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The age of zircon from crustal granitoids of the Vovcha and Huliaipole blocks: the history of the Earth crust formation of the Azov domain of the Ukrainian Shield

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The studied area comprises the junction zone of the Huliaipole granite-greenstone block with the Vovcha and Remivka granulite-gneiss blocks. The Vovcha and Remivka blocks are composed of Archean quartz-feldspathic gneisses (>80%), also containing remnants of high-metamorphic rocks of the West-Azov series. The Huliaipole Block is composed of rocks of the West-Azov series and a Mesoarchaean granite-greenstone complex (3,2–3,0 Ga), which includes the Kosivtseve greenstone structure and TTG rocks of the Shevchenko complex. Granitoids are widespread in the area. Archean TTG rocks of the Shevchenko Complex were formed by partial melting of a mafic protolith. The later granitoids of the southern part of the Vovcha block and Dobropillya Complex are still poorly studied. According to petrological data, granitoids of the Dobropillya Complex were formed due to high degree (>50%) melting of the older crust, which consisted of granitoids and metamorphosed ultramafic and mafic rocks. In the Dobropillya granitoids, inherited zircon significantly prevails and, therefore, it is hard to determine the time of crystallization of these rocks. Seventy-nine LA-ICP-MS determinations of U-Pb isotope ages were performed on zircon from granite-porphyry of the Vovcha block. The age of this rock has been estimated by the modal 207Pb/206Pb age of the main zircon population as 2840±10 Ma. A small amount of older (up to 3624 Ma) grains has also been detected. Seventy-six LA-ICP-MS U-Pb age determinations were performed on zircon from granodiorite of the second intrusive phase of the Dobropillya massif. In this rock, four main zircon populations can be distinguished. The two oldest peaks (3905 and 3435 Ma) correspond to zircons inherited from an ancient protolith. The main zircon population has a weighted average 207Pb/206Pb age of 2847±20 Ma. Thus, the main zircon populations in the crustal granitoids of both the Vovcha and Huliaipole blocks have an age of 2.8–2.9 Ga. Granitoids of this age have not yet been found in this area and, therefore, there is no clear interpretation of their source. The Archean crust, from which the crustal granitoids of the Vovcha and Huliaipole blocks might have been melted, also included Eoarchean (3.9 and 3.8 Ga), Paleoarchean (3.6–3.2 Ga), and Mesoarchean (3.15–2.95 Ga) rocks. A small group of younger (2350–2135 Ma) zircons reflects the influence of Paleoproterozoic processes, either partial loss of radiogenic lead or the crystallization of a new zircon population. The obtained geochronological data indicates that the Early Precambrian crust of the west-Azov block was formed from 3.9 to 2.1 Ga.

Keywords: *crustal granite; West Azov; Vovcha block; Huliaipole block; Dobropillya massif; zircon; U-Pb age LA-ICP-MS method.*

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Introduction

The Ukrainian Shield forms the southern part of Sarmatia, one of the three building blocks of the East European Craton (Bogdanova, 1993; Bogdanova et al., 2016). The Ukrainian Shield is composed of several Archean domains with ages ranging between c.3.8 and 2.7 Ga, and intervening Pa oldest crustal units are the Paleo- to Mesoarchean Podillya Domain in the southwestern part of the Shield and the Azov Domain in the southeast. Both these domains have evolved through several events of high-grade metamorphism and multiphase Archean and Paleoproterozoic magmatism. In contrast, the Middle Dnieper Domain in the central part of the Shield is dominated by Meso- to Neoarchean granite–greenstone belts that are less reworked by subsequent metamorphism and virtually untouched by Paleoproterozoic orogeny. In the Orikhiv-Pavlohrad shear zone, which separates the Middle Dnieper and Azov domains remnants of Eo- and Paleoarchean rock complexes were found (Lobach-Zhuchenko et al., 2014). Several folded structures occur in the Orikhiv-Pavlohrad structure, the main of which are the Novopavlivka and Tokmak antiform structures and the Orikhiv, Vasynivka and Vasylkivka synform structures (Nekryach, 1980; Kiktenko, 1982). The antiform structures are composed of Eoarchean (3670 Ma) (Bibikova, Williams, 1990) and Paleoarchean (3500 Ma) (Lobach-Zhuchenko et al., 2014) tonalites. In the Novopavlivka area, Eoarchean tonalites include remnants of older metabasic rocks and metapyroxenites (Shcherbak et al., 1984). Synform structures are composed of rocks of the Temryuk Formation, the Orikhiv-Pavlohrad structure also contains strongly compressed Chystopillya and Novohorivka Mesoarchean greenstone belts. The geological structure of the Western and Central parts of the Azov Domain, similarly to the Middle Dnieper Domain, is dominated by the Mesoarchean granite-greenstone complexes

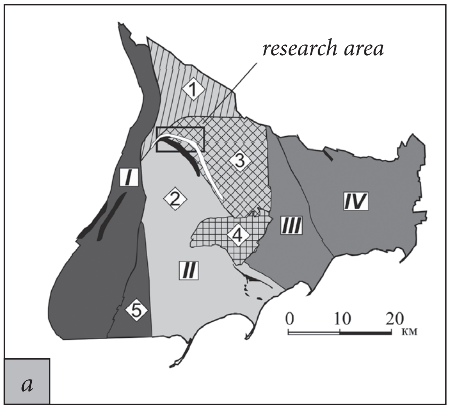
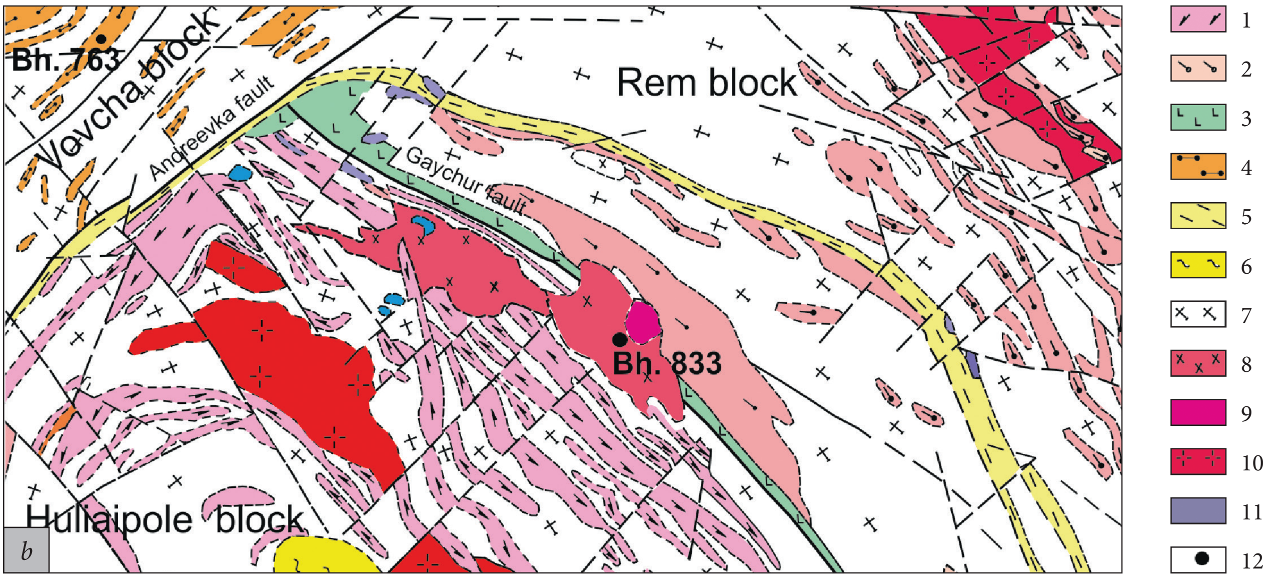


