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The U-Pb age and hafnium isotope composition of zircon from metamorphozed andesite of the Chortomlyk Formation and rhyodacite hypabyssal intrusion of the Sura Complex, Chortomlyk Greenstone Belt

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U-Pb вік та ізотопний склад гафнію циркону з метаморфізованого андезиту чортомлицької світи та ріодацитів гіпабісальної інтрузії сурського комплексу (Чортомлицький зеленокам'яний пояс)

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Ключові слова: Середньопридніпровський домен; Чортомлицький зеленокам'яний пояс; метаморфізовані андезити; чортомлицька світа; конкська серія; гіпабісальна інтрузія; ТТГ; Новомиколаївський масив; сурський комплекс; циркон; U-Pb вік; ізотопний склад Hf.

Andesites and felsic volcanic rocks are observed at all stratigraphic levels of the Konka and Bilozerka groups, which comprise greenstone structures in the Middle Dnieper Domain. Their nature and age are still poorly known. The youngest felsic volcanic rocks of the Solone Formation of the Konka Group and comagmatic with the tonalite-trondhjemite-granodiorite (TTG) association of the Sura Complex hypabyssal intrusions were previously dated by the U-Pb zircon SHRIMP method at ca. 3.1 Ga. The purpose of this study is to determine the U-Pb zircon age and geochemical features of i) metamorphosed andesites of the Chortomlyk Formation and ii) low-alkaline metarhyodacite hypabyssal intrusions that cut the rocks of the Sura Formation of the Konka Group. In the Chortomlyk Greenstone Belt, the thickness of volcanogenic rocks of the Chortomlyk Formation (dacite-andesite-tholeiite association) reaches 2000 m. The youngest felsic volcanic rocks of the Solone Formation and comagmatic hypabyssal intrusions are located within three large volcanic fields located near the Novomykolaivka* massif. Using the LA-ICP-MS method, U-Pb ages of two zircon populations from metamorphosed andesites of the Chortomlyk Formation were dated. Twenty-three crystals of transparent colourless zircon crystals yielded a concordant age of (3222 ± 6) Ma. The U-Pb age of the second population of large, brown, opaque zircon crystals is 3132–3073 Ma. Interpretation of the obtained ages is not straightforward and at least two options can be proposed: 1). The studied metaandesites are differentiated mafic magmas and the age of their formation is defined by the older zircon population, and the young population corresponds to the time of superimposed thermal processes during later intrusion of plagioclase granitoids of the Novomykolaivka massif; 2). The age of the metaandesite is defined by the younger population, while the older population is inherited from the protolith. We consider the second option as being far more likely. The first option contradicts the stratigraphic position of the dated rock. The studied metaandesite is low in potassium and belongs to the sodium series. Relative to TTG, they have higher Nb (16.2 ppm) and Y (25.9 ppm). Rare earth elements are weakly differentiated, $(La/Yb)_N = 3.91$ with a strongly negative Eu anomaly, Eu/Eu* = 0.44. The U-Pb zircon age from the low-alkaline rhyodacite hypabyssal intrusion that cuts the Sura Formation of the Konka Group is (3085 ± 6) Ma. It has a highly differentiated REE pattern, $(La/Yb)_N = 16.2$ and a positive Eu anomaly, Eu/Eu* = 1.21. The Nb (6.7 ppm) and Y (10.8 ppm) contents are low. They chemically resemble TTGs of the Sura Complex. Based on our data, the andesites of the Chortomlyk Formation of the Konka Group and the low-alkaline rhyodacite hypabyssal intrusions have the same U-Pb age, but different origins. The former were produced by the melting of older crustal rocks, and the latter were formed due to the partial melting of metabasites with garnet-bearing restite. Hafnium isotope composition in zircon from both samples reveals their juvenile nature, i.e., they crystallized from partial melts of rocks with short crustal residence times. Our isotope data agrees with the neodymium isotope composition of the felsic volcanic rocks of the Sura greenstone belt, which yielded εHf values of +1.8. These values are lower than the depleted mantle isotope composition at this time (3200–3000 Ma).

**Novomykolaivka massif was formerly known as Chkalove massif.*

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Introduction

Andesites and felsic volcanic rocks are an important element of volcanic sequences and can represent an indicator of the geodynamic regime during greenstone belt formation. They occur at different stratigraphic levels of the Konka and Bilozerka Groups, which comprise the greenstone belts sections in the Middle Dnieper domain (Semenenko et al., 1967). In the lower part of the Konka Group (Sura Formation), thin bodies (10s of cm) of intermediate and felsic volcanic rocks are rhythmically interlayered with mafic and ultramafic volcanic rocks and sedimentary rocks (Semenenko et al., 1967). In the overlying Chortomlyk Formation of the Konka Group, the thickness of intermediate and felsic volcanic rocks reaches several thousand meters (Semenenko et al., 1967; Kushinov, Kuz V.D, 1988; Koliy et al., 1990). In the Solone sub-formation at the top of the Konka Group, only felsic volcanic rocks occur, with a thickness of a few hundred meters (Bobrov, 1993a, 1993b). In the Bilozerka Group, which unconformably overlies the Konka Group, the thickness of felsic volcanic rocks is a few tens of meters (Semenenko et al., 1967; Strueva, Skarzhinskaya, 1979). The nature and age of the andesites and felsic volcanic rocks are still poorly known.

Most of the previous geochronological and isotope geochemistry studies of greenstone belts in the Middle Dnieper Domain of the Ukrainian Shield were conducted in the 1980 – early 1990s e.g., (Shcherbak et al., 1987, 1989; Zhuravlev et al., 1987; Samsonov et al., 1993). According to these data, the maximum depositional age of the metasedimentary rocks and the age of mafic and ultramafic volcanic rocks in the Konka Group was ca. 3.15 Ga. The mafic-ultramafic rocks yielded an εNd value of 1.8. Rocks of the Solone sub-formation yielded U-Pb zircon ages of 3.14–3.10 Ga with εNd = 1.8. The zircon U-Pb age of the trondhjemite intrusions cutting the Chortomlyk Formation was defined at (3115 ± 10) Ma. Finally, the maximum depositional age of the metasedimentary rocks of the Bilozerka Group was defined at ca. 3.0 Ga. Recent works, mostly based on the results of LA-ICP-MS zircon dating (Bibikova et al., 2010; Artemenko et al., 2014, 2020, 2023, 2024) allowed maximum depositional ages of sedimentary rocks in the Chortomlyk (ca. 3.1 Ga), Bilozerka (ca. 3.05 Ga) and Vysokopillya (ca. 3.06 Ga) greenstone belts to be defined.

Research objectives. Previous geochronological studies of the greenstone belts in the Middle Dnieper Domain of the Ukrainian Shield were focused, with a few exceptions, on investigations of metasedimentary rocks and mafic and ultramafic volcanic rocks. The 2000 m thick dacite-andesite-tholeiite association in the Chortomlyk Formation overlying the komatiite-tholeiite association of the Sura Formation marks an important stage in the evolution of greenstone belts in the Middle Dnieper Domain, however its age remains unknown. The purpose of this work was to define the U-Pb LA-ICP-MS zircon age and the geochemical features of metamorphosed andesites of the Chortomlyk Formation and of hypabyssal metamorphosed dacites cutting the volcano-sedimentary rocks of the Sura Formation.

Geological structure of the study area. The Chortomlyk greenstone belt is a northeast-trending syncline with a total width of 15–18 km and an area of up to 500 km^2 (Semenenko et al., 1967) (Fig. 1). It is affected by folding and faulting. The most significant structures in the belt are the Solone syncline (I), the Kyslychuvate anticline (II), the Chortomlyk tectonic wedge (an asymmetric, isoclinal syncline, III), and in the south – the Hrushivka (IV) and Oleksiivka (V) tectonic wedges (see Fig. 1). In the Chortomlyk greenstone belt, volcanic structures (central and fissure types) formed on older basement (Honchar, 1979; Bobrov, 1993a, 1993b; Kushinov, Kuz, 1988; Kornienko et al., 2001). The initial stages of the outpouring of the komatiite-basalt lavas of the Sura Formation were confined to linear fractures (>30 km) associated with deep fault zones (Fig. 2). In contrast, formation of the dacite-andesite-tholeiite association of the overlying Chortomlyk Formation was related to the central-type volcanoes (Bobrov, 1993a, 1993b; Kushinov, Kuz, 1988). The volcanic rocks of the Sura and Chortomlyk formations are intruded by plagioclase granites of the Novomykolaivka massif (Kushinov, Kuz, 1988). The youngest rocks are felsic volcanic rocks of the Solone Formation and hypabyssal intrusions, formed within three large volcanic fields located around the Novomykolaivka massif (North-Novomykolaivka, West-Novomykolaivka, and East-Novomykolaivka) (Bobrov, 1993a, 1993b; Bobrov et al., 2004). In the Middle Dnieper Domain, metamorphosed andesites and felsic volcanic rocks of the Konka Group are most voluminous in the Chortomlyk greenstone belt, which has been less affected by erosion than other belts.

