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THE FIRST DATA ON THE U-PB AGE (TIMS AND LA-ICP-MS) OF RUTILE FROM THE ICHETJU POLYMINERAL OCCURRENCE, THE MIDDLE TIMAN

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A study on the U-Pb age of rutile from the Ichetju polymineral occurrence has been done for the first time by LA-ICP-MS and TIMS methods. It was established that rutile originates from various sources with different ages (presumably, ca. 1000, 1660, 1860 and 1980 Ma), but all the rutile types have undergone a common thermal event at ca. 580 Ma. Obtained results are consistent with U-Pb zircon data for the Ichetju occurrence and the Pizhemskoe deposit. According to modern concepts, the closure temperature for the U-Pb system in rutile is higher than 500 °C, which suggests fairly high-temperature conditions of the rutile hydrothermal transformation during the formation of the deposits in Riphean. Obviously, a placer hypothesis of formation of titanium deposits of the Middle Timan which is supported by a number of researchers does not explain such temperature of rutile alteration.

Key words: rutile; U-Pb dating; TIMS, LA-ICP-MS; Ichetju occurrence; the Middle Timan

Introduction and problem statement. The widely known Pizhemskoe titanium deposit and the Ichetju polymineral occurence, located in the Middle Timan (Komi Republic), promise to be in a great demand both in terms of giant titanium and quartz sandstones of glass quality resources and the possible expansion of the list of promising mineral components (rare metals – yttrium, zirconium, niobium, rare earth elements, diamonds, etc.). Despite the fact that both deposits over the past years are the subject of the geological survey and assessment, as well as various, mainly technological, mineralogical and geochemical studies, the questions of the mineralization genesis and the age are still open [2, 6, 7, etc.].

A complex approach, including the usage of a number of mineral-geochronometers (for example, [10]) is used in the complicated procedure of mineralization and hydrothermal process dating. Along with zircon, known as a universal geochronometer, rutile is widely used for these purposes [9, 12, 17, 21, etc.].

In the present work, the first U-Pb dating results of the rutile from the polymineral ore deposit Ichetju (the Middle Timan) are given.

Geological characteristics. The polymineral diamond-gold-rare metal-rare-earth-titanium ore occurrence Ichetju is a conglobreccia horizon with a complex spot, striated and lenticular morphology and sustained thickness from 0.2 to 1.5 m. The rocks of the deposit are represented by light grey quartz sandstones, gritstones, conglomerates and conglobreccias, bedding between two thick layers at the base of the Pizhma glass quality quartz sandstones (D2pg) and higher than the ilmenite-leucoxene-quartz titaniferous stratum Malorucheiskaya of the Pizhemskoe deposit of Middle Timan [7, 8]. According to Rb-Sr isotopic data, the age of the titaniferous strata was determined as late Riphean – 685 ± 30 Ma [1]. The Ichetju rocks show a variety of mineral composition. The main minerals among the 50 indicated are quartz, rutile, anatase, niobium rutile, ilmenite, zircon, monazite, columbite, garnets, chromespinelide, tourmaline, staurolite, gold with silver impurities, rounded diamonds of the Urals-Brazilian type [8].

The content of TiO_2 in ore sandstones varies from 2 to 13.5 wt.%. Titanium minerals are represented by a number of evolving phases from ilmenite through Fe-rutile, pseudorutile to leucoxene (this phase consists of the rutile and quartz sagenite lattice) to pure acicular rutile [7, 8]. The quartz content in Pizhma leucoxene varies from 15 to 30 %. The schematic reaction of ilmenite transformation into leucoxene, which comes under a high temperature (510 ± 35) °C (the titanium-zircon geothermometer data [20]), can be represented as follows:

