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GEOLOGY

In Situ U–Pb (SHRIMP) Dating of Zircons from Granosyenite of the Troitsk Pluton, Kvarkush–Kamennogorsk Anticlinorium, Central Urals

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The Troitsk granosyenite pluton is located among the Neoproterozoic sedimentary sequences of the Kvarkush–Kamennogorsk Anticlinorium on the western slope of the Urals. The sedimentary sequences comprise the Kedrovka and Basegi groups of the Upper Riphean and the Serebryanka and Sylvitsa groups of the Vendian [1, 2]. In the mid-1980s, the Troitsk pluton was used as a reference intrusive body for timing the lower boundary(620 ± 15 Ma) of the Upper Vendian [3]. However, later on, the validity of the Rb–Sr whole-rock isochron age of carbonated granosyenites was questioned [4]. In addition to the Troitsk pluton, a number of other igneous complexes (Shpalorezov, Dvoretsk, Blagodatny, Kus'ya, Zhuravlik, and others) are localized in the Vendian sedimentary rocks of the Kvarkush–Kamennogorsk Anticlinorium. Their petrology, geochemistry, and age are discussed in many publications. The results of geological mapping under the supervision of Suslov [5] made an important contribution to recognition of the geological position of some igneous complexes. The most reliable correlation of the Late Riphean and Vendian igneous complexes in the Kvarkush–Kamennogorsk Anticlinorium was given in [6–8]. Karpukhina et al. [9] made an attempt to reconstruct geodynamic settings of the Dvoretsk, Kus'ya, and Blagodatny complexes and estimated their Sm–Nd and Rb–Sr ages. The modern data on geochemistry, geodynamics, and geochronology of the Neoproterozoic igneous complexes on the western slope of the central Urals are summarized in [10].

The Troitsk pluton, situated in the middle reaches of the Kos'va River (Fig. 1), is an oval, elongated in the near-meridional direction, intrusive body 9.5 ± 2.5 km in area with a slight pinch in its central part. The pluton includes numerous xenoliths and roof pendants with hematite–magnetite ore occurrences and deposits. The intrusive body is composed of relatively uniform granosyenites that consist of microcline, quartz, plagioclase, and biotite; apatite and magnetite are the most abundant accessory minerals. Granosyenite is altered to various degrees and often foliated. The rocks are characterized by carbonation of two stages. The early (primary) carbonation is pervasive as carbonate grains mainly developed in interstices between tabular feldspar crystals. The secondary carbonation is developed along crush zones as cement for granosyenite fragments and cavity filling in fissures. Granosyenites of the Troitsk pluton are classified as subalkali (K- and Na-bearing) plutonic rocks with a high content of Ti and low contents of Mg and Ca [10].

Geological study of plutonic and country rocks began in 1821, when skarn magnetite ores were found in the outer contact zone of the granosyenite pluton near the former Settlement of Troitsk. By the end of the 19th century, the iron deposits were almost completely exhausted and L. Duparc was invited to estimate outlooks for discovery of new deposits. He concluded that the granosyenite body is older than the shales in its framework. G.A. Bazhenov conducted geological exploration in the Troitsk iron ore district in 1928 and 1929. A.I. Krotov undertook geological mapping on a scale of 1 : 100 000 in this district. They pointed out that the pebbles of the Troitsk granosyenite are contained in conglomerates of the Tanin Formation at the base of the Serebryanka Group. They found no indications of contact metamorphism in low-carbonaceous shales of the Garev Formation of the Serebryanka Group at the contact with the Troitsk pluton. On the contrary, based on