Fig. 1. *a* – Geological and structural scheme of the Azov Domain (numbers in squares): *I* – Orikhiv-Pavlohrad zone, *II* – West Azov antiform structure, *III* – Central Azov synform structure, *IV* – East Azov antiform structure. Blocks of the III order of West Azov antiform structure (numbers in the diamonds): *1* – Vovcha block; *2* – Huliaipole-Saltycha block; *3* – Remivka block; *4* – Bilotserkivka block; *5* – Korsak block. *b* – A schematic geological map of the junction zone of the Huliaipole, Vovcha and Rem blocks (Pereverzev, 2014), with changes and addition: *1* – Petrivka strata; *2* – West Azov Series; *3* – Kosivtseve strata; *4* – Temryuk Suite of the Central Azov Series; *5* – Ternuvate Strata; *6* – Huliaipole Suite; *7* – Tokmak Complex; *8* – Dobropillya Complex, phase I; *9* – Dobropillya Complex, phase II; *10* – Shevchenko Complex; *11* – Serhiivka Complex; *12* – borehole



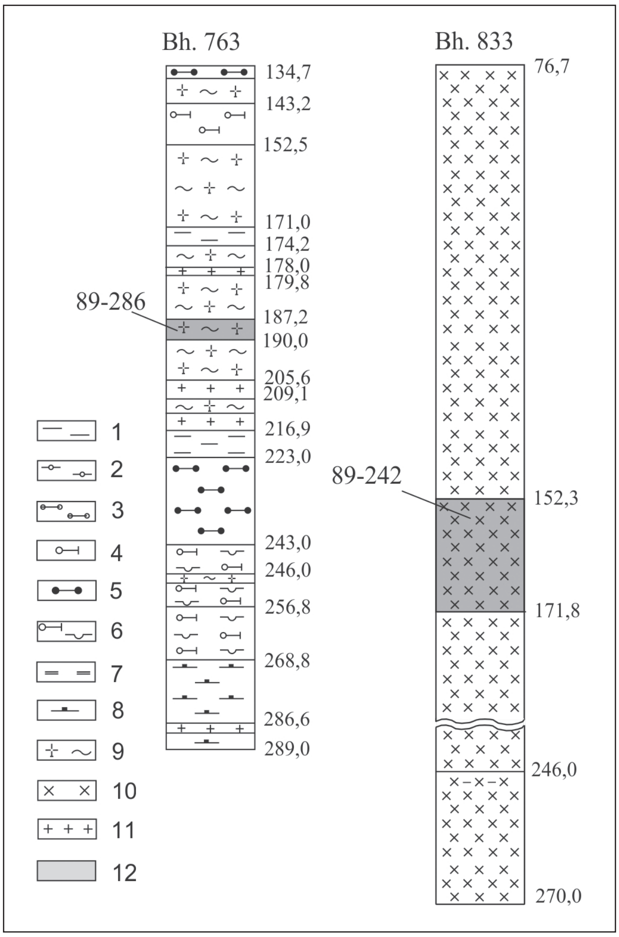


Fig. 2. Schematic borehole logs by (Kinshakov, 1990): *1* – biotite plagioclase gneiss; *2* – two-mica gneiss; *3* – sillimanite-bearing two-mica gneiss; *4* – sillimanite-garnet-biotite plagioclase gneiss; *5* – garnet-biotite plagioclase gneiss; *6* – garnet-graphite-bearing amphibole-biotite plagioclase gneiss; *7* – quartzite; *8* – amphibolite; *9* – garnet-bearing biotite granite-porphyry; *10* – granodiorite; *11* – biotite granite; *12* – sampling intervals

(Eynor et al., 1971). These are surrounded by large remnants of the Paleoarchean tonalites (3.3 Ga) (Artemenko et al., 2014; Artemenko, Shumlyanskyy, 2021). Rocks of the Central Azov series compose in this area the Korsak and Central Azov synform structures, as well as smaller structures within the Vovcha block (Eynor et al., 1971).

The studied area is located in the West Azov Domain of the Ukrainian Shield, in the junction zone of the Huliaipole granite-gneiss block with the Vovcha and Remivka granulite-gneiss blocks (Kinshakov, 1990) (Fig. 1, *a, b*). The Vovcha block occurs as an anticlinal uplift in the northwestern part of the Azov Domain. In the west, it borders the Orikhiv-Pavlohrad structure, and in the east, the northern continuation of the Central Azov synform. The northwest-trending fault system played an important role in the formation of the structure of the area. The faults follow northwest trending dome- and graben-shaped structures. The dome-shaped structures comprise Archean gneisses of the West Azov Series and plagioclase granitoids of the Shevchenko Complex, while graben-shaped structures comprise metamorphosed sedimentary rocks of the Central Azov Series (Nekryach, 1980; Kiktenko, 1982). The rocks of the Central Azov Series are cut by pegmatoid granitoids of the Anadol Complex (2067 Ma) (Artemenko et al., 2018). In the southern part of the Vovcha block, strip-like bodies of granitoids were revealed by drilling. These are represented by plagioclase granites, granites, plagioclase migmatites and migmatites of biotite and amphibole-biotite nature, rarely with garnet (Kinshakov, 1990).

The Remivka block is an antiform structure. It is composed of rocks of the West Azov Series and plagioclase granitoids of the Remivka Complex. This structure is still poorly studied, geochronological data is lacking. The Huliaipole block differs from the Remivka one by the occurrence of an Archean granite-greenstone association. The Huliaipole block is composed of rocks of the West Azov Series, TTGs of the Shevchenko Complex, sedimentary-volcanogenic rocks of the Kosivtseve Strata and granitoids of the Dobropillya Complex. There are also small bodies of granitoids of the Anadol Complex. In the northwest, the Huliaipole block is bordered by the arcuate Haichur (Ternuvate) tectonic structure (72 km long), which is composed of metamorphic rocks of the Ternuvate Strata, that continues further to the east in the Remivka block. The Huliaipole synform structure is situated in the central part of the block and is composed of rocks of the Huliaipole Suite. Granitoids are widespread in the area. The Archean (3.0–2.92 Ga) plagioclase granitoids of the Shevchenko Complex (TTG rocks) were formed due to the partial melting of a mafic protolith (Artemenko et al., 2018). The later granitoids of the Remivka and Dobropillya complexes are still poorly studied. The Dobropillya massif is confined to the Dobropillya fault, which separates the Remivka and Huliaipole blocks. It is a hypabyssal intrusion (Fig. 2) having an area of ca. 26 km^2 (Kinshakov, 1990).

Two intrusive phases have been distinguished in the massif. Phase I comprises quartz diorite, granodiorite, quartz monzonite, and tonalite, whereas phase II is represented by granodiorite, low-alkaline granite, granite, quartz syenite and quartz monzonite.

(Bobrov et al., 2006; Stepanyuk et al., 2007, 2013) have determined the Paleoproterozoic age of the mantles on zircon crystals from subalkaline granitoids (2101±15 Ma) and tonalites (2078±20 Ma) of Phase I of the Dobropillya massif. Granitoids of the Dobropillya Complex have been formed due to the high degree of melting of the older TTG rocks in crustal conditions (Artemenko et al., 2008). Intrusive rocks of the first phase occur in the northwestern part of the massif, whereas tonalities of the second intrusive phase compose the central and southeastern parts of the massif (Kinshakov, 1990).

