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THE U-Pb AGE AND Lu-Hf ISOTOPE SYSTEMATICS OF ZIRCON FROM THE HULIAIPOLE METAVOLCANICS, THE AZOV DOMAIN OF THE UKRAINIAN SHIELD: EVIDENCE FOR THE PALEOARCHEAN-HADEAN CRUST

The Azov Domain occurs as a part of a larger Mesoarchean (3.2-3.0 Ga) craton, fragments of which are preserved in the eastern part of the Ukrainian Shield and as a block of the Kursk Magnetic Anomaly (KMA). In the Neoproterozoic-Palaeoproterozoic time, it was fragmented into several tectonic blocks: Vovcha, Remivka, Huliaipole, Bilotserkivka, and Saltych. The northern part of the Huliaipole Block is composed of tonalite-trondhjemite-granodiorite (TTG) rock association, that hosts the Kosivtsevo greenstone structure. It is composed of metamorphosed rocks of the jaspilite-komatiite-tholeiite association (the Kosivtsevo unit), which corresponds to the Sura Suite of the Konka Series of the Middle Dnieper Domain. The Neoproterozoic-Palaeoproterozoic formations are represented by volcano-sedimentary rocks of the Huliaipole Suite and granitoids of the Dobropillya and Anadol complexes. Granitoids of the Dobropillya complex host numerous pyroxenite, gneiss, and plagioclase granite xenoliths. The U-Pb zircon age of granitoids of the Dobropillya Complex is 2040 Ma and inherited zircon has an age up to 3400 Ma. Small intrusions of two-feldspar granites of the Anadol Complex are widespread in the Ternuvate structure. Their U-Pb monazite age is 2190 Ma. In the central part of the Huliaipole Block, the NW-striking Huliaipole syncline (3.5 × 9 km) occurs. This structure is composed of volcano-sedimentary rocks of the Huliaipole Suite, which unconformably overlie Archean TTG. Felsic and intermediate metavolcanics are confined mainly to ferruginous quartzites of the middle Subsuites. To a limited extent, meta-andesites and felsic metavolcanics are also found in the lower and upper Huliaipole Subsuites. Zircons from meta-andesites and felsic metavolcanics of the Huliaipole Suite are very heterogeneous, indicating their crustal derivation. The U-Pb age of zircon populations from metadacite of the Huliaipole Suite was determined using the LA-ICP-MS method at 3085-2850 and 3700-3360 Ma. In addition, the age of the two crystals exceeded 3800 Ma. According to geological and geochronological data, the Huliaipole Block, 30 × 50 km in size, is composed of rocks and relicts of the Hadean, Archean, and Palaeoproterozoic eons. The oldest nucleoid of the Azov Domain

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has probably been formed between 3.97 to 3.3 Ga. The unique peculiarity of this structure is that it has never experienced granulite stage of metamorphism. This allows consideration of the Huliaipole block as an example of the continental crust that has been formed in a plume geodynamic regime. During the Mesoproterozoic (3.2-3.0 Ga), it became a part of the Middle Dnieper-Azov-Kursk granite-greenstone terrane. Felsic and intermediate volcanics of the Huliaipole Suite could have formed due to melting of the sialic crust, including rocks of the Hadean and Archean age, as a result of underplating of basic melts during the formation of the Neoproterozoic to Paleoproterozoic rift structures.

Keywords: The West Azov; the Huliaipole block, Hadean; Archean; the Ukrainian Shield; the U-Pb age.

Introduction

In the Ukrainian Shield, rocks of the Earth's early crust were found in the Azov and Dniester-Bouh domains (Bibikova and Williams, 1990; Claesson et al., 2015, 2019; Shumlyanskyy et al., 2021). In the Dniester-Bouh Domain, they are highly metamorphosed and represented by enderbites and mafic schists reaching in age 3.8 Ga. A special feature of the Archean rocks in the Azov Domain is a relatively low metamorphic grade, not exceeding the epidote-amphibolite to amphibolite facies. Here, tonalites with ages of 3.67, 3.5, and 3.3 Ga have been identified (Bibikova and Williams, 1990; Artemenko et al., 2002, 2014; Lobach-Zhuchenko et al., 2010). Metaterrigenous rocks in the Soroki greenstone structure (GS) and Neoproterozoic to Palaeoproterozoic troughs contain detrital zircon varying in age from 3.8 to 3.3 Ga (Bibikova et al., 2010), which indicate the presence in the Azov Domain of ancient rocks yet undiscovered. Some researchers suggested that ancient granulite-gneissic complexes of the Azov and Dniester-Bouh domains, as well as of the Voronezh Crystalline Massif, represented fragments of one of the oldest protocratons (Nozhkin and Krestin, 1984). Claesson et al. (2015) suggested a model of the autonomous evolution of the "Early Archean cores" of the Azov and Dniester-Bouh domains, which has been supported by the recent geological data.

Geological setting of the Azov Domain

The Azov Domain occurs as a part of a larger Mesoproterozoic (3.2-3.0 Ga) craton, fragments of which are preserved in the eastern part of the Ukrainian Shield and as a block of the Kursk Magnetic Anomaly (KMA). In the Neoproterozoic-Palaeoproterozoic time, it was fragmented into several tectonic blocks: Vovcha, Remivka, Huliaipole,

Bilotserkivka, and Saltych. Size of the Huliaipole block is 30 × 50 km. To the west, north, and east, it is bordered by the Orekhiv-Pavlohrad structure, the Vovcha and Remivka blocks, respectively (Fig. 1). The Haichur fault of NW strike separates the Huliaipole and Remivka blocks; the Mesoproterozoic Kosivtsevo greenstone structure is confined to this fault. To the south, the Huliaipole Block is bordered by the Bilotserkivka Syncline and Korsak-Stulneve Anticline. Analyzing the geological position of greenstone belts in this area, which are characterized by a concentric shape and distinct confinement to the faults, (Berzenin, 1990) was the first to assume that they developed on the Neoproterozoic granulite-gneissic basement above the mantle plume. The northern part of the Huliaipole Block comprises tonalite-trondhjemite-granodiorite (TTG) rock association, which hosts fragments of greenstone structures, while its central and southern parts are almost completely composed of younger granitoids. In the central part of the Huliaipole Block, the Huliaipole syncline (3.5 × 9 km) of the NW strike occurs (Zhukov et al., 1978). Syncline limbs are plunging to the centre at an angle of 50-70°. According to geophysical data, the fold extends down to the depth of 2.1-2.3 km. This structure is composed of a 1700 m thick volcano-sedimentary sequence of the Huliaipole Suite, unconformably overlying Archean TTG. The Huliaipole Suite consists of three subsuites. The lower one (250 m thick) is composed of two-mica and andalusite-staurolite quartzites and schists; the middle one (450 m thick) consists of ferruginous quartzites and felsic to intermediate metavolcanics; the upper one (1000 m thick) is composed of biotite schists, often graphite-bearing, rarely high-Al quartzites and quartzite schists with flysch-like alternations. To a limited extent, meta-andesites and felsic metavolcanics reaching 70 m in thickness are also found in the lower and upper Huliaipole subsuites (Glevasskiy et al., 1985). A lateral replacement

