and pseudorutile (quartz is white, light brown siderite segregation in the centre)

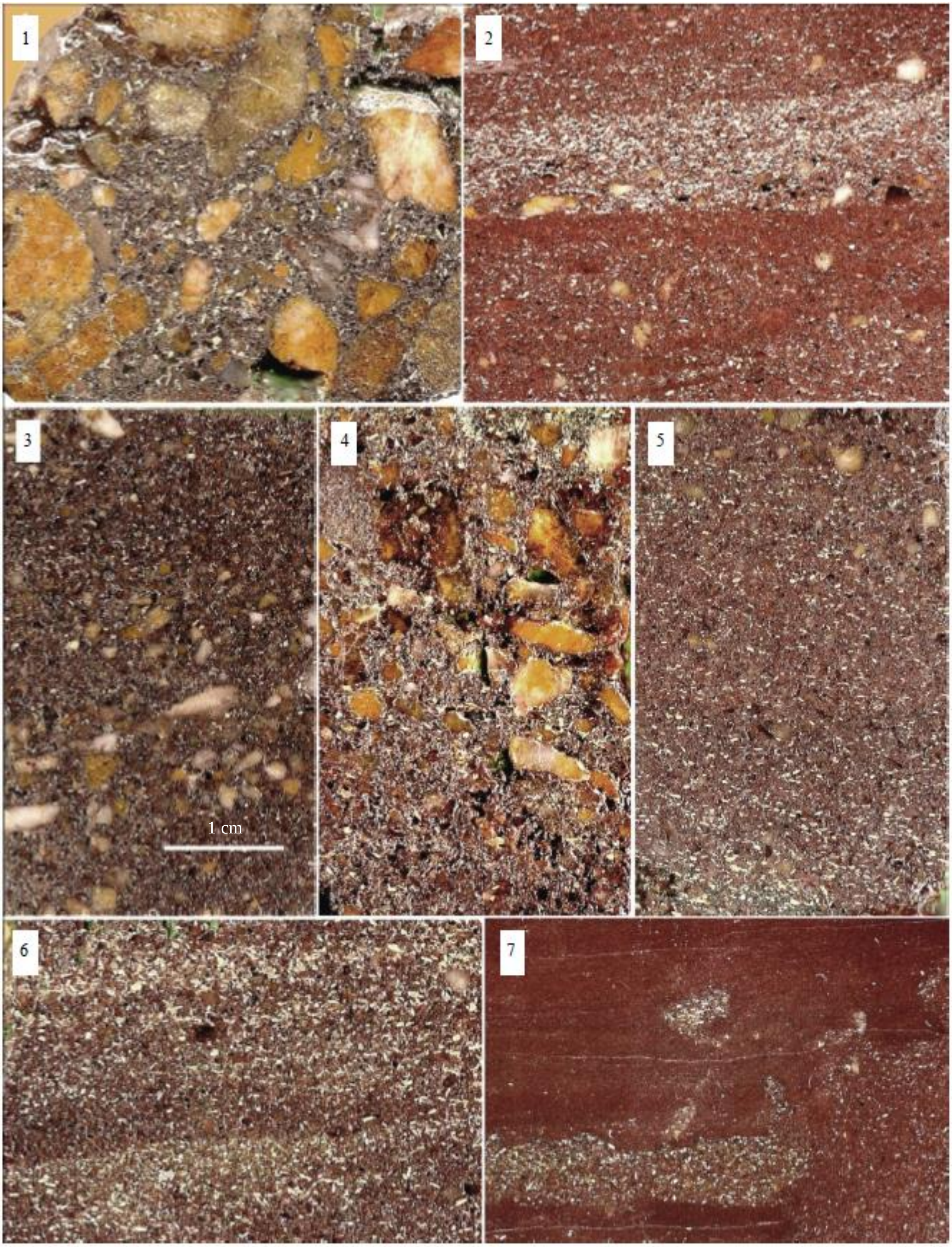

Fig.3. Morphological features of titanium-bearing rocks of the Pizhma deposit

Clastogenic psephytes of the lower red-colouredPR_3mr^1 Malorucheiskaya sequence and matrix are detritalvein quartz and quartzite, the filler is small fragments of the same quartz of the sandy fraction: 1 – conglobreccia; 2-4 – gritstones; 5, 6 – sandstones; 7 – silty-sandstone. Fines of yellow rutile leucoxene with a grain size of 100-500 µm, modal size 300 µm (the image shows scanned polished rock pieces 4-5 cm with the same magnification) inability of titanium transfer by hydrothermal fluid is considered a premature solution. One of the latest models suggests that the Yarega sandstones are of Neoproterozoic age, and the source of the ore material was lamprophyres for titanium phases and granites for zircon and other rare and rare earth minerals [22].

