The chemical composition and age of monazite and kularite from titanium ore of Pizhemskoye and Yarega deposits (Middle and Southern Timan)

A.B. Makeyev1*, S.E. Borisovsky1, A.O. Krasotkina2

1Institute of Ore Geology, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences, Moscow, Russian Federation
2Institute of Precambrian Geology and Geochronology of the Russian Academy of Sciences, Saint-Petersburg, Russian Federation

Abstract. A study on the typomorphic characteristics and age of the monazite the two giant titanium deposits of the Timan – Pizhemskoye and Yarega, which revealed differences in morphology in the species composition of the inclusions, the grain size, distribution of chemical types of a mineral associated with conditions of crystallization and different sources of the substance. The isochronous Th-Pb monazite age was calculated using the cHIME method. For Yarega monazite built three isochrones with age 1301, 1105 and 778 Ma; for Pizhemsky monazite-kularite one isochrone with age 782 Ma. Source of high-Th monazite Yarega oil-titanium deposit could be ancient granite batholith and the origin Yarega less-Th monazite and Nd-Ce-monazite-kularite Pizhemskoye deposit with an age of ~ 780 Ma could be related to the hydrothermal conversion of the weathering crusts on lamprophyres close in age with lamprophyre (spessartite and kersantite) of Chetlasmky Kamen.

Keywords: Pizhemskoye titanium, Yarega oil-titanium deposits, Timan, monazite, kularite, chemical composition, age

Recommended citation: Makeyev A.B., Borisovsky S.E., Krasotkina A.O. (2020). The chemical composition and age of monazite and kularite from titanium ore of Pizhemskoye and Yarega deposits (Middle and Southern Timan). Georesursy = Georesources, 22(1), pp. 22-31. DOI: https://doi.org/10.18599/grs.2020.1.22-31

Monazite is a phosphate of cerium-group light rare-earth elements. It is a rare but very informative compositionally variable mineral occurring in Timan titanium deposits and occurrences. Its typomorphic characteristics are studied to better understand the genesis, age and sources of the substance in titanium deposits (Makeyev, 2016; Makeyev, Dudar, 2001; Makeyev et al., 2008; Skublov et al., 2018). The goal of the present project is to study monazite from two Russia’s giant titanium deposits: Pizhemskoye and Yarega. The deposits are similar in geological structure and possibly genesis but are different from other titanium deposits in the non-standard phase-mineral composition (ilmenite-pseudorutile-leucoxene-quartz and siderite-leucoxene-quartz) of titanium ores. The non-standard phase composition of titanium ores (Ignatiev, Burtsev, 1997; Kalyuzhny, 1982; Makeyev, 2016; Makeyev, Dudar, 2001) from these deposits would require a preliminary chemical stage to remove silicon from leucoxene and pseudorutile, to manufacture commercial products (artificial porous rutile, etc.) and to launch the economic mining of these deposits that are highly important for Russia. As monazite is a principal recoverable constituent of titaniferous sandstone (because it occurs in the ore as free grains), the economic profitability and cost price of the economic mining of the above deposits will undoubtedly increase.

The goal of the present study is to better understand the chemical composition pattern of monazite grains from the Yarega and Pizhemskoye deposits and to estimate the time of their formation using the CHIME – chemical Th-U-total Pb isochrone method (chemical isochrone method) proposed by K. Suzuki (Suzuki, Adachi, 1991; Suzuki, Kato, 2008).

Method for monazite grain analysis
Monazite was analyzed at the Institute of Ore Geology, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences (IGEM RAS), on a JXA-8200 wave microprobe. Fifty-nine analyses of the composition of monazite grains from two industrial samples per 15 constituents: matrix (P₂O₅, La₂O₃, Ce₂O₃, Pr₂O₃, Nd₂O₃, Sm₂O₃, Y₂O₃, ThO₂) and trace constituents (CaO, SiO₂, UO₂, PbO, FeO, MnO, SO₃) were done.
The chemical composition and age of monazite and kularite... A.B. Makeyev, S.E. Borisovsky, A.O. Krasotkina

Special analytical conditions were as follows: ThO$_2$, UO$_2$, PbO: an accelerating voltage of 20 kV, a probe current of 150 nA and a PET analyzer crystal (Table 1).

Age was calculated from the results of electron-probe X-ray spectral determination of ThO$_2$, UO$_2$ and PbO using the CHIME method. The positive results of our studies based on this method are described in (Votyakov et al., 2011; Makeyev, Viryus, 2013; Pilyugin, Mukhanova, 2008; Popova et al., 2010; Williams et al., 2007, etc).

Calculations of estimated $\omega$(ThO$_2^*$) concentration for constructing an isochrone were made using the formula:

$$\omega(\text{ThO}_2^*) = \omega(\text{ThO}_2) + \omega(\text{UO}_2) \cdot M(\text{ThO}_2)/M(\text{UO}_2) \cdot \left\{\left[\frac{e^{\lambda_{232} t} + 137.88 \cdot e^{\lambda_{238} t}}{138.88}\right] - 1\right\}/(e^{\lambda_{232} t} - 1),$$

where $\omega(\text{ThO}_2)$ and $\omega(\text{UO}_2)$ are the mass fraction of thorium oxide (IV) and uranium oxide (IV) in monazite; $M(\text{ThO}_2)$ and $M(\text{UO}_2)$ are the molar masses of thorium oxide (IV) and uranium oxide (IV); $\lambda_{232}$ and $\lambda_{238}$ are decay constants for thorium and uranium isotopes, respectively; it is the time taken by the decay.