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

The paper presents the results of isotope-geochemical studies of rutile from four samples selected only within the southern section of the Ichetju ore occurrence along a 3 km meridional line between the extreme sampling points: UM-212 – river Umba, right bank, the Bolshoy quarry; MU-08/7 – river Umba, left bank, quarry K-150; MU-08/4 – river Umba, left bank, near the ditch KU-1; SM-215 – river Srednjaya, right bank, quarry K-100. The thickness of the ore-bearing layer at the sampling points is 40, 30, 30, and 150 cm, respectively. The bedding of the strata differs by almost 40 m at different altitudes, which is determined by the topography of the basement and the faults amplitude. All samples were selected in clearing walls of the quarries by the method of a continuous channel, the conglobreccia volume in each sample was 20 litres. The samples were weighted, screening, washed in the field up to the grey concentrate. Then in the laboratory samples were separated in bromoform, the volume the heavy fraction was determined, and the mineralogical analysis was carried out. The volume of the heavy fraction was, respectively, 1245; 765; 358; 975 g/m^3. The heavy fractions of four samples provided several dozen of short-prismatic of rutile crystals or its fragments.

Analytical techniques. Representative rutile grains manually picked under a light microscope were implanted in epoxy resin (2.5 cm in diameter) and polished out up to approximately half of its thickness. The quantitative chemical composition of rutile was determined by the SEM-EDS method in Institute of Precambrian Geology and Geochronology RAS (analyzed by O.L.Galankina and N.M.Korolev) using a JEOL JSM-6510LA with an EDS JED-2200. The epoxy resin disks with implanted rutile grains were covered with carbon. The local minerals composition analysis was performed using an electron beam with an accelerating voltage of 20 kV and a current of 1 nA, the spot size was 3 μm. A set of natural minerals, pure oxides and metals was used for standardization. The data were corrected using the ZAF-algorithm.

LA-ICP-MS analysis. Some of the rutile grains previously studied by the SEM-EDS method were analyzed by the LA-ICP-MS method (Fig.1, Table 1). In situ U-Pb dating of rutile was performed at the Swedish Museum of Natural History, Stockholm, using a Nu Instruments Nu Plasma II Multicollector (MC) ICP-MS coupled to an ESI NWR193UC excimer laser ablation system.

Masses 202, 204, 206, 207 and 208 were measured on ion counters, and masses 232, 235, and 238 were measured on Faraday collectors. Mounted rutile grains were ablated for 30 s using 4 J/cm^2, and pulsing at 8 Hz on spots of 60-80 μm. Helium was used as a sample carrier gas (0.3 l/min) to flush the laser cell and was mixed with Argon sample gas (0.9 l/min) before entering the ICP-MS.
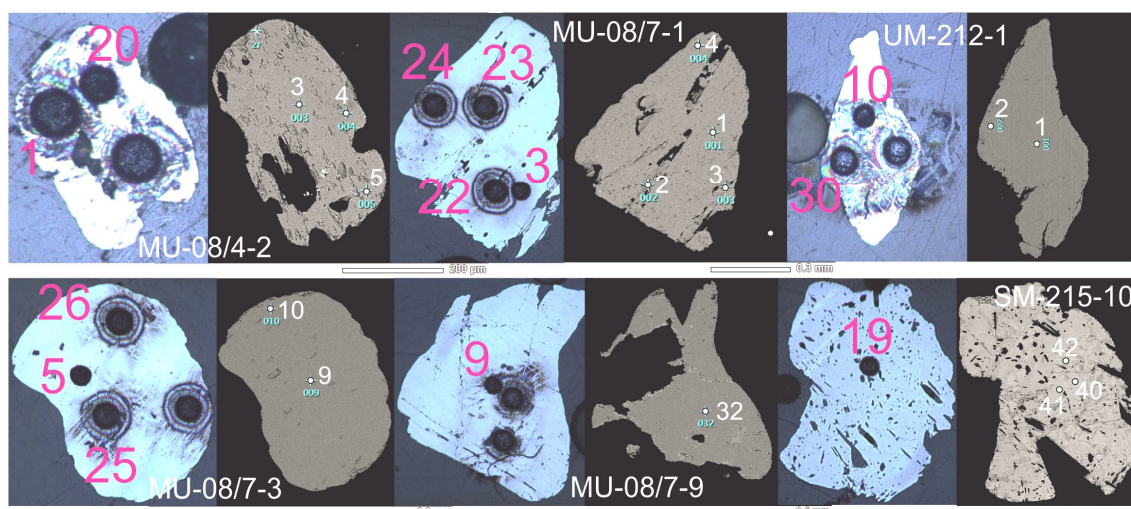