According to FGBU VIMS classification [27], metamorphogenic titanium deposits with leucoxene (one of which is the Yarega oil-titanium field) belong to leucoxene-quartz (according to the main mineral forms) bedrock deposits. The Pizhma deposit differs from the Yarega deposit in a more complex polymineral composition [3].

The Pizhemskoye deposit is unique in terms of reserves and mineral composition of ores: the main titanium phases are pseudorutile and leucoxene. There are no other similar deposits in the world. In the classification of titanium ore deposits, one should distinguish a new genetic subtype, pseudorutile-leucoxene-quartz, among metamorphogenic deposits [1, 6].

The Chetlassky ridge, 60 km southwest of the Volsk-Vym ridge (distance from the Pizhemskoye deposit), along with shales, is composed of thick quartzite strata that emerge on the day surface. This sequence of the Late and Middle Proterozoic rocks (Chetlasskaya, Anyugskaya, Vizingskaya, Novobobrovskaya, Svetlinskaya formations) is 100-200 Ma older than the shales of the Lunvozhskaya Fm. (PR_3lv) and 816.3 ± 5.2 Ma Volsk-Vym ridge [20, 28]. It can be assumed that these older strata compose the deeper part of the Volsk-Vym ridge. In this case, it is the quartzites from the older formations that do not emerge on the day surface in the Volsk-Vym ridge that can serve as a source of quartz sandstones and conglobreccias of ore sequences. Then follows the assumption of a deep vertical transportation of material.

An interesting feature of the Ichetyu and Pizhemskoye deposits is the composition of monazite [22, 29]. In contrast to monazite from placers all over the world, which has a high content of thorium in their composition (5-10 wt.% ThO_2), a characteristic feature of monazite from the Ichetyuoccurrence and Pizhemskoye deposits is low ThO_2 content (0.5 wt.% on average). The acicular, brittle form of the newly formed rutile in the Pizhma deposit ores indicates the formation of rutile *in situ* [30].

Doubts about the placer nature of the Pizhemskoye deposit are caused by the morphology of its ores, a limited area (spread over 6×18 km, i.e., about 90 km^2) with ore beds thickness from 30 to 140 m, an island bowl-shaped structure of ore bodies.

The hydrothermal-metamorphic (fluidization) model of the Yarega and Pizhemskoye deposits formation occurs in a series of works [1, 3, 31, 32]. The fluidization model should be shownexemplified by the Ichetyu occurrence, located strictly above the Pizhemskoye titanium deposit. Its analogues with respect to the mineral composition and features of formation structure are unknown. The mineral (species) composition of the Pizhemskoye deposit and Ichetyu occurrence coincides by about 80 %. The polymineral Ichetyu occurrence (diamond-gold-rare-earth-rare-metal-titanium) is an intermediate reservoir (0.5-1.5 m thick) of unusual genesis, structure, and mineral composition with a discontinuous spotty-lentiformshape, composed of conglobreccia from slightly rounded pebbles, quartz sandstone fragments with sandy quartz filler.

Heavy fraction yield is 0.2-2.0 kg/m^3. The conglobreccia combines six paragenetic mineral associations from several primary endogenous sources: gold-quartz; diamond (with indicator minerals); titanium (Mg, Mn, V, Nb, Cr-ilmenite-Fe-rutile-pseudorutile-leucoxene); niobium (Nb-rutile-rutile-columbite); zircon (with staurolite, tourmaline, amphibole, and garnet); rare earth (xenotime-monazite-coularite-florensite). The ratio of mineral associations in heavy concentrate samples over the area of conglobrecciabed distribution varies greatly. It can be assumed that under the study region of the Pizhemskoye deposit, in the Riphean quartzite-shale sequence, there were several endogenous occurrences at different depths in the vertical column of the crystalline basement. They could serve as a source of mineral associations that are separated in time from each other, but as a result of a single fluidization process, they are all combined in the Ichetyu conglobreccia bed.