Age calculation:

$$T = \frac{\ln(m \cdot [M(\text{ThO}_2)/M(\text{PbO})] + 1)}{\lambda_{232}},$$

where $m$ is the inclination of the isochrone.

Analytical results for monazite composition and age calculations are shown in Tables 2 and 3. U and Pb were not estimated in all the grains analyzed because of their low concentrations. Therefore, 52 monazite analyses out of 59 were used for age estimation and isochrones construction.

Table 1. Analytical conditions for certain elements in monazite composition. The monazite samples were analyzed at IGEM RAS, on a JXA-8200 wave microanalyzer with five X-ray spectrometers at a voltage of 20 kV and a current of 150 mA. The probe diameter is 5 µm.

| Elements in composition | Analytic line | Analyzer crystal | Exposure Line/background, s | Standard | Limit of detection 3 σ (ppm) |
|------------------------|--------------|------------------|-----------------------------|---------|-----------------------------|
| Th                     | ThMα         | PETJ             | 50/25                       | ThO$_2$ | 210                         |
| U                      | UMβ          | PETH             | 100/50                      | UO$_2$  | 150                         |
| Pb                     | PbMα         | PETH             | 150/75                      | PbCrO$_4$ | 120                        |
| La                     | LaLα         | PETJ             | 10/5                        | LaPO$_4$ | 900                         |
| Ce                     | CeLα         | PETJ             | 10/5                        | CePO$_4$ | 950                         |
| Pr                     | PrLβ         | LiF              | 60/30                       | PrPO$_4$ | 725                         |
| Nd                     | NdLα         | LiF              | 50/25                       | NdPO$_4$ | 500                         |
| Sm                     | SmLβ         | LiF              | 60/30                       | SmPO$_4$ | 600                         |
| Y                      | YLα          | TAP              | 30/15                       | YPO$_4$  | 200                         |
| P                      | PKα          | TAP              | 10/5                        | Apatite | 270                         |
| Ca                     | CaKα         | PETH             | 10/5                        | CaAl$_2$Si$_2$O$_6$ | 120             |
| Si                     | SiKα         | TAP              | 10/5                        | NaFeSi$_2$O$_6$ | 200             |
| Fe                     | FeKα         | LiF              | 10/5                        | NaFeSi$_2$O$_6$ | 400             |
| Mn                     | MnKα         | LiF              | 10/5                        | Mn$_2$Al$_2$[SiO$_4$]$_3$ | 400          |
| S                      | SKα          | PETH             | 10/5                        | BaSO$_4$ | 180                         |

Material Yarega monazite. The grains and crystal fragments of Yarega monazite were extracted from an ultra-heavy fraction of a big (several tons) industrial sample. They are small in size (84×49 – 110×80, average size 93×63 µm) and display an isometric to mildly elongated irregular shape with a perfect cleavage; no other phases, except for scarce quartz inclusions, were found inside the grains (Fig. 1). Yarega monazite is concentrated to form a fine (< 0.125 µm) non-magnetic leucoxene fraction together with zircon and rutile. The chemical composition of monazite is shown in Table 2.

Fig. 1. Electron microscopy images (backscattered electron regime) of nine Yarega monazite grains. Ce-La-Th-monazite grains (1-3) are zonal. Thorium is more abundant in the cores than on the margins. Points indicate the location of microprobe analyses, whose symbols coincide with numbers in Table 2.
Table 2. Chemical composition (wt. %) and age (Ma) of nine Yarega monazite grains. Lack of sum in the analyses of monazites is due to the absence of the estimation of the middle members of the REE series, Gd$_2$O$_3$ and Eu$_2$O$_3$, the presence of which in the same grains was confirmed earlier on a JSM-7300 electron microscope with a Link ED-spectrometer (Makeyev, Magazina, 2019).