Fig.1. The LA-craters in rutile grains are signed in red colour on the reflected light images.
The microprobe analytical points on BSE image of rutile grains are signed in white colour.
The numbers of the analysis points correspond to table 1 (SEM-EDS) and table 2 (LA-ICP-MS)

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Table 1

The composition of rutile (wt. %), SEM-EDS data

Sample	Grain	Point	SiO$_2$	TiO$_2$	Al$_2$O$_3$	Cr$_2$O$_3$	FeO*	Nb$_2$O$_5$	WO$_3$	∑
MU-08/4	2	3	0.02	98.98	–	–	0.30	0.70	–	100.00
	2	4	–	99.31	–	–	0.51	0.18	–	100.00
	2	5	0.16	98.87	–	–	0.23	0.74	–	100.00
MU-08/7	1	1	0.31	90.99	–	3.55	0.39	4.76	–	100.00
	1	2	0.47	94.65	0.72	2.52	1.37	0.27	–	100.00
	1	3	0.64	94.30	0.70	1.02	1.26	2.07	–	100.00
	1	4	0.29	90.21	0.22	3.51	0.44	5.33	–	100.00
	3	9	–	99.62	–	–	0.38	–	–	100.00
	3	10	–	99.36	–	–	0.64	–	–	100.00
	9	32	–	99.35	–	–	0.39	0.26	–	100.00
UM-212	1	1	–	99.67	–	–	0.33	–	–	100.00
	1	2	–	99.37	–	–	0.30	–	0.33	100.00
SM-215	10	40	–	82.43	–	–	4.01	13.56	–	100.00
	10	41	0.40	83.67	–	–	3.70	12.23	–	100.00
	10	42	0.29	89.28	–	–	2.67	7.77	–	100.00

Dash – content is below the detection limit; FeO* – total iron

This study follows the mass bias and elemental fractionation correction protocols of Kooijman et al. [12]. Data were reduced using an in-house Excel spreadsheet [13]. The R10 rutile standard [18] was used for normalization and indicated external reproducibility of 2.0 % RSD (n = 25). Accuracy was assessed by analyzing the secondary standard R19 (519 Ma [18]) and yielded 507 ± 29 Ma (n = 5), which is within uncertainty of the published value. All uncertainties are reported at the 2σ level. A total of 36 local analyzes of rutile were performed, 13 of which were suitable for U-Pb dating (Table 2).

Table 2

U-Pb rutile isotope data (LA-ICP-MS)

Sample	Grain	Point	Isotopic ratio						Rho	Age, Ma					
			^{207}Pb/^{206}Pb	±2σ	^{207}Pb/^{235}U	±2σ	^{206}Pb/^{238}U	±2σ		^{206}Pb/^{238}U	±2σ	^{207}Pb/^{235}U	±2σ	^{207}Pb/^{206}Pb	±2σ
MU-08/4	2	1 (1*)	0.1098	0.0017	4.857	0.144	0.3209	0.0082	0.86	1794	40	1795	25	1796	28
	2	20 (2*)	0.1134	0.0014	5.156	0.164	0.3298	0.0097	0.92	1837	47	1845	27	1855	22
MU-08/7	1	3 (3*)	0.0633	0.0014	0.868	0.032	0.0995	0.0030	0.82	612	18	635	18	717	46
	1	22 (4*)	0.0616	0.0015	0.815	0.032	0.0960	0.0030	0.80	591	17	605	18	659	50
	1	23 (5*)	0.0618	0.0025	0.815	0.043	0.0956	0.0033	0.65	589	19	605	24	668	86
	1	24 (6*)	0.0661	0.0030	0.858	0.047	0.0941	0.0030	0.58	580	18	629	26	810	94
	3	5 (7*)	0.0602	0.0013	0.729	0.026	0.0880	0.0024	0.77	543	14	556	15	609	48
	3	25 (8*)	0.0634	0.0019	0.814	0.035	0.0932	0.0028	0.71	574	17	605	20	722	64
	3	26 (9*)	0.0632	0.0028	0.805	0.042	0.0924	0.0028	0.57	570	16	599	24	714	93
	9	9 (10*)	0.0534	0.0146	0.670	0.184	0.0909	0.0034	0.14	561	20	521	112	348	434
UM-212	1	10 (11*)	0.0691	0.0015	1.226	0.043	0.1287	0.0035	0.78	781	20	812	20	900	45
	1	30 (12*)	0.0795	0.0023	1.327	0.078	0.1210	0.0062	0.87	736	36	858	34	1186	57
SM-215	10	19 (13*)	0.1215	0.0033	5.767	0.234	0.3443	0.0103	0.74	1907	50	1941	35	1978	49