Not a single manifestation with similar mineral associations is knownon the day surface in the studied region of the Volsk-Vym ridge (except for the Pizhemskoye titanium deposit). However, there are analogues in the neighbouring ridge (Chetlassky Kamen) 60-80 km southwest of the Ichetyu manifestation, in the older Neoproterozoic shale-quartzite sequence of the Vizingskaya Fm. (PR_3vs). This suggests that a similar PR_3vs sequence occurs below the Neoproterozoic PR_3lv shales in the Volsk-Vym ridge. The destruction and vertical transportation of the material in such a section could give a diverse mineral species composition (more than 50 mineral species) of the Ichetyu occurrence.

The Ichetyu occurrence is a younger formation in the bottom part of the Middle Devonian Pizhemskaya Fm. (D_2pz) quartz sandstone sequence. It was intruded into it, probably, in the Late Devonian synchronously with basalts. This is proved by the following facts and observations:

1. Discontinuous spotty-lenticular shape of bodies.

2. Presence of boudins of Pizhemskaya sandstones (to 1 m in size) inside the Ichetyu body, presence of quenching clarified thermal contacts of boudins and covering them from all sides with conglobreccia material (for example, in the Zolotoy Kamen outcrop).

3. A case of a vertical position of diamond-bearing conglobreccia body and its intersection with the underlying rocks of the PR_3mr^3 Malorucheiskaya sequence was documented (stripping in K-100 open pit, right side of the Srednyaya River). The size of a bed fragment, similar to a concrete vertical wall, in the stripping: length – 6 m; thickness – 0.5 m; traced to the depth of the vertical penetrationof the bed for 2.5 m. The length and depth of the body were penetrated partially due to technical capabilities. This is a direct observation of the introduction channel of conglobreccia or sill foot, that is, the rock intruded from below.

4. The presence of the Riphean rocks fragments in the conglobrecciacomposition: shales; weakly rounded quartzites; quartz veins; weakly rounded quartz crystals to 1-3 cm; sandstones of the Pizhemskaya Fm.; fresh basalts (similar in appearance to the Late Devonian basalts). The shape of rock pebbles is irregular spherical or slightly elongated elliptical (with concave curved surfaces), and not flattened, which excludes the assumption of the bed genesis as a "sea beach placer".

5. Clastogenic coarse grains of quartz in the composition of the reservoir filler prove the nearby provenance of this material.

6. The quantitative composition of isomorphic admixture elements in fine-grained quartz of the reservoir filler (Al, Ge, Ti) according to electron paramagnetic resonance data is sharply different from the rounded quartz grains of the Pizhemskaya Fm. D_2pz.

7. The results of determining the age of zircon with wide variations in values from Late Proterozoic to Early Archean [30] in the absence of Phanerozoic values indicate in favour of the vertical upward transportation of material during the Ichetyu bed formation.

All these facts prove the late injection of the Ichetyu reservoir into the consolidated lithified sequence of the Middle Devonian sandstones as fluidisites or tuffizites. The fluidisite material had an elevated temperature, as evidenced by the thermal quenching contacts of boudins (to 1 m in size) and fragments of host quartz sandstones of the Pizhemskaya Fm. (2-10 cm in size) in the composition of the conglobreccia bed, as well as hydrothermal alteration of some ore minerals in the conglobreccia: high-yttrium zircon [30, 31]; recrystallization with purification of niobium-rutile from admixtures [32]; baddeleyite rims on zircon; zinc rims on chrome spinel [33]; florensite rims on cularite and diamond [15]; small druses of anatase on leucoxene, etc.

The point of view about the placer nature of the Ichetyu occurrence and titanium deposits turns on another problem:determination of the lateral direction of material removal and the facies belonging of "pseudo-placers" (alluvial, deltaic, eolian, sea beach, etc.).

We also consider the point of view that the oil-titanium Yarega field is a direct analogue of the Pizhemskoye deposit to be erroneous [12, 17]. The conditionally sedimentary origin of the Yarega deposit is proved by numerous finds of remains of biota (spores and pollen) of both the Middle and Late Devonian. However, we can assume that Devonian pollen could have been brought by oil (whose own age is Permian-Jurassic [21]) migrating into ancient superporous sandy titaniferous reservoirs. The leucoxene-quartz rocks of the Pizhemskoye deposit never were primary sedimentary. The aggressive environment during the deposit formation did not contribute to any life and the preservation of its remains.