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Research methods. Zircon was separated from a metamorphosed andesite (sample 85-335) and a low-alkaline metarhyodacite from a hypabyssal intrusion (sample 85-313) 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 and their morphology was studied under an optical microscope. The U-Th-Pb analyses were conducted by laser ablation-inductively coupled mass spectrometry (LA-ICP-MS) on crystals in epoxy mounts at the Department of Geology, Trinity College, Dublin, Ireland. A Photon Machines Analyte Excite 193 nm ArF excimer laser-ablation system with a HelEx 2-volume ablation cell, coupled to an Agilent 7900 mass spectrometer was employed. Line scans on NIST612 standard glass were used to tune the instrument, by obtaining a Th/U ratio close to unity and low oxide production rates (i.e., ThO+/Th+ typically <0.15%). A circular laser spot of 24 μm, a repetition rate of 11 Hz and a fluence of 2.25 J/cm^2 were employed. The helium carrier gas was fed into the laser cell at ~0.4 l/min[1], and was mixed with ~ 0.6 l/min Ar make-up gas and 11 ml/min N_2. Each analysis comprised 27.3 s of ablation (300 shots) and 12 s of wash out time and the latter portions of the washout were used for baseline measurements. The data reduction of raw U-Th-Pb isotopic data was undertaken using the freeware IOLITE package (Paton et al., 2011), with the "Vizual Age" data reduction scheme (Petrus et al., 2012). The primary U-Pb zircon calibration reference material was 91500 zircon (^{206}Pb-^{238}U age of (1065.4 ± 0.6) Ma (Wiedenbeck et al., 1995, 2004) and the secondary reference materials were Plešovice zircon (^{206}Pb-^{238}U age of (337.13 ± 0.37) Ma (Sláma et al., 2008) which yielded an age of (338.7 ± 1.0) Ma (^{206}Pb-^{238}U age weighted mean age, n = 109) and WRS 1348 zircon (^{206}Pb-^{238}U age of (526.26 ± 0.70) (Pointon et al., 2012) which yielded an age of (526.6 ± 2.0) Ma (^{206}Pb-^{238}U age weighted mean age, n = 130). Final ages were calculated using Isoplot (Ludwig, 2011).

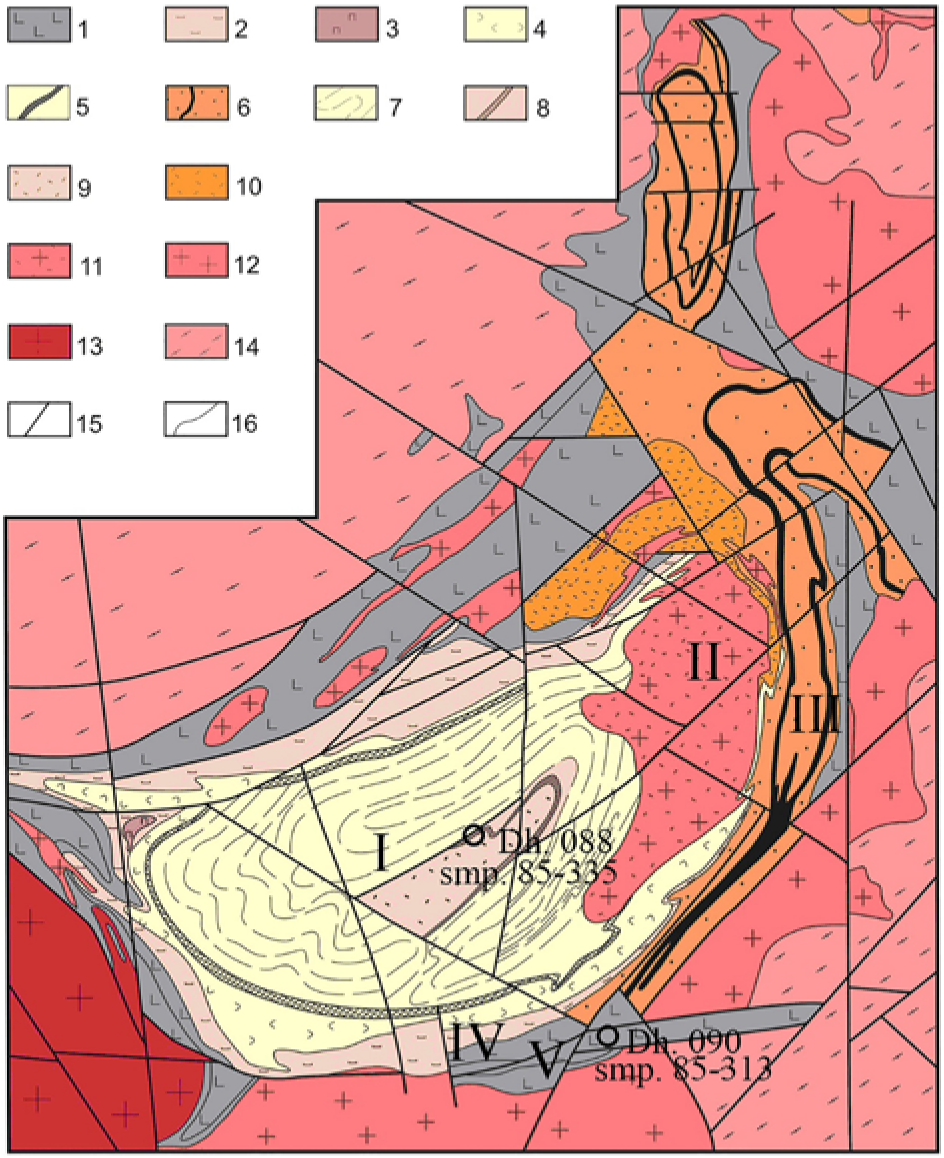

Fig. 1. Schematic geological map of Chortomlyk greenstone belt modified from (Kornienko et al., 2001; Bobrov et al., 2004). *Metakomatiite association*: *1* – complex KT-1, *2* – complex KT-2, *3* – dunite-harzburgite association, *4* – complex KT-3, *5* – complex KT-4, *6* – complex of shale-jaspilite-tholeiite SDT; *7* – metadacite-tholeiite-andesite association DAT: *8* – lower complex, *9* – upper complex; *10* – rhyodacite and tonalite-plagioclase granite association; *11* – subvolcanic facies RD; *12* – hypabyssal facies; *13* – granite of the Tik massif; *14* – granite-gneissic basement; *15* – faults; *16* – geological boundaries. Geological structures: *I* – Solone syncline; *II* – Kyslychuvate anticline; *III* – Chortomlyk syncline; IV – Hrushivka tectonic wedge; *V* – Oleksiivka tectonic wedge. Locations of the drill holes 088, 090 and of the samples collected for geochronological studies (85-335, 85-313) are indicated

