Prospects for the titanium carrying Triassic formations of the Bolshaya Synya depression of the Pre-Uralian marginal flexure

M Sokerin¹, V Saldin¹, I Golubeva¹, N Sokerina¹, E Korolev²

¹Institute of Geology, FIC Komi Scientific Center, Ural Branch of the Russian Academy of Sciences, Syktyvkar, Russia
²Kazan Federal University, Kazan, Russia

E-mail: sokerin@geo.komisc.ru

Abstract. It was established potentially industrial titanium-containing terrigenous rocks from the Lower and Middle Triassic formations of the southern part of the Bolshaya Synya depression, Pre-Uralian marginal flexure. Sandstones contain the bulk of productive mineralization and makeup about 80% of the Triassic section. Sandstones are represented by weakly lithified, finely grained lithoclast greywackes scattered in the hands with weakly rounded unsorted fragments, with pore, film, and contact type of cement form by hydrogetite and illite and chlorite. The proportion of relatively strong sandstones with calcite-siderite cement does not exceed 10% of the studied section. The deposits are formed in alluvial and pluvial, lacustrine depositional environments within the wide alluvial plain. The rocks belong to the upper part of the thick Permo-Triassic continental molasses formed in compensated depressions as a result of the destruction of the Paleo Uralian Orogeny. The main minerals of the heavy fraction are epidote, ilmenite, titanomagnetite, and amphibole; the minor minerals are chlorite, goethite, martite, pyroxene, chrome spinel and a group of garnets. The share of zircon does not exceed the first percent. The main mineral concentrator of titanium is ilmenite, the minor minerals are manganilmenite, titanomagnetite, titanite, leucoxene aggregates, rutile, and pyrophanite. The hypothetical primary source of ilmenite was epidote and amphibole contains shale or epidote containing amphibolite formed from a mafic substrate. The thickness of titanium contains layers is 1–4 m with an ilmenite content of more than 30 kg/m³. At the local level, ilmenite and titanomagnetite mineralization is concentrated in the form of small jets, lenses, puffs, and interlayer bodies. The average contents of ilmenite are comparable with those of the well-known titanium and zirconium placer deposits in Russia. The data presented in the article make it possible to predict the existence of new titanium contains region in the Triassic deposits of the south part of the Bolshaya Synya depression. The productivity of the region should be associated with continental ilmenite placers.

1. Introduction

In Russia, titanium is a deficit type of strategic mineral resources, although it has one of the leading places in the world in terms of balance reserves, almost all reserves of titanium are purchased abroad. The main industrial types of titanium deposits in the world are modern and ancient Upper Cretaceous and Paleogene-Quaternary ilmenite-zircon-rutile coastal-marine and continental placers with complex
titanium-zirconium mineralization. In Russia, similar objects are known in the Paleogene-Neogene deposits of the Stavropol Uplift, Trans-Urals, Northern Ustyurt, Northern Aral Sea, the southwestern part of the West Siberian Plate, the Paleogene and Mesozoic of the Chulym-Yenisei Depression and the Amur-Zeya Depression, the Yenisei part of the West Siberian Plate, Irkutsk coal-bearing basin. The share of total reserves is only 3-4%. This is almost an order of magnitude less compared to global indicators. Also, with the quality of resources comparable to world analogs, they are characterized by a deeper occurrence, difficult mining and geological and hydrogeological conditions of exploitation. Therefore, the search for such objects remains very relevant. One of the promising new titanium contains regions is the Bolshaya Synya Depression. In the east and south of depression were found rich ilmenite contains rocks in the Triassic units.

