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Discovery of metamorphosed Devonian volcanic rocks in the Prypyat-Dnieper-Donets Rift

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ABSTRACT:

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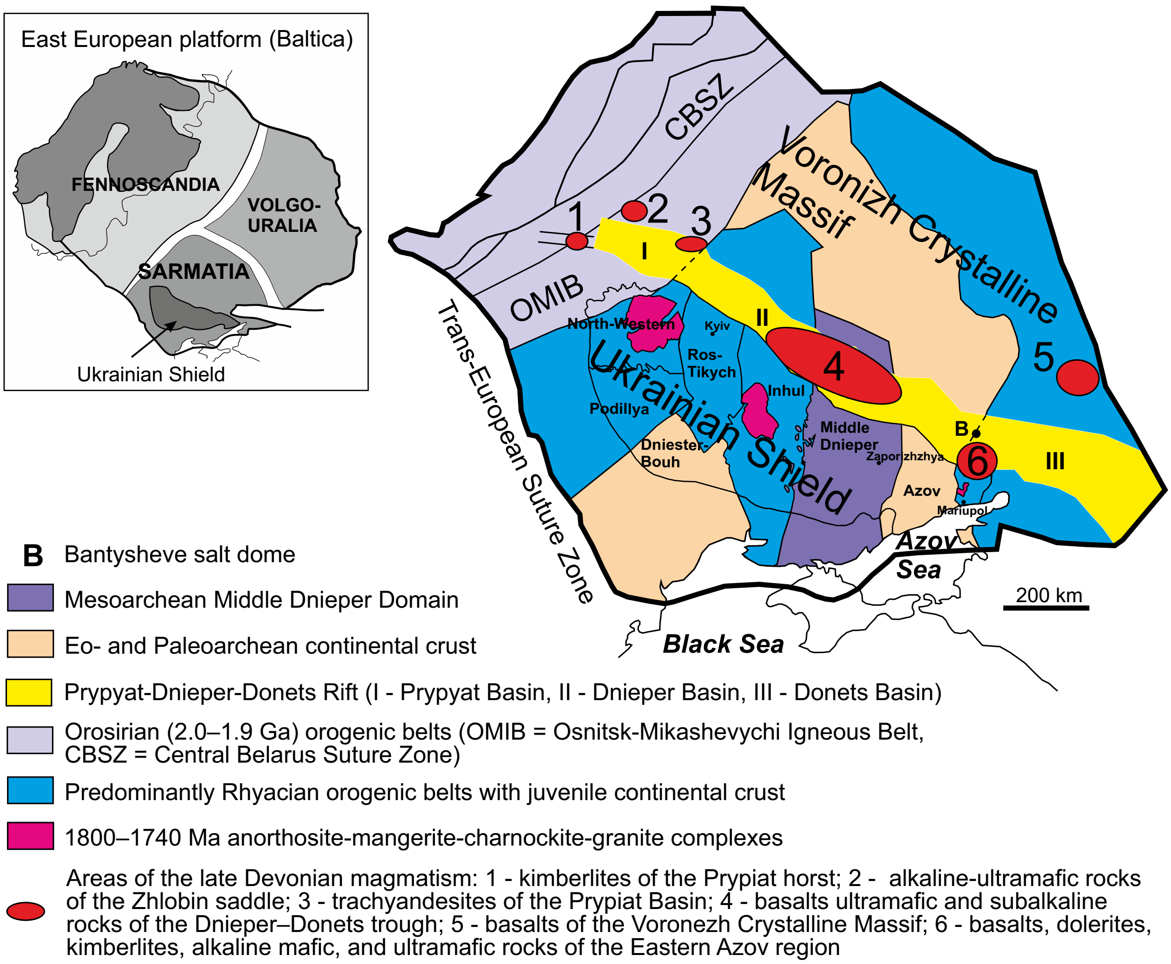
The Late Devonian Prypyat-Dnieper-Donets Rift is a significant tectonic structure on the East European platform. Devonian salt domes are extensively developed within the Rift and create a system of associated traps, which often accommodate oil and gas fields. Associated with these salt domes hydrothermal deposits and occurrences of mercury and base metals are also found in the south-eastern part of the Rift, near the Donets inversion-folded structure. Diapiric breccias (cap rocks) frequently contain fragments of various rocks, which remain poorly studied. The authors examined a fragment of metamorphosed mafic rock collected from a cap rock of the Bantysheve salt dome, situated in north-western Donbas, at the transition zone to the Dnieper Basin. The rock was identified as hornblende schist, metamorphosed at a relatively high temperature of 775–730°C and low pressure of 1.4–1.0 kBar, corresponding to the hornfels facies of metamorphism. The U-Pb age of the metamorphic crystallisation of titanite from the schist was determined at 370 ± 17 Ma. This age matches the magmatism in the Prypyat-Dnieper-Donets Rift. Data obtained suggest that the most probable protolith for the studied schist is the Late Devonian picritic basalt or picritic dolerite, which is associated with the development of the Rift.