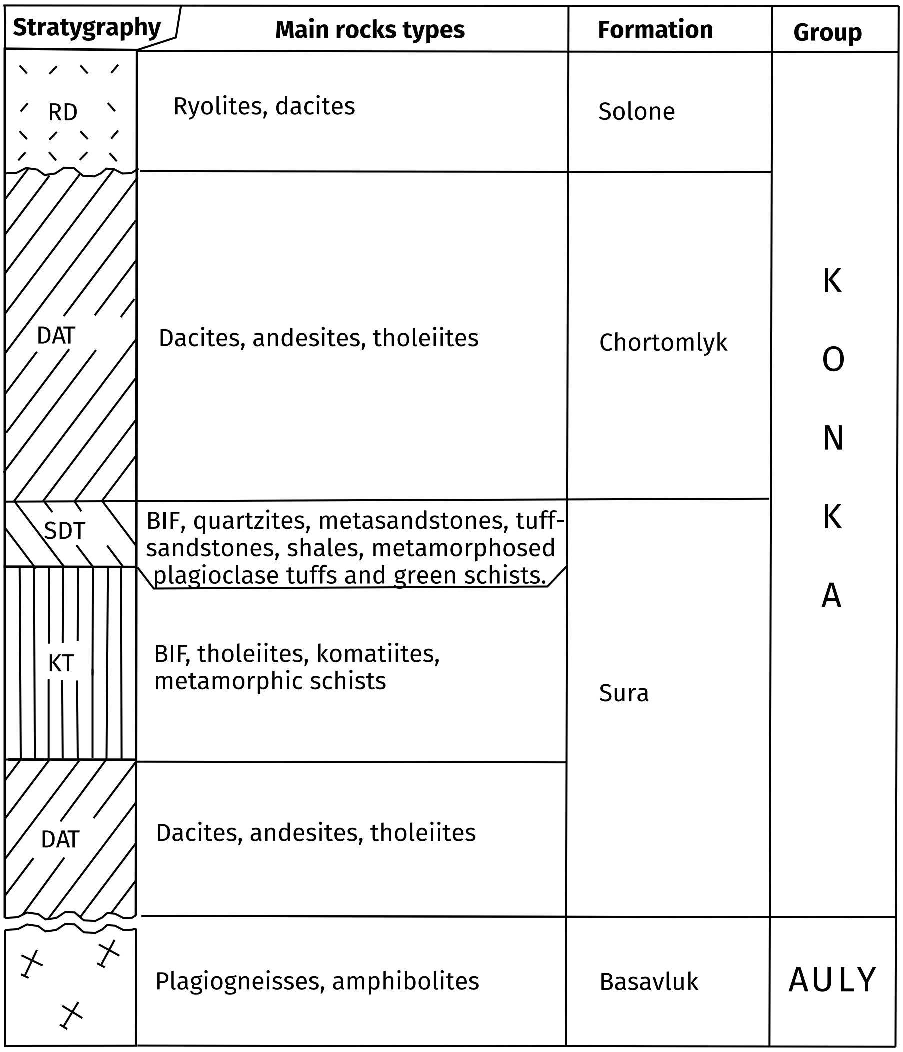

Fig. 2. Schematic stratigraphic column of the sedimentary-volcanogenic succession in the Chortomlyk greenstone belt (southern profile) according to (Sivoronov et al., 1990 with modifications). Metamorphosed associations: DAT – dacite-andesite-tholeiite; KT – komatiite-tholeiite; K – komatiite; SDT – schist-jaspilite-tholeiite, RD – rhyolite-dacite

Lutetium-hafnium isotope analyses in zircon were performed by LA-MC-ICP-MS at the MILESTONE Laboratory (RéGEF ISOTOP-MTP, Geosciences Montpellier, France). A Thermo Scientific Neptune XT was coupled to a Teledyne Cetac Analyte Excite+ Excimer laser (193 nm), which was equipped with an optional X-Y Theta dynamic aperture allowing rectangular-shaped beams of any aspect ratio and orientation to be generated. Analyses were carried out on top of the U-Pb ablation pits, using a 40×40 μm beam, a laser frequency of 5 Hz and an energy density of 6 J/cm^2. Each analysis included a 30 s background measurement and a 60 s ablation period of 60 cycles of 1 s each. The accuracy and long-term reproducibility of the measurements were gauged by performing repeated analyses of three zircon reference standards: Mud Tank (^{176}Hf/^{177}Hf = (0.282512 ± 17), n = 55); Plešovice (^{176}Hf/177Hf = (0.282485 ± 15), n = 57), and Temora-2 (^{176}Hf/^{177}Hf = (0.282673 ± 24), n = 29). The data agree with the accepted ^{176}Hf/^{177}Hf ratios for Mud Tank (0.282504 ± 44) (Woodhead and Hergt, 2005), Plešovice (0.282482 ± 13) (Sláma et al., 2008) and Temora-2 (0.282680 ± 24) (Woodhead et al., 2004). All errors are given at 2 s.d.level. ^{176}Hf/^{177}Hf initial ratios were calculated using the ^{176}Lu decay constant quoted in Söderlund et al. (2004). Only analyses with a precision better than 150 ppm (2 s.d.) were considered for this study. εHf(t) values were calculated using ^{176}Lu/^{177}Hf = 0.0336 and ^{176}Hf/^{177}Hf = 0.282785 for the CHUR (Bouvier et al., 2008).

Research results. Volcanogenic rocks of the Chortomlyk Formation were described as a differentiated dacite-andesite-tholeiite association (Sivoronov et al., 1981a, 1981b; Kushinov, Kuz, 1988; Lobach-Zhuchenko et al., 1988;). The formation is dominated by the packs comprising multiple repetitions of andesite + basalt paragenesis. The three-component basalt + andesite + dacite paragenesis is of subordinate importance (Kushinov, Kuz, 1988). Metamorphosed andesites of this formation were studied from Drill hole 088, drilled in the central part of the Chortomlyk structure, where andesites alternate with dacites in the section (Fig. 3).

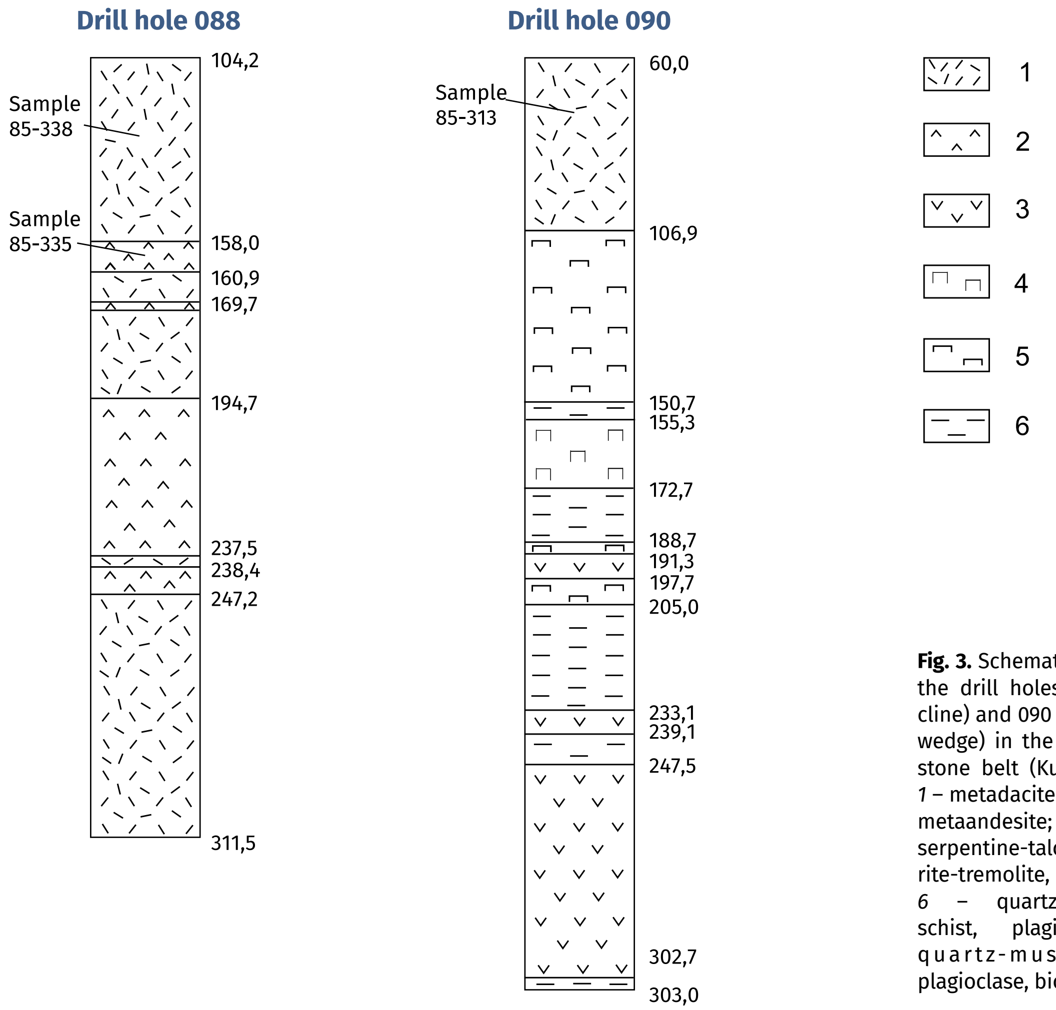

Fig. 3. Schematic geological log of the drill holes 088 (Solone syncline) and 090 (Oleksiivka tectonic wedge) in the Chortomlyk greenstone belt (Kushinov, Kuz, 1988): *1* – metadacite and rhyodacite; *2* – metaandesite; *3* – amphibolite; *4* – serpentine-talc, talc rock; *5* – chlorite-tremolite, tremolite schists; *6* – quartz-biotite-plagioclase schist, plagioclase-hornblende, quartz-muscovite-biotite-plagioclase, biotite microgneisses

