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

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Abstract. A study on the typomorphic characteristics and age of the monazite the two giant titanium deposits of the Timan – Pizhemskiye 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 isochrone with age 1301, 1105 and 778 Ma; for Pizhemskiye monazite-kularite one isochrone with age 782 Ma. Source of hith-Th monazite Yarega oil-titanium deposit could be ancient granite batholith and the origin Yarega less-Th monazite and Nd-Ce-monazite-kularite Pizhemskiye 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 Chetlasky Kamen.

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

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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: Pizhemskiye 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 Pizhemskiye 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 (P_2O_5 , La_2O_3 , Ce_2O_3 , Pr_2O_3 , Nd_2O_3 , Sm_2O_3 , Y_2O_3 , ThO_2) and trace constituents (CaO, SiO_2 , UO_2 , PbO, FeO, MnO, SO_3) were done.

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Special analytical conditions were as follows: ThO₂, UO₂, 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 ThO₂, UO₂ 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 ThO₂* concentration for constructing an isochrone were made using the formula:

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

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); λ_{232} and λ_{238} are decay constants for thorium and uranium isotopes, respectively; it is the time taken by the decay.

Age calculation:

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

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.

Materials

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.

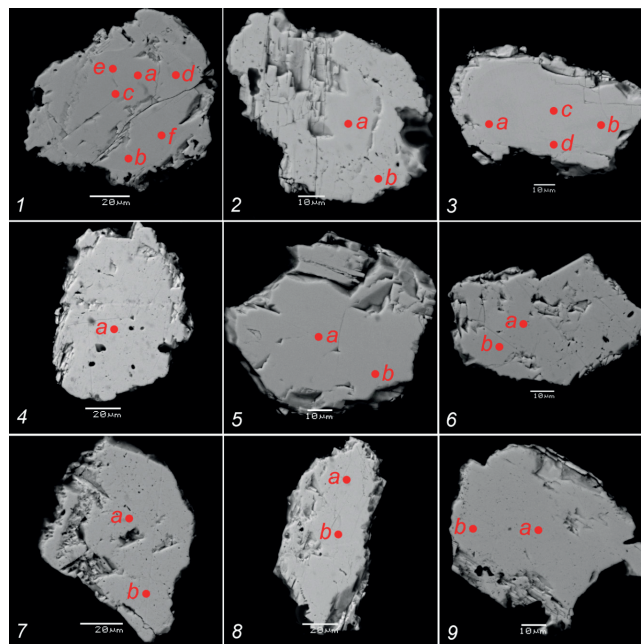


Fig. 1. Electron microscopy images (backscattered electron regime) of nine Yarega monazite grains. Ce-La-Th-monazite grains (1-3) are zonal. Thorium is more abundant in the cores than on the margins. Points indicate the location of microprobe analyses, whose symbols coincide with numbers in Table 2.

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 ₈	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 ₃ Al ₂ [SiO ₄] ₃	400
S	SKα	PETH	10/5	BaSO ₄	180

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.