| No | P$_2$O$_5$ | La$_2$O$_3$ | Ce$_2$O$_3$ | Pr$_2$O$_3$ | Nd$_2$O$_3$ | Sm$_2$O$_3$ | Y$_2$O$_3$ | UO$_2$ | ThO$_2$ | PbO | CaO | SiO$_2$ | FeO | MnO | SO$_3$ | Total | ThO$_2^*$ | Age |
|----|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------|--------|------|-----|---------|-----|------|-------|-------|---------|-----|
| 1 a | 30.84 | 12.11 | 25.84 | 2.99 | 11.75 | 2.05 | 2.68 | 0.305 | 6.496 | 0.353 | 1.52 | 0.16 | 0.01 | 0.03 | 0.01 | 97.13 | 7.553 | 1071.6 |
| 1 b | 30.88 | 12.53 | 26.65 | 3.09 | 12.09 | 2.10 | 2.29 | 0.367 | 5.593 | 0.333 | 1.33 | 0.13 | 0.00 | 0.01 | 0.00 | 97.39 | 6.870 | 1111.6 |
| 1 c | 31.25 | 12.12 | 25.68 | 2.97 | 11.63 | 2.11 | 2.80 | 0.425 | 6.422 | 0.384 | 1.60 | 0.15 | 0.02 | 0.04 | 0.00 | 97.61 | 7.901 | 1112.4 |
| 1 d | 31.51 | 13.02 | 26.40 | 3.05 | 11.42 | 1.98 | 2.79 | 0.430 | 4.760 | 0.282 | 1.27 | 0.10 | 0.00 | 0.04 | 0.01 | 97.05 | 6.247 | 1047.6 |
| 1 e | 31.20 | 12.06 | 25.74 | 3.00 | 11.74 | 2.06 | 2.82 | 0.357 | 6.299 | 0.369 | 1.47 | 0.17 | 0.00 | 0.03 | 0.00 | 97.31 | 7.544 | 1134.0 |
| 1 f | 31.44 | 12.28 | 25.53 | 2.98 | 11.68 | 2.08 | 2.47 | 0.360 | 6.792 | 0.333 | 1.33 | 0.13 | 0.00 | 0.01 | 0.00 | 97.83 | 8.051 | 1166.8 |
| 2 a | 31.27 | 13.01 | 26.67 | 3.23 | 12.36 | 2.23 | 2.57 | 0.305 | 4.078 | 0.266 | 0.98 | 0.14 | 0.01 | 0.04 | 0.00 | 97.15 | 5.147 | 1194.8 |
| 2 b | 31.52 | 22.17 | 31.84 | 2.58 | 7.87 | 0.69 | 0.31 | 0.059 | 1.375 | 0.24 | 0.04 | 0.03 | 0.04 | 0.00 | 98.80 | 1.575 | 783.6 |
| 3 a | 30.99 | 14.45 | 28.70 | 3.07 | 11.34 | 1.80 | 1.71 | 0.202 | 4.459 | 0.293 | 0.96 | 0.28 | 0.00 | 0.00 | 0.00 | 98.27 | 5.174 | 1294.0 |
| 3 b | 31.10 | 13.82 | 28.20 | 3.09 | 11.57 | 1.95 | 1.82 | 0.216 | 4.937 | 0.325 | 0.96 | 0.34 | 0.00 | 0.01 | 0.00 | 98.34 | 5.701 | 1290.8 |
| 3 c | 31.18 | 13.61 | 28.06 | 3.13 | 11.72 | 1.96 | 1.82 | 0.209 | 5.096 | 0.340 | 0.99 | 0.33 | 0.00 | 0.00 | 0.00 | 98.45 | 5.839 | 1314.2 |
| 3 d | 31.16 | 13.79 | 28.09 | 3.02 | 11.68 | 1.91 | 1.80 | 0.217 | 5.028 | 0.324 | 1.00 | 0.35 | 0.02 | 0.00 | 0.02 | 98.39 | 5.796 | 1289.6 |
| 4 a | 31.07 | 8.11 | 28.79 | 4.43 | 19.33 | 3.61 | 0.69 | 0.168 | 0.369 | 0.029 | 0.19 | 0.11 | 0.00 | 0.06 | 0.02 | 96.98 | 0.934 | 721.4 |
| 4 b | 31.20 | 15.91 | 31.47 | 3.46 | 13.30 | 2.37 | 0.35 | 0.000 | 0.035 | 0.006 | 0.04 | 0.03 | 0.01 | 0.04 | 0.01 | 98.23 | 3593 |
| 5 a | 31.44 | 15.70 | 31.01 | 3.43 | 13.36 | 2.37 | 0.38 | 0.012 | 0.126 | 0.000 | 0.08 | 0.04 | 0.02 | 0.03 | 0.01 | 98.02 | 3593 |
| 5 b | 31.33 | 10.09 | 32.40 | 4.39 | 16.91 | 2.38 | 0.54 | 0.055 | 0.227 | 0.001 | 0.19 | 0.00 | 0.01 | 0.04 | 0.02 | 98.59 | 3593 |
| 6 a | 31.25 | 17.92 | 33.64 | 3.10 | 10.16 | 1.38 | 0.39 | 0.069 | 0.430 | 0.015 | 0.13 | 0.00 | 0.00 | 0.04 | 0.00 | 98.71 | 0.655 | 351.0 |
Table 3. Chemical composition (mas. %) and age (Ma) of Pizhemsy monazite-kularite. The first analytical result in the line is shown for the probe point in the centre of the grain and the second result – for the margin of the same grain.