Key words: Prypyat-Dnieper-Donets Rift; Salt dome; Diapiric breccia; U-Pb age; Titanite; Hornblende schist.

INTRODUCTION

The Prypyat-Dnieper-Donets Rift is a more than 1000 km long tectonic structure that extends from northwest to southeast, separating the Voronizh crystalline massif from the Ukrainian Shield and dividing the Sarmatian segment of the East European Platform approximately in half (Text-fig. 1). Within the Rift, three main segments are distinguished: the Prypyat, Dnieper, and Donets basins, which vary in the amount and composition of sedimentary and igneous rocks, as well as in the degree of deformation (Chalot-Prat *et al.* 2007; de Boorder *et al.* 1996; Wilson and Lyashkevich 1996; Kusznir *et al.* 1996; Stephenson *et al.* 2006). The boundaries between these segments coincide with the boundaries between the main crustal blocks that form the basement for the rift and extend beneath it from the Ukrainian Shield to the Voronizh Massif.

According to Wilson and Lyashkevich (1996), alkaline-ultramafic and mafic magmatism associated with the initiation and development of the rift occurred alongside the emplacement of the mantle plume during the Late Frasnian time, while regional uplift began earlier, in the Middle Frasnian.



Text-fig. 1. Schematic map of Sarmatia according to Shumlyanskyy *et al.* (2021c) showing the position of the Prypyat-Dnieper-Donets Rift and associated magmatism.

Devonian igneous rocks are common within the rift and in adjacent areas, such as the Azov Domain of the Ukrainian Shield, the Voronizh crystalline massif, and the Prypyat horst (Korzun and Makhnach 1977; Buturlinov 1979; Mikhailov *et al*. 2011; Sheremet *et al*. 2015; Yutkina *et al*. 2017; Sazonova *et al*. 2019; Shumlyanskyy *et al*. 2021a, c).

In the Prypyat-Dnieper-Donets Rift, Devonian salt domes (cryptodiapirs and diapirs) are extensively developed (e.g., Kityk 1970; Stovba 2005). Oil and gas fields are primarily associated with them, and in the southeastern part of the Rift, near the Donets inversion-folded structure, salt-dome structures host deposits and occurrences of mercury and base metals (Kyrykylytsya and Laskov 1970; Shumlyanskyy and Bezuhla 1995; Fedorchuk 1984).

The oldest rocks of the salt dome structures are clastic, evaporitic, and effusive formations of Middle and, partly, Late Devonian age. Deep boreholes have recovered them as rock salt stocks or as fragments and blocks in diapiric tectonic breccias that surround the stocks or form their cap rocks. In some locations, fragments of volcanic rocks are found directly within the salt. In the Adamivka stock (Sloviansk anticline) area, a borehole recovered a block approximately 50 m thick of slightly altered diabase. Similar fragments and blocks have also been observed in the Bantysheve, Kurulka, Petrivske, Bilyaivka, Stepok, and other anticlines (Kyrykylytsya and Laskov 1970; Shumlyanskyy and Bezuhla 1995).

The volcanic rocks composing the fragments and blocks include diabase, basalt, trachydolerite, and porphyrite. They are typically grey and show signs of hydrothermal alteration, characterised by albitization, propylitization, and carbonatization. In addition to volcanic rocks, two large fragments of granitoids were described in the diapiric breccia of the Sloviansk structure (Fedorchuk 1984). Limestones with a Givetian fauna were also discovered (Kyrykylytsya and Laskov 1970).