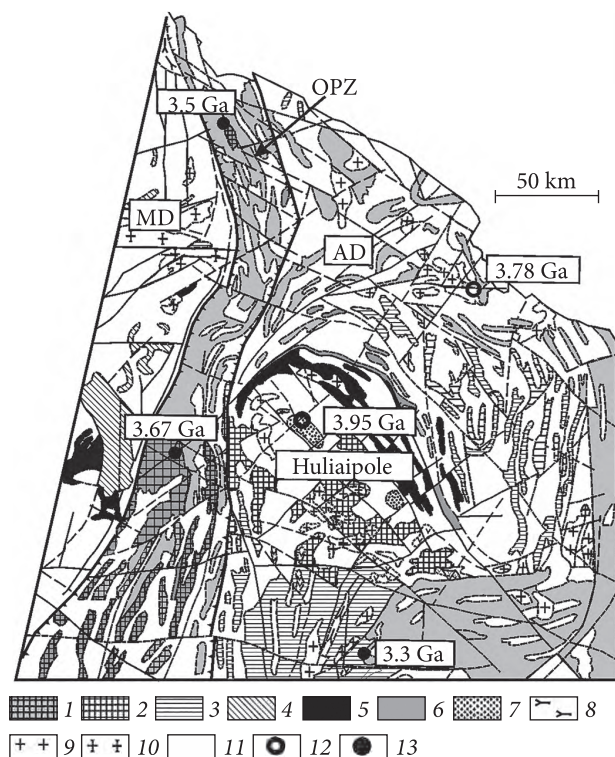


Fig. 1. Schematic geological map of the northern part of the West Azov area (Geological map..., 2014) with changes and additions). MD — the Middle-Dnieper Domain, OPZ — the Orekhiv-Pavlohrad Zone: 1 — the Novopavlivka unit, 2 — the Novopavlivka Complex, 3 — the West Azov Series, 4 — the Auly Series, 5 — greenstone belts, 6 — the Central-Azov Series, 7 — the Huliaipole Suite, 8 — alkaline intrusions, 9 — Paleoproterozoic K-Na granites, 10 — archaean K-Na granites. 11 — plagioclase migmatites of the Shevchenko and Dnipro complexes, 12 — tonalite dating sites, 13 — dating sites of detrital and xenogenic zircons in felsic metavolcanics

of ferruginous quartzites by metavolcanics is observed from the margins towards the centre of the structure. In the same direction, in the lower and upper subsuites, clay-rich facies are replaced by sandy ones. The multi-grain detrital zircon fractions from quartzites of the Lower Huliaipole Subsuite yielded the U-Pb (TIMS) age of 2.9 ± 0.1 Ga; the metamorphism of these rocks was dated at 2.14 Ga (Tatarinova et al., 2001).

Analytical methods

Zircon has been extracted from the rock using a shaking table, heavy liquids and magnetic separator to produce the heavy non-magnetic fraction. Zircons were hand-picked under a binocular microscope. Silicate rock analyses were carried out at the

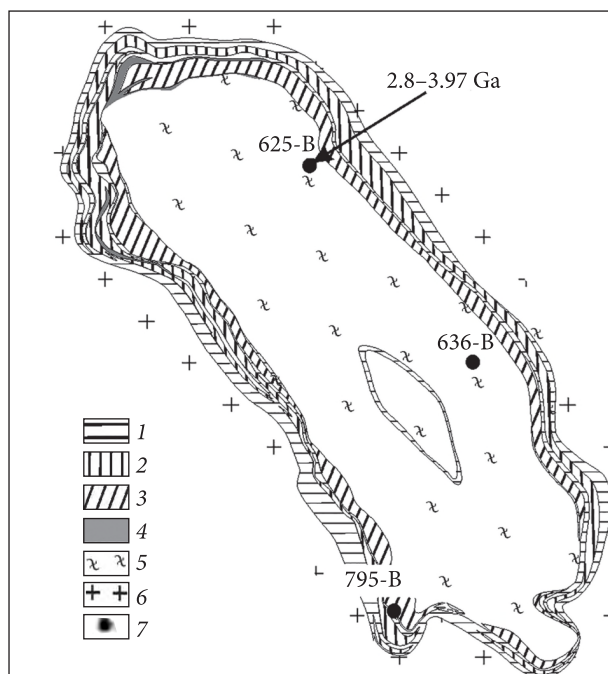


Fig. 2. A schematic geological map of the Huliaipole syncline (Glevassky et al., 1985): 1 — quartzites, meta-sandstones; 2 — andalusite-biotite-magnetite shales; 3 — magnetite, silicate-magnetite quartzites; 4 — magnetite-silicate quartzites; 5 — quartz-feldspar-biotite shales; 6 — amphibole-biotite plagiogranites; 7 — drill-hole numbers

IGMOF of NAS of Ukraine, Kyiv. Concentrations of rare and trace elements in the rocks were determined using the ICP-MS method in the Institute of Microelectronics Technology and High-Purity Materials of the Russian Academy of Sciences (IMTM RAS), Chernogolovka, Russia. The validity of analyses was checked by the means of determination of international and Russian reference samples GSP-2, VM, SGD-1A, ST-1. Concentration measuring errors were 3 to 5 wt% for most elements.

Zircon morphology has been studied under an optical microscope, whereas the internal structure was documented using cathodoluminescence. U-Pb zircon and monazite geochronology were performed at the University of California, Santa Barbara, using a Nu Plasma HR MC-ICPMS and a Photon Machines Excite 193 excimer ArF laser-ablation system equipped with a HeLex sample cell. Spots were ablated during a 15-second analysis, run at 4 Hz and ~ 1 j/cm², yielding a pit depth of ~ 5 μ m. Sample analyses were preceded by a 15-second baseline measurement and unknown analyses were corrected with the 91 500 reference material

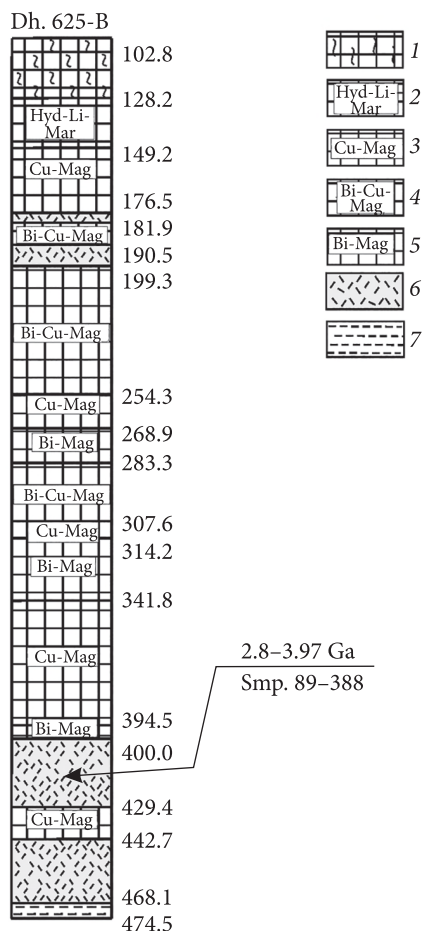


Fig. 3. A schematic log of the drill-hole 625-B: 1 — weathering crust of barren quartzites; 2 — quartzites with hydromica-limonite-martite (Hyd-Li-Mar, iron-rich weathering crust); 3 — quartzites with cummingtonite-magnetite (Cu-Mag); 4 — quartzites with biotite-cummingtonite-magnetite (Bi-Cu-Mag); 5 — quartzites with biotite-magnetite (Bi-Mag); 6 — metamorphosed felsic volcanics; 7 — biotite schist

(1062 Ma; Wiedenbeck et al., 1995) approximately every 10 analyses. For quality control, secondary RMs included GJ-1(602 Ma; Jackson et al., 2004; Kylander-Clark et al., 2013), and Plešovice (337 Ma; Sláma et al., 2008), and returned ages within 2% of the accepted $^{206}\text{Pb}/^{238}\text{U}$ ages. All age errors reported are 2σ .