The age of the Pizhemskoye deposit, as shown by Rb-Sr isotope-geochemical studies, is much older than it is commonly believed, Riphean (685 ± 30 Ma) [23]. The considered model of the Pizhma deposit and the Ichetyu occurrence formation provides for the vertical transportation of huge masses of material like mud volcanoes in a continuous pulsating mode and the filling of negative topographic features of the crystalline basement composed of shale.

Structure of the Pizhemskoye deposit ore bed is similar to a fluidisate caldera structure. Such a unusual structure of the titaniferous Malorucheiskaya Fm. was revealed during geological exploration using exploratory drilling in 2011-2013 on a license block of 35 km^2, carried out by FGUNPP Aerogeologiaby the order of RUSTITAN JSC (the owner of a license for titanium prospecting, exploration, and production). Computer simulation enabled to construct a 3D model of the ore bed and specifythe morphology of the titaniferous Malorucheiskaya Fm. [1]. The ore sequence has a cellular structure and infills all the negative forms in the rugged topography of the Riphean basement, the difference in the absolute elevations of the roof of which exceeds 300 m. The most complete section of titaniferous rocks with a three-member division of the Malorucheiskaya Fm. (PR_3mr^{1-3}) is observed only in the negative forms of the basement topography, where the Ichetyu conglobreccia bed is present.

An analogy with the structure of mud volcanoes, which form volcanic cones (from their slopes the material slides into the lowlands), is noted. Such hills and bowl-shaped depressions are numerous; they create a cellular structure of the ore bed. There are no morphological signs of the presence of ancient river valleys. The bowl-shaped structures of the titaniferous strata occurrence are also visible in the geological sections [1]. It is assumed that the bedrock source of titanium and many other indicator minerals were dikes of lamprophyres (spessartites and comptonites), whose fields are widespread in the neighbouring ridge (Chetlassky Kamen) [16, 34] and, presumably, lie in depth the Volsk-Vym ridge as well. The evidence is provided by the typomorphic features of indicator minerals in the Pizhemskoye titanium deposit [3] and the Ichetyu polymineral ore occurrence (Mg, Mn, V, Nb, Cr-ilmenite, Zn-chromium spinel [33], rare garnet with a majorite component, a indicator mineral of diamond [16], biotite, amphiboles, etc.), coinciding in chemical composition with rock-forming and accessory minerals of lamprophyres [15, 30].

The driving factor of the fluidization process could be metamorphic waters, which met with intruding hot magmas or lamprophyres, which intruded at the age boundary of 600-800 Ma (this is exactly the age of the Chetlassky Kamen lamprophyres) [34]. The superheated fluid destroyed and disintegrated lamprophyres with the formation of quartz, kaolinite, hydromica, titanium ore minerals, etc. All these phases rushed upward in the fluidized flow, captured in ancient strata quartz grains from quartzites, veined quartz with gold, ore minerals (monazite, xenotime, niobium rutile, columbite, rutile) from small occurrences, diamonds from intermediate reservoirs. Zircon could be extracted sequentially from various rocks (including granites) in the entire basement sequence of different ages, from Archean to Late Proterozoic.

Aggressive superheated water-carbon dioxide fluid transformed ilmenite into leucoxene at a high temperature of 510±35 °C, based on the calculation using a titanium-zircon geothermometer [35, 36] according to the scheme [1, 6]:

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$$3FeTiO_3 + 2SiO_2 + O_2 + CO_2 \rightarrow \text{leucoxene } 2[TiO_2]\cdot[SiO_2] + FeCO_3 + Fe_2O_3 + TiO_2.$$

The Pizhemskoye deposit could have been formed for a long time; the alteration of minerals continued both at depth in the presence of a high-temperature fluid and during a low-temperature hydrothermal stage already on the surface. The source of iron for the formation of siderite-hematite cement of sandstones in the lower stratum of the Malorucheiskaya Fm. (PR_3mr^1) could be destroying micas and ilmenite. The ferruginization of sandstones occurred in the hydrothermal stage. Carbon dioxide had a deep origin, as evidenced by the isotopic composition of carbon in siderite [18], close to the carbon composition of diamonds from the Ichetyu occurrence, which originate from mantle eclogites [37]. The hydrothermal-metamorphic model of the Pizhemskoye deposit and Ichetyu occurrence formation eliminates many contradictions of the placer model.