| No | P 2 O 5 | La 2 O 3 | Ce 2 O 3 | Pr 2 O 3 | Nd 2 O 3 | Sm 2 O 3 | Y 2 O 3 | UO 2 | Th O 2 | Total | Th O 2* | Age       |
|----|---------|----------|----------|----------|----------|----------|---------|------|--------|--------|----------|-----------|
| 1  | 30.34   | 14.32    | 32.57    | 3.73     | 13.67    | 2.74     | 0.71    | 0.044| 0.13   | 97.28  | 1.242    | 823.4     |
| 2  | 30.19   | 8.84     | 18.09    | 4.44     | 0.47    | 0.06     | 0.03    | 0.00  | 0.02   | 99.71  | 0.633    | 695.0     |
| 3  | 30.18   | 14.32    | 32.57    | 3.73     | 0.18    | 0.06     | 0.044   | 0.2   | 0.02   | 99.71  | 0.633    | 695.0     |
| 4  | 29.83   | 5.68     | 23.62    | 4.50     | 23.40    | 6.92     | 0.57    | 0.114 | 0.06   | 95.51  | 0.653    | 815.4     |
| 5  | 30.83   | 10.35    | 31.53    | 4.37     | 17.71    | 2.73     | 0.43    | 0.112 | 0.02   | 98.49  | 0.868    | 721.4     |
| 6  | 30.47   | 13.78    | 31.22    | 4.37     | 18.60    | 2.91     | 0.64    | 0.01  | 0.02   | 98.16  | 0.666    | 746.8     |
| 7  | 30.18   | 8.84     | 18.09    | 4.44     | 0.47    | 0.06     | 0.03    | 0.00  | 0.02   | 99.71  | 0.633    | 695.0     |
| 8  | 30.49   | 14.32    | 32.57    | 3.73     | 0.18    | 0.06     | 0.044   | 0.2    | 0.02   | 99.71  | 0.633    | 695.0     |
| 9  | 29.83   | 5.68     | 23.62    | 4.50     | 23.40    | 6.92     | 0.57    | 0.114 | 0.06   | 95.51  | 0.653    | 815.4     |
| 10 | 30.83   | 10.35    | 31.53    | 4.37     | 17.71    | 2.73     | 0.43    | 0.112 | 0.02   | 98.49  | 0.868    | 721.4     |
| 11 | 30.47   | 13.78    | 31.22    | 4.37     | 18.60    | 2.91     | 0.64    | 0.01  | 0.02   | 98.16  | 0.666    | 746.8     |
| 12 | 30.18   | 8.84     | 18.09    | 4.44     | 0.47    | 0.06     | 0.03    | 0.00  | 0.02   | 99.71  | 0.633    | 695.0     |
| 13 | 30.49   | 14.32    | 32.57    | 3.73     | 0.18    | 0.06     | 0.044   | 0.2    | 0.02   | 99.71  | 0.633    | 695.0     |
| 14 | 29.83   | 5.68     | 23.62    | 4.50     | 23.40    | 6.92     | 0.57    | 0.114 | 0.06   | 95.51  | 0.653    | 815.4     |
| 15 | 30.83   | 10.35    | 31.53    | 4.37     | 17.71    | 2.73     | 0.43    | 0.112 | 0.02   | 98.49  | 0.868    | 721.4     |
| 16 | 30.47   | 13.78    | 31.22    | 4.37     | 18.60    | 2.91     | 0.64    | 0.01  | 0.02   | 98.16  | 0.666    | 746.8     |
| 17 | 30.18   | 8.84     | 18.09    | 4.44     | 0.47    | 0.06     | 0.03    | 0.00  | 0.02   | 99.71  | 0.633    | 695.0     |
| 18 | 30.49   | 14.32    | 32.57    | 3.73     | 0.18    | 0.06     | 0.044   | 0.2    | 0.02   | 99.71  | 0.633    | 695.0     |
| 19 | 30.34   | 10.22    | 32.57    | 3.73     | 0.18    | 0.06     | 0.044   | 0.2    | 0.02   | 99.71  | 0.633    | 695.0     |
There are three chemical varieties of Yarega monazite: neodymium-cerium, lanthanum-thorium-cerium and lanthanum-cerium. The latter is the most common variety (over 60% of cases). A high positive correlation between cerium, lanthanum, thorium, yttrium and calcium, on the one hand, and between neodymium, praseodymium, samarium, europium and gadolinium, on the other hand, is observed (Makeyev, Magazina, 2019). The tetrad rule in the chemical composition of Yarega high-thorium monazite is violated in both the first (La-Ce-Pr-Nd) and second (Sm-Eu-Gd-Tb) tetrads because of a negative cerium anomaly associated with the isomorphic replacement Th+Y+Ca → Ce and a negative Eu-anomaly in the second tetrad. The typochemical characteristics of Yarega high-thorium monazite with a distinctive Eu-anomaly are typical of monazite, which is genetically related to granitoids (Skublov et al., 2018; Schandl, Gorton, 2004; Williams et al., 2007).

Pizhemsky monazite-kularite. Pizhemsky monazite grains were extracted from the magnetic ilmenite-pseudorutile concentrate of the grey-coloured sandstone of an industrial sample weighing 250 kg. They are much bigger (521×446 ÷ 228×130, average size is 375×278 µm) than the grains and crystal fragments of Yarega monazite; they are often amoeba-shaped, rounded or ellipsoid and are grey or brown in color. Individual grains are filled with quartz inclusions (up to 10-15 %, Fig. 2) and are similar in shape, color and internal morphology to leucoxene grains. This morphological variety of monazite is called kularite. In addition to quartz, it contains florencite, muscovite and pseudorutile inclusions. Monazite-kularite grains are magnetized by pseudorutile and are concentrated to form an electromagnetic fraction together with ilmenite, pseudorutile and siderite (Lutoev, Makeyev, 2019). The chemical characteristics of monazite-kularite are shown in Table 3. There are three chemical varieties of Pizhemsky monazite: lanthanum-cerium, neodymium-samarium-cerium and neodymium-cerium. The latter is the most common (over 80% of cases). There is a high positive correlation between cerium and lanthanum, on the one hand, and between praseodymium, neodymium, samarium, gadolinium and europium, on the other (Makeyev, Magazina, 2019). The tetrad rule in Pizhemsky monazite-kularite is violated: there is no bending between the first (La-Ce-Pr-Nd) and second (Sm-Eu-Gd-Tb) tetrads, which seems to be due to elevated Nd and Sm concentrations. This could have been provoked by the hydrothermal transformation of the mineral in the weathering crust of the primary source and the removal of some of the constituents.