Research objectives and methods

The questions regarding the timing of formation of the crustal granitoids widespread in the junction zone of the Huliaipole, Vovcha and Remivka blocks, and the age of their protolith remain unresolved. In this study, we focus on LA-ICP-MS zircon dating of granitoids revealed by drilling 8 km northwest of the Ternuvate structure in the southern part of the Vovcha block (borehole 763, sample 89-286), and granitoids of the second intrusive phase of the Dobropillya Complex (borehole 833, sample 89-242).

Analytical methods. Zircon has been extracted from the rock using a shaking table, heavy liquids, and a magnetic separator to produce a heavy non-magnetic fraction. Zircons were hand-picked under a binocular microscope. Zircon morphology has been studied under an optical microscope, whereas the internal structure was documented using cathodoluminescence. U-Pb isotopic data were collected using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in the GeoHistory Facility, John de Laeter Centre, Curtin University. Zircon was ablated using a Resonetics RESOlution M-50A-LR system, incorporating a COMPex 102–193 nm excimer UV laser that was coupled to an Agilent 8900 QQQ mass spectrometer. Zircon standard OG1 (3465±0.6) Ma; (Stern et al., 2009); all uncertainties at 2σ) was utilized as the primary reference material and analyzed in blocks with secondary standards GJ-1 ((601.2±0.4) Ma; (Jackson et al., 2004), and Plešovice ((337.13±0.37) Ma; (Sláma et al., 2008)). The secondary standards yielded weighted mean 207Pb/206Pb ages and 238U/206Pb ages within an uncertainty of the recommended values. The time-resolved mass spectra were reduced using Iolite 3.7™ (Paton et al., 2011) with final ages calculated using Isoplot. Silicate rock analyses were carried out at the IGMOF of NAS of Ukraine, Kyiv. Trace elements, were analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) on an Elan 6100 mass spectrometer at the VSEGEI Central Laboratory in 2009.

Geochemistry and origin of granitoids

Garnet-bearing biotite granite-porphyry (Vovcha block, sample 89-286) is composed of (vol. %) albite (30–32), quartz (22–25), microcline (27–30), biotite (7–9) and sporadic grains of garnet, zircon, magnetite and titanite. Sericite develops after plagioclase. Porphyries are represented by quartz, microcline and garnet.

Table 1. **Chemical composition of the studied garnet-bearing granite-porphyry and granodiorite**

Oxide, %	Sample 89-286 (1)	Sample 89-242 (2)
SiO_2	70.91	67.20
TiO_2	0.34	0.42
Al_2O_3	13.65	14.69
Fe_2O_3	0.47	1.16
FeO	2.59	2.74
MnO	0.04	0.09
MgO	1.66	2.70
CaO	2.62	3.29
Na_2O	3.25	4.20
K_2O	3.39	2.60
S_{tot}	0.02	0.06
P_2O_5	0.06	0.24
CO_2	0,38	–
H_2O-	0.01	0.13
LOI	0.53	0.75
Total	*99.92*	*100.27*

Notes: 1 – garnet-bearing granite-porphyry, Vovcha Block, borehole 763, depth 187.2–190.0 m (sample 89-286); 2 – granodiorite, II intrusive phase of the Dobropillya Complex, Dobropillya massif, borehole 833, depth 152.3–171.8 m. Chemical analyzes were carried out in the chemical laboratory of the IGMOF NAS of Ukraine.

Table 2. **Trace elements concentrations in garnet-bearing granite-porphyry (sample 89-286)**

Element	Concentration, ppm	Element	Concentration, ppm	Element	Concentration, ppm
Rb	133	Ni	23.6	Eu	1.05
Sr	318	Cu	27.4	Gd	4.51
Ba	1030	Zn	42.3	Tb	0.53
Nb	13.7	Sn	1.2	Dy	1.91
Y	8.2	Sb	0.1	Ho	0.31
Zr	174	Cs	1.8	Er	0.88
Ga	21.5	Hf	4,7	Tm	0.11
Ge	1.4	Ta	0.66	Yb	0.76
Pb	16.5	W	<0.15	Lu	0.13
Th	42.6	Tl	0.47		
U	1.7	La	71.3		
Mo	0.9	Ce	136		
V	41.3	Pr	14.3		
Cr	76.5	Nd	46.2		
Co	9.2	Sm	7.04		

Ratios:
(La/Yb)N = 67.3
Eu/Eu* = 0.57
Rb/Sr = 0.42

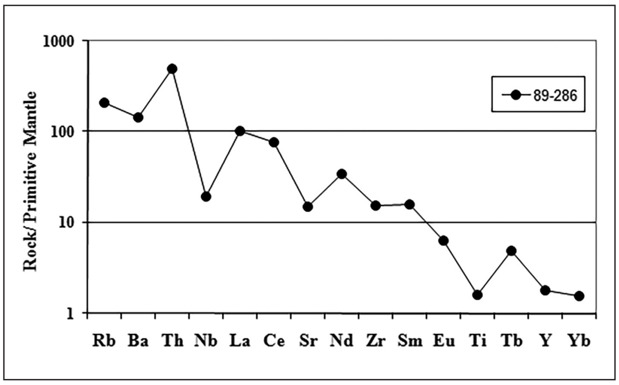


Fig. 3. Primitive-mantle normalized (Sun, McDonough, 1989) multi-element patterns for garnet-bearing granite-porphyry (sample 89-286)

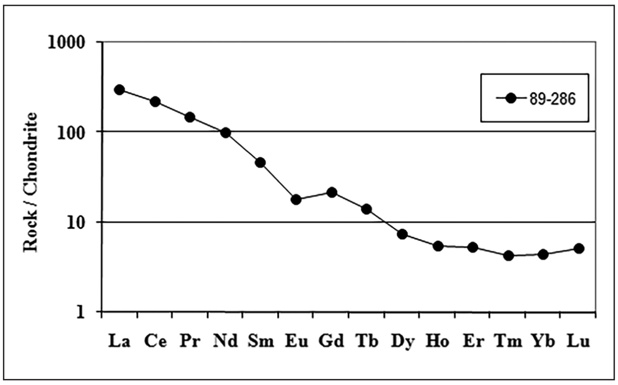


Fig. 4. Chondrite (C1) normalized (Sun, McDonough, 1989) REE patterns for garnet-bearing granite-porphyry (sample 89-286)

In terms of chemical composition, garnet-bearing biotite granite-porphyry (samples 89-286) correspond to low alkaline granite of the normal (SiO_2 – 70.91; $Na_2O + K_2O$ = 6.64%) of the K-Na series (Na_2O/K_2O = 0.96) (Table 1) (Igneous…, 1987). It is characterized by a high Rb/Sr ratio of 0.42. (Table 2). They also have high Ba (1030 ppm) and HFSE content (Y – 8.18 ppm, Nb – 13.7 ppm, Yb – 0.76 ppm, Th – 42.6 ppm). Negative anomalies of Nb, Sr and Ti stand out on the spidergram (Fig. 3). Rare-earth elements are strongly differentiated: (La/Yb)N = 67.3 (Fig. 4). The negative Eu anomaly (Eu/Eu* = 0.57) has also been found, which, together with the negative Sr anomaly, indicates plagioclase fractionation in the crustal magmatic source.

Granodiorite of the Dobropillya Massif (intrusive phase II, sample 89-242) has a hypidiomorphic granular texture. The rock mineral composition (vol.%) is as follows: plagioclase 45–47; quartz 15–18; amphibole 12–15; biotite 8–10; microcline 7–11; epidote 2–3; sericite and muscovite 1–1.5; apatite 1–1.5; carbonate, chlorite, zircon, allanite, magnetite and leucoxene occur in sporadic grains. Zircon and allanite are always found as inclusions in biotite and amphibole.

In terms of chemical composition, this rock corresponds to granodiorite of the normal (SiO_2 – 67.91; Na_2O+K_2O = 6.80%) K-Na series (Na_2O/K_2O = 1.6) (see Table 1) (Igneous…, 1987).