The Lu-Hf isotope composition was measured on a Nu Plasma II multi-collector inductively coupled plasma mass spectrometer in the John de Laeter Centre, Curtin University, Australia. All isotopes (^{180}Hf , ^{179}Hf , ^{178}Hf , ^{177}Hf , ^{176}Hf , ^{175}Lu , ^{174}Hf , ^{173}Yb , ^{172}Yb and ^{171}Yb) were counted on the Faraday collector array. Contributions of ^{176}Yb and ^{176}Lu were removed from the 176-mass signal using

$^{176}\text{Yb}/^{173}\text{Yb} = 0.7962$ and $^{176}\text{Lu}/^{175}\text{Lu} = 0.02655$ with an exponential-law mass bias correction assuming $^{172}\text{Yb}/^{173}\text{Yb} = 1.35274$ (Chu et al., 2002). The interference-corrected $^{176}\text{Hf}/^{177}\text{Hf}$ was normalised to $^{179}\text{Hf}/^{177}\text{Hf} = 0.7325$ (Patchett and Tatsumoto, 1980) for mass bias correction. Zircon crystals from the Mud Tank carbonatite were analysed together with the samples in each session to monitor the accuracy of the results. Zircons 91500; Plešovice; GJ- 1 and R33 were also run as secondary reference standards. All reference material yielded $^{176}\text{Hf}/^{177}\text{Hf}$ ratios within an uncertainty of their respective reported values. Calculation of initial $^{176}\text{Hf}/^{177}\text{Hf}$ and ϵHf values for unknown zircons employed the measured $^{207}\text{Pb}/^{206}\text{Pb}$ spot date; a $\lambda^{176}\text{Lu}$ decay constant of 1.867×10^{-11} (Söderlund et al., 2004); and a present-day Chondritic Uniform Reservoir (CHUR) $^{176}\text{Hf}/^{177}\text{Hf} = 0.282785$ and $^{176}\text{Lu}/^{177}\text{Hf} = 0.0336$ (Bouvier et al., 2008).

Results

A possible presence of an ancient crust in the Huliaipole Block is supported by a large number of xenoliths in the granitoids of the Dobropillya Complex and the ubiquitous presence of xenocrystic zircons (Shcherbak et al., 2000). The Palaeoarchean age of 3.3 Ga of xenocrystic zircon (multiple zircon grain method) was determined by Shcherbak et al. (2000) and of 3.4 Ga (SHRIMP U-Pb method) by Stepanyuk et al. (2007). A large amount of xenocrystic zircon was also found in metamorphosed andesites and dacites of the Huliaipole Suite. These zircons were dated in this study applying the LA-ICP-MS method. For the most ancient zircons, the age was also confirmed by secondary ion mass spectrometry (SIMS).

Petrography

The sampled interval is composed of metadacites (sample 89-388, drill-hole 625-B, int. 424.4-429.4 meters) (Figs 2, 3). The texture of the rock is blastoporphyrictic with a lepidogranoblastic groundmass (Fig. 4 a, b, c). Phenocrysts are represented by albite. Phenocrysts are often granulated and transformed into an aggregate of fine grains. Secondary minerals in phenocrysts are biotite, sericite, muscovite, chlorite, carbonate, and magnetite. The groundmass is composed of (vol. %): quartz + albite — 75-77, biotite — 20-22, apatite — 3-5,

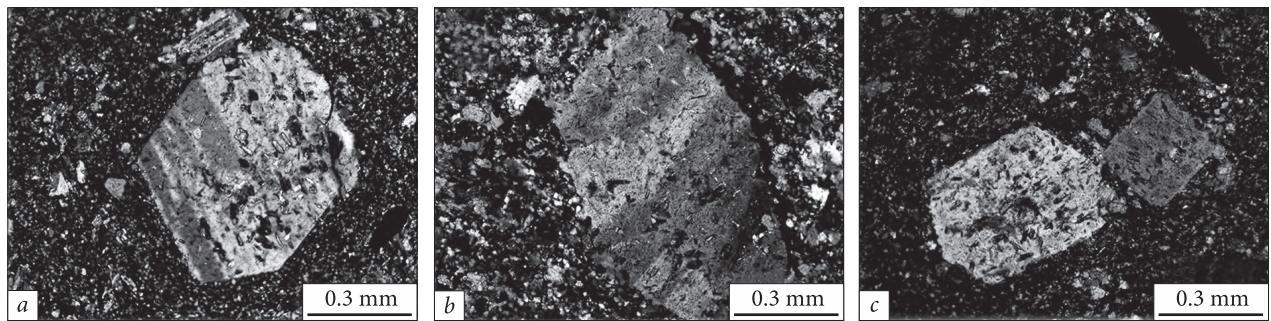


Fig. 4. Photomicrographs of thin sections of metadacites of the Huliaipole Suite, drill-hole 625-B: *a* — sample 89-384, depth 424.8 m; *b* — sample 89-385, depth 427.4 m; *c* — sample 89-386, depth 428.6 m. Images were taken using a polarizing microscope ECLIPSE LV100 POL. Crossed analyzers

Table 1. Chemical composition of metavolcanics of the Huliaipole Suite

%	89-156	89/463	89/381	89/388	%	89-156	89/463	89/381	89/388
SiO ₂	60.70	62.58	63.98	65.70	K ₂ O	3.52	3.60	6.00	3.18
TiO ₂	0.74	0.46	0.47	0.57	S _{обит}	0.30	0.23	0.24	0.13
Al ₂ O ₃	14.60	13.74	13.36	13.93	P ₂ O ₅	0.36	0.24	0.10	0.24
Fe ₂ O ₃	0.35	0.72	0.65	1.41	CO ₂	2.69	2.24	0.07	1.30
FeO	4.70	3.60	3.38	3.38	H ₂ O-	traces	0.08	0.12	traces
MnO	0.08	0.06	0.05	traces	LOI	0.34	0.56	2.64	0.59
MgO	1.90	2.26	1.24	1.79	Total	99.68	99.67	99.58	99.62
CaO	5.10	3.96	3.50	3.62	Mg#	40.3	48.7	35.8	40.7
Na ₂ O	4.30	5.34	3.78	3.78					