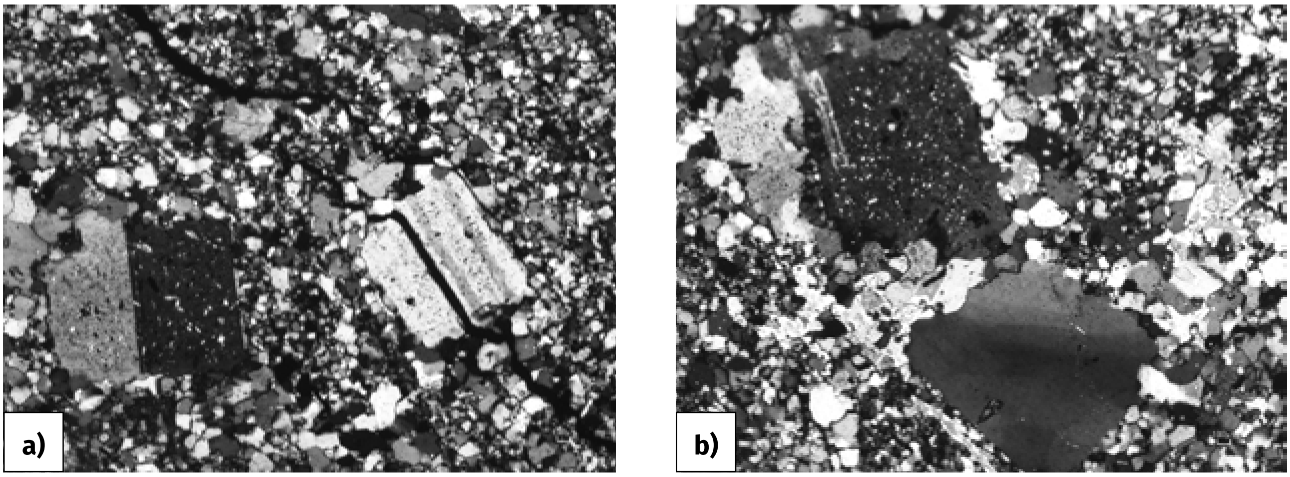

Fig. 4. Photomicrographs under cross-polarised light of metamorphosed quartz-plagioclase porphyrite (andesite) of the Chortomlyk Formation of the Konka Group: *a)* drill hole 088, depth 158,5 m; *b)* drill hole 088, depth 160 m. Images are taken using an ECLIPSE LV100 POL polarizing microscope

Metaandesite, sample 85-335 (Chortomlyk Formation of the Konka Group, drill hole 088, depth 158,0–160,9 m). The rock has a schistose structure. The texture is blastoporphyritic with lepidogranoblastic texture in the groundmass (Fig. 4, a, b). The phenocrysts are represented by quartz and plagioclase. The mineral composition (vol. %) of the groundmass: chlorite – 6; muscovite – 7; carbonate – 15–18; quartz + albite – 70; biotite – 1; magnetite, apatite, zircon – single grains.

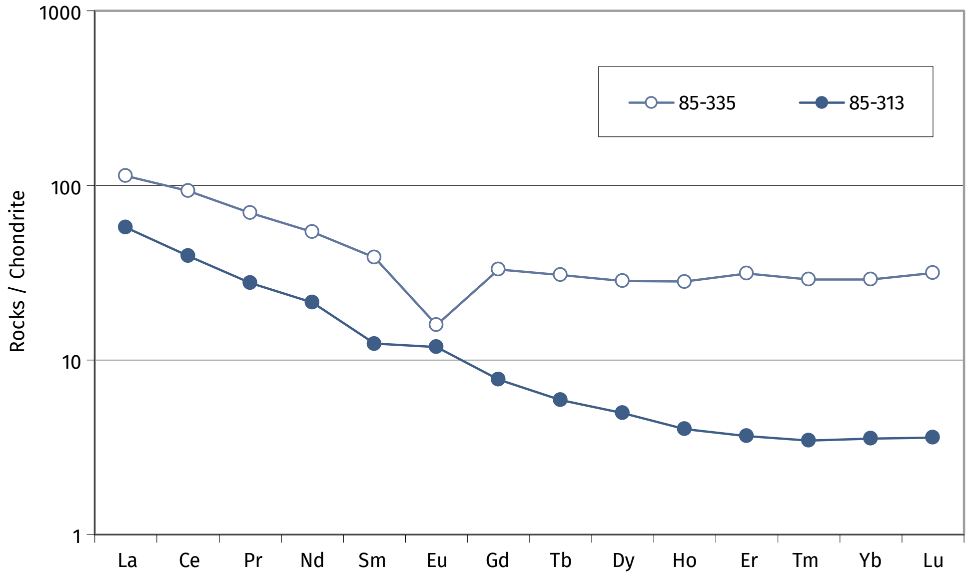

Fig. 5. Chondrite-normalized REE pattern for the metamorphosed andesite (sample 85-335) of the Chortomlyk Formation and metamorphosed low-alkaline rhyodacite hypabyssal intrusion (sample 85-313). Chondrite composition is after Sun & McDonough (1989)

In terms of chemical composition, they correspond to andesite of the calc-alkaline series (Na_2O/K_2O = 3.8) (Bogatikov, Gonshakova, 1987) (Table 1). They are high-magnesian, Mg# = 0.49, and poor in Rb (31.7 ppm), Sr (92.2 ppm), Ba (81.9 ppm), as well as in transition elements V (5.68 ppm), Cr (10.4 ppm), Ni (15.7 ppm) (Table 2). They are rich in Nb (16.2 ppm) and Y (25.9 ppm). Rare earth elements are weakly differentiated, (La/Yb)N = 3.9, with a strongly negative Eu anomaly, Eu/Eu* = 0.44 (Fig. 5).

There are two populations of zircon crystals in the andesite: small, transparent, colorless and large, brown, opaque. The average size of the small transparent zircons is 0.6 × 0.03 mm. Shapeless zircon grains predominate; subhedral zircon is much less common. Their internal structure is homogeneous. Crystals of brown opaque zircon reach a size of up to 0.25 x 0.17 mm. They exhibit a zonal structure (Fig. 6).

A total of 30 zircon crystals were analysed in this sample (Table 3). Of these, 24 small transparent colourless zircon crystals were dated and a concordant age of (3222.3 ± 6.0) Ma was calculated for 23 zircon crystals (Fig. 7). The U-Pb ages of six large, brown, opaque zircons range from 3132–3073 Ma (Table 3). The concordia age of the three youngest results is (3082 ± 10) Ma.

The hafnium isotope composition was measured in 10 spots, 6 of them represent zircons having a concordant age of (3222 ± 6) Ma, while the rest was obtained for crystals with younger ages. All zircon crystals irrespective of their age yielded positive εHf values, varying from +3.2 to +1.5 (Table 4, Fig. 8).

Table 1. Chemical composition of the volcanic and intrusive hypabyssal rocks, Chortomlyk greenstone structure

Oxides, %	1/ 85-335	2/ 85-313
SiO_2	59.02	68.67
TiO_2	0.76	0.46
Al_2O_3	14.06	16.22
Fe_2O_3	0.79	2.27
FeO	6.05	1.87
MnO	0.14	0.07
MgO	3.67	2.02
CaO	5.02	1.51
Na_2O	3.80	4.0
K_2O	1.00	0.99
P_2O_5	0.30	0.08
Stot.	0.10	–
CO_2	–	1.76
H_2O^-	0.02	0.09
LOI	5.16	0.12
Total	**99.89**	**100.13**
Mg#	0.49	0.48

**Note.* *1 – metamorphosed andesite, Chortomlyk Formation, Solone syncline, drill hole 088, depth 158–160.9 m (sample 85-335); 2 – metamorphosed low-alkaline rhyodacite hypabyssal intrusion, Oleksiivka tectonic wedge, drill hole 090, depth 65–97 m (sample 85-313). Mg# = Mg/(Mg+Fe) (molar ratio).*

Table 2. Trace element composition of volcanic and intrusive hypabyssal rocks from the Chortomlyk greenstone belt

Concentration, ppm	1/ 85-335	3/ 85-313
V	5.7	72
Cr	10.4	93
Co	2.1	18.9
Ni	15.7	38
Cu	15.2	102
Zn	88	24.5
Ga	15.5	–
Rb	32	39
Sr	92	171
Y	25.9	10.8
Zr	175	121
Nb	16.2	6.7
Mo	2.5	0.9
Sb	0.1	–
Cs	0.44	1.40
Ba	82	294
La	26.9	13.6
Ce	57.1	24.1
Pr	6.61	2.62
Nd	25.3	9.97
Sm	5.91	1.90
Eu	0.92	0.69
Gd	6.80	1.59
Tb	1.15	0.22
Dy	7.22	1.26
Ho	1.59	0.23
Er	5.20	0.61
Tm	0.74	0.09
Yb	4.93	0.60
Lu	0.80	0.09
Hf	8.52	3.28
Ta	1.29	0.62
W	0.52	-
Pb	2.63	4.57
Th	6.92	3.52
U	1.70	0.90
ΣREE	151.17	57.57
(La/Yb)N	3.91	16.2
Eu/Eu*	0.44	1.21