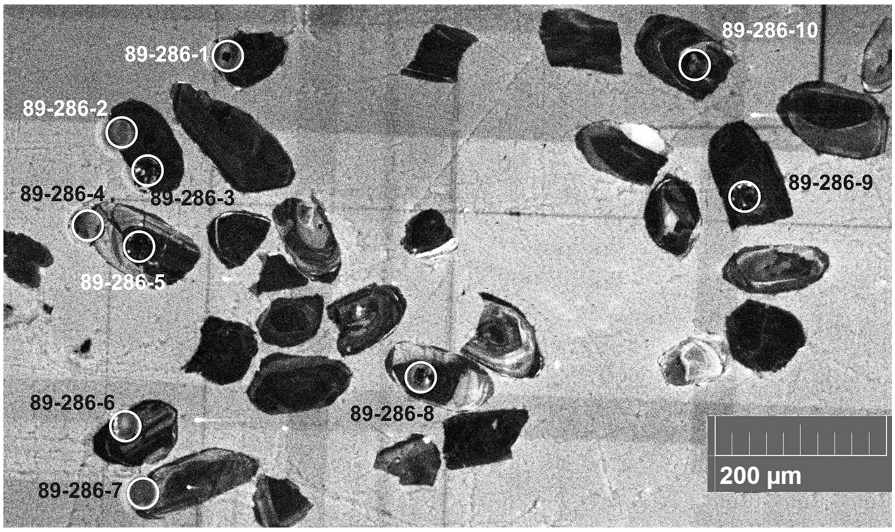


Fig. 5. Cathodoluminescent image of the studied zircon crystals from garnet-bearing granite-porphyry (sample 89-286). The numbers of the analyzes are as in Table 3

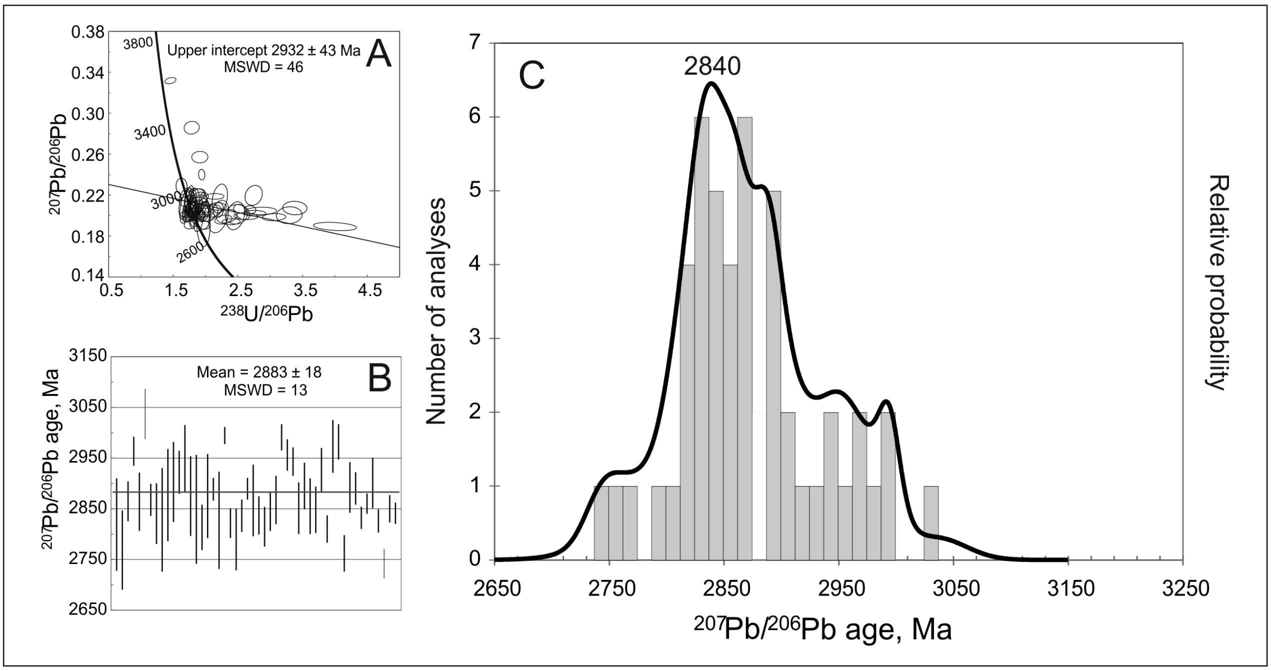


Fig. 6. *A* – U-Pb concordia diagram for zircon from garnet-bearing granite-porphyry (sample 89-286); *B* – weighted average $^{207}Pb/^{206}Pb$ age of concordant zircons; *C* – distribution of $^{207}Pb/^{206}Pb$ concordant ages

Zircon characterization and results of geochronological studies

Garnet-bearing biotite granite-porphyry (the Vovcha block, borehole 763, depth 187.2–190.0 m, sample 89-286) contains euhedral zircon, slightly corroded (Fig. 5)and strongly fissured. Prism {100} prevails over {110}. L4 size = 0.15–0.25 mm, elongation factor = 3.0. The surface is smooth. The color is pinkish-brown, with matte lustre; transparent and translucent (up to opaque). The internal structure is often heterogeneous, with shadowy dark brown cores.

In total, we performed 79 U-Pb age determinations for zircons from granite porphyry (sample 89-286) (Table 3). The upper intercept age calculated for all obtained results is 2932±43 Ma (Fig. 6, *A*). However, this age is somewhat overestimated because zircons contain ancient (inherited) cores as old as ~3600 Ma. Some of the obtained results are discordant whereas most of the analytic results (50) are concordant and clustered at 2750–3000 Ma. For this group of results, we calculated a weighted average $^{207}Pb/^{206}Pb$ age of 2883±18 Ma (Fig. 6, *B*).

Table 3. **Results of U-Pb isotope dating of zircon from garnet-bearing granite-porphyry (sample 89-286) and granodiorite (sample 89-242)**