1.1. History of exploring the area

The evidence of ilmenite (up to 30% of the volume of the piece of ore sample) was found in slightly lithified Triassic sandstones in the south of the Bolshaya Synya depression, in the river basin Bolshaya Synya, by the geological survey party of B. V. Gribanov in 1957. Later, in 1961 ilmenite was found in the Lower Triassic sandstones on the right bank of the Pechora River, near Byzova village. I.S. Muravyev during geological surveying expedition discovered a placer with the content of ilmenite up to 320 kg/m³ and zircon up to 20 kg/m³. In 1963-1964 the Byzovskaya geological group confirmed the titanium content of these formations, by the leadership of B.I. Kostyushko (Fig. 1A). This served as the basis for the creation of the Pechorogorod gold-titanium ore-placer potential area within the Lower Triassic rocks in the southern part of the Bolshaya Synya depression [2].

In 2013-2014, we identified 8 mineralization points with a high content of ilmenite and proved the feasibility of isolating Bolshaya Synya titanium-placer in the basin of Bolshaya Synya river (Fig. 1B), during the geological exploration in the area Q-40-XXIX, scale 1: 200 000 (GDP-200).

1.2. Geological settings

The research area is located in the eastern part of the Bolshaya Synya depression of the Pre-Uralian marginal flexure (Fig. 1B). The Lower Triassic rocks in the modern erosion profile have a steep western or sub-vertical dip, forming the eastern wing of the asymmetric fold. The Middle-Upper Triassic formations of the Syninskaya formation have subhorizontal, but near the eastern boundary of the depression, the angles of incidence increase to 40°. The section of Triassic rocks is composed of sandstones, siltstones, claystones, and clays. The deposits are formed in alluvial and pluvial, lacustrine depositional conditions within the wide alluvial plain [3]. Formational, the rocks belong to the upper part of the thick Permo-Triassic continental molasses formed in compensated depression as a result of the destruction of the Paleo-Uralian orogen.

2. Materials and methods

Material for research is represented by samples from coastal outcrops. Intervals were tested with increased magnetic susceptibility relative to the background. The chemical composition of the rocks was determined on an XRF-1800 X-ray fluorescence spectrometer (Shimadzu) with correction according to the control sample with verification by silicate analyzes (12% of samples). It showed good convergence of the results (90-100% according to TiO₂ and ΣFeO). Data used by B.I. Kostyushko (Report of the Byzovsk search party for 1963-1964) was determined by the colorimetric method, the contents of TiO₂ and ZrO₂. For the study of the mineral composition was used binocular magnifier and an optical microscope Nikon EKLIPSE LV100ND. The mineral composition was studied using Tescom Vega 3 LMN and Jeol JSM-6400 scanning electron microscopes at the Institute of Geology, FIC Komi Scientific Center, Ural Branch of the Russian Academy of Sciences. The gross contents of ilmenite and
zircon were calculated according to the standard method of normative mineral recalculations of the results of chemical analyses. Calculations of the contents of these minerals showed their significant underestimation (on average 4 times) due to large losses of the material of thin (less than 0.05 mm) fractions already at the stage of sample elutriation using, according to a quantitative mineralogical analysis of the heavy fraction.

Figure 1. A - geological scheme of the southern part of the Bolshaya Synya depression
Figure 1. B - the work area GDP-200. Compiled from materials [2]. 1 – Syninskaya formation. Slightly lithified polymineral sandstones with intercalations of siltstones and clays. 2 – Krasny Kamen’ and Keryamael’ combined formations. Red clay, polymineral sandstones, siltstones, claystones. 3 – Byzovskaya formation. Polymineral sandstones and conglomerates. 4 – Ust’berezovskaya formation, polymineral sandstones, clay, conglomerates in the base of formation. 5 – Combined formation of the Krasny Kamen’, Keryamael, Byzovskaya formations and the Ust’berezovskaya formation. 6 - Khudorechenskaya formation. Sandstones, siltstones, claystones, limestone. 7 – Undivided Bolshoy Elmach, Kyrta.shor. Ust’pereborskaya and Vertny formations. Below – interbedded sandstones, polymineral siltstones; in top – sandstones, calcareous sandstones with coal. 8 – Not divided Kyrta.shor and Bolshoy Elmach formations. Polymineral sandstones, siltstones, interlayers of limestone and gravelites. 9 – Saryugya formation. Limestones, clayey limestones, interlayers of siltstones, claystones. 10 – Asyvvozh, Shaytanovskaya, Uldorkyrt formations, undivided Morchanovskaya, and Kozhvelderskaya formations. Carbonate breccias, limestones. 11 – Combined siliceous-carbonate, terrigenous and carbonate formations. Limestones, sandstones, siltstones, claystones, and dolostones. 12 – Placer with ilmenite. 13 – Work area of the Byzovskaya geological survey.
3. Results