Ppm	89-156	89/463	89/381	89/388	Ppm	89-156	89/463	89/381	89/388
Cs	—	18.53	—	4.8	La	32.50	29.05	35.9	38.3
Li	—	14.88	—	23	Ce	62	57.07	68.1	76.0
Be	—	1.94	—	1.4	Pr	7.07	6.36	7.60	7.9
Rb	97.10	96.90	102.6	174	Nd	26.60	24.87	26.7	29
Sr	816	742.9	812.1	647	Sm	4.75	4.15	4.52	4.5
Ba	1400	1953	2116	2327	Eu	1.70	1.26	1.23	1.1
V	64.50	64.78	67	42.5	Gd	3.61	3.81	3.14	3.4
Cr	21.30	70.42	—	41.7	Tb	0.49	0.39	0.36	0.41
Co	7.29	12.55	9.6	7.5	Dy	1.98	2.11	1.45	1.6
Ni	15	33.61	27.2	19.3	Ho	0.30	0.38	0.23	0.26
Cu	—	26.93	17.4	30.2	Er	0.73	1.09	0.60	0.66
Zn	—	70.31	60	58.2	Tm	0.092	0.14	0.08	0.088
Ga	—	47.55	—	16.6	Yb	0.51	0.95	0.53	0.54
As	—	2.13	—	0.48	Lu	0.072	0.14	0.06	0.08
Sc	—	18.53	—	4.1	Mo	—	0.83	0.2	0.49
Ge	—	—	—	—	Ag	—	70.43	<0.1	—
Y	8.19	8.17	7.0	7.5	Ta	0.37	—	0.3	0.42
Nb	6.49	4.82	5.0	6.7	Pb	—	17.70	9.5	19.2
Zr	160	116.4	162.6	190	W	—	0.44	—	7.5
Hf	—	3.48	3.3	4.9	(La/Yb) _N	45.7	21.9	48.6	50.9
U	1.41	1.83	1.4	1.4	Eu/Eu*	1.26	0.97	1.0	0.97
Th	6.71	7.25	5.6	6.5	Nb/La	0.20	0.17	0.14	0.17
Sn	—	0.70	—	1.1	Nb/Ce	0.11	0.08	0.07	0.09
Sb	—	0.12	—	0.25	Th/Yb	13.2	7.4	10.6	12

Note. 1 — meta-andesite, drill-hole 636-B, depth 384.5-384.7 m (sample 89-156); 2 — meta-andesite, drill-hole 795-B, depth 392-395.7 m (sample 89-463); 3 — meta-andesite, drill-hole 625-B, depth 424.4-429.4 m (sample 89-388); 4 — metadacite, drill-hole 625-B (sample 89-381). Mg# is Mg/(Mg + Fe_{total}) in cation mole percent.

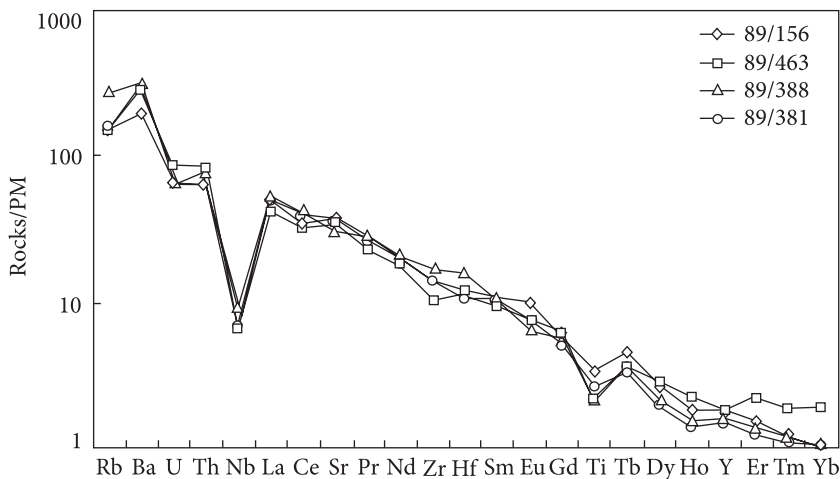


Fig. 5. Primitive mantle-normalized (Sun, McDonough, 1989) multi-element plot for meta-andesites and metadacites of the Huliaipole Suite

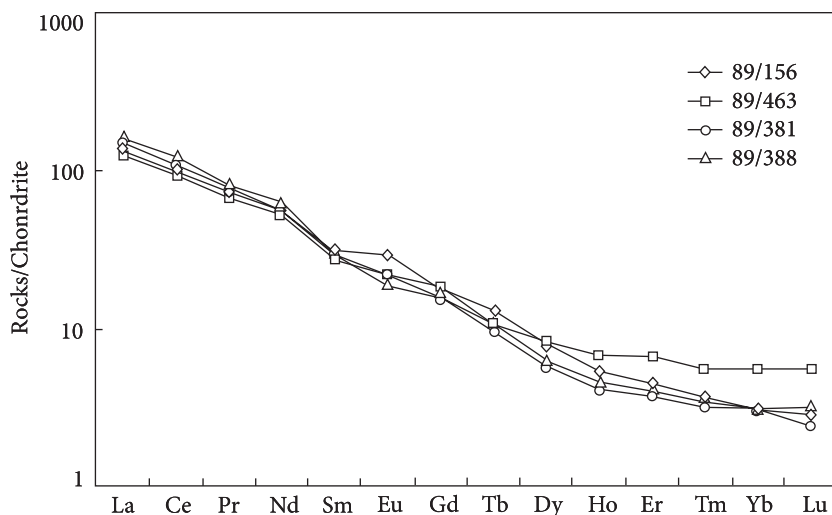


Fig. 6. Chondrite-normalized REE pattern for meta-andesites and metadacites of the Huliaipole Suite (Sun, McDonough, 1989)

magnetite — up to 1, chlorite and titanomorphite — fractions of %, muscovite and zircon — rare grains. Quartz and albite form aggregates of isometric grains having 0.02 mm in size. Biotite and chlorite are unevenly distributed, forming clusters of elongated lenticular and irregular shape. Patchy segregations of magnetite, zircon, and titanomorphite are confined to biotite accumulations. An interesting feature of the rock is the high content of apatite (up to 5%).

Geochemistry

In terms of chemical composition, metavolcanics of the Huliaipole Suite are middle-Mg# (35,8-48,7) andesites and dacites of the normal potassium-sodium series (Igneous rocks., 1983) (Table 1). On the SiO₂-K₂O plot, they fall into the fields of high-K andesites and dacites of the calc-alkaline series. They have high concentrations of Sr (743-816 ppm)

and Ba (1400-2116 ppm), and moderate content of Rb (97-103 ppm) (Table 1). The amounts of transition elements, Ni (15-34 ppm) and Cr (21-70 ppm), are close to their content in TTGs. Negative anomalies of Nb and Ti are prominent on the multi-element plots (Fig. 5). Rare earth elements in meta-andesites and metadacites are highly differentiated: (La/Yb)_N = 21.9-50.9 (Fig. 6). The sample 89-156 shows a prominent positive Eu anomaly, Eu/Eu* = 1.26; the rest of the samples lack positive Eu anomaly. The high Th/Yb ratio (7.4-13.2) and low Nb/La (0.14-0.20) indicate crustal contamination (Table 1).