In this paper, we explore the geochronology and petrology of a previously unreported metamorphic rock fragment. Determining the origin of these rocks is crucial for understanding the ore-forming processes associated with salt-dome structures and the formation and evolution of these structures.

RESEARCH METHODS

Titanite was extracted from the sample at the M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation, Kyiv, Ukraine, using standard separation methods, including a shaking table, heavy liquids, and a magnetic separator. The titanite U-Pb isotopic age was determined at Trinity College Dublin Isotope Laboratory, Dublin, Ireland. The laser ablation system used was a Photon Machines Analyte Excite 193 nm ArF laser system, equipped with a 2-volume HelEx ablation cell, and connected to an Agilent 7900 mass spectrometer. The laser beam size was set at 36 µm. The analytical results were processed using the IOLITE package (Paton *et al.* 2011) with the VizualAge UcomPbine data reduction scheme (Chew *et al.* 2014), which can account for variations in total Pb in a standard sample.

The chemical analysis for major oxides and trace elements was performed using ICP-MS at Bureau Veritas Commodities Canada Ltd's commercial laboratory (https://www.bvna.com). Electron microprobe analyses, as well as backscattered electron and secondary electron images, were produced using the ZEISS Ultra Plus Scanning Electron Microscope at the GFZ Helmholtz Centre for Geosciences, Potsdam, Germany. The acceleration voltage was set at 15 kV.

The parameters of amphibole crystallisation were calculated using MagMin_PT Excel macros (Gündüz and Asan 2023), and whole-rock spidergrams were plotted with PetroGram Excel macros (Gündüz and Asan 2021).

RESULTS

Petrography

The Bantysheve anticline (dome) is situated on the northwestern edge of the Donets Basin, near its transition to the Dnieper Basin (Text-fig. 1). It forms part of a chain of anticline structures that extends from the Holovna (Main) and Druzhkivka-Kostyantynivka anticlines of the Donbas towards the northwest (Belous and Kyrykylytsya 1975). The dome is elongated towards the northwest, with an azimuth of 320–330°. Its length along the cap rock breccia is about 2800 m, and its width varies from 900 to 1100 m. The formation of the salt dome began in the Early Permian, with salt mass movement continuing into the Neogene (Belous and Kyrykylytsya 1975). Within the Bantysheve mercury-base metal occurrence, a fragment of rock initially described as diabase was collected from borehole No. 9365 at a depth of 694 m, originating from the cap rock diapir breccia. The breccia contained mercury mineralisation.

During microscopic studies, the rock was identified as a hornblende schist. It has a fine-grained, uniform to slightly uneven-grained nematoblastic texture and schistose structure. The mineral composition is as follows (wt. %): hornblende – 80, quartz – up to 5–6, sulphides – up to 8, titanite – up to 2, plagioclase – 2, carbonate – 2, biotite – single crystals.

The rock consists of an aggregate of small (0.1–0.2 mm) short prismatic crystals of hornblende, which are pleochroic, ranging from yellow-green to grass-green. In places rather large (up to 1–1.5 mm) prismatic crystals of hornblende occur; these are partially fragmented and replaced by crystals of the same mineral. Small (0.05–0.1 mm) isometric crystals of opaque minerals and titanite, as well as larger (0.2–0.3 mm) rounded crystals of quartz, carbonate, and plagioclase, are found between hornblende grains. Biotite in the sample appears as a single crystal with intense pleochroism in brown shades.

Mineral chemistry

Amphibole, the most abundant mineral in the studied rock, is a magnesian-iron hornblende with impurities of Na, K, and Ti (Table 1).

Spot #	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O
02–01	46.42	1.31	8.54	16.72	13.20	11.61	1.39	0.80
01–13	47.28	1.04	8.79	15.80	12.52	12.29	1.67	0.60
03–09	46.88	1.15	7.41	16.75	13.26	12.25	1.12	0.58

Table 1. Amphibole chemical composition, wt. %.