The diagrams (Figs. 3 and 4) show the correlations of the constituents used to distinguish between the typochemical characteristics of the above two deposits. Pizhemsky monazite contains more neodymium and samarium, while Yarega monazite carries more lanthanum, thorium, yttrium, calcium, uranium and lead.

Results of monazite dating by the CHIME method

The results of monazite dating, based on 18 and 35 analyses, are shown in Tables 2 and 3. The average age of Yarega monazite, based on “point” determinations in three combinations, is: 1) 1304±22; 2) 1107±39;
The chemical composition and age of monazite and kularite…

A.B. Makeyev, S.E. Borisovsky, A.O. Krasotkina

3) 837±147 Ma. The average age of Pizhensky monazite-kularite from 33 points (if 2 marginal points on both sides, which are not in the 3σ interval, are removed) T is 777±110 Ma. Figures 5 and 6 show the correlations of PbO and ThO₂* for samples from the two deposits. These data were used to calculate and construct corresponding isochrones. The three isochrones constructed for Yarega monazite are:

**Isochrone I** with parameters: T = 1301 Ma, y = 0.0566x, R² = 0.906;
**Isochrone II** with parameters: T = 1105 Ma, y = 0.0481x, R² = 0.901;
**Isochrone III** with parameters: T = 778 Ma, y = 0.0335x, R² = 0.931.

The first two isochrones were constructed for high-thorium monazite grains, while the last one for low-thorium grains. This evidence, together with data on the chemical composition of monazite, suggests that monazite grains from three primary sources, considerably differing in age by ~200 and ~320 Ma, occur together in the Yarega deposit.

Only one isochrone (Fig. 6), showing an age (T) of 782 Ma, can be constructed for the Pizhensky deposit, based on the results obtained. Statistical analysis was done to calculate two isochrones similar in age: one with a free member PbO = -0.007+0.0345·ThO₂*, R² = 0.908; and the other which has no free member and approaches zero, – PbO = 0.0337·ThO₂*, R² = 0.9084. Let us choose the latter isochrone, as is accepted in this type of study. It should be noted that it is a perfect case, when the isochrones for Pizhensky monazite closely coincide with the average “point” age of the entire combination. Another feature of the present study is that the age values in isochrone III for Yarega monazite coincide with the only isochrone for Pizhensky monazite-kularite. This may indicate the close nature of the geological object of one of the indigenous primary sources of monazite of the two Timan deposits.

**Discussion**

The most similar object for discussion of the results obtained is the well-known and well-studied Ichetyu base mineral gold-diamond-rare earth-rare metal-titanium deposit. It is a 0.2-1.5 m thick breccio-conglomerate horizon resting directly on the Malorucheiskaya rock sequence of the Pizhensky deposit (Makeyev, 2016; Makeyev, Dudar, 2001). Isotopic (Pb-Th and Pb-U) and chemical age estimations (CHIME method) for La-Ce-monazite and Nd-Ce-monazite-kularite from the horizon are known (Krasotkina, 2018; Makeyev, Viryus, 2013; Skublov et al., 2018). Local dating of monazite yielded two peaks of 206Pb/238U age values: a major peak with an
age of 1000-1060 Ma and a minor peak with a maximum of about 570 Ma. $^{206}\text{Pb} - ^{238}\text{U}$ age, estimated at the same points as $^{206}\text{Pb} - ^{238}\text{U}$ age, yielded only one peak with an age of 500-700 Ma (Skublov et al., 2018). In addition to monazite, the isotope-geochemical characteristics of rutile and zircon were analyzed (Krasotkina, 2018). It has been shown that the isotope systems and trace element compositions of all the three mineral-chronometers studied (zircon, rutile and monazite) from the Ichetyu ore occurrence are indicative of a major hydrothermal event dated at ~600 Ma. The event does not manifest itself in the rocks that underlie titanium deposits, and is understood as an age similar to the age of formation of Middle Timan titanium deposits.

The distribution of data on individual age calculations (CHIME) for Ichetyu monazites at the «pointo» (Makeyev, Viryus, 2013) shows three modes. Hence, the samples can be divided into three groups and their average age can be calculated: 1) 955±124 Ma, 2) 706±76 Ma, 3) 401±88 Ma. The isochrone method of calculation also yields three sets that are consistent with three isochrones:
- **isochrone I** with parameters: 967 Ma ($y = 0.0414x$, $R^2 = 0.9669$);
- **isochrone II** with parameters: 737 Ma ($y = 0.0314x$, $R^2 = 0.9434$);
- **isochrone III** with parameters: 522 Ma ($y = 0.0221x$, $R^2 = 0.9840$).