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	0.406	1.56	0.21	0.00	0.03	0.01	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	0.053	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	1341.2
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
5 a	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 b	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		no
6 a	31.03	15.61	31.88	3.58	13.42	1.81	0.61	0.003	0.577	0.016	0.17	0.05	0.02	0.03	0.01	98.82	0.587	797.0
6 b	31.25	16.25	32.16	3.47	12.86	1.63	0.51	0.013	0.418	0.008	0.17	0.05	0.00	0.04	0.01	98.84	0.461	608.2
7 a	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		no
7 b	31.52	15.70	34.72	3.53	11.49	1.35	0.50	0.070	0.219	0.020	0.12	0.00	0.02	0.01	0.02	99.28	0.466	997.4
8 a	31.23	13.46	34.97	3.74	12.73	1.54	0.50	0.066	0.000	0.004	0.16	0.08	0.01	0.03	0.00	98.52	no	no
8 b	31.00	12.77	34.88	3.90	13.52	1.61	0.50	0.070	0.024	0.004	0.13	0.17	0.00	0.06	0.01	98.65		no
9 a	31.37	10.52	32.90	4.26	16.33	2.24	0.49	0.072	0.218	0.018	0.16	0.05	0.02	0.01	0.00	98.67	0.460	997.4
9 b	31.45	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 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, Gd₂O₃ and Eu₂O₃, 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	30.34	10.06	30.46	4.25	17.37	2.91	0.93	0.231	0.458	0.044	0.13	0.05	0.02	0.03	0.01	97.28	1.242	823.4
	30.43	14.32	32.57	3.73	13.67	1.86	0.68	0.143	0.153	0.019	0.12	0.02	0.02	0.01	0.00	97.71	0.633	695.0
2	30.19	8.84	30.28	4.44	18.09	2.74	0.71	0.034	0.291	0.015	0.24	0.23	0.43	0.06	0.01	96.59	0.407	848.2
	30.18	9.37	30.67	4.33	17.38	2.51	0.64	0.033	1.147	0.039	0.23	0.32	0.03	0.03	0.00	96.93	0.633	721.8
3	30.49	19.34	32.78	3.12	10.12	1.09	0.50	0.078	0.260	0.013	0.08	0.09	0.13	0.00	0.00	98.10	0.519	578.2
	30.43	14.93	32.78	3.71	13.20	1.67	0.52	0.095	0.247	0.019	0.11	0.05	0.03	0.02	0.00	97.81	0.568	777.0
4	30.18	5.68	23.62	4.50	23.40	6.92	0.57	0.114	0.266	0.023	0.14	0.05	0.01	0.06	0.00	95.51	0.653	815.4
	29.83	4.84	21.03	4.30	24.60	9.00	0.61	0.145	0.151	0.022	0.07	0.03	0.00	0.05	0.01	94.66	0.643	793.4
5	30.83	10.35	31.53	4.37	17.71	2.73	0.43	0.225	0.112	0.027	0.05	0.05	0.02	0.06	0.00	98.49	0.868	721.8
	30.47	9.53	29.97	4.37	18.05	3.04	0.69	0.151	0.552	0.040	0.13	0.02	0.06	0.04	0.00	97.10	1.066	870.2
6	30.35	6.46	24.92	4.64	23.13	5.39	0.60	0.103	0.865	0.039	0.16	0.01	0.04	0.06	0.01	96.77	1.212	748.6
	30.22	6.80	25.46	4.65	22.76	5.07	0.41	0.066	0.700	0.032	0.13	0.00	0.00	0.06	0.00	96.36	0.924	804.2