The deep source of material provides information about the origin of clastogenic quartz from sandstones of psammite and gritstone dimensions (Fig.3), which is absent on the surface and in shales. The same applies to all ore minerals, the manifestations of which are unknown in the underlying shale of the Lunvozhskaya Fm. Diamonds in the Ichetyu conglobreccia can not originate from non-diamond-bearing kimberlite pipes (Umbinskaya, Srednenskaya, and Vodorazdelnaya) 12-14 km southeast of the ore field, since the age of the pipes is the Late Devonian, and the Ichetyu conglobreccia is localized in the Middle Devonian sandstones. Diamonds found in the Ichetyu occurrence have a different, deep origin, along with other mineral components of the deposits under consideration. The Ichetyu ore occurrence is promising in terms of resources of zircon, Au, Y, Nb, Ce, La, Nd. Among the mineral diversity of the Ichetyu occurrence, zircon makes up more than 50 wt.% of the heavy concentrate in a number of samples in the fraction of 0.10-0.25 mm and is of commercial interest.

Zircon deserves special attention both from the point of view of genetic information and commercial analysis. Zircon reserves in C_2 category on an area of 12 km^2 in the Central plot of the Pizhemskoye deposit amounted to 151 Kt of ZrO_2 [1]; in P_1 category, only in the license block of the Pizhemskoye deposit with an area of 35 km^2, they approach 1 Mt (according to RUSTITAN JSC). The probable source of zircon is the Timan basement rocks. It is proved by its characteristic geochemical features, isomorphism of rare earth elements according to the xenotime scheme [30, 31]:

$$Zr^{4+} + Si^{4+} \rightarrow (Y^{3+} + REE^{3+}) + P^{5+}.$$

Probably, this source was granites of about 1200 and 1500 Ma, corresponding to the most intense peaks in the age diagrams for both sites. This circumstance does not allow zircon transportation from adjacent regions, since no such geochemical varieties of zircon have been found either in the Urals or on the Fennoscandian Shield.

It is difficult to imagine that huge zircon masses were transported by wind or sea currents thousands of kilometres away from the Baltic Shield or the Urals, forming the Pizhemskoye zircon-titanium deposit and the overlying Ichetyu diamond-gold-rare-metal-rare-earth-titanium occurrence. The morphological features of zircon, medium roundness and good preservation, suggest that zircon grains and crystals have a nearby provenance. The direction of ore masses transportation was vertical, not lateral.

Based on the conducted mineralogical and geochronological studies, it can be assumed that the Middle Timan basement (the most probable source of zircon) is composed of the Proterozoic rocks and, probably, is a continuation of the Belomorian mobile belt. Thus, the Paleoproterozoic collisional structure, oriented in the northwest direction, continues under the Mezen syneclise and Middle Timan. The isotope geochemical age determinations of zircon from the Pizhemskoye deposit and Ichetyu occurrence (570-3200 Ma) [30, 31] characterize namely the age features of the rocks that make up the Timan basement. Close correlations between the age characteristics of zircon from the

Pizhemskoye deposit and the Ichetyu ore occurrence allow us to conclude that both ore sites have a common source of zircon. Age boundaries (from the Archean to the Riphean-Vendian) are repeated in the isotope geochemical determinations of zircon, monazite, rutile, and platinoids [30-32].

The experience of foreign researchers is useful to establish the genetic and rock affiliation of grains of accessory zircons from the studied titaniferous deposits of Timan. Examples of compositionally anomalous zircons from rocks of different composition and age are united by the impact of fluids enriched in incompatible elements (HFSE and REE), which are usually immobile during magmatic and metamorphic processes [38]. Zircons from the metasediments of the Dalradian complex in Scotland showed a high content of Y (to 5 wt.% Y_2O_3), which was formed during intensive fluid processing of rocks [39]. The Th/U ratio, close to 0.1-0.3 for zircons with sectorial zoning and zircon cores, corresponds to the range of Th/U ratios for metamorphic zircons [40]. Granulite zircons are distinguished from other populations by their colour: they are mostly colourless or light pink grains with a "diamond" lustre. They are characterized [41, 42] by an isometric or rounded shape of zircon grains resembling a ball. A high degree of LREE fractionation for the population of zircons that are dark in the CL image [43], the zones of alteration in them and some of the nuclei in the discriminant diagrams Ca-U, Sm_N/La_N-La, and others fall into the field of hydrothermal zircons and into the region of porous zircons formed as a result of intensive fluid processing.