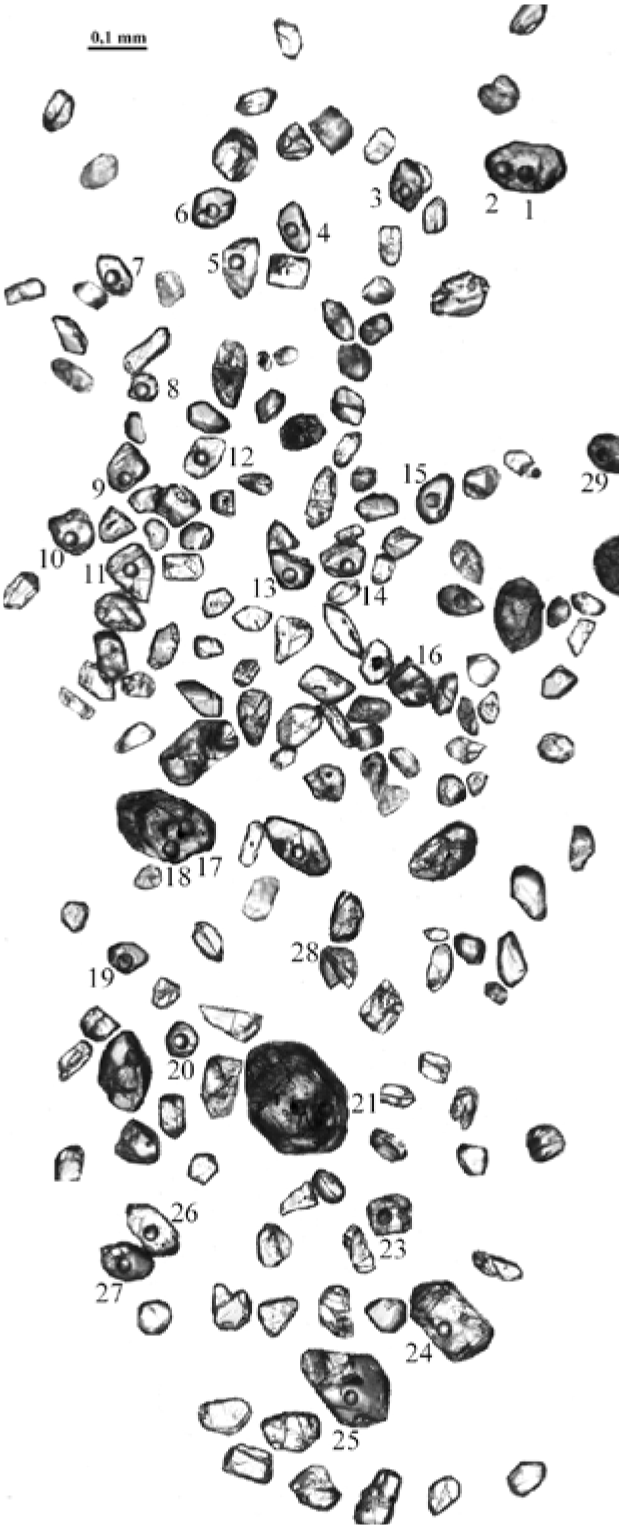

Fig. 6. Optical image of the studied zircon crystals from meta-andesite of the Chortomlyk Formation (Chortomlyk greenstone structure, drill hole 088, depth 158.0–160.9 m, sample 85-335) with location of U-Pb analytical spots indicated (see Table 3)

Table 3. Results of LA-ICP-MS U-Pb dating of zircon from volcanic and intrusive hypabyssal rocks, Chortomlyk greenstone structure

# analysis	Concentration, ppm			Th/U	Isotope ratio							Isotopic age, Ma					
	U	Pb	Th		$^{207}Pb/^{235}U$	2σ	$^{206}Pb/^{238}U$	2σ	Rho	$^{207}Pb/^{206}Pb$	2σ	$^{207}Pb/^{235}U$	2σ	$^{206}Pb/^{238}U$	2σ	$^{207}Pb/^{206}Pb$	2σ
Sample 85-335, metamorphosed andesite, drill hole 088, depth 158-160.9 m																	
1	316	280	186	0.6	21.83	0.26	0.6603	0.0100	0.76508	0.2410	0.0023	3175	12	3267	37	3126	15
2	687	647	460	0.7	21.32	0.35	0.6390	0.0130	0.62151	0.2420	0.0028	3152	16	3191	53	3132	18
3	163	199	148	0.9	22.21	0.28	0.6570	0.0140	0.42759	0.2486	0.0040	3192	12	3265	51	3174	25
4	134	124	86	0.6	22.82	0.27	0.6490	0.0120	0.55010	0.2557	0.0034	3219	12	3231	44	3219	21
5	121	126	91	0.8	22.81	0.27	0.6534	0.0080	0.65816	0.2561	0.0030	3218	12	3240	32	3223	18
6	163	182	132	0.8	22.65	0.25	0.6422	0.0080	0.78963	0.2554	0.0021	3211	11	3196	32	3218	13
7	149	159	106	0.7	22.81	0.31	0.6521	0.0090	0.60552	0.2530	0.0030	3218	13	3241	33	3202	19
8	184	196	133	0.7	23.16	0.42	0.6510	0.0110	0.68510	0.2565	0.0031	3235	17	3232	43	3224	19
9	158	141	94	0.6	22.92	0.38	0.6580	0.0110	0.603710	0.2558	0.0045	3227	15	3259	44	3233	27
10	177	195	135	0.8	22.70	0.22	0.6496	0.0090	0.69142	0.2530	0.0025	3213.4	9.5	3230	36	3205	15
11	107	118	82	0.8	22.84	0.23	0.6530	0.0110	0.64003	0.2535	0.0029	3219.6	9.6	3240	42	3205	18
12	92	72	48	0.5	23.46	0.32	0.6770	0.0110	0.31520	0.2523	0.0041	3245	13	3338	42	3196	26
13	145	135	93	0.6	22.75	0.29	0.6477	0.0100	0.73949	0.2536	0.0027	3217	13	3222	38	3206	17
14	123	92	62	0.5	22.81	0.27	0.6527	0.0100	0.57620	0.2549	0.0034	3218	12	3237	38	3213	21
15	108	96	64	0.6	23.25	0.25	0.6595	0.0100	0.60169	0.2542	0.0030	3237	10	3264	38	3210	19
16	74	71	44	06.	22.91	0.31	0.6535	0.0090	0.69446	0.2527	0.0027	3222	13	3245	37	3200	17
17	178	141	128	0.7	19.60	0.37	0.6010	0.0140	0.69860	0.2385	0.0041	3071	18	3031	56	3108	27
18	158	173	167	1.1	19.96	0.36	0.6140	0.0100	0.72046	0.2332	0.0028	3088	18	3086	41	3073	19
19	152	158	114	0.8	22.61	0.24	0.6460	0.0100	0.56269	0.2553	0.0032	3209	10	3212	40	3215	20
20	77	65	44	0.6	23.02	0.28	0.6590	0.0130	0.54659	0.2545	0.0041	3227	12	3263	49	3211	26
21	154	140	83	0.5	20.38	0.26	0.6149	0.0080	0.57607	0.2405	0.0030	3110	12	3088	33	3123	21
22	223	138	107	0.5	19.73	0.34	0.6090	0.0160	0.69906	0.2374	0.0036	3077	16	3064	62	3101	25
23	286	400	250	0.9	23.59	0.25	0.6768	0.0100	0.75242	0.2523	0.0024	3251	10	3331	37	3199	15
24	237	382	246	1.0	22.68	0.22	0.6517	0.0080	0.71407	0.2530	0.0023	3212.5	9.5	3234	32	3205	15
25	91	78	52	0.6	23.04	0.30	0.6567	0.0090	0.63754	0.2549	0.0036	3227	13	3259	37	3215	23
26	93	96	59	0.6	23.22	0.50	0.6610	0.0160	0.64286	0.2540	0.0047	3235	21	3269	60	3208	30
27	80	66	48	0.6	22.79	0.30	0.6488	0.0100	0.60856	0.2523	0.0028	3221	13	3226	37	3197	18
28	139	145	95	0.7	22.73	0.27	0.6508	0.0090	0.52722	0.2546	0.0026	3214	11	3230	33	3212	16
29	74	50	32,5	0.4	23.18	0.50	0.6700	0.0150	0.66009	0.2521	0.0053	3238	22	3302	59	3195	34
30	158	270	230	1.5	22.79	0.28	0.6463	0.0090	0.70892	0.2546	0.0023	3217	12	3212	35	3212	14

Table 3. Results of LA-ICP-MS U-Pb dating of zircon from volcanic and intrusive hypabyssal rocks, Chortomlyk greenstone structure (continuation)