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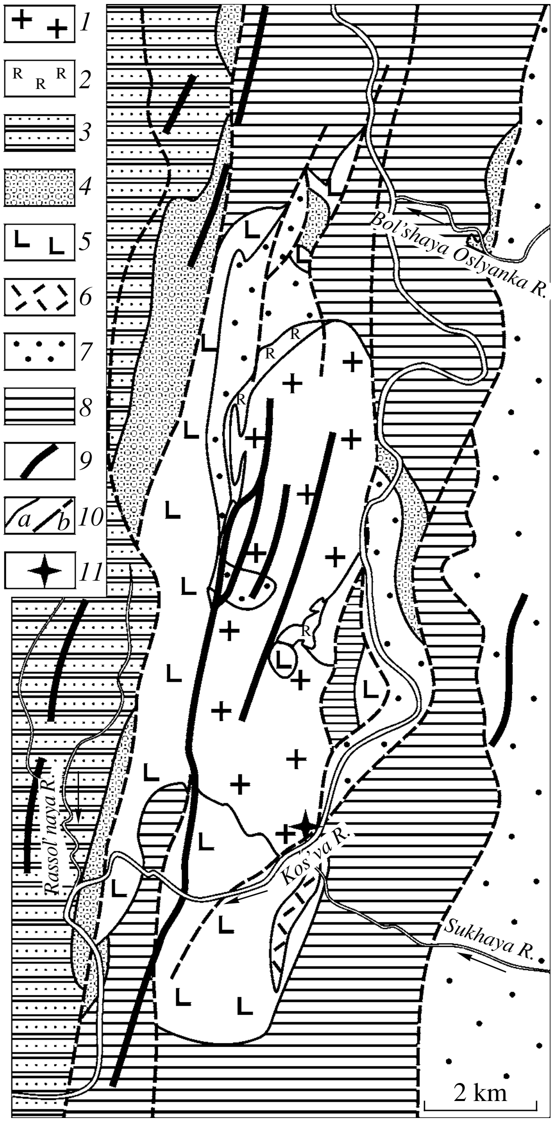

Fig. 1. Geological sketch-map of the Troitsk pluton. Compiled by G.A. Petrov using the data reported by A.M. Zilberman, B.K. Ushakov, and I.P. Teterin. (*1*) Porphyritic granosyenite of the Troitsk pluton; (*2*) hornfels; (*3*) Garevaya Formation of the Serebryanka Group: gray silty shale with sandstone interbeds; (*4*) Taninsky Formation of the Serebryanka Group: polymictic conglomerate; (*5, 6*) Shchegrovity Formation of the Basegi Group: (*5*) trachybasaltic lava and tuff and (*6*) rhyolite; (*7*) Us'va Formation of the Basegi Group: silty shale, arkosic sandstone, and matrix-supported conglomerate; (*8*) Fedotovo Formation of the Basegi Group: black and dark gray silty shales; (*9*) dolerite and gabbrodolerite dikes; (*10*) geological boundaries (*a*) and faults (*b*); (*11*) location of samples for dating.

the data obtained by V.L. Leonov-Vendrovsky and N.P. Starkov in the mid-1960s, Iblaminov and Lebedev [8] indicated the presence of intrusive contacts of the Troitsk pluton with the Tanin Formation at the base of the Serebryanka Group and suggested a Silurian age of this pluton. A.M. Zilberman, who carried out geological mapping on a scale of 1 : 50 000 in this district in 1960 and 1968, also suggested a young (probably, post-Vendian) age of the pluton. Thus, the geological literature of the mid-1980s was dominated by the opinion that the Troitsk pluton intrudes the lower part of the Lower Vendian Serebryanka Group (Tanin and Garev formations). The relationships with the overlying Koiva, Buton, and Kernos formations of the Serebryanka Group remained ambiguous [11, 12]. However, judging from indirect evidence, the Troitsk pluton predated the Upper Vendian sequence of the Sylvitsa Group [3].

We analyzed the available data and found that there is no reliable evidence in favor of active contacts of the Troitsk pluton with the Vendian sedimentary sequences. Our field observations indicate that the pluton is localized in the Upper Riphean rocks of the Basegi Group (trachybasalt lavas and tuffs and rhyolites of the Shchegrovit Formation, arkosic sandstones of the Us'va Formation, and dark gray phyllites of the Fedotov Formation). Iron ore deposits and occurrences known along the Troitsk pluton periphery are mainly hosted in the hornfelsized and skarnized volcanics of the Shegrovit Formation. The Vendian sedimentary rocks have tectonic contacts with granosyenites.