Rho – correlation coefficient of the ^{207}Pb/^{235}U and ^{206}Pb/^{238}U ratios errors; starred numbers in brackets are points Numbers in Fig.3, *c*

TIMS analysis. The set of rutile grains was purified from impurities under a binocular. The samples were washed in a highly diluted hydrochloric acid solution in an ultrasonic bath for 10 minutes. The rutile decomposition was carried out in a Teflon liner with a metal case in concentrated HF with the addition of HNO$_3$ in a thermostat at a temperature of 220 °C for two days. The extraction of Pb and U from rutile was carried out on a BioRad AG 1×8 100-200 mesh anion ex-

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change resin in the HBr form by the special procedure [16] followed by the U extraction on the anion exchange resin UTEVA. The Pb and U contents measurement was carried out by isotopic dilution using a mixed tracer enriched with ^{235}U-^{208}Pb isotopes. Pb and U isotopes measurements were carried out in the Laboratory of Geochronology and Geochemistry of Isotopes (IPGG RAS) on the TRITON TI multicollector mass spectrometer. Laboratory contamination did not exceed 50 pg of Pb and 5 pg of U in current measurements. Calculations of isotopic ratios and U-Pb rutile age were performed according to a standard procedure with a measurement error of Pb/U ratios of about 0.5 % (2σ) according to the K.Ludvig's programs [14, 15].

Results and discussion. There is a wide variety of shapes, sizes and colours (light brown, dark brown, black and dark red) of rutile grains under study. Along with well-cut crystals with growth striation on the faces, there are rounded rutile grains. Such diversity may indicate multistage processes of rutile formation (alteration) or their various sources. Earlier, a detailed study (SEM-EDS) of rutile grains from the Ichetju ore samples was carried out [11]. As a result, rutile types were determined depending on the Fe and Nb content. Hydrothermal alteration of highly niobium rutile containing up to 24 wt% Nb_2O_5, leads to a significant removal of Nb, down to a decrease in the Nb_2O_5 content to values not exceeding 1 % by weight. The decrease in Nb content is accompanied by the Fe reduction in the ferrirutile, which forms the crosscutting veins in the niobium-containing rutile. Two mineral associations are revealed: the first one is represented by niobium rutile and columbite; the second one is ilmenite replaced by ferri-rutile and pseudorutile, which is purified from the Fe and transformed to a leucoxene phase under hydrothermal conditions, as evidenced by the transition of ferri-rutile to anatase [11].

The second association of titanium bearing minerals is analogous to the association of the underlying Pizhemskoe titanium deposit [7]. This indicates that the titaniferous sandstones of the Malorucheiskaya stratum of the Pizhemskoye deposit were the bedrock of these minerals.