Analysis #	Isotope ratios					Isotope ages, Ma				Concentrations, ppm	
	$^{238}U/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	ρ	$^{207}Pb/^{206}Pb$	2σ	$^{238}U/^{206}Pb$	2σ	U	Pb
Sample 89-286											
UA-2-1	3.3792	0.1534	0.2073	0.0054	-0.04	2874	41	1712	67	1700	1465
UA-2-2	1.9681	0.0840	0.1911	0.0175	-0.05	2819	91	2697	102	209	237
UA-2-3	1.9403	0.0404	0.2399	0.0043	-0.07	3120	30	2683	47	715	498
UA-2-4	1.8929	0.0585	0.1949	0.0086	0.39	2769	78	2761	67	155	127
UA-2-5	2.5571	0.1020	0.2034	0.0062	-0.38	2840	49	2135	61	995	935
UA-2-6	1.7273	0.0284	0.2060	0.0050	0.32	2865	39	2953	39	607	174
UA-2-7	1.9726	0.0389	0.2176	0.0037	-0.23	2964	29	2655	43	1060	164
UA-2-8	1.7701	0.0543	0.2070	0.0071	0.04	2864	57	2912	66	381	133
UA-2-9	1.6299	0.0707	0.2285	0.0066	-0.05	3037	50	3127	121	734	125
UA-2-10	3.2925	0.1624	0.2003	0.0067	0.06	2821	60	1742	67	640	286
UA-2-11	1.8338	0.0302	0.2059	0.0040	0.20	2868	32	2814	38	641	547
UA-2-12	2.7434	0.1092	0.2197	0.0080	0.18	2971	61	2038	66	484	166
UA-2-13	1.9873	0.0602	0.2043	0.0076	0.27	2840	60	2652	64	204	233
UA-2-14	1.9711	0.0876	0.2014	0.0123	0.05	2828	102	2673	83	120	117
UA-2-15	1.8092	0.0784	0.2122	0.0119	0.21	2877	91	2853	104	83	143
UA-2-16	1.7299	0.0469	0.2142	0.0106	0.30	2903	79	2963	65	110	135
UA-2-17	1.7989	0.0348	0.2135	0.0056	0.37	2922	43	2860	43	346	195
UA-2-18	2.4609	0.1178	0.1998	0.0112	0.25	2795	90	2257	94	152	125
UA-2-19	1.7482	0.0540	0.2174	0.0095	0.51	2948	67	2944	71	102	76
UA-2-20	1.7875	0.0467	0.2089	0.0110	0.35	2875	79	2875	67	151	163
UA-2-21	1.6804	0.0636	0.2081	0.0128	0.44	2849	108	3051	87	71	105
UA-2-22	1.8514	0.0416	0.1988	0.0058	0.33	2813	45	2799	54	402	1027
UA-2-23	2.1969	0.0652	0.2056	0.0061	0.06	2858	48	2432	67	324	193
UA-2-24	1.8066	0.0454	0.2112	0.0114	0.25	2875	83	2848	61	121	110
UA-2-25	1.9908	0.0466	0.2070	0.0052	-0.14	2872	41	2628	47	427	357
UA-2-26	1.9021	0.0315	0.2082	0.0029	0.13	2888	22	2731	37	1644	72
UA-2-27	1.8155	0.0588	0.2020	0.0120	0.18	2827	96	2860	76	75	102
UA-2-28	1.7278	0.0249	0.2222	0.0024	0.09	2994	17	2950	34	2379	327
UA-2-29	1.8288	0.0281	0.2001	0.0036	0.20	2822	29	2819	35	671	162
UA-2-30	2.6930	0.0702	0.2058	0.0032	-0.12	2868	25	2051	44	1747	967
UA-2-31	1.8119	0.0373	0.1980	0.0070	0.26	2789	61	2845	46	251	85
UA-2-32	1.7696	0.0225	0.2004	0.0040	0.30	2836	32	2887	31	754	205
UA-2-33	1.7743	0.0264	0.2084	0.0027	0.13	2890	22	2888	35	1991	4503
UA-2-34	1.6685	0.0656	0.2071	0.0093	0.10	2866	71	3073	94	123	115
UA-2-35	1.9155	0.0308	0.2024	0.0046	0.26	2837	38	2715	36	587	175
UA-2-36	2.2202	0.0971	0.2166	0.0116	0.28	2971	77	2444	83	144	28
UA-2-37	1.9415	0.0363	0.1997	0.0048	0.11	2815	39	2688	41	525	307
UA-2-38	1.6743	0.0233	0.2033	0.0047	0.09	2844	38	3025	34	611	216
UA-2-39	1.8190	0.0426	0.2067	0.0059	0.03	2867	48	2841	55	373	338
89-286-1	4.0000	0.2720	0.1893	0.0033	-0.28	2730	28	1433	62	1769	1427
89-286-2	2.4752	0.1409	0.2012	0.0078	0.07	2823	67	2184	63	334	580
89-286-3	2.3310	0.1304	0.1992	0.0054	0.26	2816	42	2303	59	460	910
89-286-4	2.2026	0.1261	0.1990	0.0130	0.37	2810	100	2408	70	67	41
89-286-5	2.2758	0.1088	0.1960	0.0036	0.27	2789	30	2350	27	519	316
89-286-6	1.8657	0.1009	0.2219	0.0036	-0.07	2991	26	2761	61	775	380
89-286-7	2.0534	0.1138	0.2026	0.0068	0.30	2849	58	2562	62	161	56
89-286-8	3.0581	0.1496	0.1984	0.0028	0.13	2811	23	1823	29	1680	1220
89-286-9	1.9120	0.1024	0.2571	0.0046	0.02	3223	28	2707	60	330	150
89-286-10	1.9290	0.0930	0.2178	0.0042	0.12	2956	31	2695	31	284	69
89-286-11	2.8571	0.1959	0.2045	0.0030	0.05	2858	24	1922	82	1000	726
89-286-12	2.1459	0.1151	0.2187	0.0023	0.02	2969	17	2460	52	958	401
89-286-13	2.6247	0.1516	0.1993	0.0027	-0.09	2816	22	2082	58	1020	351

Table 3. **Results of U-Pb isotope dating of zircon from garnet-bearing granite-porphyry (sample 89-286) and granodiorite (sample 89-242)** *(continuation)*

Analysis #	Isotope ratios					Isotope ages, Ma				Concentrations, ppm	
	$^{238}U/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	ρ	$^{207}Pb/^{206}Pb$	2σ	$^{238}U/^{206}Pb$	2σ	U	Pb
89-286-14	1.8939	0.1004	0.2134	0.0038	0.15	2943	28	2727	54	356	212
89-286-15	1.7832	0.0890	0.2027	0.0063	0.17	2851	51	2867	38	104	139
89-286-16	1.7800	0.0887	0.2061	0.0057	0.31	2895	46	2876	40	136	125
89-286-17	1.4573	0.0701	0.3318	0.0025	0.33	3624	12	3367	23	2370	353
89-286-18	2.0182	0.0978	0.1989	0.0038	0.27	2813	32	2594	24	371	138
89-286-19	1.7483	0.0886	0.2020	0.0070	0.35	2855	55	2920	46	107	73
89-286-20	1.9562	0.0957	0.2032	0.0057	0.43	2848	46	2660	35	160	257
89-286-21	1.9113	0.0950	0.2133	0.0056	0.18	2926	44	2711	32	196	253
89-286-22	1.7578	0.0834	0.1980	0.0032	0.12	2810	27	2902	29	287	556
89-286-23	1.7007	0.0897	0.2182	0.0073	0.37	2973	52	2990	54	85	16
89-286-24	1.8797	0.0954	0.2200	0.0050	0.27	2982	35	2753	45	249	107
89-286-25	1.7737	0.0849	0.1920	0.0041	0.30	2762	36	2881	29	299	492
89-286-26	1.8519	0.0960	0.2070	0.0068	0.39	2892	50	2787	49	87	129
89-286-27	2.0040	0.0964	0.2030	0.0035	0.21	2847	28	2609	25	530	130
89-286-28	1.8034	0.0878	0.2081	0.0041	0.02	2890	32	2842	30	386	1019
89-286-29	1.7857	0.0957	0.2858	0.0051	0.07	3389	28	2869	60	483	75
89-286-30	1.7376	0.0815	0.2009	0.0026	0.30	2832	22	2930	21	841	227
89-286-31	2.1160	0.1030	0.2046	0.0050	0.16	2856	40	2493	30	205	147
89-286-32	2.7548	0.1442	0.2022	0.0022	-0.02	2843	18	1993	45	2264	1103
89-286-33	1.7844	0.0860	0.2044	0.0026	0.07	2860	20	2867	28	939	960
89-286-34	1.7658	0.0873	0.2096	0.0063	0.33	2901	50	2890	40	136	207
89-286-35	1.8921	0.0895	0.2005	0.0028	0.12	2826	23	2737	18	658	195
89-286-36	1.9646	0.0926	0.1908	0.0034	-0.12	2742	29	2652	25	484	310
89-286-37	2.3958	0.1148	0.1940	0.0024	0.09	2775	21	2247	27	1860	579
89-286-38	1.8275	0.0902	0.2037	0.0033	0.28	2850	27	2812	32	457	537
89-286-39	1.7091	0.0818	0.2020	0.0027	0.36	2841	21	2971	28	723	313
89-286-40	2.1882	0.1101	0.2088	0.0030	-0.02	2897	25	2424	38	738	1950
Sample 89-242											
UA-3-1	1.4362	0.0242	0.3051	0.0091	0.25	3484	47	3407	42	225	213
UA-3-2	1.8259	0.0723	0.2789	0.0060	-0.22	3350	33	2861	90	421	491
UA-3-3	2.3284	0.0948	0.2013	0.0079	0.11	2814	65	2343	75	303	67
UA-3-4	1.6143	0.0397	0.2375	0.0097	0.32	3092	63	3127	61	208	138
UA-3-5	1.5144	0.0353	0.2935	0.0101	0.14	3430	51	3274	63	199	341
UA-3-6	1.6410	0.0460	0.3646	0.0131	0.18	3752	55	3081	73	179	142
UA-3-7	1.4441	0.0341	0.2899	0.0065	0.02	3410	35	3409	58	524	606
UA-3-8	1.8037	0.0396	0.2038	0.0047	0.22	2849	37	2857	50	659	239
UA-3-9	1.1903	0.0297	0.3988	0.0063	0.40	3901	24	3954	75	427	521
UA-3-10	4.2261	0.3649	0.2909	0.0079	-0.18	3411	43	1518	126	710	136
UA-3-11	1.8156	0.0378	0.2149	0.0040	0.13	2943	32	2841	48	633	256
UA-3-12	2.2073	0.1064	0.2084	0.0127	0.30	2859	94	2453	98	117	136
UA-3-13	1.8707	0.0745	0.2156	0.0125	0.38	2899	95	2794	98	77	65
UA-3-14	1.7593	0.0250	0.2251	0.0054	0.31	3008	39	2907	33	672	331
UA-3-15	2.0564	0.0781	0.1976	0.0094	0.26	2770	84	2596	85	138	82
UA-3-16	2.2317	0.0586	0.2034	0.0075	0.24	2833	62	2395	54	268	377
UA-3-17	2.0672	0.0599	0.1988	0.0058	-0.16	2803	48	2566	59	427	123
UA-3-18	2.0270	0.1053	0.1793	0.0108	-0.30	2586	109	2657	109	116	137
UA-3-19	1.8866	0.0583	0.2082	0.0084	0.32	2868	64	2768	67	225	256
UA-3-20	3.3533	0.1620	0.2097	0.0117	0.33	2859	90	1733	78	188	117
UA-3-21	1.7950	0.0553	0.2049	0.0128	0.23	2826	100	2870	78	80	80
UA-3-22	1.8973	0.0427	0.2072	0.0062	0.42	2879	52	2733	47	225	87
UA-3-23	1.7971	0.0321	0.2001	0.0065	0.36	2821	55	2861	42	275	187
UA-3-24	1.3988	0.0370	0.3020	0.0104	0.25	3464	52	3500	73	138	173