U-Pb geochronology and Lu-Hf isotope composition

The LA-ICP-MS method was applied to determine the U-Pb age and Hf isotopic composition in zircons from metadacites of the Huliaipole Suite

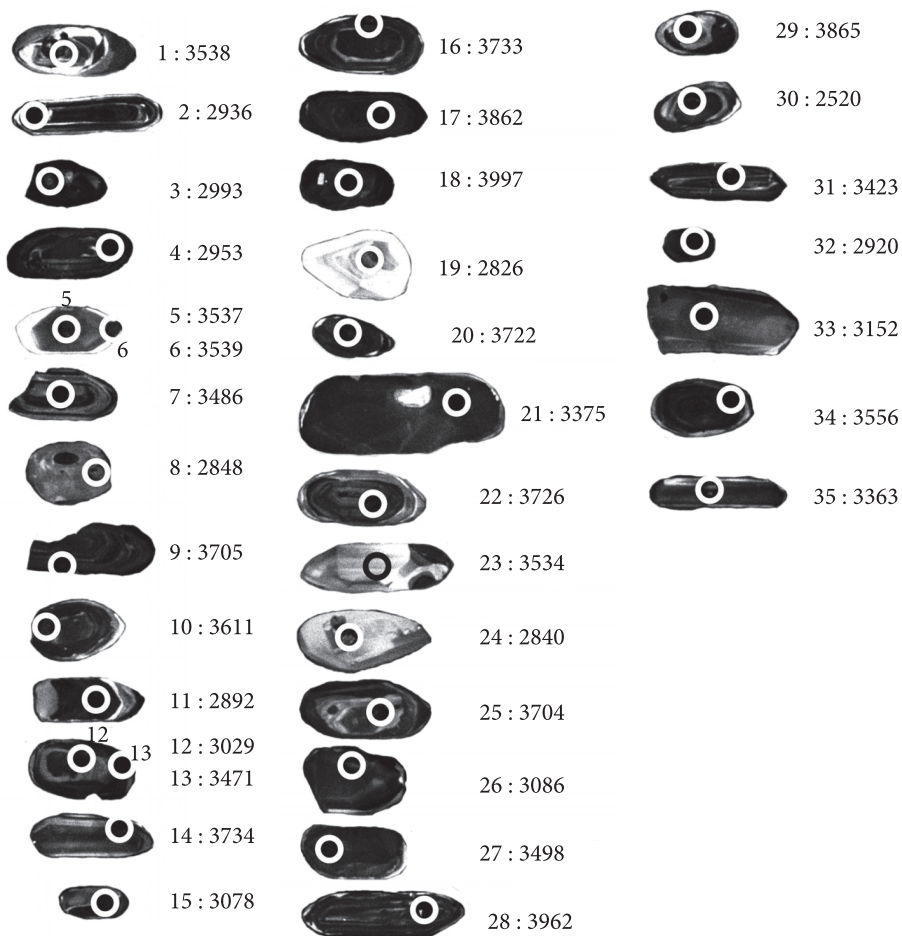


Fig. 7. Cathodoluminescence images of the studied zircon crystals from metadacites of the Huliaipole Suite (drill-hole 625-B, depth 424.4-429.4 m, sample 89-388). Numbers of the analyzes and $^{207}\text{Pb}/^{206}\text{Pb}$ ages are shown

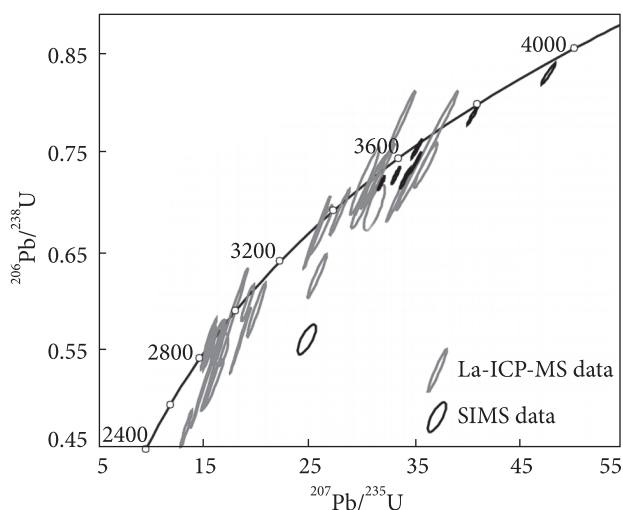


Fig. 8. U-Pb diagram with concordia for zircons from metadacites of the Huliaipole Suite (Drill-hole 625-B, depth 424.4-429.4 meters, sample 89-388)

(Table 2). A total of 34 zircon crystals was analyzed. In two crystals both core and rim parts have been analysed. In one case both core and rim yielded

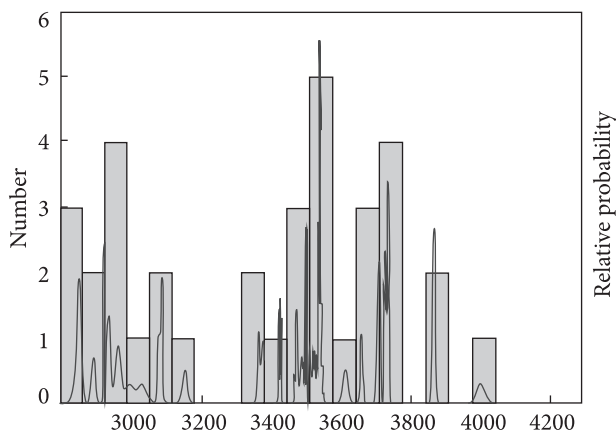


Fig. 9. $^{207}\text{Pb}/^{206}\text{Pb}$ age distribution for zircons from metadacites of the Huliaipole Suite (Drill-hole 625-B, depth 424.4-429.4 meters, sample 89-388)

identical within the error results (analyses 5 and 6). However, in the second crystal, the rim yielded the of 3471 Ma which was significantly older than the $^{207}\text{Pb}/^{206}\text{Pb}$ age of the core (3029 Ma, analyses 12 and 13).

The oldest ages, exceeding 3800 Ma, have been obtained for the core parts of zircon grains. However, several ages exceeding 3700 Ma have been produced in the rim parts of the crystals (Fig. 7). The age of the most ancient zircons was confirmed by dating with the secondary ion mass spectrometry (SIMS) method (Fig. 8).

According to the obtained data, two main populations of zircon can be distinguished (Fig. 8, 9). The first population embraces zircons with an age in the range of 3085-2850 Ma. The Hf isotopic

composition varies within wide limits: 6 crystals have ϵHf values from 6.2 to -0.5 ; other 6 have values from -7.5 to -21 (Table 3, Fig. 10). Thus, zircons of this group have been derived from rocks of different genesis: some of them were of juvenile origin, while others were formed due to reworking of an ancient crust. The second population comprises zircons with an age of 3700-3360 Ma, which also have variable Hf isotope characteristics: from juvenile (ϵHf up to 1.6) and negative ϵHf values (down to -7.7 at an age of 3705 Ma).