Preliminary results of zircon dating by the U-Pb method (SHRIMP-II, CIR VSEGEI) from shales of the Riphean basement under the Pizhemskoye deposit give an age range of 1.1-2.2 Ga with two clear maxima, 1100-1200 and 1450-1550 Ma, which are close to the same peaks for zircon in the described sites. According to other researchers of the Northern [44], Middle [28], and Southern Timan [45], there are no zircon younger than 1000-1100 Ma in the basement rocks. These data are fundamentally different from the results of studying zircon from the Ichetyu ore occurrence and the Pizhma deposit. The latter containsa considerable proportion of younger grains (570-1000 Ma) that could not have been brought from the neighbouring provinces.

By all indications, the underlying Riphean shales of the Lunvozhskaya Fm. could not be the bedrock source of zircon and titanium for the formation of the giant Pizhemskoye zircon-titanium deposit. Data obtained from zircon of the Pizhemskoye deposit and Ichetyuoccurrence, namely, young stable datings with an age of about 600 Ma and the features of the rare element composition of this zircon, as well as the age of a single event determined from rutile and monazite, reveal the time limit of the hydrothermal alteration of these minerals, about 600 Ma [29]. This age can be considered as the time of intense hydrothermal alteration of the bedrock sources, which determined the Pizhemskoye deposit and Ichetyu occurrence formation. It can be assumed that there was a single local bedrock source of minerals of titanium (Mg, Mn, V, Nb, Cr-ilmenite-Fe-rutile-pseudorutile-leucoxene), zircon, and rare earth associations for both objects of the Pizhemskoye deposit and Ichetyu ore occurrence.

The titanium assemblage of minerals in the Ichetyu conglobrecia originates either from the Malorucheyskaya (PR_3mr) titaniferous sequence of the Pizhemskoye deposit or from a similar bedrock source. The collection area of the minerals present in them may be somewhat different. Judging by the age of zircon from the Ichetyu occurrence (the presence of the Archean grains), it can be assumed that the source of some minerals (diamonds, zircon, etc.) is deeper.

In the adjacent region of the Middle Timan, there are no visible outcropping mineral manifestations, the destruction of which and the transportation towards the Ichetyuoccurrence and Pizhemskoye deposit could contribute to the formation of the observed commercial concentrations. It remains to assume only a deep source of ore material for the sites under consideration. In terms of typomorphic features, many minerals are close to the rock-forming and accessory minerals of lamprophyres [3, 16]; therefore, it is assumed that one of the bedrock sources of both sites was precisely lamprophyres, which form large dike fields with an area of several tens of square km in the Chetlassky Kamen ridge [16, 34]. It is likely that similar large dike fields of lamprophyres are deep under the Pizhemskoye deposit, and they could be the bedrock source of these sites. The most famous and studied in the Chetlassky Kamen are the Kosyu, Bobrovskoe, and Oktyabrskoe dike fields of lamprophyres. According to Rb-Sr isotopic data, a large set of lamprophyre samples forms an isochronewith Neoproterozoic age of 819 ± 19 Ma [34]. There are also lamprophyre dikes about 606 ± 10 Ma in age, coeval with the Chetlassky carbonatites. The most probable source of the ore material, apart from the high-Ti Chetlassky lamprophyres (spessartites and comptonites), may also be the alkaline basalts of the Volsk-Vym ridge [16]. The age of ore minerals (thorite, monazite, and tantalum-niobates) from the Novobobrovsky complex rare-metal-thorium-rare-earth deposit in the Middle Timanwas determined by the Sm-Nd method as 581 ± 47 Ma [46]. This indicates an extended period of lamprophyre magma generation in the Middle Timan, covering a period of about 200 Ma [16, 34]. However, this is not the only possible source of ore minerals in the deposits under consideration. The source of monazite, zircon, columbite, rutile, and other minerals could be the other, echeloned at different depths, small occurrences of such minerals.