The results obtained were interpreted as follows. Consistent with isochrones I are mostly ellipsoidal grains of a neodymium-cerium variety (except for two thorium grains and two lanthanum-cerium monazite grains). Consistent with isochrone II are only grains of a neodymium-cerium variety (monazite-kularite). Consistent with isochrone III are all three monazite varieties, but thorium and lanthanum-cerium varieties prevail over a neodymium-cerium variety. The early isochrones (I) seem to indicate the time of formation of rare metal – rare earth high-temperature hydrothermal-metasomatic mineralization in Neoproterozoic shales, which are similar to the Bobrovskoye and Oktyabskoye Chetlasky Kamen deposits, Middle Timan.

The middle isochrones (II) can be correlated in age with Chetlasky lamprophyres, whose intrusion time was estimated by the Rb-Sr method at 815 Ma (Makeyev et al., 2009). Chetlasky carbonatites (600 Ma), in which monazite is one of the most common accessory minerals, were derived in the same period of time.

The latest isochrones for monazite (III) are consistent with the intrusion age of Devonian basalts and probably with the age of formation of the Ichetyu occurrence proper. During this phase monazite could have recrystallized and lost part of radiogenic lead. This assumption is consistent with the geological knowledge of the structure of a productive breccio-conglomerate horizon (in which basalt fragments occur) and shows that Ichetyu breccio-conglomerates are of volcanic-fluidisate origin and were formed simultaneously with the intrusion of basalt sills.

These data should be compared with new age dates for monazite and zircon from the Pizhemskoye and Yarega deposits to more precisely date the deposits themselves. Interestingly, the age values for Nd-Ce-monazite-kularite from the Ichetyu occurrence and the Pizhemskoye deposit are very similar and seem to indicate a common primary source.

With respect to Timan igneous rocks, only Chetlasky lamprophyres are the most similar in isotope age (Makeyev et al., 2008; 2009) to the chemical age of Yarega low-thorium monazite and Pizhemsky monazite-kularite. Rb-Sr-data show that the largest group of Chetlasky lamprophyre samples forms an isochrone with a Neoroterozoic age of 819±19 Ma (Makeyev et al., 2009). Hence, it is Neorotozoic lamprophyres, most similar in age and the mineral composition of accessories (Makeyev, 2016; Makeyev et al., 2008;
2009; 2016), that could have provided a source of ore matter for the two titanium deposits. The prospecting and exploration of the northern Volsk-Vymskaya Ridge is likely to reveal Chetlassky-like lamprophyres beneath titaniferous sequences.

The species composition of micron-sized mineral inclusions in Yarega zircon (Makeyev, Zhilicheva, 2018), which is closely associated in titaniferous sandstone with the monazite studied, is: quartz, muscovite, F-REE-apatite, xenotime, chlorite, K-feldspar, biotite – PASE (phlogopite-annite-siderophyllite-eastonite) – series mica (according to a new nomenclature, International Mineralogical Association). This clearly shows that the entire association is bimica granite. Well-known criteria (Krasotkina, 2018; Skublov et al., 2018; Schandl, Gorton, 2004; Williams et al., 2007), such as extremely low Th concentration, U/Th ration and the absence of Eu-anomaly, the chemical compositions of Pizhemsky monazite-kularite and Yarega low-thorium monazite are indicative of their hydrothermal genesis. According to the same criteria, a bedrock source for Yarega high-thorium monazite could have been provided by old Timan granitic batholiths that seem to occur in Timan’s crystalline basement and are not exposed on the day surface.

It was thought earlier that oil-saturated leucoxene sandstones from the Yarega deposit are of Middle Devonian age, as shown by spore-and-pollen analysis. However, O.P. Telnova of the Yushkin Institute of Geology of Komi Science Center of Ural Branch of Russian Academy of Sciences (personal communication), has recently conducted extensive studies of core samples from prospecting holes, which showed that the samples contain both Middle and Late Devonian microfossils. This ambiguity suggests that microfossils were carried to Yarega titaniferous sandstones and distributed there by migrating oil, which was squeezed out from Devonian parent rock and migrated to porous sandstones as the most favorable collector (an anticlinal trap formed by the Yarega tectonic structure). The mineral compositions of leucoxene sandstones of oil and water grades were identical. It means that oil later filled the upper anticlinal portion of the Yarega deposit and that it was not genetically related to the formation of the titaniferous sequence itself. Here, oil also fills the upper ore-free quartz sandstone bed in the anticlinal trap. It is safe to assume that oil carried a mixture of Middle and Late Devonian plant spores and pollen while migrating. So, the Middle Devonian age of the Yarega deposit is not proven. The question remains open. To correctly approach the problem, further isotope-geochemical studies, similar to those carried out earlier in the Pizhemsky deposit (Chernyshov et al., 2010), are needed.