Table 2. Results of U-Pb isotope dating of zircons from metadacites of the Huliaipole Suite arranged in descending

# analysis	Concentration, ppm		Mass ratio	Isotopic ratio						
	U	Th		Th/U	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	Rho	$^{207}\text{Pb}/^{206}\text{Pb}$
89-388-18	176	109	0.62	49.900	2.507	0.84	0.03	0.98	0.424	0.011
89-388-29	61	38	0.62	42.280	1.157	0.79	0.02	0.98	0.389	0.008
89-388-17	165	96	0.58	44.000	1.409	0.81	0.02	0.97	0.388	0.008
89-388-14	148	76	0.51	37.430	1.096	0.77	0.02	0.99	0.356	0.007
89-388-16	188	73	0.39	37.060	0.923	0.76	0.02	0.99	0.356	0.007
89-388-22	295	74	0.25	37.080	0.980	0.75	0.02	0.98	0.354	0.007
89-388-20	171	136	0.79	38.590	1.232	0.79	0.02	0.98	0.354	0.007
89-388-9	276	85	0.31	36.400	2.412	0.76	0.05	0.99	0.350	0.007
89-388-25	245	15	0.06	36.250	0.910	0.74	0.02	0.96	0.349	0.007
89-388-34	490	7	0.01	33.720	1.009	0.71	0.02	0.99	0.339	0.007
89-388-10	357	122	0.34	31.390	0.822	0.70	0.02	0.79	0.329	0.007
89-388-6	48	16	0.33	34.070	0.984	0.79	0.02	0.99	0.314	0.006
89-388-1	70	28	0.40	31.250	0.938	0.72	0.02	0.98	0.313	0.006
89-388-5	117	83	0.71	31.060	0.843	0.72	0.02	0.98	0.313	0.006
89-388-23	60	23	0.38	32.040	1.009	0.74	0.02	0.99	0.313	0.006
89-388-30	234	170	0.73	30.330	0.957	0.70	0.02	0.94	0.310	0.006
89-388-27	209	153	0.73	30.350	0.686	0.71	0.02	0.99	0.305	0.006
89-388-7	167	39	0.23	30.480	1.120	0.73	0.03	0.97	0.303	0.006
89-388-13	624	24	0.04	25.900	0.748	0.63	0.02	0.96	0.300	0.006
89-388-31	163	76	0.47	28.060	0.752	0.69	0.02	0.98	0.291	0.006
89-388-21	201	79	0.39	26.330	0.876	0.68	0.02	0.96	0.282	0.006
89-388-35	68	52	0.76	25.920	1.030	0.67	0.03	0.99	0.280	0.006
89-388-33	193	77	0.40	20.120	0.706	0.59	0.02	0.97	0.245	0.005
89-388-26	230	244	1.07	18.620	0.820	0.56	0.03	1.00	0.235	0.005
89-388-15	187	63	0.34	19.300	0.471	0.60	0.01	0.93	0.234	0.005
89-388-12	426	38	0.09	16.020	0.825	0.52	0.02	0.95	0.227	0.006
89-388-3	97	38	0.39	16.850	0.451	0.55	0.01	0.52	0.222	0.006
89-388-28	139	32	0.23	17.100	1.832	0.56	0.06	1.00	0.218	0.005
89-388-4	129	57	0.44	16.500	0.542	0.56	0.02	0.82	0.216	0.006
89-388-2	258	119	0.46	15.500	1.336	0.53	0.05	1.00	0.214	0.004
89-388-32	512	441	0.86	16.590	0.520	0.56	0.02	1.00	0.212	0.004
89-388-11	105	5	0.05	13.470	0.450	0.47	0.02	0.97	0.208	0.004
89-388-8	63	81	1.28	15.610	0.615	0.56	0.02	0.99	0.203	0.004
89-388-19	46	71	1.54	15.680	0.485	0.55	0.02	0.98	0.203	0.004
89-388-24	39	41	1.05	15.720	0.414	0.56	0.01	0.94	0.202	0.004

Two zircon crystals with the age exceeding 3800 Ma have been found (3805 Ma with $\epsilon_{\text{Hf}} = -3.3$, and 3971 Ma with $\epsilon_{\text{Hf}} = -1.3$). These zircons are the oldest ones so far found in the Ukrainian Shield. Their isotopic characteristics indicate the presence of Hadean material within the Azov Domain of the Ukrainian Shield. The minimum model age for the crystallization of this material, calculated at $\text{Lu}/\text{Hf} = 0$ for zircons with the lowest ϵ_{Hf} values in each age population, is about 4.1 Ga (Fig. 10).

Discussion

Two main zircon populations found in metovolcanics of the Huliaipole Suite resemble in terms of their U-Pb and Hf isotope systematics zircons from the Archean metasedimentary rocks of the Soroki Greenstone Belt of the Azov Domain (Claesson et al., 2015), and quartzites of the Bouh Series of the Dniester-Bouh Domain of the Ukrainian Shield (Shumlyansky, 2012a; Shumlyansky et al., 2015). At the same time, the older

order of $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Drill-hole 625-B, depth 424.4-429.4 meters, sample 89-388)

		Isotopic age, Ma								Mass ratio
$^{208}\text{Pb}/^{232}\text{Th}$	2σ	$^{207}\text{Pb}/^{235}\text{U}$	2σ	$^{206}\text{Pb}/^{238}\text{U}$	2σ	$^{208}\text{Pb}/^{232}\text{Th}$	2σ	$^{207}\text{Pb}/^{206}\text{Pb}$	2σ	Discordance, %
0.213	0.006	3986	49	3940	100	3897	78	3997	25	2.2
0.198	0.006	3831	20	3739	59	3644	84	3865	4	3.4
0.211	0.006	3863	25	3832	66	3866	81	3862	7	1.8
0.212	0.007	3704	21	3662	56	3888	92	3734	5	2.1
0.215	0.005	3695	15	3637	36	3940	50	3733	4	2.6
0.192	0.006	3695	17	3609	47	3551	72	3726	4	3.3
0.209	0.006	3740	22	3748	58	3831	79	3722	5	0.8
0.217	0.019	3667	62	3620	170	4050	340	3705	9	2.3
0.229	0.011	3677	17	3575	43	4160	170	3704	6	3.8
0.169	0.014	3601	22	3464	66	3150	240	3656	7	4.8
0.209	0.010	3531	17	3411	50	3830	150	3611	15	4.4
0.218	0.008	3611	21	3749	59	3980	120	3539	8	-2.8
0.197	0.008	3526	22	3510	62	3630	110	3538	6	1.5
0.201	0.006	3520	18	3501	48	3707	65	3537	3	1.5
0.188	0.008	3551	24	3551	66	3490	130	3534	7	1.0
0.187	0.005	3496	24	3432	62	3471	65	3520	10	2.8
0.185	0.004	3498	10	3462	33	3436	33	3498	3	2.0
0.198	0.006	3500	30	3513	88	3654	71	3486	11	0.6
0.197	0.007	3342	20	3141	53	3635	89	3471	5	7.0
0.183	0.005	3421	18	3394	51	3395	59	3423	5	1.8
0.177	0.005	3358	27	3323	57	3298	67	3375	8	2.0
0.182	0.009	3341	34	3310	100	3370	150	3363	7	1.9
0.159	0.004	3096	29	2999	77	2976	50	3152	15	4.1
0.119	0.023	3019	39	2902	95	2250	420	3086	4	4.9
0.182	0.005	3056	14	3031	35	3371	64	3078	7	1.8
0.153	0.006	2885	43	2712	64	2884	99	3029	26	7.0
0.206	0.010	2926	17	2837	33	3790	150	2993	27	4.0
0.166	0.013	2920	110	2860	240	3100	220	2962	12	3.1
0.121	0.005	2905	25	2864	60	2308	78	2953	28	2.4
0.060	0.009	2838	72	2720	180	1170	170	2936	6	5.2
0.153	0.005	2910	24	2875	58	2879	75	2920	3	2.2
0.067	0.013	2712	26	2511	41	1320	250	2892	11	8.4
0.163	0.006	2851	33	2860	76	3058	79	2848	7	0.7
0.150	0.004	2856	23	2839	52	2826	58	2852	9	1.6
0.152	0.004	2860	16	2878	38	2864	44	2840	13	0.4