The rutile from four samples studied by LA-ICP-MS differs in the content of impurity elements (Table 1). The maximum concentration of Fe and Nb is characteristic for the sample SM-215. Rutile from the sample MU-08/7 shows the lower Fe and Nb content, as well as the additional presence of Al and Cr. The content of Fe and Nb is even lower in the rutile from the MU-08/4 sample. Rutile from the sample UM-212 is the purest and contains the negligible quantity of Fe and W. The rutile from the sample UM-212 shows the absence of Si, which is considered as a common impurity in the all other samples.
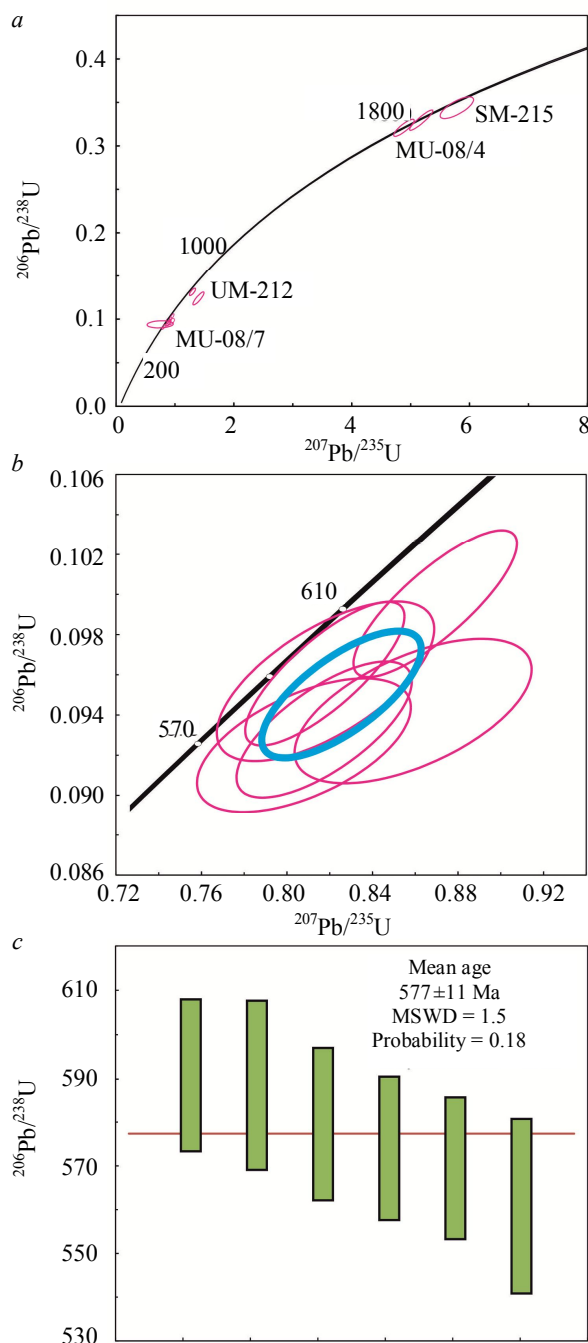

Fig.2. Results of the rutile LA-ICP-MS isotope study:
a – concordia plot illustrating the results of all analyses;
b – concordia plot of the subconcordant points cluster, sample MU-08/7; *c* – calculation of the weighted average age for the subconcordant cluster of points for the MU-08/7 sample. The measurement error ellipses correspond to 2σ, including the error of the decay constant

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LA-ICP-MS analysis. In situ dating was performed for the 13 rutile grains from the four samples divided into several groups (Fig.2, *a*). The age values (^{207}Pb/^{206}Pb age) of about 1980 Ma (sample SM-215) and 1800-1850 Ma (sample MU-08/4) are closest to the concordant age and characteristic for the Paleoproterozoic rutile. The results of single rutile analysis from the samples SM-215 and MU-08/4, presented in Table 2 and in Fig.2, *a*, indicate the Paleoproterozoic age of the rutiles source (presumably, crystalline basement).

Rutile from the sample UM-212 is discordant (^{207}Pb/^{206}Pb age is 900-1185 Ma, ^{206}Pb/^{238}U age is 740-780 Ma (Table 2)). The analytical points of rutile from the MU-08/7 sample form a single subconcordant cluster with a weighted average age of 577±11 Ma (MSWD = 1.5, Fig.2, *b*, *c*).