The isotopic ages of rocks and minerals of the Troitsk pluton obtained before 1980 are characterized by a wide range. The K–Ar age of feldspars from granosyenites yielded 360–378 Ma, and whole-rock determinations for hornfels gave 680 Ma [11]. The Rb–Sr whole-rock isochron age of the pluton is 621 ± 12 Ma [11, 13]. The thermoisochron $^{207}Pb/^{206}Pb$ method applied to zircon monofractions from granosyenites yielded 650 ± 20 and 630 ± 20 Ma [14] at $^{207}Pb/^{206}Pb$ ratios equal to 0.060 and 0.059, respectively. (However, these ages are most likely incorrect, because the aforementioned $^{207}Pb/^{206}Pb$ ratios fit the ages of 604 and 567 Ma, respectively.) The data presented above clearly indicate that the available geochronological data on the Troitsk granosyenite pluton require revision on a modern metrological basis.

To solve this problem, zircons were recovered from five granosyenite samples taken on the right bank of the Kos'va River (Fig. 1) and processed in compliance with the traditional technology using a concentrator, isodynamic magnetic separator, and heavy liquids. The main varieties of zircon crystals were hand picked under a binocular microscope. They were fixed by Epofix resin in a pellet (25 mm in diameter) together with zircon standards SL13, 91500, and TEMORA. Then, the pellet was polished up to the point of exposure of crystals at the surface. The cathodoluminescence (CL) images of zircons obtained with a CamScan MX2500 SEM equipped with a CLI/QUA2 Bentham cathodoluminescent system allowed us to choose the most suitable points for the high-precision SHRIMP II analysis at the Center of Isotopic Studies of the All-Russia Research Institute of Geology. The most representative crystals of the selected community of zircons are shown in Fig. 2.