The mechanism of vertical transportation of significant material masses is a complex issue. There is an assumption that lamprophyres under the influence of aggressive fluids could be destroyed, forming disintegrated rocks (weathering crusts at depth). In this case, biotite from lamprophyres could transform into kaolinite and hydromuscovite-illite, and ilmenite into leucoxene, siderite, and hematite. These are the main rock-forming and ore minerals in the Pizhemskoye deposit rocks. Metamorphic fluids (water and carbon dioxide) were the driving factor for the transportation of mineral material upwards; thermal energy was provided by the intruding Riphean magmas or divergent phases of the lamprophyres themselves. Two phases of magmatic activity can be assumed, Riphean (800-600 Ma) and Late Devonian (370-360 Ma). The first led to the formation of the Pizhemskoye deposit, the second caused the separation of ore material to form the Ichetyu occurrence and its movement up the section. The second phase of intrusion exploited the already developed permeable fault zone. The high activity of carbon dioxide in the proposed process is evidenced by the huge masses of siderite in the Pizhemskoye deposit and the overlying Late Devonian basalt tuffs (D_3vl) of the Valsovskaya Fm saturated with calcite.

Conclusion. Unique in terms of reserves Timan titanium deposits, Yarega and Pizhemskoye, belong to the same genetic type of metamorphic bedrock leucoxene-quartz deposits. Pizhemskoye deposit belongs to a special subtype, pseudorutile-leucoxene-quartz.

The primary mineral in both deposits is ilmenite. Leucoxene, as the final phase of ilmenite alteration, formed in a multistage chemical hydrothermal process with the participation of carbon dioxide fluid. Iron is removed from the primary mineral (ilmenite → Fe-rutile → pseudorutile → leucoxene+rutile) in the form of bicarbonate, which is transformed into siderite and, together with kaolinite, hydromuscovite, and hematite, forms a strong cement of ore titaniferous sandstones.

The Yarega and Pizhemskoye deposits cannot be considered placers, since they do not meet the necessary criteria: the minerals, titanium phases, were not transported in water flows (they are brittle) and formed on site, as well as the main rock-forming mineral of sandstones, clastogenic unrounded quartz (abrasive material). Secondary hydrothermal siderite forms a strong bond (cement) between all minerals; therefore, ore sandstones do not meet the second sign of placers, useful components are not found in loose rock in the form of free grains (additional technological methods are required to extract them from aggregates).

The Riphean shales cannot be the bedrock source of titanium in the two Timan deposits, since they do not form thick classical, zonal chemical weathering crusts sufficient for reserves accumulation. As for the accessory ilmenite in the Riphean shales (“clean” from usual typomorphic admixtures), it has a different chemical appearance, in contrast to the relict ilmenite (rich in Mg, Mn, V, Nb, Cr) in both deposits. Anatase-leucoxene, which develops after shale ilmenite, is minimally distributed in titaniferous sandstones of bedrock deposits, where rutile-leucoxene predominates.

Igneous mafic and alkaline-ultramafic rocks can be the most suitable as the bedrock source for the material of these deposits in terms of the accessory mineral spectrum. Weathering crusts along dike fields of lamprophyres, similar to Chetlassky ones, could be one of the material sources in titanium deposits.

The hydrothermal alteration of accessory minerals-geochronometers (zircon, rutile, and monazite) and (Mg, Mn, V, Cr, Nb)-ilmenite from the Ichetyu occurrence and Pizhemskoye deposit occurred at about 600 Ma. The isotope-geochemical study of zircon from the Ichetyu occurrence and Pizhemskoye deposit allows us to make an important conclusion: zircon from the Ichetyu ore occurrence is similar to zircon from the Pizhemskoye deposit in terms of the increased content of non-formular elements (Y, REE, P, Nb, Ti, and Ca) and the presence grains with U-Pb ages of about 600 Ma. The obtained isotopegeochemical data on accessory minerals do not contradict the model suggesting intensive hydrothermal fluid processes during the Ichetyu ore occurrence and Pizhemskoye deposit formation.

This study does not put an end to the discussion about the genesis of titanium deposits in the Middle Timan. Each of the considered hypotheses has its own rational grain, but there are also serious contradictions. The development of a reliable model for the formation of titanium deposits in the Middle Timan requires additional geological and mineralogical studies, in particular, the study of accessory and ore minerals by modern isotope geochemical and other methods.

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