7	30.70	15.18	33.88	3.53	12.12	1.67	0.45	0.067	0.508	0.018	0.11	0.04	0.00	0.02	0.00	98.29	0.731	571.8
	30.46	14.39	33.81	3.63	12.16	1.60	0.50	0.071	1.031	0.039	0.17	0.02	0.01	0.01	0.00	97.90	1.270	715.4
8	30.44	12.77	32.64	3.88	14.17	1.80	0.35	0.048	1.565	0.054	0.15	0.00	0.12	0.02	0.01	98.01	1.727	729.4
9	30.32	17.14	33.20	3.29	11.05	1.23	0.33	0.039	0.776	0.000	0.08	0.10	0.24	0.05	0.59	98.44		Not det.
	30.65	19.93	33.02	2.99	9.82	0.94	0.27	0.065	0.670	0.031	0.08	0.00	0.03	0.00	0.00	98.49	0.890	807.8
10	30.40	12.59	32.26	3.94	14.83	2.09	0.61	0.108	0.631	0.033	0.14	0.10	0.06	0.04	0.00	97.82	0.996	769.0
	30.44	10.64	31.19	4.20	16.74	2.66	0.58	0.154	0.173	0.022	0.09	0.07	0.17	0.04	0.01	97.18	0.692	737.0
11	30.45	10.38	32.47	4.46	17.22	2.38	0.41	0.132	0.010	0.012	0.04	0.04	0.05	0.05	0.02	98.11	0.450	614.2
	30.21	6.84	26.04	4.49	21.43	5.90	0.62	0.092	0.368	0.026	0.11	0.09	0.06	0.03	0.01	96.31	0.682	881.8
12	28.73	8.10	26.60	3.94	16.38	3.18	0.61	0.159	0.274	0.020	0.32	1.48	0.39	0.05	0.01	90.23	0.803	579.0
13	30.02	5.76	24.18	4.57	23.47	6.20	0.70	0.210	0.124	0.031	0.05	0.02	0.02	0.05	0.01	95.41	0.838	856.6
	30.41	5.69	23.70	4.67	24.42	6.36	0.48	0.027	0.246	0.017	0.18	0.04	0.04	0.05	0.00	96.32	0.340	1142.6
14	30.35	18.09	32.84	3.23	10.86	1.25	0.60	0.149	0.600	0.038	0.08	0.04	0.11	0.00	0.00	98.24	1.105	799.4
	30.42	17.83	33.61	3.36	11.22	1.24	0.47	0.085	0.169	0.005	0.08	0.00	0.04	0.03	0.00	98.54	0.445	255.0
15	30.44	12.34	32.10	3.92	14.74	1.88	0.53	0.094	0.622	0.038	0.12	0.32	0.03	0.02	0.01	97.19	0.944	932.2
	30.40	8.94	30.76	4.62	18.97	2.81	0.40	0.118	0.382	0.035	0.06	0.01	0.00	0.03	0.00	97.52	0.789	1023.8
16	29.58	7.88	27.96	4.40	18.71	3.16	0.73	0.073	0.398	0.021	0.16	0.55	0.01	0.03	0.01	93.66	0.644	754.6
	29.92	8.55	29.74	4.59	19.43	3.27	0.49	0.068	0.408	0.023	0.13	0.04	0.07	0.04	0.01	96.76	0.639	832.6
17	30.08	10.42	30.60	4.35	17.66	2.48	0.54	0.235	0.650	0.058	0.10	0.01	0.01	0.06	0.01	97.26	1.454	925.4
	30.34	9.82	30.73	4.53	18.57	2.81	0.33	0.083	0.348	0.018	0.10	0.01	0.01	0.06	0.00	97.75	0.626	666.2
18	31.33	11.78	32.41	4.18	16.02	2.29	0.47	0.133	0.061	0.017	0.08	0.18	0.00	0.03	0.01	98.99	0.510	769.0
	30.27	12.23	33.29	4.28	15.80	1.96	0.28	0.072	0.044	0.008	0.03	0.01	0.00	0.02	0.00	98.29	0.285	641.0
19	30.27	7.73	29.05	4.68	20.67	3.80	0.42	0.024	0.393	0.019	0.15	0.09	0.02	0.05	0.00	97.37	0.475	920.6
	30.34	8.99	31.35	4.63	19.15	2.82	0.45	0.054	0.013	0.008	0.06	0.03	0.02	0.04	0.00	97.94	0.198	919.6