Sandstones, which have at least 80% of the entire section, are poorly lithified, finely grained greywacke with weakly rounded and unsorted fragments. Cement is represented by hydrogetite, illite-chlorite and clay minerals. The proportion of relatively strong sandstones with calcite-siderite cement does not exceed 10% of the thickness of the studied section. The content of lithoclastic material in sandstones varies in the range from 50 to 70 vol. % These are mainly silicates, microquartzites, and phyllites. The share of the remaining rocks does not exceed the first percent (quartz, sericite and quartz, chlorite crystalline shales, effusives, and granitoids). Mineral fragments occupant 10-30 vol. % and represented mainly by quartz and pelletized potassium feldspar. The main minerals of the heavy fraction are epidote, ilmenite, titanomagnetite, and amphibole; the minor ones are chlorite, goethite, martite, monoclinic and rhombic pyroxene, chromspinelides and a group of garnets (Fig. 2). Apatite, monazite, xenotime, and serpentine are found as accessory minerals.

![Figure 2. Shares of the heavy fraction (rel.%). 1 - Ti-magnetite; 2 - ilmenite; 3 - amphibole; 4 - pyroxene; 5 - epidote; 6 - martit; 7 - goethite; 8 - chromspinelids; 9 - garnet; 10 - chlorite. A – sandstones of the Byzovskaya formation (38 analysis), B – rocks of the Keryamael’ formation (2 analysis), C - sandstones of the Bolshaya Synya formation (5 analysis), D – ore sands of the Bolshaya Synya formation (2 analysis).](image)

Mineral associations of ilmenite, especially quantitative ratios with titanomagnetite, significantly depend on the age of the rocks. If in the Lower Triassic of Byzovskaya formation the ratio of ilmenite, titanomagnetite, and epidote is in approximately equal proportions, in younger rocks, ilmenite is 5–20 times predominant over titanomagnetite and 3–10 times over epidote. The proportion of zircon does not exceed the first percent, only in one sample was established in a 20 percent ratio to ilmenite. According to the regulatory recalculation of chemical analyzes, the zircon content usually ranges from 0.5 to 0.7 kg/m³. The main concentrator of titanium minerals are ilmenite, and secondary minerals are manganilmenite, titanomagnetite, titanite, leucoxene, rutile, and pyrophanite. The total fraction of titanite and rutile concerning the amount of ilmenite does not exceed 5 vol. %. The content of TiO₂ in titanomagnetite is not more than 5 wt. % of the total amount in the studied samples. Thus, about 90 wt. % of the gross amount of titanium is located for ilmenite.

Ilmenite is represented by angular isometric fragments (Fig. 3A, B) in cement, rarely tabular grains that save the primary morphology of crystals. The maximum grain size is 0.5 mm; at least 70% is a fraction of less than 0.05 mm. The mineral doesn’t have secondary changes, except for rare cases of leucoxenization (Fig. 3C, D).
Most of the studied ilmenite grains are characterized by a homogeneous structure (Fig. 4A). Decay structures are rare in ilmenite-hematite composition. Structures were noted with two stages of solid solution decomposition, where in the lamellas of hematite and ilmenite of the first generation form microinclusions of ilmenite and hematite of the second generation (Fig. 4B). Sometimes are observed regenerative ilmenite rims on hematite. Of the inclusions in ilmenite were diagnosed, apatite and baddeleyite.