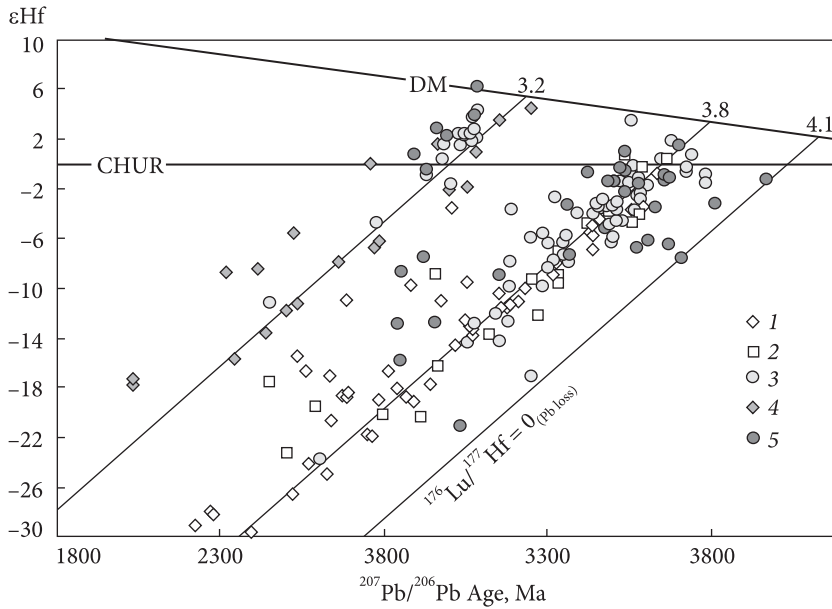


Fig. 10. Hf isotope systematics of zircons from metadacites of the Huliaipole Syncline. Zircons from other rock complexes of the Ukrainian Shield are shown for comparison. 1 — eoarchaean enderbite of the Dniester-Bouh Series (Claesson et al., 2015); 2 — mafic granulite of the Dniester-Bouh Series (Lobach-Zhuchenko et al., 2016); 3 — archaean metasediments of the Azov Domain (Bibikova et al., 2013); 4 — bouh Series quartzite (Shumlyansky et al., 2015); 5 — metavolcanics of the Huliaipole Suite

Table 3. Results of Hf isotope study of zircons from metadacites of the Huliaipole Suite (Drill-hole 625-B, depth 424.4-429.4 meters, sample 89-388)

Spot	²⁰⁷ Pb/ ²⁰⁶ Pb age, Ma	¹⁷⁶ Lu/ ¹⁷⁷ Hf	¹⁷⁶ Yb/ ¹⁷⁷ Hf	¹⁷⁶ Hf/ ¹⁷⁷ Hf	±1s	¹⁷⁶ Hf/ ¹⁷⁷ Hf _T	eHf _T	±2s	T(DM), Ma	T(DM) ^c _{felsic} , Ma	T(DM) ^c _{mafic} , Ma
1	3538	0.000459	0.015200	0.280460	0.000022	0.280429	-2.2	1.5	3801	3913	4185
2	2936	0.000596	0.021500	0.280912	0.000015	0.280878	-0.5	1.0	3214	3327	3611
3	2993	0.000313	0.010570	0.280934	0.000023	0.280916	2.2	1.6	3162	3232	3407
4	2953	0.001262	0.047000	0.280591	0.000019	0.280519	-12.9	1.4	3704	3988	4733
5	3537	0.001653	0.065200	0.280591	0.000029	0.280478	-0.5	2.0	3742	3820	4027
6	3539	0.001384	0.050200	0.280609	0.000019	0.280514	0.9	1.4	3691	3751	3905
7	3486	0.001236	0.045700	0.280568	0.000017	0.280485	-1.4	1.2	3732	3830	4080
8	2848	0.000489	0.018410	0.280529	0.000017	0.280502	-15.9	1.2	3713	4061	4932
9	3705	0.000803	0.028720	0.280481	0.000022	0.280423	1.6	1.6	3806	3849	3954
10	3611	0.000896	0.032600	0.280327	0.000019	0.280264	-6.3	1.3	4020	4188	4606
11	2892	0.000366	0.013140	0.280963	0.000015	0.280943	0.8	1.0	3128	3225	3467
12	3029	0.001140	0.042600	0.280301	0.000022	0.280235	-21.2	1.6	4080	4483	5522
13	3471	0.001016	0.035600	0.280459	0.000020	0.280391	-5.2	1.4	3857	4012	4405
14	3658	0.000912	0.032600	0.280440	0.000023	0.280375	-1.2	1.6	3872	3960	4180
15	3078	0.000699	0.023900	0.280946	0.000023	0.280905	3.8	1.6	3177	3217	3319
16	3682	0.000983	0.036800	0.280433	0.000019	0.280363	-1.1	1.4	3888	3972	4183
17	3805	0.001652	0.063100	0.280341	0.000021	0.280219	-3.3	1.5	4081	4188	4466
18	3971	0.001608	0.063780	0.280287	0.000023	0.280163	-1.3	1.6	4149	4219	4400
19	2852	0.001137	0.042850	0.280766	0.000022	0.280704	-8.7	1.5	3457	3687	4290
20	3626	0.000507	0.018830	0.280368	0.000017	0.280332	-3.5	1.2	3926	4054	4365
21	3375	0.000883	0.029840	0.280451	0.000018	0.280393	-7.4	1.3	3854	4048	4536
22	3576	0.001103	0.039860	0.280497	0.000022	0.280421	-1.6	1.6	3815	3911	4155
23	3534	0.000670	0.023100	0.280504	0.000018	0.280458	-1.2	1.3	3763	3859	4095
24	2840	0.000375	0.012860	0.280614	0.000020	0.280594	-12.9	1.4	3590	3896	4656
25	3704	0.000986	0.038100	0.280234	0.000020	0.280163	-7.7	1.4	4153	4336	4794
26	3086	0.001012	0.036830	0.281026	0.000017	0.280966	6.2	1.2	3095	3099	3108
27	3498	0.000838	0.032050	0.280536	0.000021	0.280479	-1.4	1.5	3737	3835	4080
28	2962	0.001820	0.071000	0.281057	0.000025	0.280953	2.8	1.8	3119	3175	3330

Spot	²⁰⁷ Pb/ ²⁰⁶ Pb age, Ma	¹⁷⁶ Lu/ ¹⁷⁷ Hf	¹⁷⁶ Yb/ ¹⁷⁷ Hf	¹⁷⁶ Hf/ ¹⁷⁷ Hf	±1s	¹⁷⁶ Hf/ ¹⁷⁷ Hf _T	εHf _T	±2s	T(DM), Ma	T(DM) ^c _{felsic} , Ma	T(DM) ^c _{mafic} , Ma
29	3574	0.000850	0.030710	0.280338	0.000025	0.280279	-6.7	1.8	4001	4176	4612
30	3520	0.000580	0.019600	0.280537	0.000019	0.280498	-0.2	1.3	3711	3791	3988
31	3423	0.001443	0.055600	0.280645	0.000020	0.280550	-0.6	1.4	3648	3735	3963
32	2920	0.000643	0.024400	0.280728	0.000024	0.280692	-7.5	1.7	3463	3681	4231
33	3152	0.000923	0.034900	0.280554	0.000022	0.280498	-8.9	1.6	3721	3947	4521
34	3656	0.000795	0.027630	0.280445	0.000020	0.280389	-0.8	1.4	3853	3935	4139
35	3363	0.001620	0.061500	0.280619	0.000023	0.280514	-3.3	1.7	3701	3828	4166

(3700–3360 Ma) zircon population reveal similarity to zircons from the Eoarchean enderbites of the Dniester-Bouh Domain (Claesson et al., 2015; Shumlyansky, 2012b; Shumlyansky et al., 2021). One of the zircon crystals found in the metasedimentary rocks of the Soroki Greenstone Belt (Claesson et al., 2015) resembles the oldest zircon crystals from the metavolcanic rocks of the Huliaipole Suite and has a minimum hafnium model age of ca. 4.1 Ga.