Table 3. Chemical composition (mas. %) and age (Ma) of Pizhemy 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.

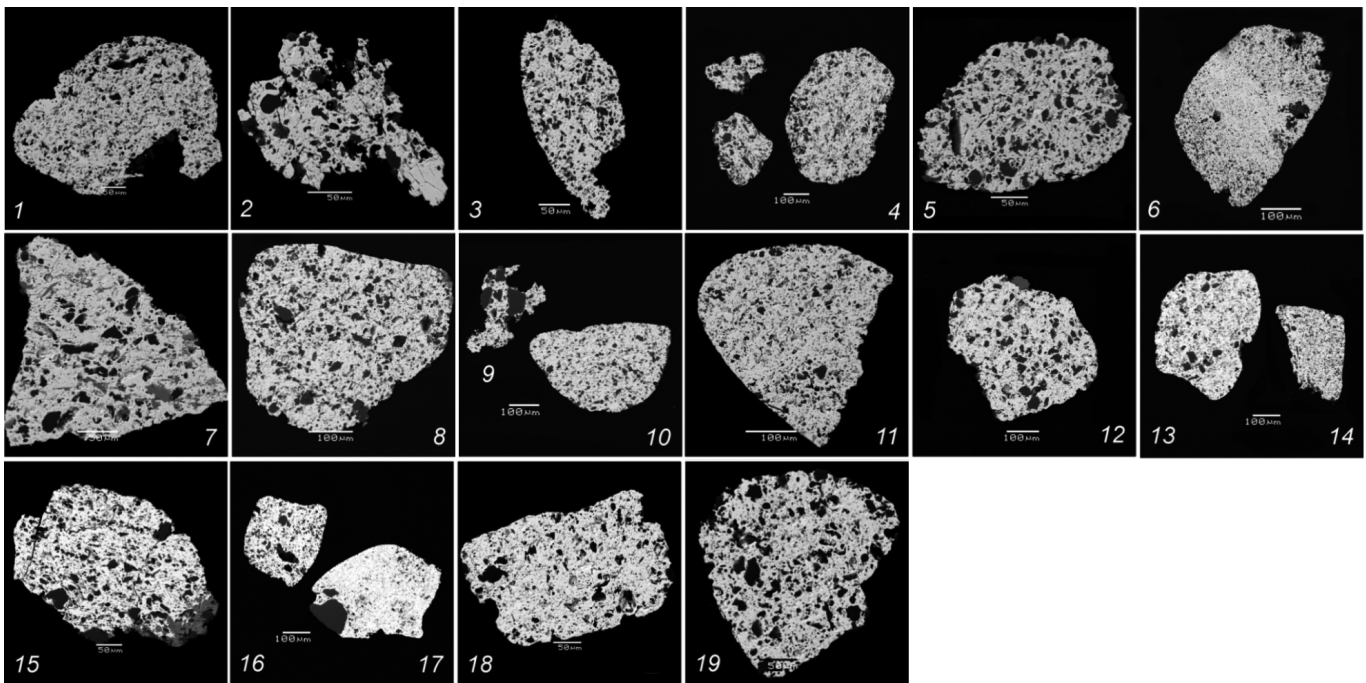


Fig. 2. Electron microscopy images (BSE regime) of 19 Pizhemy monazite-kularite grains with quartz (black) and florencite (light-grey in grains 7 and 15) inclusions. Grain numbers coincide with analytical numbers in Table 3.

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 $\text{Th} + \text{Y} + \text{Ca} \rightarrow \text{Ce}$ 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).

Pizhemy monazite-kularite. Pizhemy 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 ($521 \times 446 \div 228 \times 130$, average size is $375 \times 278 \mu\text{m}$) 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 Pizhemy 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 Pizhemy 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. Pizhemy 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 ;

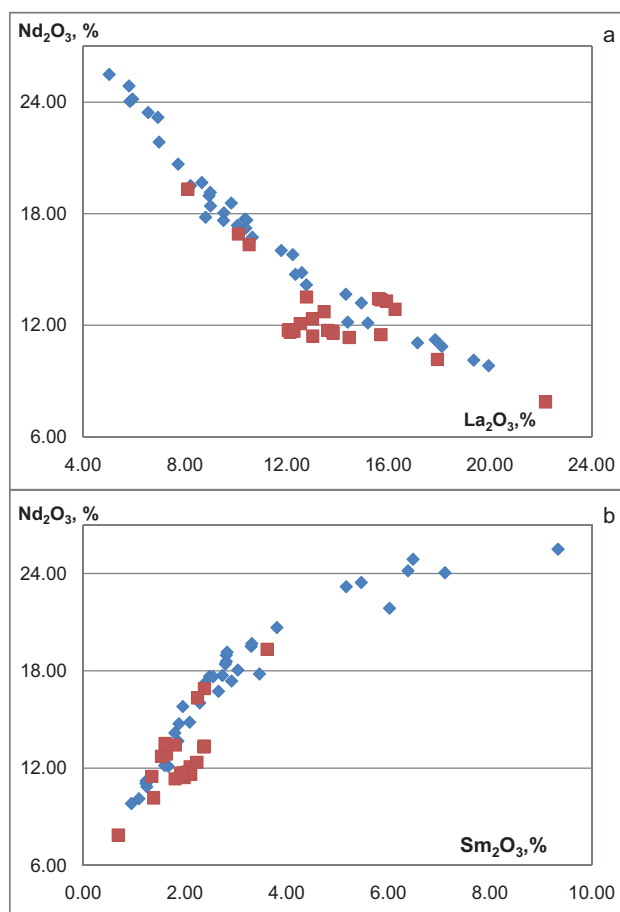


Fig. 3. Oxide ratios: a – La_2O_3 - Nd_2O_3 ; b – Sm_2O_3 - Nd_2O_3 in Yarega (squares) and Pizhensky (rhombs) monazites.