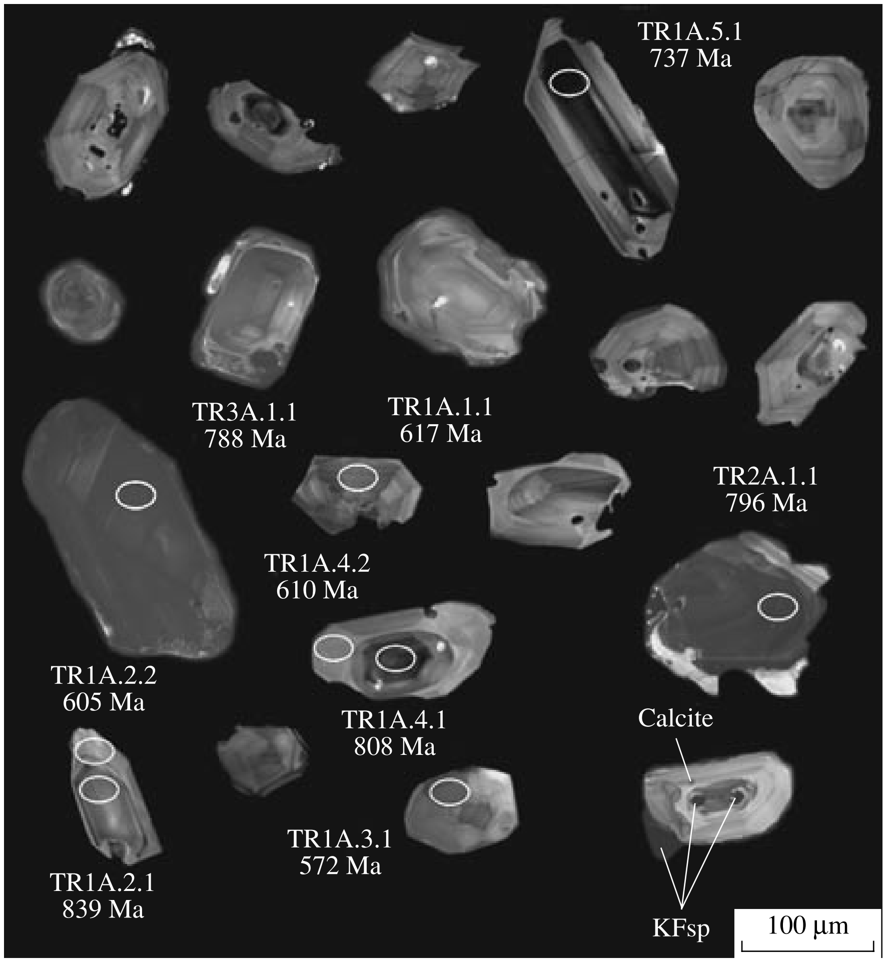

Fig. 2. Cathodoluminescent images of the most representative zircon crystals from granosyenite of the Troitsk pluton. White ellipses (long axes are up to 30 μm) demonstrate crater location within a crystal. Age in Ma, based on $^{207}Pb/^{206}Pb$.

The maximum length of the studied crystals reached 230 μm, while the minimum length was 70 μm. The crystals are euhedral, subhedral, or isometric with the elongation coefficient varying from 2.7 to 1.1. Judging from CL images, the sampling includes both homogeneous and inhomogeneous crystals. The cores of some crystals are characterized by a low CL intensity, whereas the outer zones are distinguished by high CL values. Some crystals reveal a distinct sectorial zoning. K-feldspar and calcite inclusions were detected in several zircon grains.

The measurements were performed during two stages. At the first stage, after completion of all adjustments and calibrations, the Pb isotopic compositions and U/Pb ratios were measured in standards. The obtained reference values were used further for the calculation of the U–Pb age of samples. In each measurement series, we recorded five to seven mass-peak spectra of $^{90}Zr_2O$, ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{238}U, $^{232}Th^{16}O$, and $^{238}U^{16}O$. At the second stage, the primary ion beam was focused on the CL-based region (spot) on the zircon crystal surface. The Pb isotopic composition and U/Pb ratio were measured at each point for 10–15 min to achieve the necessary statistics. The zircon standards (TEMORA, 91500, and SL13) were analyzed after each 4–5 analyses of the tested samples. The obtained analytical information was processed with SQUID and ISOPLOT/EX software.

In total, the U–Th–Pb isotopic compositions were studied at nine local spots in seven zircon crystals from three granosyenite samples (TR1A, TR2A, and TR3A). The maximum size of the elliptical spots was <30 μm (Fig. 2).

The U–Pb isotopic results (Table 1) plotted in $^{207}Pb/^{235}U$–$^{206}Pb/^{238}U$ coordinates (Fig. 3) are localized near concordia within the error interval of ±1σ with the $^{206}Pb/^{238}U$ age value ranging from 650 ± 13 to 789 ± 14 Ma (the discordance interval varies from –20 to +22%). The formal approximation of all data points (Table 2) defines a discordia with the lower intercept at 679 ± 100 Ma and the upper intercept at 946 ± 280 Ma (MSWD = 0.97). If we exclude the data points corresponding to craters TR1A.2.2, TR1A.1.1, and TR2A.1.1, the remaining U–Pb data may be regarded as concor-