The genesis and ages of the two deposits studied are problems of animated debate. It was assumed earlier that the deposits are old placers, but this point of view has not been generally accepted. According to the existing classification of Russia’s titanium deposits, the Yarega is clearly a metamorphogenetic bedrock deposit. The two deposits are identical in geological structure and are similar in mineral composition (and possibly age and genesis). The titaniferous sequence of the Pizhemsky deposit is barren and contains no organic remains. Therefore, its Devonian age was tentatively accepted earlier. The Malorucheiskaya sequence is overlain by the Middle Devonian terrigenous rocks of the Pizhemsky suite (D.pz) that contain Middle Devonian pollen. Many scholars estimate the age of the Malorucheiskaya titaniferous sequence of the Pizhemskoye deposit from indirect evidence in the Early Devonian – Neoroterozoic time span. Isotope methods were used to precisely date the titaniferous sequence of the Pizhemsky deposit from a Rb-Sr-isochrone as Neoroterozoic, $T = 685\pm30$ Ma (Chernyshov et al., 2010). Material for age determination was provided by ore-hosting rocks, such as siltstone and argillite-like clay, as well as leucoxene ore concentrate proper. Thus, the chemical age obtained for monazite supports our earlier data on the isotope age of zircon, monazite and leucoxene. Hence, the Pizhemsky titanium deposit is much older (most probably 600-700 Ma) and was formed in Neoroterozoic time ($PR,mt$).

The authors of the publications that saw the light in the past few years tried to provide arguments in favor of the bedrock rather than other (not placer) genesis of the Pizhemsky deposit (Makeyev, 2016; Makeyev et al., 2008; 2009; 2016, etc). One of their arguments is the complete absence of the roundness of quartz (at both localities) a major mineral in terms of ore volume. It is sharply angular and clastic – a feature indicative of the short-distance transport of the entire material. Some of the mineral phases, e.g. leucoxene and monazite-kularite, may display the pseudo-rounded shape of grain produced by the hydrothermal reworking of the material and the vertical movement of the material in a vertical flow. Therefore, the rounded shape of grains is a convergent feature, which cannot be accepted as strong evidence for the placer origin of ore occurrences and the movement of the material in subhorizontal water flows. The sizes of quartz and other non-metallic and ore minerals (0.1-2.0 mm) are much greater than those of minerals from Riphean fine-grained (0.01-0.10 mm) shale (bedrock). Furthermore, the shale does not contain sufficient amounts of ore constituents. Therefore, the weathering crust after the shale could not have been a bedrock source of the matter that made up the overlying ore sequence. Calculations show that to create current TiO$_2$ concentration in the deposits, the volume of weathering crusts after shale should have been tens of times the volume and thickness of the titaniferous sequences. Thick weathering crusts...
The reaction was as follows:

\[
\text{FeTiO}_3 + \text{H}_2\text{O} + \text{C}_2 \text{O}_2 + \text{Si}_2 \text{O}_2 \rightarrow (2\text{Ti}_2\text{O}_5\cdot\text{Si}_2\text{O}_5) + \text{Ti}_2 \\
+ \text{Fe}_2\text{O}_3 \rightarrow \text{Fe(OH)}_3 + \text{Fe}_2\text{O}_3 + \text{C}_2 \text{O}_2.
\]

The aforementioned geological, geochemical and mineralogical features and proofs are convincing enough to argue that the Pizhemsuy titanium deposit is of volcanic (phreato-magmatic) origin. Its formation of a mud volcano type was contributed to by water vapour and carbon dioxide. The deposit formed after the substrate of the weathering crusts of lamprophyres followed by the long (hundreds of millions of years) metamorphism of ore sequences (Makeyev, 2016).

Thus, two Timan’s giant structurally similar titanium deposits, Yarega and Pizhemsuy, resting directly on Neoroterozoic shales, overlain by Middle and Upper Devonian sedimentary rocks and erroneously interpreted earlier as Middle Devonian, are indeed Neoroterozoic. One of the most probable sources of ore matter could have been provided by Chetlassky-like lamprophyres similar in the age, species composition and typomorphic characteristics of accessory indicator minerals.

Conclusions

The typomorphic characteristics and age of monazite samples from Timan’s giant Pizhemsky and Yarega titanium deposits were studied. Differences in morphology (Yarega monazite occurs as crystal fragments, while Pizhemsky monazite is present as hydrothermally altered ellipsoid grains), the species composition of inclusions (quartz inclusions make up 10-15% of Pizhemsky kularites), grain size (Pizhemsky monazite is 4 times bigger) and the distribution of the chemical characteristics of the mineral (a large portion of Yarega monazites occurs as high-thorium and lanthanum varieties, while Pizhemsky monazite-kularite occurs as neodymium and samarium varieties) were revealed.

The isochrone Th-Pb age of monazite was estimated using the CHIME method. Three isochrones for Yarega monazite with the ages of 1301, 1105 and 778 Ma and one isochrone for Pizhemsuy monazite-kularite with an age of 782 Ma were constructed. These differences are due to monazite crystallization conditions and a difference in the sources of the matter. A source for Yarega high-thorium monazite could have been provided by old granitic batholiths, and the origin of Yarega low-thorium monazite and ~780 Ma Pizhemsky Nd- Ce-monazite-kularite could have been associated with the hydrothermal alteration of weathering crusts after lamprophyres resting presumably beneath the deposits in the shale-quartzite sequence of the crystalline basement, which is similar in age to Chetlassky Kamen lamprophyres (spessartite and kersantite). The free form of monazite grains in both deposits allows us to develop technological methods for extracting the mineral from concentrates, which will certainly increase the profitability of their mining.

Acknowledgements

The authors are sincerely grateful to A.N. Konilov for help in calculating the age of monazite grains and constructing isochrones according to his own program and A.V. Lalomonov for the useful discussion of the article and comments.