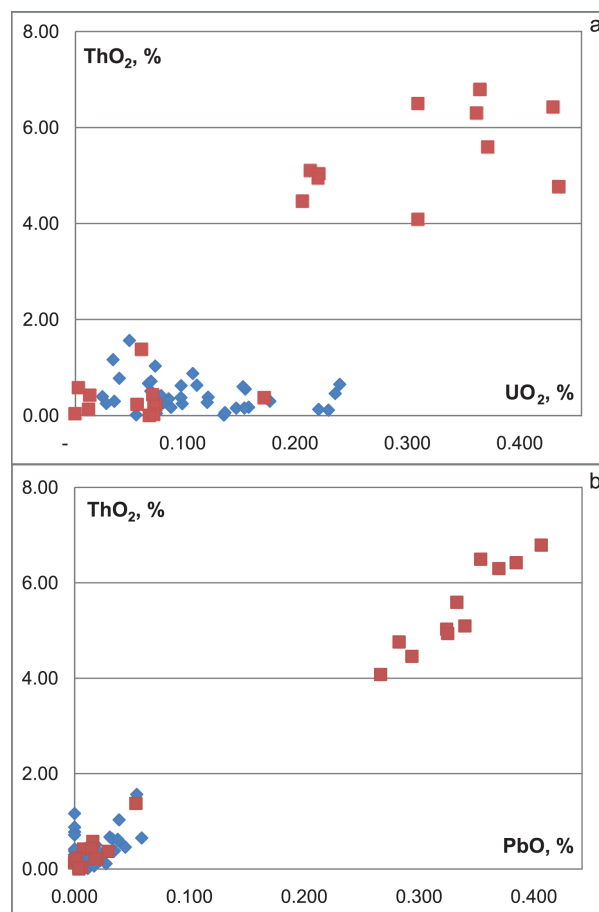


Fig. 4. Oxide ratios: a – UO_2 - ThO_2 ; b – PbO - ThO_2 in Yarega (squares) and Pizhensky (rhombs) monazites.

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 ThO_2^* 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,
 $y = 0.0566x$, $R^2 = 0.906$;

Isochrone II with parameters: $T = 1105$ Ma,
 $y = 0.0481x$, $R^2 = 0.901$;

Isochrone III with parameters: $T = 778$ Ma,
 $y = 0.0335x$, $R^2 = 0.931$.

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 $\text{PbO} = -0.007 + 0.0345 \cdot \text{ThO}_2^*$, $R^2 = 0.908$;

and the other which has no free member and approaches zero, $-\text{PbO} = 0.0337 \cdot \text{ThO}_2^*$, $R^2 = 0.9084$. 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 ^{206}Pb - ^{238}U age values: a major peak with an

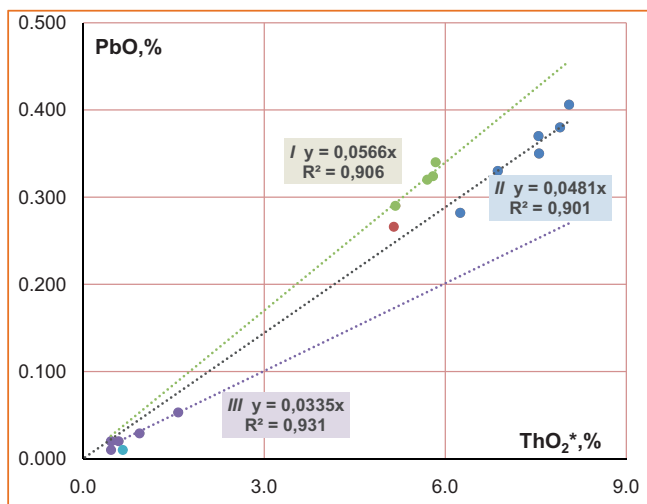


Fig. 5. Isochrones for Yarega monazite: **I** – $T = 1301$ Ma, **II** – $T = 1105$ Ma (high-thorium); **III** – $T = 778$ Ma (low-thorium).