The end Table 3

Analysis #	Isotope ratios					Isotope ages, Ma				Concentrations, ppm	
	$^{238}U/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	ρ	$^{207}Pb/^{206}Pb$	2σ	$^{238}U/^{206}Pb$	2σ	U	Pb
UA-3-25	1.9432	0.1160	0.2202	0.0171	-0.61	2901	120	2786	145	193	138
UA-3-26	1.9591	0.0748	0.2097	0.0087	0.30	2878	66	2698	82	124	131
UA-3-27	2.4386	0.1787	0.2446	0.0086	-0.44	3132	56	2300	113	265	405
UA-3-28	1.4377	0.0324	0.3297	0.0075	0.00	3608	35	3420	60	215	173
UA-3-29	1.9504	0.1106	0.2797	0.0110	-0.01	3351	59	2758	127	141	83
UA-3-30	1.4508	0.0297	0.2908	0.0089	0.32	3417	50	3382	59	205	212
89-242-1	1.6611	0.0828	0.2458	0.0055	0.26	3152	36	3036	40	257	297
89-242-2	1.4213	0.0687	0.3050	0.0048	0.26	3491	25	3432	34	256	591
89-242-3	1.8727	0.0947	0.1969	0.0081	0.31	2783	68	2760	46	106	153
89-242-4	2.6015	0.1354	0.1841	0.0074	0.07	2683	67	2094	41	169	165
89-242-5	2.1834	0.1192	0.2251	0.0058	-0.30	3004	43	2426	58	447	123
89-242-6	1.9073	0.0946	0.1946	0.0044	0.40	2780	38	2719	31	289	150
89-242-7	1.9596	0.0960	0.1976	0.0057	0.37	2812	47	2660	35	217	266
89-242-8	1.8349	0.1077	0.2580	0.0072	-0.81	3226	46	2817	75	680	392
89-242-9	2.7435	0.1430	0.1913	0.0046	-0.67	2741	41	2001	42	744	445
89-242-10	4.7870	0.2292	0.1468	0.0040	-0.13	2303	47	1222	20	962	796
89-242-11	4.1152	0.3387	0.2954	0.0050	0.12	3440	26	1392	86	951	317
89-242-12	2.8474	0.1459	0.1784	0.0062	-0.49	2644	56	1938	40	482	337
89-242-13	1.3004	0.0626	0.3999	0.0046	0.17	3906	17	3674	39	816	1044
89-242-14	2.6288	0.1382	0.2073	0.0092	0.04	2867	74	2075	43	124	132
89-242-15	2.0964	0.1099	0.2034	0.0067	0.17	2862	56	2519	46	189	321
89-242-16	1.9157	0.0991	0.2025	0.0065	-0.12	2838	52	2703	47	132	366
89-242-17	1.6447	0.1136	0.2654	0.0055	-0.60	3285	33	3040	120	545	655
89-242-18	1.8986	0.0937	0.2066	0.0048	0.39	2873	39	2730	33	282	279
89-242-19	1.9524	0.0991	0.1908	0.0059	0.21	2741	53	2664	41	174	163
89-242-20	1.8553	0.0929	0.1965	0.0063	0.37	2783	52	2778	45	117	225
89-242-21	2.8433	0.1455	0.1699	0.0062	0.30	2559	62	1945	40	187	296
89-242-22	2.0534	0.1096	0.1981	0.0036	-0.27	2815	28	2565	57	495	320
89-242-23	2.2573	0.1783	0.1950	0.0160	-0.87	2660	130	2340	120	328	187
89-242-24	3.7313	0.2367	0.1955	0.0080	0.43	2777	70	1527	59	307	70
89-242-25	3.7175	0.1797	0.1324	0.0027	0.31	2135	34	1535	20	851	541
89-242-26	4.8780	0.3807	0.2052	0.0047	-0.07	2868	36	1210	68	514	133
89-242-27	5.0505	0.2500	0.1320	0.0035	0.09	2127	48	1164	17	662	223
89-242-28	1.8416	0.0882	0.2014	0.0049	0.14	2840	38	2799	28	182	77
89-242-29	3.1172	0.1555	0.1406	0.0054	0.21	2218	69	1796	28	146	119
89-242-30	1.9120	0.0987	0.2298	0.0083	0.34	3037	58	2707	52	75	56
89-242-31	3.4341	0.1769	0.1414	0.0065	0.49	2245	80	1646	27	141	63
89-242-32	1.4144	0.0740	0.3012	0.0095	0.31	3469	48	3449	58	61	43
89-242-33	1.8416	0.1017	0.1920	0.0110	0.24	2721	95	2797	68	30	52
89-242-34	2.4096	0.1568	0.2760	0.0051	-0.24	3338	30	2236	89	190	125
89-242-35	2.9940	0.3586	0.2558	0.0079	-0.32	3220	50	1830	170	196	87
89-242-36	3.5524	0.1893	0.2053	0.0049	-0.45	2862	43	1596	39	698	107
89-242-37	1.6367	0.0830	0.4045	0.0084	0.17	3918	31	3071	53	119	77
89-242-38	1.8587	0.1002	0.3258	0.0091	0.20	3588	43	2770	58	110	54
89-242-39	1.4514	0.0716	0.3202	0.0042	0.31	3567	20	3377	46	176	99
89-242-40	2.0942	0.1053	0.2113	0.0058	0.08	2925	44	2513	43	103	105
89-242-41	1.4347	0.0741	0.2929	0.0050	-0.57	3430	28	3402	58	200	105
89-242-42	2.1863	0.1099	0.2050	0.0035	0.05	2864	27	2426	35	265	171
89-242-43	2.0538	0.1055	0.2188	0.0050	0.05	2961	37	2555	40	237	192
89-242-44	2.5316	0.1923	0.3030	0.0071	-0.03	3480	37	2130	110	235	22
89-242-45	2.2075	0.1511	0.2923	0.0059	-0.49	3422	32	2390	100	290	72
89-242-46	2.5025	0.1315	0.1489	0.0041	0.04	2327	49	2164	42	198	73