Another intriguing observation is that similarly to the iron-bearing metasedimentary successions of the Middle Dnieper Domain, no zircons younger than ca. 2800 Ma were found either in the greenstone belts of the Azov Domain or the metavolcanics of the Huliaipole Suite (e.g., Bibikova et al., 2010; Bobrov et al., 2011; Stepanyuk et al., 2020; Artemenko et al., 2020), supporting a common geological history of these two domains in the Neoproterozoic and Paleoproterozoic.

The high Th/Yb (7.4–13.2) and low Nb/La (0.14–0.20) ratios in the metavolcanics of the Huliaipole Suite and the presence of the old inherited from the source rocks zircons reaching in age almost 4.0 Ga can be explained by predominantly crustal source of the initial melts. There is a group of crystals that have Hadean ‘felsic crust’ model ages calculated using average continental crust ¹⁷⁶Lu/¹⁷⁷Hf value of 0.015 (Griffin et al., 2004), and ‘mafic crust’ model ages calculated using ¹⁷⁶Lu/¹⁷⁷Hf value of 0.021 (Kemp et al., 2006; Table 4). Such crystals provide strong evidence of the presence of Hadean material in the Azov Domain. However, six crystals belonging to the young popu-

lation have εHf values characteristic to chondritic to depleted mantle sources, indicating significant input of the juvenile mantle material into the source of metavolcanic rocks of the Huliaipole Suite.

The obtained data have shown that the Huliaipole block, despite its relatively small size (30 × 50 km) hosts mineral and rock relicts belonging to the Eoarchean, Paleoproterozoic, and Mesoproterozoic eras (ca. 4000–2900 Ma), that indicates prolonged evolution of the Archean crust, probably within the single nucleoid structure. The unique peculiarity of this structure is that it has never experienced granulite stage metamorphism. This allows consideration of the Huliaipole block as an example of the continental crust that has been formed in a plume geodynamic regime.

Conclusions

The Huliaipole Block of the Azov Domain of the Ukrainian Shield carries evidence for a protracted geological evolution from the Hadean to the Paleoproterozoic. The Azov Domain indicates the existence of the cratonic nucleus formed from 3.97 to 3.3 Ga ago. In the Mesoproterozoic (3.2–3.0 Ga), the Huliaipole Block was a part of the Middle-Dnieper-Azov-Kursk granite-greenstone craton. Felsic and intermediate volcanic rocks of the Huliaipole Suite could have formed due to melting of the sialic continental crust, including components of the Hadean and Archean age, as a result of underplating by mafic magmas during the formation of Neoproterozoic–Paleoproterozoic extension-related rift structures.

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U-Pb ВІК ТА Lu-Hf ІЗОТОПНА СИСТЕМАТИКА
ЦИРКОНУ З МЕТАВУЛКАНІТІВ ГУЛЯЙПІЛЬСЬКОГО БЛОКУ,
ПРИАЗОВСЬКИЙ ДОМЕН УКРАЇНСЬКОГО ЩИТА:
СВІДЧЕННЯ ПРО ПАЛЕОАРХЕЙ-ГАДЕЙСЬКУ КОРУ

Приазовський район є частиною мезоархейського (3,2—3,0 млрд років) кратону, фрагменти якого збереглися в східній частині «Українського Щита» і на блоці Курської магнітної аномалії. У неоархеї-палеопротерозої він був фрагментований на кілька тектонічних блоків — Вовчанський, Ремівський, Гуляйпільський, Білоцерківський і Салтичанський. Північна частина Гуляйпільського блоку складена тоналіт-грондіт-гранодіоритовою

асоціацією порід (ТТГ), серед яких знаходиться Косивцівська зеленокам'яна структура. Вона складена метаморфізованими породами джеспіліт-коматит-толеїтової асоціації (косивцівська товща), яку співставляють з сурською світою конкської серії Середньопридніпровського району. Неоархей-палеопротерозойські утворення представлені осадово-вулканогенними породами гуляйпільської світи і гранітоїдами добропільського і анатольського комплексів. Гранітоїди добропільського комплексу містять велику кількість ксенолітів піроксенітів, гнейсів і плагіогранітоїдів. U-Pb ізотопний вік за цирконом гранітоїдів добропільського комплексу — 2040 млн років. Ксеногенний циркон має вік до 3400 млн років. Невеликі інтрузії двопольовошпатових гранітів поширені у Тернуватській структурі. U-Pb вік двопольовошпатових гранітів за монацитом — 2190 млн років. У центральній частині Гуляйпільського блоку розташована Гуляйпільська брахісинкліналь (3,5×9 км), яка витягнута в ПнЗ напрямку. Ця структура складена осадово-вулканогенними породами гуляйпільської світи, які залягають з неузгодженням на мезоархейських ТТГ. Метавулканіти кислого і середнього складу приурочені, в основному, до залізистих кварцитів середньогуляйпільської підсвіти. В обмеженій кількості вони також зустрічаються в нижньогуляйпольській і верхньогуляйпільській підсвітах. Циркон з метаандезитів і кислих метавулканітів гуляйпільської світи дуже гетерогенний, що вказує на його коровий генезис. Методом LA-ICP-MS визначено U-Pb вік популяцій циркону з метадацитів гуляйпільської світи — 3085—2850 і 3700—3360 млн років. Крім того, виявлено два кристали циркону віком понад 3800 млн років. Згідно з геологічними і геохронологічними даними, Гуляйпільський блок, який має розміри 30 × 50 км, складений породами і їх реліктами гадейського, архейського і палеопротерозойського еонів. Найдавнішим фундаментом Приазовського мегаблоку є, ймовірно, породи нуклеїдної структури, яка формувалася від 3,97 до 3,3 млрд років. Унікальною особливістю цієї структури є те, що вона ніколи не зазнавала метаморфізму гранулітової фації. Це дозволяє розглядати Гуляйпільський блок як приклад континентальної кори, яка сформувалася у плюмовому геодинамічному режимі. У мезоархеї (3,2—3,0 млрд років) вона стала частиною Середньопридніпровсько-Приазовсько-Курського граніт-зеленокам'яного терейну. Вулканіти кислого і середнього складу гуляйпільської світи могли утворитися при плавленні порід сіалічної кори, що включала породи гадейського та архейського віку, в результаті андерплейтінга базитових розплавів при формуванні неоархей-палеопротерозойських рифтогенних структур.

Ключові слова: Західне Приазов'я; Гуляйпільський блок; гадей; архей; палеопротерозой; Український щит; U-Pb вік.