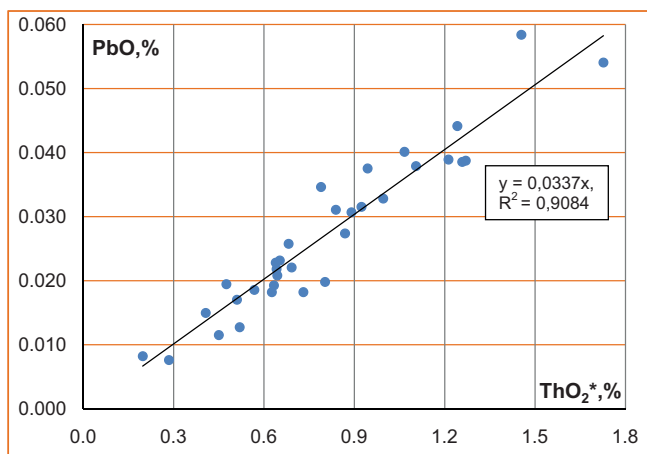


Fig. 6. Isochrone for Pizhensky monazite-kularite: $T = 782$ Ma.

age of 1000-1060 Ma and a minor peak with a maximum of about 570 Ma. ^{208}Pb - ^{232}Th age, estimated at the same points as ^{206}Pb - ^{238}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 «point» (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 Chetlassky Kamen deposits, Middle Timan.

The middle isochrones (**II**) can be correlated in age with Chetlassky lamprophyres, whose intrusion time was estimated by the Rb-Sr method at 815 Ma (Makeyev et al., 2009). Chetlassky 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 Pizhenskoye 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 Pizhenskoye deposit are very similar and seem to indicate a common primary source.

With respect to Timan igneous rocks, only Chetlassky lamprophyres are the most similar in isotope age (Makeyev et al., 2008; 2009) to the chemical age of Yarega low-thorium monazite and Pizhensky monazite-kularite. Rb-Sr-data show that the largest group of Chetlassky lamprophyre samples forms an isochrone with a Neoproterozoic age of 819 ± 19 Ma (Makeyev et al., 2009). Hence, it is Neoproterozoic 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 Pizhemsy 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.

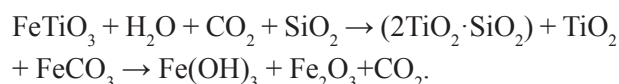
It was thought earlier that oil-saturated leucoxene sandstones from the Yarega deposit are of Middle Devonian age, as shown by spore-and-pollen analysis. However, O.P. Telnova of the Yushkin Institute of Geology of Komi Science Center of Ural Branch of Russian Academy of Sciences (personal communication), 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 Pizhemsy 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 Pizhemsy 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 Pizhemsy suite (D₂pz) that contain Middle Devonian pollen. Many scholars estimate the age of the Malorucheiskaya titaniferous sequence of the Pizhemsy deposit from indirect evidence in the Early Devonian – Neoroterozoic time span. Isotope methods were used to precisely date the titaniferous sequence of the Pizhemsy deposit from a Rb-Sr-isochrone as Neoroterozoic, T = 685±30 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 Pizhemsy titanium deposit is much older (most probably 600-700 Ma) and was formed in Neoroterozoic time (PR₃mr).

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 Pizhemsy 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 TiO₂ 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

after Riphean shales have never formed on Timan, and nobody has ever seen them. The underlying shales of the Lunvozhskaya suite (PR₃In) were dated by the Rb-Sr method at $T = 816.3 \pm 5.2$ Ma (Makeyev et al., 2018). No other ore concentrations, which could be a source of ore matter, have been revealed on the day surface near the Pizhensky deposit. Hence, the probable source (it could be weathering crusts after lamprophyre) was at some depth beneath the deposits, and the ore masses must have moved vertically. Another convincing evidence for the contribution of hydrothermal processes to the formation of both titanium deposits is the presence (3-15 % by volume) of porous and veined siderite with the endogenic isotope composition of carbon (Makeyev, Nosik, 2009). The decay of ilmenite as a primary ore mineral, which gave rise to leucoxene, took place in a hydrothermal process in the presence of endogenic CO₂. The reaction was as follows:



The aforementioned geological, geochemical and mineralogical features and proofs are convincing enough to argue that the Pizhensky 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 Pizhenskoye, resting directly on Neoproterozoic shales, overlain by Middle and Upper Devonian sedimentary rocks and erroneously interpreted earlier as Middle Devonian, are indeed Neoproterozoic. 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 Pizhensky and Yarega titanium deposits were studied. Differences in morphology (Yarega monazite occurs as crystal fragments, while Pizhensky monazite is present as hydrothermally altered ellipsoid grains), the species composition of inclusions (quartz inclusions make up 10-15 % of Pizhensky kularites), grain size (Pizhensky 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 Pizhensky 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 Pizhensky 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 Pizhensky 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.

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