TIMS analysis. The studied rutile shows a high content of common lead, which is reflected in the low ^{206}Pb/^{204}Pb ratios (from 20.5 to 90.8, table 3). There are no values of U-Pb ratio for the three samples (points 6-8), presented in Table 3, due to the very low ^{206}Pb/^{204}Pb values, which do not allow common lead correction.

The absence of minerals suitable for initial lead correction complicates the correct determination of U-Pb dependencies. Common lead correction was performed assuming an initial Pb composition taken from the model of Stacey & Kramers [19] at the age of the sample.

The discordia plotted on three points of the sample MU-08/4 (Table 3, points 1-3) yields two intersections with the concordia and the U-Pb ages of 590±11 Ma and 1659±6 Ma (MSWD = 0.97). The Pb/U ratios for two of the three points are close to the concordant values (Fig. 3a). This result clearly demonstrates the presence of different-aged rutile grains within one sample.

The age calculated from the two points of sample UM-212 (Table 3, points 5, 6) and two points of sample MU-08/7 (Table 3, points 7, 8) in ^{207}Pb/^{204}Pb-^{206}Pb/^{204}Pb coordinates, is estimated in 947±71 Ma (MSWD = 0.09, Fig.3, *b*).

Figure 3 shows the geochronological results obtained by both LA-ICP-MS in situ analysis (Table 2) and conventional TIMS technique (Table 3). There is a wide range of age results in the range from about 600 to 2000 Ma. Discordia constructed from the set of points of different rutile samples obtained by the TIMS and LA-ICP-MS are characterized by the upper intersection with the concordia at points with different age values of about 1000, 1660, 1860, and 1980 Ma (Fig.3, *c*). At the same time, the points of the lower intersection of all discordia with concordia converge within an error in the region corresponding to approximately 580 Ma.
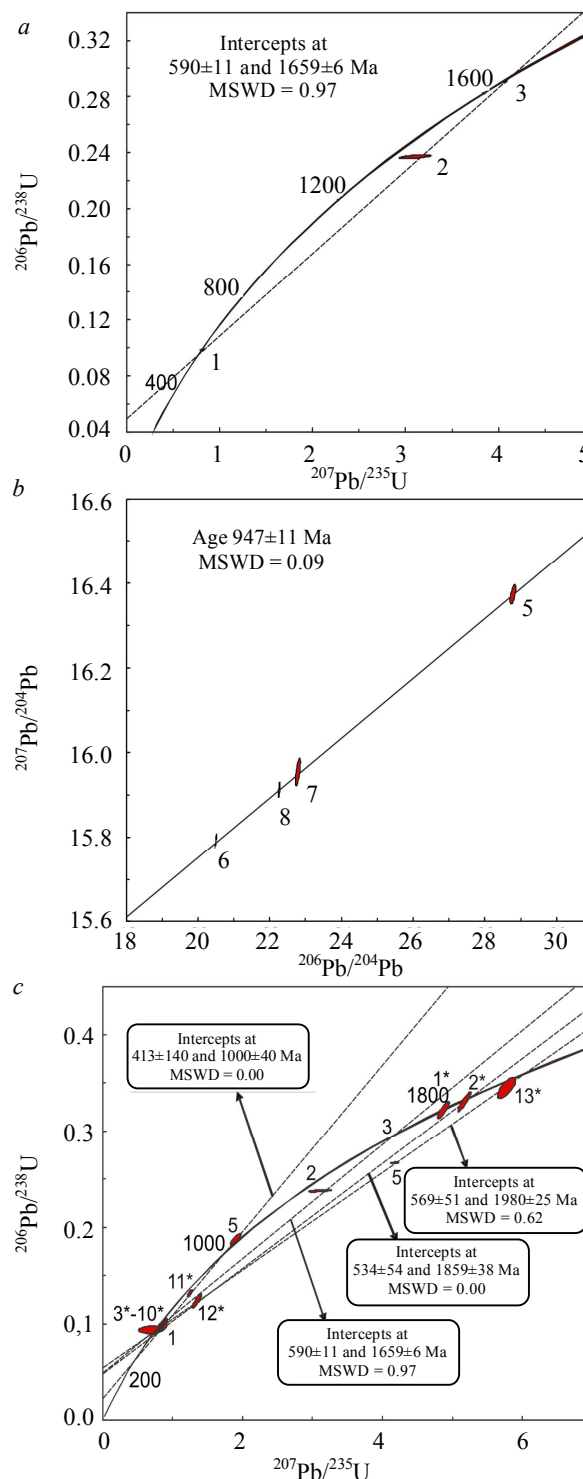