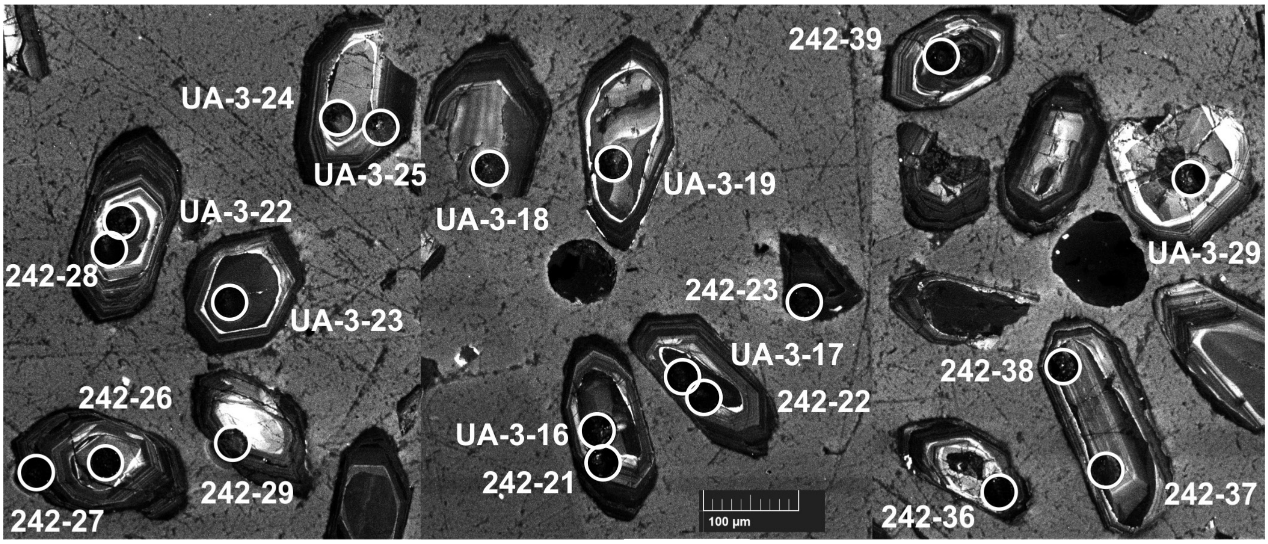


Fig. 7. Cathodoluminescent images of the studied zircon crystals from granodiorite of the intrusive phase II of the Dobropillya Massif (sample 89-242, borehole 833, depth 152.5–171.8 m). Numbers of the analyzes as in Table 3

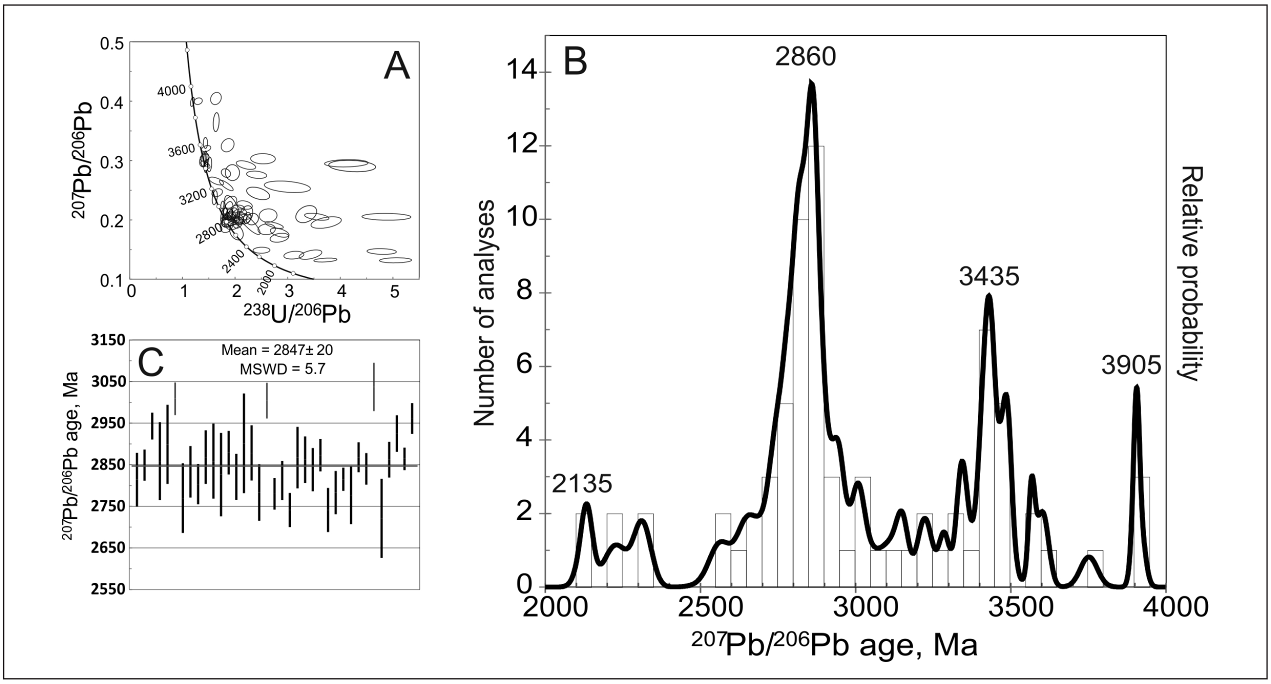


Fig. 8. *A* — U-Pb concordia diagram for zircon from granodiorite (sample 89-242); *B* — multimodal distribution of concordant $^{207}Pb/^{206}Pb$ ages; *C* — weighted average 207Pb/206Pb ages of the most abundant zircon population

However, as can be seen in Fig. 6, *C*, the distribution of ages in this group is not statistically normal with an anomalous «tail» towards the older ages. Therefore, the most probable age of granite-porphyry crystallization is not the weighted average, which is shifted toward the older age, but the modal $^{207}Pb/^{206}Pb$ age, which is 2840±10 Ma. The appearance of the ancient «tail» is linked to the presence of older, variably reset, cores.

Granodiorite of the intrusive phase II of the Dobropillya massif (borehole 833, depth 152.3–171.8 m, sample 89-242). Zircon from granodiorites is heterogeneous in terms of crystal morphological characteristics. Some of the zircons from this sample have inclusions (cores) of older zircon.