Table 1. Results of U–Pb (SHRIMP) measurements

Sample, crystal, crater	$^{206}Pb_c$, %	U, ppm	Th, ppm	$^{232}Th/^{238}U$	$^{206}Pb^*$, ppm	Age, Ma		
						$^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$	$^{208}Pb/^{232}Th$
TR1A.2.2	0.31	141	88	0.64	12.9	651 ± 13	605 ± 71	619 ± 22
TR1A.1.1	0.08	169	291	1.78	16.0	672 ± 8	617 ± 60	670 ± 11
TR1A.3.1	1.82	53	71	1.38	5.44	713 ± 13	572 ± 198	709 ± 29
TR1A.4.2	1.50	33	32	0.99	3.37	713 ± 16	610 ± 259	709 ± 47
TR1A.5.1	0.29	268	353	1.36	26.0	687 ± 14	738 ± 78	676 ± 19
TR1A.2.1	0.01	56	69	1.26	5.45	687 ± 13	839 ± 208	711 ± 37
TR3A.1.1	0.11	512	845	1.71	52.1	721 ± 13	788 ± 49	730 ± 16
TR1A.4.1	0.06	133	222	1.73	13.9	741 ± 10	808 ± 76	755 ± 15
TR2A.1.1	0.02	949	330	0.36	106	789 ± 14	796 ± 43	805 ± 17
Sample, crystal, crater	*D*, %	$^{207}Pb^*/^{206}Pb^*$	±%	$^{207}Pb^*/^{235}U$	±%	$^{206}Pb^*/^{238}U$	±%	*Rho*
TR1A.2.2	−7	0.0600	3.3	0.879	3.3	0.1062	2.1	0.64
TR1A.1.1	−8	0.0604	2.8	0.914	2.7	0.1098	1.2	0.43
TR1A.3.1	−20	0.0591	9.1	0.953	9.2	0.1169	2.0	0.22
TR1A.4.2	−14	0.0602	12	0.970	12	0.1169	2.4	0.20
TR1A.5.1	7	0.0639	3.7	0.991	3.7	0.1125	2.2	0.60
TR1A.2.1	22	0.0670	10	1.040	10	0.1125	2.0	0.20
TR3A.1.1	9	0.0654	2.4	1.068	2.3	0.1184	2.0	0.85
TR1A.4.1	9	0.0660	3.6	1.109	3.7	0.1218	1.4	0.39
TR2A.1.1	1	0.0657	2.1	1.179	2.1	0.1302	1.9	0.92

Note: Uncertainties are indicated at the 1σ level. Uncertainty in the calibration of standards was 0.43%. The correction for common lead was introduced by ^{204}Pb. (Pb_c, Pb*) Common and radiogenic lead, respectively; (*D*) discordance; (*Rho*) correlation coefficient.

dant ones (the observed ellipses overlap one another within error limits) fitting the age of 718 ± 17 Ma (at 95% confidence level with allowance made for uncertainties of the decay constant). This estimate is characterized by a relatively high value of the concordance parameter (MSWD = 7.6) and, correspondingly, a low probability of concordance (0.006), suggesting a low reliability of the age obtained. The introduction of CL data allows us to constrain the procedure of U–Pb age calculation.

Indeed, even the finest growth zones are characterized by different CL characteristics due to the nonuniform incorporation of microadmixtures in the process of zircon crystallization. Therefore, we can discern the growth zones, recognize the internal morphology of crystals, and record the evolution of crystallographic forms. The SEM-based cathodoluminescence images allowed us to specify eventually the coordinates of the spots for microprobe analysis within zircon crystals and to avoid the shifts of isotopic characteristics of polychronous sectors of the crystal lattice of a single grain because of different sets and concentrations of microadmixtures, their valence state, and structural defects. In other words, the CL images of zircons from the Troitsk granosyenite revealed the individual mineralogical features and made it possible to differentiate the U–Pb dates for the specified age calculations.

Let us consider the following essential points. First, the U–Th–Pb isotopic system is different in two zircon crystals analyzed (TR1A.2 and TR1A.4). Both crystals are characterized by different CL intensities in the cores and marginal zones. The cores have older $^{207}Pb/^{206}Pb$ ages (839 and 808 Ma), whereas the outer shells are younger (605 and 610 Ma, respectively). Second, the $^{207}Pb/^{206}Pb$ age for crater TR1A.1.1 (zircon crystals with the most perfect euhedral morphology of the entire community), which overlaps two zones with different CL intensities, is 617 Ma. This value is close to the age of the outer shells in zircon grains TR1A.2 and TR1A.4. The U–Pb data for TR1.A.1.1, TR1A.2.2, and TR1A.4.2 overlap one another in the concordia diagram and yield an age of 671 ± 24 Ma (at 95% confidence level with allowance made for uncertainties of the decay constant and MSWD = 2.8). Third, the U–Pb data for craters in cores TR1A2.1 and TR1A.4.1 and subhedral (relatively homogeneous) crystals TR1A.3, TR2A1, and TR3.1 are characterized by the partial mutual