# analysis	Concentration, ppm			Th/U	Isotope ratio							Isotopic age, Ma					
	U	Pb	Th		$^{207}Pb/^{235}U$	2σ	$^{206}Pb/^{238}U$	2σ	Rho	$^{207}Pb/^{206}Pb$	2σ	$^{207}Pb/^{235}U$	2σ	$^{206}Pb/^{238}U$	2σ	$^{207}Pb/^{206}Pb$	2σ
Sample 85-313, metamorphosed low-alkaline rhyodacite from the hypabyssal intrusion, drill hole 090, depth 65-97 m																	
2	266	269	142	0.5	19.82	0.25	0.6203	0.0100	0.50837	0.2350	0.0034	3084	12	3110	38	3084	23
3	293	292	159	0.5	20.05	0.34	0.6210	0.0110	0.87670	0.2340	0.0025	3092	17	3111	46	3081	18
4	221	162	105	0.5	19.87	0.49	0.6180	0.0240	0.70808	0.2327	0.0055	3083	24	3116	90	3068	37
5	167	137	90	0.5	19.92	0.19	0.6195	0.0080	0.52481	0.2338	0.0024	3086.6	9.2	3111	32	3079	17
6	193	184	127	0.7	20.06	0.37	0.6180	0.0120	0.82565	0.2360	0.0023	3094	18	3098	48	3092	16
7	140	99	68	0.5	19.96	0.32	0.6100	0.0120	0.77850	0.2370	0.0028	3088	16	3072	46	3103	18
9	230	165	121	0.5	20.04	0.28	0.6200	0.0100	0.64450	0.2338	0.0029	3092	13	3108	40	3076	20
10	258	248	169	0.7	20.32	0.31	0.6260	0.0120	0.80007	0.2352	0.0030	3106	15	3132	46	3093	20
11	238	173	126	0.5	20.23	0.32	0.6170	0.0120	0.69247	0.2372	0.0030	3101	15	3098	49	3100	20
12	214	178	132	0.6	19.78	0.36	0.6180	0.0110	0.77389	0.2339	0.0025	3084	17	3101	43	3080	17
13	297	276	212	0.7	19.63	0.41	0.6070	0.0120	0.76414	0.2376	0.0038	3076	19	3055	49	3102	25
14	76	42,3	44,7	0.6	19.76	0.24	0.6145	0.0070	0.41757	0.2326	0.0027	3079	12	3087	29	3074	20
15	163	131	117	0.7	18.75	0.34	0.5760	0.0140	0.69150	0.2366	0.0047	3028	18	2933	57	3095	32
16	138	131	90	0.7	20.45	0.31	0.6240	0.0140	0.72916	0.2395	0.0036	3112	15	3123	54	3119	23
17	193	154	116	0.6	19.35	0.30	0.5910	0.0100	0.80174	0.2366	0.0023	3058	15	2991	41	3097	16
19	115	77	81	0.7	18.11	0.28	0.5607	0.0090	0.63706	0.2370	0.0029	2995	15	2869	36	3099	20
20	95	77	54	0.6	19.14	0.26	0.6007	0.0090	0.61929	0.2310	0.0028	3048	13	3031	34	3060	19
21	238	196	164	0.7	19.37	0.37	0.6050	0.0130	0.82027	0.2341	0.0027	3062	19	3056	52	3082	19
22	210	202	176	0.8	19.33	0.27	0.6040	0.0120	0.70105	0.2357	0.0029	3058	13	3043	48	3090	19
23	171	112	81	0.5	19.84	0.27	0.6112	0.0070	0.57383	0.2354	0.0030	3086	13	3074	28	3090	20
24	146	182	128	0.9	19.90	0.32	0.6176	0.0100	0.60898	0.2341	0.0030	3087	16	3098	38	3078	21
25	223	149	125	0.6	18.15	0.43	0.5580	0.0120	0.63657	0.2379	0.0048	3000	22	2855	48	3102	32
26	153	161	110	0.7	20.39	0.75	0.6170	0.0220	0.70696	0.2407	0.0061	3115	33	3094	88	3122	40
27	120	78	64	0.5	20.08	0.41	0.6210	0.0130	0.88555	0.2337	0.0023	3094	20	3111	53	3076	15
28	192	166	160	0.8	17.61	0.35	0.5400	0.0120	0.75326	0.2351	0.0033	2967	19	2781	50	3086	22
29	215	134	101	0.5	19.89	0.36	0.6150	0.0140	0.45738	0.2354	0.0045	3089	18	3086	57	3087	31
30	161	112	83	0.5	19.71	0.52	0.6060	0.0250	0.73408	0.2404	0.0061	3080	25	3050	100	3128	38
34	133	99	69	0.5	20.28	0.34	0.6270	0.0120	0.75278	0.2341	0.0029	3103	16	3134	47	3078	20
35	403	631	496	1.2	20.04	0.31	0.6130	0.0120	0.68281	0.2362	0.0035	3092	15	3079	46	3092	24

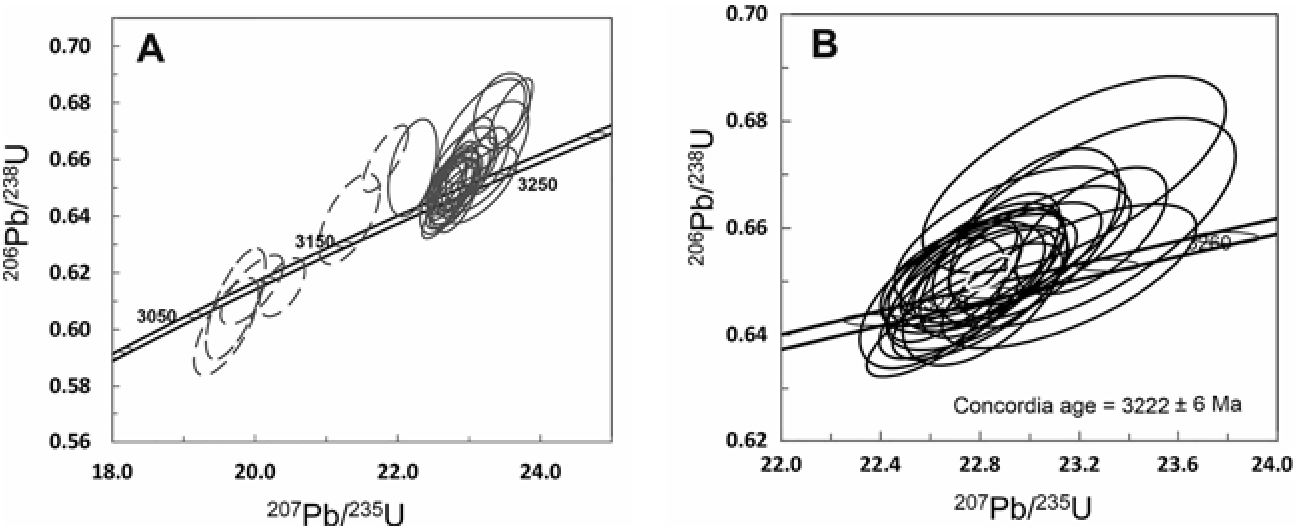

Fig. 7. U-Pb diagram for concordant zircon from metaandesite of the Chortomlyk Formation (sample 85-335, drill hole 088, depth 158.0–160.9 m). A – all obtained data. Dashed ellipses indicate results obtained for big brown zircon grains; B – concordant data from the small, colourless population

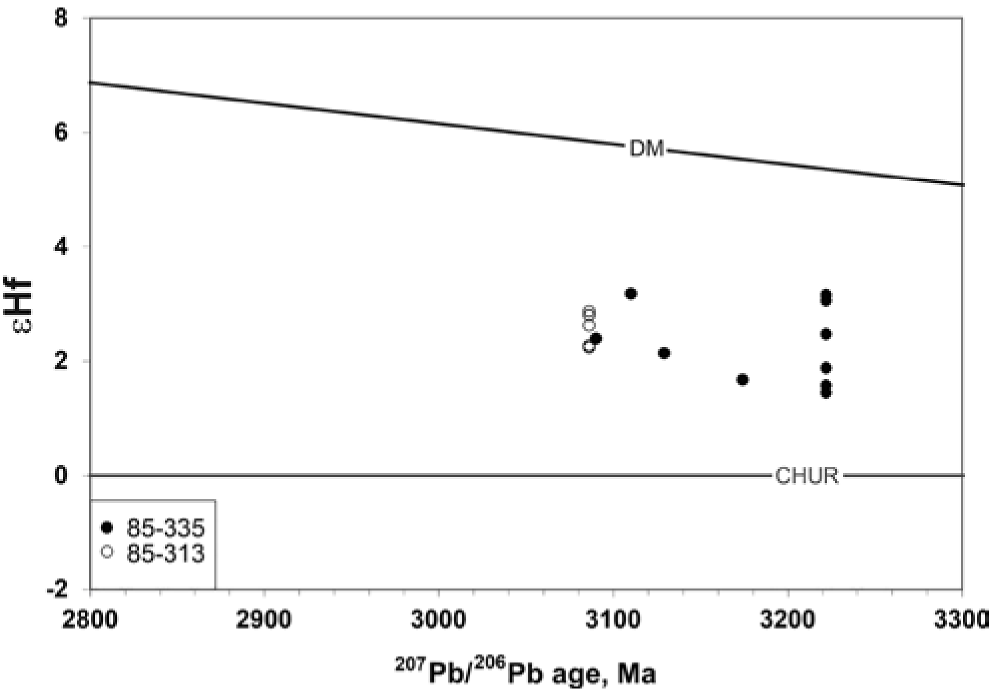

Fig. 8. Hafnium isotope composition in the studied samples of metaandesite (sample 85-335, drill hole 088, depth 158.0–160.9 m) and rhyodacite (sample 85-313, drill hole 090, depth 65–97 m)