We performed 76 U-Pb isotopic analyses of zircon from granodiorite (sample 89-242) (Fig. 7,

Table 3). The results have revealed a complex geological history of the rock. The multimodal distribution of zircon concordant ages (Fig. 8, *A, B*) allows the identification of at least four stages of its formation. The two oldest peaks (3905 and 3435 Ma) correspond to zircons inherited from an ancient protolith. The main zircon population has a weighted average 207Pb/206Pb age of 2847±20 Ma (Fig. 8, *C*), while the modal age of this population is 2860 Ma (see Fig. 8, *B*). Finally, a small group of younger zircons (2350–2135 Ma) reflects the influence of the Paleoproterozoic processes, i.e., either the partial loss of radiogenic lead or igneous crystallization of a new zircon population.

Discussion and conclusions

A geochronological study of the crustal granitoids in the southern part of the Vovcha Block and the Dobropillya massif was carried out. These granitoids were formed due to a high degree (>50%) melting of the older crust, which consisted of granitoids and metamorphosed ultramafic and mafic rocks. Garnet-bearing biotite granite-porphyries are characterized by an increased content of HFSE. The negative Eu anomaly (Eu/Eu* = 0.57) has also been found, which, together with the negative Sr anomaly, indicates plagioclase fractionation in the crustal magmatic source. The increased content of Th and light REE is probably due to the metasomatic enrichment. Granitoids of the Dobropillya massif are subject to microclinization. In these granitoids, inherited zircon significantly prevails and, therefore, it is hard to define the time of crystallization of these rocks. The age of garnet-bearing biotite granite-porphyry has been estimated by the modal $^{207}Pb/^{206}Pb$ age of the main zircon population, which is 2840±10 Ma. For granodiorite of the Dobropillya massif, four main zircon populations can be distinguished. The two oldest peaks (3905 and 3435 Ma) correspond to zircons inherited from an ancient protolith, i.e., the rock that produced the magmatic melt from which the granodiorites have crystallized. The main zircon population has a weighted average $^{207}Pb/^{206}Pb$ age of 2847 ± 20 Ma (see Fig. 8, *C*) and modal age of 2860 Ma (see Fig. 8, *B*).

Thus, the main population of zircon in the crustal granitoids of both the Vovcha and Huliaipole has an age of 2.8–2.9 Ga. In this respect, it is interesting to compare studied zircons with those from metavolcanic rocks of the Huliaipole Formation (Artemenko et al., 2021; Shumlyanskyy et al., 2020). Metadacites of the Formation contain numerous zircons of the Paleoarchean and Eoarchean ages, while the main zircon population crystallized at ca. 2.85–2.90 Ga. The obtained data indicate that the studied granitoids and metavolcanic rocks of the Huliaipole Formation may have crystallized from melts produced due to fusion of the same crustal source. The oldest rocks known in the Ukrainian Shield possibly having Hadean prehistory were present in this source (Artemenko et al., 2021; Shumlyanskyy et al., 2020).

Several individual grains and mantles on zircon crystals from the Dobropillya massif have yielded the Paleoproterozoic age. This age corresponds to the ages of the mantles on zircons from subalkaline granitoids (2101±15 Ma) and tonalites (2078±20 Ma), which has been interpreted as the age of magmatic crystallization (Bobrov et al., 2006; Stepanyuk et al., 2007, 2013). Notably, the age of the core parts of these crystals ranged from 3.6 to 2.8 Ga. The age of the formation of young mantles in the studied zircons from granodiorites of the Dobropillya massif coeval to the well-known metamorphism and accompanying granitoid magmatism (Ponomarenko et al., 2014; Artemenko et al., 2018).

The defined age (2.8 Ga) of the main zircon population in granitoids of the Vovcha and Huliaipole blocks indicates the importance of the 2.8 Ga stage in the geological history of the Ukrainian Shield. At that time, felsic magmatism, accompanied by metamorphism and metasomatic processes, was manifested in nearly all parts of the Shield (Ponomarenko et al., 2010; Stepanyuk et al., 2020 a, b; Claesson et al., 2015, 2016; Shumlyanskyy et al., 2012, 2021). The obtained geochronological data indicate that the Early Precambrian crust of the west-Azov block was formed from 3.9 to 2.1 Ga.

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Вік циркону з корових гранітоїдів Вовчанського і Гуляйпільського блоків: історія формування земної кори Приазовського району Українського щита

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Район досліджень охоплює зону зчленування Гуляйпільського граніт-зеленокам'яного блока з Вовчанським та Ремівським грануліт-гнейсовими блоками. Вовчанський та Ремівський блоки складені архейськими кварцпольовошпатовими гнейсами (понад 80 %) з останцями високометаморфізованих порід західноприазовської серії. Гуляйпільський блок представлений породами західноприазовської серії та мезоархейським граніт-зеленокам'яним комплексом (3,2–3,0 млрд років), що включає Косивцівську зеленокам'яну структуру та ТТГ. Значний об'єм у геологічній будові цього району займають гранітоїди. Архейські ТТГ, представлені шевченківським комплексом, утворились в результаті часткового плавлення базитового субстрату. Гранітоїди Добропільського масиву та південної частини Вовчанського блока, що проривають ТТГ, вивчені ще недостатньо. За петрологічними даними вони утворились в результаті високого ступеня (понад 50 %) плавлення більш давньої кори, що складалась з гранітоїдів та метаморфізованих ультраосновних і основних порід. У цирконі з цих гранітоїдів значно переважає реліктовий циркон і тому визначити час формування цих гранітів надзвичайно складно. Згідно з результатами наших досліджень, граніт-порфіри південної частини Вовчанського блока характеризуються високим відношенням Rb/Sr – 0,42, високим вмістом Ba – 1030 ppm, підвищеним вмістом високозарядних елементів Y – 8,18; Nb – 13,7; Yb – 0,76, Th – 42,6 ppm та негативною європієвою аномалією – Eu/Eu* = 0,57. Виконано 79 визначень ізотопного U-Pb віку цирконів з граніт-порфірів методом LA-ICP-MS. Вік цих порід було оцінено у 2840 ±10 млн років за модальним 207Pb/206Pb віком головної популяції цирконів. Для цирконів з гранодіоритів другої інтрузивної фази Добропільського масиву виконано 76 визначень U-Pb віку методом LA-ICP-MS. В цій породі можна розпізнати чотири головні популяції цирконів. Два найдавніших піки (3905 та 3435 млн років) були успадковані з давнього джерела магматичного розплаву. Головна популяція цирконів має середньозважений $^{207}Pb/^{206}Pb$ вік у (2847±20) млн років. Таким чином головною популяцією циркону в корових гранітоїдах як Вовчанського, так Гуляйпільського блоків переважає циркон віком 2,8–2,9 млрд років. Гранітоїди такого віку ще не виявлено в цьому районі і тому однозначна інтерпретація щодо їх джерела неможлива. В складі архейської кори, з яких виплавились корові гранітоїди Вовчанського та Гуляйпільського блоків, були також породи еоархею 3,9 і 3,8 млрд років, палеоархею 3,6–3,2 млрд років та мезоархею 2,95–3,15 і 2,7–2,9 млрд років. Невелика група молодших (2350–2135 млн років) цирконів може інтерпретуватися як час накладених палеопротерозойських процесів – часткову втрату радіогенного свинцю або ж магматичну кристалізацію нової популяції цирконів. Одержані геохронологічні дані вказують на те, що ранньодокембрійська кора Західноприазовського блока формувалась від 3,9 до 2,1 млрд років.

Ключові слова: *корові граніти; Західне Приазов'я; Вовчанський блок; Гуляйпільський блок; Добропільський масив; циркон; U-Pb вік; LA-ICP-MS метод.*