Fig.3. Results of the TIMS rutile isotope study (sample numbers correspond to Table 3):
a – concordia plot for rutile from a sample MU-08/4;
b – Pb-Pb isochrone for rutile from samples UM-212 and MU-08/7; *c* – combined plot of concordia and the results of LA-ICP-MS (the starred samples numbers correspond to the Table 2)

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Table 3

U-Pb rutile isotope data (TIMS)

Sample		Weight, mg	Contents, ppm		Isotopic ratio				Rho	Th/U	Age, Ma		
			Pb	U	$^{206}Pb/^{204}Pb^a$	$^{207}Pb/^{204}Pb^a$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$			$^{206}Pb/^{238}U$	$^{207}Pb/^{235}U$	$^{207}Pb/^{206}Pb$
MU-08/4	1	1.55	0.68	2.50	53.625(2.6)	17.722(0.58)	0.79629(1.7)	0.09635(0.63)	0.44	0.54	593±4	595±10	601±33
	2	4.67	7.42	5.22	28.382(0.27)	16.530(0.35)	3.0904 (4.5)	0.23603(0.47)	0.58	1.32	1366±6	1430±64	1527±80
	3	0.87	11.1	21.1	90.813(0.46)	22.961(0.23)	4.0668(0.35)	0.29010(0.23)	0.72	0.25	1642±4	1648±6	1655±5
SM-215	4	3.08	32.1	13.9	23.748(0.06)	16.175(0.09)	4.1615 (1.1)	0.26538(0.27)	0.56	3.33	1517±4	1667±19	1860±18
UM-212	5	2.04	3.97	3.03	28.777(0.22)	16.372(0.12)	1.8828 (3.2)	0.18556 (2.7)	0.87	3.15	1097±30	1075±34	1030±32
	6	1.10	23.5	3.40	20.457(0.07)	15.786(0.92)	–	–	–	–	–	–	–
MU-08/7	7	2.75	1.49	0.74	22.750(0.26)	15.949(0.17)	–	–	–	–	–	–	–
	8	3.89	3.62	1.77	22.230(0.09)	15.907(0.10)	–	–	–	–	–	–	–

Isotopic ratios have been adjusted to blank and fractionation; The error in measurement (± 2σ) is indicated in percent in parentheses

An analogous dating was obtained in the U-Pb isotopic study of zircon from the Ichetju ore occurence (sample MU-08/4). This zircon has shown a wide range of age values in the range from about 700 to 3280 Ma [5]. These data are consistent with the age of zircon from the underlying titanium ores of the Pizhemskoe deposit [3]. In addition to the age correlation, the trace element compositions of zircons from both objects are quite similar. There are high-Y and low-Y zircon types in the Ichetju and Pizhemskoe deposits. These zircons are characterized by the correlation of Y and REE with P (so-called, xenotime isomorphic scheme [4]). The results of the isotopic and geochemical study provide evidence of a single zircon source in two deposits, while zircon could come from the horizons of the underlying crystalline basement, bedding at the different depth.

Conclusions. The first isotope and geochemical study of rutile from the Ichetju polymineral occurrence highlighted that rutile has various sources of different ages (presumably with an age of about 1000, 1660, 1860 and 1980 Ma). Rutile has undergone a common thermal event at ca. 580 Ma. Obtained results are consistent with the earlier U-Pb dating of zircon from the Ichetju occurrence and the Pizhemskoe deposit [3, 5]. According to modern concepts, the closure temperature for U-Pb system in rutile is higher than 500 °C [12], which suggests fairly high-temperature conditions of the rutile hydrothermal alteration during the deposits formation in Riphean time.

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