Low-alkaline metarhyodacite (sample 85-313) was collected from a hypabyssal body intruding the sedimentary-volcanogenic rocks of the Sura Formation (Oleksiivka tectonic wedge, Dh. 090, depth 65–97 m) (see Fig. 1, 3). The texture is porphyritic and the phenocrysts are represented by quartz and plagioclase (Fig. 9). The groundmass is fine-grained and composed of quartz, plagioclase, biotite, muscovite, opaque minerals, apatite and zircon.

In terms of chemical composition, this rock belongs to the sodium series (Na_2O/K_2O = 4.0) (Bogatikov, Gonshakova, 1987) (see Table 1). It is highly magnesian, Mg# = 0.48. REEs are differentiated with (La/Yb)N = 16.2, and a positive europium anomaly is observed with Eu/Eu* = 1.21 (see Fig. 5). The rock is poor in Nb (6.7 ppm) and Y (10.8 ppm), has moderate concentrations of Ni (38 ppm) and Cr (93 ppm), and relatively rich in Cu (102 ppm) and Zn (24.5 ppm) (see Table 2).

Table 4. Results of Hf isotope composition studies of zircon from volcanic and intrusive hypabyssal rocks, Chortomlyk greenstone structure

#	Age, Ma	$^{176}Hf/^{177}Hf$	±1σ	$^{176}Lu/^{177}Hf$	±1σ	$^{176}Yb/^{177}Hf$	$^{176}Hf/^{177}Hf_T$	εHf_T	±2 σ	T(DM), Ma	$T(DM)^c_{felsic}$, Ma	$T(DM)^c_{mafic}$, Ma
Sample 85-335, metamorphosed andesite, drill hole 088, depth 158–160.9 m												
1	3129	0.280875	0.000007	0.001089	0.000013	0.029739	0.280824	2.1	0.5	3286	3348	3507
2	3174	0.280915	0.000015	0.002425	0.000140	0.080789	0.280781	1.7	1.2	3349	3409	3580
3	3222	0.280849	0.000012	0.001752	0.000032	0.049454	0.280755	1.9	0.9	3379	3438	3595
4	3222	0.280857	0.000009	0.002012	0.000044	0.058114	0.280746	1.6	0.7	3392	3454	3623
5	3222	0.280849	0.000009	0.001483	0.000014	0.045045	0.280771	2.5	0.6	3356	3406	3541
6	3222	0.280839	0.000009	0.001782	0.000025	0.050279	0.280743	1.5	0.6	3396	3460	3634
7	3222	0.280859	0.000011	0.001373	0.000023	0.037976	0.280788	3.1	0.8	3333	3376	3488
8	3222	0.280902	0.000010	0.002019	0.000041	0.057164	0.280790	3.2	0.7	3331	3370	3479
9	3090	0.280904	0.000009	0.001024	0.000043	0.027937	0.280857	2.4	0.7	3242	3302	3457
10	3110	0.280887	0.000007	0.000585	0.000005	0.015605	0.280866	3.2	0.5	3229	3277	3399
Sample 85-313, metamorphosed low-alkaline rhyodacite from the hypabyssal intrusion, drill hole 090, depth 65–97 m												
1	3086	0.280907	0.000008	0.000842	0.000015	0.022289	0.280871	2.8	0.6	3223	3277	3417
2	3086	0.280894	0.000009	0.000871	0.000012	0.024867	0.280856	2.3	0.7	3243	3305	3465
3	3086	0.280875	0.000008	0.000558	0.000007	0.015187	0.280856	2.3	0.6	3242	3306	3466
4	3086	0.280893	0.000008	0.000870	0.000013	0.023537	0.280855	2.2	0.6	3244	3307	3468
5	3086	0.280896	0.000008	0.000651	0.000013	0.017274	0.280871	2.8	0.6	3222	3277	3417
6	3086	0.280885	0.000008	0.000437	0.000011	0.011353	0.280873	2.9	0.6	3219	3274	3411
7	3086	0.280892	0.000008	0.000682	0.000009	0.019005	0.280866	2.6	0.6	3229	3287	3433

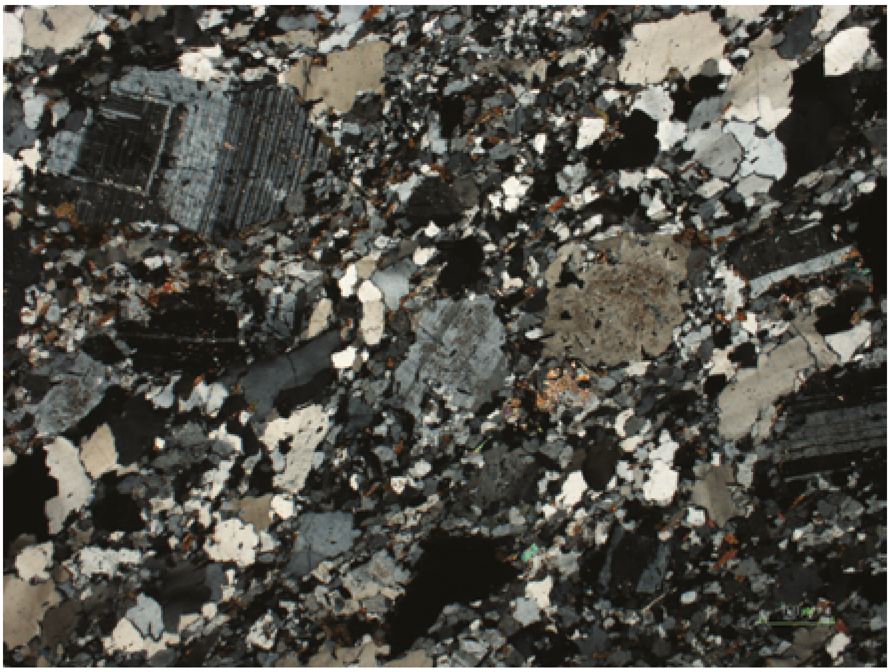

Fig. 9. Photomicrograph of metamorphosed low-alkaline rhyodacite from hypabyssal intrusion (Oleksiivka tectonic wedge, drill hole 090, depth 65–97 m, sample 85-313). Images are taken using a ECLIPSE LV100 POL polarizing microscope with crossed analysers

Fig. 10. An optical image of the studied zircon crystals from the metamorphosed low-alkaline rhyodacite (Chortomlyk greenstone belt, Oleksiivka tectonic wedge, drill hole 090, depth 65–97 m, sample 85-313) with location of U-Pb analytical spots indicated (see Table 3)

Zircon forms short-prismatic crystals with poorly defined facets. They are light brown and transparent to semi-transparent and zoned. In terms of their appearance, they resemble zircon of the second population, described in the previous sample. The zircon contains apatite inclusions (Fig. 10).

A total of 27 zircon crystals were analysed, eight of them were analysed in two spots (see Table 3). An upper intercept isochron age of (3086 ± 6) Ma was calculated for this sample (Fig. 11). The weighted mean $^{207}Pb/^{206}Pb$ age for these results is (3087.9 ± 3.9) Ma. Hafnium isotope composition was measured in 7 spots, all of which yielded positive εHf values of 2.8 to 2.2 (see Table 4).