Table 2. Versions of the calculation of U–Pb analytical data

Sample	Crystal	Crater	Age, Ma	MSWD	Note
All	All	All	946 ± 280	0.97	Upper intercept
			679 ± 100		Lower intercept
TR1A; TR3A	TR1A.3; TR1A.4; TR1A.5; TR1A.2; TR3A.1; TR1A.4	TR1A.3.1; TR1A.4.2; TR1A.5.1; TR1A.2.1; TR3A.1.1; TR1A.4.1	718 ± 17	7.60	Concordant value
TR1A	TR1A.1; TR1A.2; TR1A.4	TR1A.1.1; TR1A.2.2; TR1A.4.2	671 ± 24	2.80	Concordant value
TR1A; TR2A; TR3A	TR1A.2; TR1A.3; TR2A.1; TR3A.1; TR1A.4; TR1A.5	TR1A.2.1; TR1A.4.1; TR1A.3.1; TR2A.1.1; TR3A.1.1; TR1A.5.1	801 ± 53	0.46	Upper intercept

overlapping of the respective ellipses in $^{207}Pb/^{235}U$–$^{206}Pb/^{238}U$ coordinates and by older $^{207}Pb/^{206}Pb$ ages. This relationship allows us to integrate the U–Pb data for craters TR1A.2.1, TR1A.4.1, TR1A.3.1, TR2A.1.1, TR3A.1.1, and TR1A.5.1 into a common massif that yields the isochron age of 801 ± 53 Ma (MSWD = 0.46).

The data discussed above allow us to distinguish two episodes in the evolution of the Troitsk pluton. The age of 671 ± 24 Ma (concordant value for three zircon grains), which corresponds to the crystallization of perfect euhedral zircon crystals, is interpreted as the most probable age of the pluton formation. At approximately the same time, the outer shells were grown over the older zircon cores dated at 801 ± 53 Ma (upper intercept of discordia calculated for six data points). The U–Pb age of cores is consistent with model Nd ages of the Dvoretsk Complex based on our recalculation of the Sm–Nd data reported in [9]: 757 and 824 Ma (trachybasalt) and 797 Ma (trachyandesite). This value may be regarded as the probable age of the source for most igneous complexes known on the western slope of the central Urals, including the Troitsk pluton. The petrology and geochemistry of these complexes indicate that they are related to magma sources, which originated at different depths during the ascent of a mantle plume [9, 10].

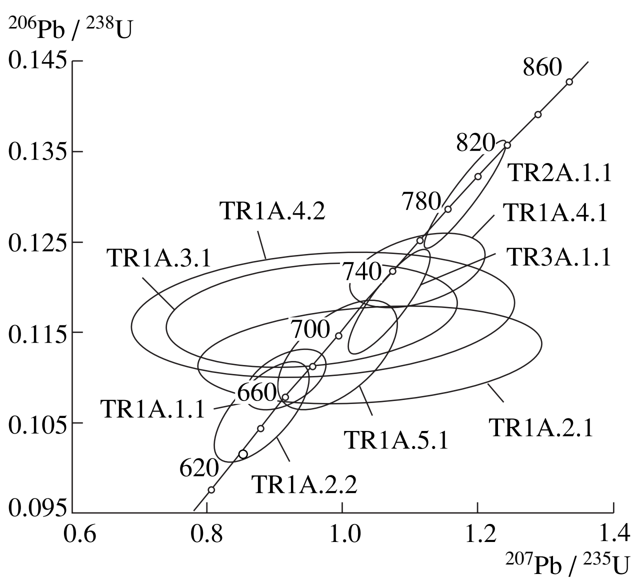

Fig. 3. U–Pb (SHRIMP) data on zircons from granosyenite of the Troitsk pluton. Ellipse dimensions correspond to analytical uncertainties (±1σ).

Thus, the performed study of the U–Pb system of zircons from the Troitsk granosyenite pluton supports its pre-Vendian (Late Karatavian) age, which is consistent with the available geological relationships, and limits the application of this pluton as a geochronological marker. The correct determination of the Lower/Upper Vendian boundary in the Urals may be realized by the dating of zircons from volcanic ash interlayers in the upper part of the Staropechninsk Formation at the base of the Sylvitsa Group [15] and from pillow basalts of the Shpalorezov Complex in the upper part of the Kernos Formation, the youngest lithostratigraphic unit of the Serebryanka Group [1, 10].

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