According to microprobe analysis, the content of TiO$_2$ in ilmenite varies (in wt.%) from 41.91 to 59.60, averaging 49.9, total iron - from 31.84 to 55.38, on average - 43.2. A constant admixture of MnO was noted (4.5 on average, excluding manganilmenite and pyrophanite). In some samples was detected the presence (in wt%) of MgO (up to 3.19), V$_2$O$_5$ (up to 1.06), Cr$_2$O$_3$ (up to 0.15).

Studies of the typomorphic properties of ilmenite and the minerals associated with ilmenite showed that the most probable primary sources were epidote and amphibole shales or epidote containing amphibolites formed from the mafic substrate. Modern analogs of such rocks are ilmenite containing crystalline shales, known in the composition of the Nerkayskogo complex of the Subpolar Ural [4]. Productive mineralization is a group of essentially ilmenite placers of near drift. This is indicated by the absence or weak degree roundness of ilmenite and the material of the host rocks and the low zircon content in ore sands.
Figure 4. The internal structure of ilmenite grains. A - typical homogeneous structure; B - hematite-ilmenite decomposition structure. Ilmenite is dark gray, hematite is gray. SEM image in the mode of backscattered electrons.

According to furrow testing of rocks, the thickness of titanium-bearing layers is 1–4 m, with an ilmenite content of more than 30 kg/m³ (cut-off grade accepted for forecast estimates). The layers are characterized by a fall position. At the local level, ilmenite-titanomagnetite mineralization is concentrated in the form of gray, dark gray fine jets with a diameter of 1-3 cm and a length of 0.3-1 m. They are inconsistent by the fall of millimeter layers, often grouped in bundles and interlayers (5-15 cm). In a point sample, the maximum content of ilmenite was 102 kg/m³, in mineralization point 2 (Fig. 1B). Often ilmenite rich intervals no differ from a relatively poor part of rocks neither in appearance and magnetic. According to mineralogical analysis, samples from these intervals characterize in the lowest concentrations of magnetite and goethite.

The distribution of ilmenite contents in most mineralization points is relatively uniform, which is confirmed by small values of the coefficient of variation calculated by the results of chemical analyzes of furrow rock samples and spot samples (Table 1).

| Point | Formation | Number of samples | Content of interval | Average content | Median value | Coeff. variations,% | Number of samples with content more than 30 kg/m³ |
|-------|-----------|-------------------|--------------------|-----------------|--------------|---------------------|-----------------------------------------------|
| 1     | Syninskaya | 3                 | 27—40              | 32              | 30           | 21                  | 2                                             |
| 2     | Syninskaya | 5                 | 8—25               | 15              | 13           | 43                  | 0                                             |
| 3     | Syninskaya | 2                 | 32—102             | 67              | —            | —                   | 2                                             |
| 4     | Keryamael` | 2                 | 19—26              | 22              | —            | —                   | 0                                             |
| 5     | Syninskaya | 1                 | 17                 | —               | —            | —                   | 0                                             |
| 6     | Syninskaya | 5                 | 17—39              | 28              | 27           | 37                  | 2                                             |
| 7     | Keryamael` | 8                 | 21—38              | 32              | 35           | 21                  | 6                                             |
| 8     | Byzovskaya | 13                | 23—72              | 37              | 36           | 40                  | 8                                             |
The average ilmenite contents are shown in Table 2. Intervals are comparable in the studied section, with those of the known titanium-zirconium placer deposits in Russia (Table 3).