The study was carried out in the framework of budget theme No. 0136-2018-0020 and partially was funded by Russian Foundation for Basic Research, project number 19-33-60001.

References

Makeyev A.B., Andreechev V.L., and Krasotkina A.O. (2018). Isotopic-geochemical features and age of accessory minerals of the Iketjou occurrence and Pizhemsuy deposit (Middle Timan). Abstract Cand. geol. and min. sci. diss. St. Petersburg, 20 p. (In Russ.)

Krasotkina A.O. (2018). Isotopic-geochemical features and accessory minerals of the Iketjou occurrence and Pizhemsuy deposit (Middle Timan). Abstract Cand. geol. and min. sci. diss. St. Petersburg, 20 p. (In Russ.)

Makeyev A.B. (2016). Mineralogical-geochemical features of minerals of Ti ores from the Pizhemskoe deposit. Mineralogiya = Mineralogy, 1, pp. 24-49. (In Russ.)

Makeyev A.B., Bryanchaninova N.I. (2009). Age of Lamprophyres of the Middle Timan: First Rb-Sr Date. Doklady Earth Sciences, 435(1). pp. 1524-1528. https://doi.org/10.1134/S1028334X10110255

Ignatiev D.V., Burtsen I.N. (1997). The leucokars of Timan: Mineralogy and problems of technology. St.Petersburg: Nauka, 215 p. (In Russ.)

Kalyuzhny V.A. (1982). Geology of new placeforming metamorphic formations. Moscow: Nauka, 264 p. (In Russ.).

Krasotkina A.O. (2018). Isotopic-geochemical features and age of accessory minerals of the Iketjou occurrence and Pizhemsuy deposit (Middle Timan). Abstract Cand. geol. and min. sci. diss. St. Petersburg, 20 p. (In Russ.)

Lytsoev V.P., Makeyev A.B. (2019). Assessment of the quality of the magnetic concentrates of the titanium ores at Pizhemsuy deposit from the point of view of the technological mineralogy. Proceedings of higher educational establishments. Geology and Exploration, (3), pp. 31-41. (In Russ.) https://doi.org/10.32454/0016-7762-2019-3-31-42

Makeyev A.B. (2016). Typomorphic features of minerals of Ti ores from the Pizhemskoe deposit. Mineralogiya = Mineralogy, 1, pp. 24-49. (In Russ.)

Makeyev A.B., Andrechev V.L., and Bryanchaninova N.I. (2009). Age of Lamprophyres of the Middle Timan: First Rb-Sr Date. Doklady Earth Sciences, 426(4). pp. 584-587. https://doi.org/10.1134/S1028334X09040163

Makeyev A.B., Bryanchaninova N.I. (2009). Lamprophyres of Chetlassky Kamen (Middle Timan). Regional Geol. Metallogeny, 37, pp. 51-73. (In Russ)

Makeyev A.B., Krasotkina A.O., Skublov S.G. (2016). Geochronometry and U-Pb-age of zircon from Pizhemskoe titanium deposit (Middle Timan). Vestnik IG Komi SC UB RAS, 5, pp. 38-52. https://doi.org/10.19110/2221-1381-2016-5-38-52 (In Russ.)

Makeyev A.B., Krasotkina A.O., Skublov S.G. (2018). Lake shales of the Lunvozhskoj suite of the Volsk-Yvm ridge (Middle Timan): composition, age, accessory zircon. Proc. Mineralogical seminar: Modern problems of theoretical, experimental and applied mineralogy (Yakhinsky readings – 2018). Syktyvkar, pp. 40-41. (In Russ.)
The chemical composition and age of monazite and kularite... A.B. Makeyev, S.E. Borisovsky, A.O. Krasotkina

Votyakov S.L., Hiller V.V., Shchapova U.V. (2012). Peculiarities of composition and chemical microprobe Dating of U-Th-bearing minerals. Part I. Monazites of a number of geological objects of the Urals and Siberia. Zapski RMO (Proceedings of the Russian Mineralogical Society), 1, pp. 45-60. (In Russ.)

Williams M.L., Jercinovic M.J., Hetherington C.J. (2007). Microprobe monazite geochronology: understanding geologic processes by integrating composition and chronology. Annu. Rev. Earth Planet. Sci., 35, pp. 137-175. https://doi.org/10.1146/annurev.earth.35.031306.140228

About the Authors

Alexander B. Makeyev – Dr. Sci. (Geology and Mineralogy), Professor, Leading Researcher, Laboratory of Ore Deposits Geology, Institute of Ore Geology, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences

35, Staromonetny Lane, Moscow, 119017, Russian Federation

E-mail: abmakeev@igem.ru

Sergey E. Borisovsky – Cand. Sci. (Geology and Mineralogy), Researcher, Laboratory of the Analysis of Minerals, Institute of Ore Geology, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences

35, Staromonetny Lane, Moscow, 119017, Russian Federation

Anna O. Krasotkina – Cand. Sci. (Geology and Mineralogy), Researcher, Head of the Project of Russian Foundation for Basic Research, Institute of Precambrian Geology and Geochronology of the Russian Academy of Sciences

2, Makarov emb., Saint-Petersburg, 199034, Russian Federation

Manuscript received 25 September 2019; Accepted 15 November 2019; Published 30 March 2020