Discussion of the results and conclusions

Results of the U-Pb dating and Hf isotope measurements in zircon from the rocks of the Chortomlyk Formation shed new light on the evolution of greenstone magmatism in the Middle-Dnieper Domain of the Ukrainian Shield. Geochronological studies of metaandesite of the Chortomlyk Formation of the Konka Group and hypabyssal intrusions of quartz-plagioclase porphyry (rhyodacite) of TTG of the Sura Complex were carried out. The prevailing zircon population in the metaandesite of Chortomlyk Formation (sample 85-335 is represented by relatively small transparent colourless crystals. This population yielded a concordant age of (3222 ± 6) Ma. This is the oldest age so far obtained for the rocks comprising the greenstone belts in the Middle Dnieper Domain. This age is older than those obtained for the TTG gneisses ((3196 ± 13) Ma and (3079 ± 9) Ma) and amphibolites ((3181 ± 5) Ma and (3078 ± 17) Ma) of the Auly Group (Samsonov et al., 1996) which comprises the basement to the greenstone belts. An age identical within age uncertainty of (3227 ± 9) Ma was obtained for tonalite of the Dnipro Complex that intrudes supracrustal rocks of the Auly Group (Bobrov et al., 2008).

The second zircon population in the metaandesite comprises relatively rare large, brown, opaque zircon crystals that resemble those found in hypabyssal intrusions cutting through the rocks of the Konka Group (sample 85-313). Zircon of this population are younger and yielded an age of 3132–3073 Ma. The concordia age of the three youngest results is (3082 ± 10) Ma. The interpretation of the ages obtained in this sample is not straightforward and at least two options can be proposed:

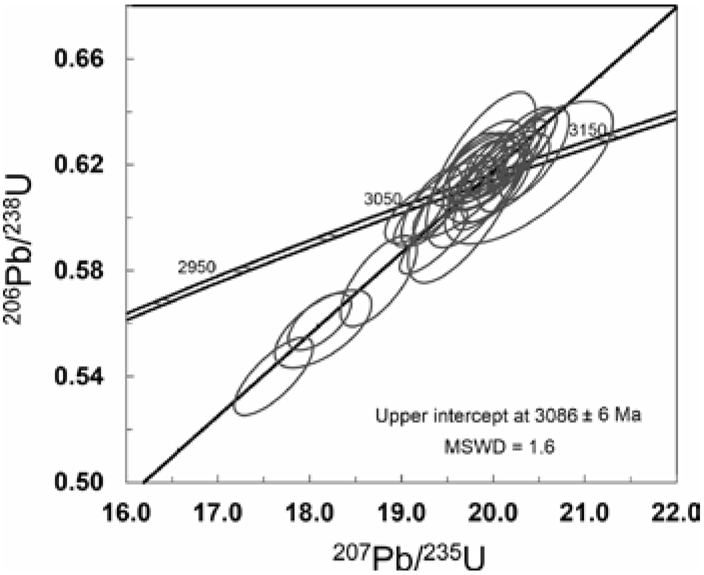

Fig. 11. U-Pb diagram for zircon from the metamorphosed low-alkaline rhyodacite hypabyssal intrusion (Chortomlyk greenstone structure, Oleksiivka tectonic wedge, Dh. 090, depth 65–97 m, sample 85-313)

1. The studied metaandesites are differentiated mafic magmas and the age of their formation is determined by dating the older zircon population and the younger population corresponds to the time of superimposed thermal processes during the intrusion of later plagioclase granitoids of the Novomykolaivka massif.
2. The age of the metaandesite is defined by the younger population, while the older population is inherited from the protolith. We consider the second option as being far more likely. In this case, the age of the metaandesite can be defined as (3082 ± 10) Ma. The first option contradicts the stratigraphic position of the dated rock.

Two models of the formation of andesites and felsic volcanics of the Chortomlyk Formation have been proposed. Lobach-Zhuchenko and Malyuk (1988) believed that magmas of the andesite-basalt, andesite, and possibly dacite composition of the Chortomlyk Formation could have formed as a result of differentiation of tholeiitic magmas according to the Bowen's trend. Another model was presented by Malyuk and Sivoronov (1990) according to which andesites and felsic volcanic rocks of the Chortomlyk Formation could have formed as a result melting of the basement of the greenstone structure during the heating of the upper crust up to 800–900 ^{o}C. Our data indicate the origin of andesites of the Chortomlyk Formation due to the melting of the older crust.

The age of zircon from the rhyodacite hypabyssal intrusion is 3085 ± 6 Ma, well in the range of ages defined for igneous rocks composing greenstone belts in the Middle Dnieper Domain by other researchers (Shcherbak et al., 1987, 1989; Zhuravlev et al., 1987; Samsonov et al., 1993; Artemenko et al., 2023). It is also in good agreement with our preferred age of the metaandesite. In terms of chemical composition, the rhyodacite is similar to rocks of the TTG association of the Sura Complex. Their primary melts could have formed as a result of partial melting of a metamorphosed mafic precursor with residual garnet and/or amphibole (Samsonov et al., 1993).

The hafnium isotope composition in zircon from both samples reveals their juvenile nature, i.e., they crystallized from the melts produced by partial melting of rocks with short crustal residence times. Our isotope data agrees with the neodymium isotope composition of the metavolcanic rocks of the Sura greenstone belt, which yielded εHf values of +1.8. These values are below the depleted mantle isotope composition at this time (3200–3000 Ma).

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Андезити та кислі вулканічні породи спостерігаються на всіх стратиграфічних рівнях конкської та білозерської серій, які складають зеленокам'яні структури Середньопридніпровського домену. Їх природа та ізотопний вік досліджені ще дуже слабо. Наймолодші кислі вулканічні породи солонівської світи конкської серії та гіпабісальні інтрузії, комагматичні до тоналіт-тронд'еміт-гранодіоритової (ТТГ) асоціації сурського комплексу за датуваннями циркону методом SHRIMP мають вік 3,1 млрд років. Метою цього дослідження є визначення U-Pb віку за цирконом та геохімічних особливостей і метаморфізованих андезитів чортомлицької світи та її метаморфізованих низькокалужних ріодацитів гіпабісальних інтрузій, які проривають породи сурської світи конкської серії у Чортомлицькому зеленокам'яному поясі. У цій структурі потужність вулканогенних порід чортомлицької світи (дацит-андезит-толеїтова асоціація) досягає 2000 м. Наймолодші кислі вулканіти солонівської світи та комагматичні до них гіпабісальні інтрузії розміщені тут у межах трьох великих вулканічних полів, розташованих по периферії Новомиколаївського* масиву. Методом LA-ICP-MS визначено ізотопний вік двох популяцій циркону з метаморфізованих андезитів чортомлицької світи. За 23 кристалами прозорого безбарвного циркону першої популяції отримано U-Pb вік (3222 ± 6) млн років. U-Pb вік другої популяції великих, коричневих, непрозорих кристалів циркону сягає 3132–3073 млн років. Інтерпретація отриманих значень віку не є однозначною і можна запропонувати принаймні два її варіанти: 1) досліджувані метаандезити є диференціатами мафітової магми і вік їх утворення визначається датуванням давньої популяції циркону, а молода популяція відповідає часу накладених теплових процесів під час інтрузії пізніших плагіогранітоїдів Новомиколаївського масиву, та 2) вік метаандезиту визначається молодою популяцією, а древня – є успадкованою від протоліту. Ми вважаємо, що другий варіант є більш ймовірним. Перший варіант суперечить стратиграфічному положенню датованої породи. Досліджені метаандезити чортомлицької світи є низькокалієвими і належать до натрієвої серії. Відносно ТТГ в них підвищений вміст Nb (16,2 ppm) і Y (25,9 ppm). Рідкісноземельні елементи слабодиференційовані – $(La/Yb)_N$ = 3,91 з глибокою негативною європієвою аномалією – Eu/Eu* = 0,44. Вік циркону з низькокалужного ріодациту з гіпабісальної інтрузії, який прориває сурську світу конкської серії (Олексіївська тектонічна луска), становить (3085 ± 6) млн років. Низькокалужні ріодацити характеризуються сильно диференційованими РЗЕ – $(La/Yb)_N$ = 16,2 та позитивною європієвою аномалією – Eu/Eu* = 1,21. В них низький вміст Nb (6,7 ppm) і Y (10,8 ppm). За геохімічними характеристиками вони аналогічні до порід ТТГ сурського комплексу. Згідно з отриманими даними, андезити чортомлицької світи конкської серії та низькокалужні ріодацити гіпабісальних інтрузій мають однаковий U-Pb вік за цирконом, але різний генезис. Перші виплавились з більш давніх корових порід, а другі – утворились при частковому плавленні метабазитів з реститом, що включав гранат. Ізотопний склад гафнію в цирконі обох досліджуваних зразків свідчить про їх ювенільну природу, тобто вони кристалізувалися з розплавів, утворених в результаті часткового плавлення порід з коротким часом перебування у корі. Наші ізотопні дані узгоджуються з ізотопним складом неодиму кислих вулканічних порід Сурського зеленокам'яного поясу, який дав значення ε Hf +1,8. Ці значення далекі від модельного ізотопного складу збідненої мантії цього віку (3200–3000 млн років).

**Новомиколаївський масив раніше був відомий як Чкалівський масив.*

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