### Table 2. The content of ilmenite in the Triassic rocks Bolshesyninsky and Pechorgorodsky potential areas (in kg/m$^3$)

| Formation                  | Number of samples | Content of interval | Average content | Coeff. variations,% |
|----------------------------|-------------------|---------------------|-----------------|--------------------|
| Bolshesyninsky titanium-placer area |                   |                     |                 |                    |
| Byzovskaya                 | 11                | 23—72               | 37              | 40                 |
| Keryamael’ and Krasny Kamen’ | 12                | 19—38               | 31              | 23                 |
| Bolshaya Synya             | 30                | 8—102               | 29              | 66                 |
| Pechorgorodsky gold-titanium ore-placer area |       |                     |                 |                    |
| Ust’berezovskaya           | 43                | 16—57               | 32              | 23                 |
| Byzovskaya                 | 255               | 16—379              | 40              | 94                 |

**Note.** The indicators for the Pechorgorodsky gold-titanium ore-placer potential area are calculated according to B.I. Kostyushko, 1964.

### Table 3. Average ilmenite contents (in kg/t) and exploitation methods for deposits of titanium-zirconium placers in Russia (according to [1])

| Index          | Deposits of the European part | Deposits of Western Siberia |
|---------------|-------------------------------|-----------------------------|
|               | Central                       | Deposits of the European part | Deposits of Western Siberia |
|               | Beshpagirskoe                 | Lukoyanovskoe               | Tuganskoye                  | Tarskoye                  | Georgievskoe            | Ordynskoye              |
| ilmenite      | 31.3                          | 21.8                        | 66                          | 30.5                      | 48.4                      | 31.6                      | 26.52                     |
| rutil         | 6.3                           | 8.4                         | 8.33                        | 4.8                       | 6.5                       | 4.5                       | 5.32                      |
| zirkon        | 5                             | 10.3                        | 21.93                       | 12.8                      | 8                         | 12.4                      | 6.95                      |
| method of exploitation | quarry + DHP           | quarry + DHP               | quarry + DHP               | DHP                       | DHP                       | DHP                       |

**Note.** DHP—downhole hydraulic production.

As shown above, it is possible to substantiate the isolation of the Bolshesyninsky titanium-placer potential area in the eastern part of the Bolshesyninsky depression. Proven resources of this area only within area Q-40-XXIX amounted to 3 million tons of ilmenite. When assessing the prospectivity of the territory of the Bolshaya Synya depression on titanium it is necessary to take into account the presence of ilmenite similar in content and mineral composition of the Byzovsky mineralization, which localized in the rocks of the Ustberezovskaya and Byzovskaya formations, in the valley of the Pechora River. A positive factor...
in the prospects of this object is also the relatively small thickness of the Cenozoic cover (up to 30 meters). It allows using the quarry mining method.

Conclusions

Thus, it is possible, in our opinion, with a certain degree of confidence to predict the discovery in the Triassic deposits of the Bolshaya Synya depression of the Pre-Uralian marginal flexure a new potential titaniferous area. The productivity of area should be associated with continental ilmenite placers such as the Irshinsky group of deposits in the Volyn’ region of Western Ukraine.

Acknowledgments

This study was performed in the context of the Russian Government Program of Competitive Growth of Kazan Federal University and partial financial support of the Russian Fund of Fundamental Research, project 18-45-110009 p_a.

References

[1] Bykhovsky L Z Titanium raw materials of Russia: problems of development and development of SMEs http://www.minsoc.ru/E2-2011-6-0/.
[2] Vodolazskaya V P, Oparenkova L I, Zarhidze D V 2013 State geological map of the Russian Federation. Scale 1: 1 000 000 (third generation). Series Ural. Sheet Q-40 - Pechora. Explanatory letter (Saint-Petersburg: Cartographic factory VSEGEI) p 365
[3] Chalyshev V I and Varyukhina L M 1966 Biostratigraphy of the Triassic of the Pechora region (Moscow: Nauka) p 150
[4] Shmakova A M, Golubeva I I, Sokerin M Yu 2018 Mineralogy of titaniferous deposits of the Middle Triassic on the river Kydzrasyu (Pre-Ural marginal deflection) Bulletin of the IG Komi Scientific Center of the Ural Branch of the Russian Academy of Sciences 2 28-37