Spot #	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	Ab	An
02–13	60.45	0.45	24.78	n.d.	6.76	7.56	66.9	33.1
02-17	59.30	n.d.	24.79	0.81	6.76	7.81	67.6	32.4
01–12	64.46	n.d.	22.45	n.d.	3.57	9.52	82.8	17.2
01–14	67.19	0.26	20.37	n.d.	0.83	11.35	96.1	3.9
03–04	62.06	0.33	24.94	n.d.	4.52	8.14	76.5	23.5

Table 2. Plagioclase chemical composition, wt. %.

Spot #	S	Fe	Ni	Si
02–14	63.84	35.74	n.d.	0.42
02–15	65.42	31.25	3.33	n.d.
02–16	64.98	35.02	n.d.	n.d.
01–15	65.24	34.34	n.d.	0.42
03–08	64.85	34.91	n.d.	0.24
04–04	64.63	35.16	n.d.	0.21
04–05	64.80	34.82	n.d.	0.38
04–08	65.63	34.09	n.d.	0.28
04–10	65.22	34.78	n.d.	n.d.
04–11	64.68	35.32	n.d.	n.d.
04–12	65.16	33.21	1.63	n.d.
04–13	64.70	35.30	n.d.	n.d.
04–14	66.30	31.02	2.68	n.d.

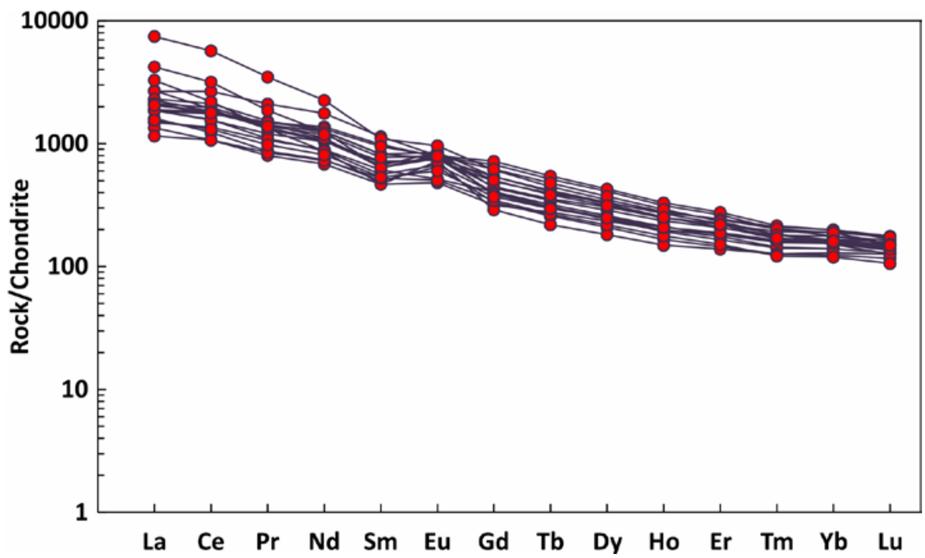
Table 3. Pyrite chemical composition, at. %.

The composition of plagioclase ranges from $An_{33}Ab_{67}$ to An_4Ab_{96} (Table 2), with a predominance of calcium-rich plagioclase. It contains noticeable impurities of Ti and occasionally Fe. Pyrite is the only sulphide mineral in the rock. It contains small impurities of Si (Table 3), while Ni content varies from 1.6 to 3.3 at. %; these elements were detected in a limited number of analysed crystals. Titanite is characterised by a noticeable (0.6–1.9 wt. %) impurity of Al and sporadic impurities of Fe, S, and Mg (Table 4).

The trace element composition of titanite is provided in Table 5. Titanites contain significant amounts of all measured trace elements, namely P – 255–1950 ppm, V – 2050–4270 ppm, Mn – 915–213 ppm, Sr – 72–405 ppm, Y – 235–450 ppm, Zr – 520–6795 ppm, and the total of REEs – 1655–7195 ppm. Meanwhile, the levels of radioactive elements are relatively low: Th – 7–72 ppm (with isolated anomalous values reach-

Spot #	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SO_3
02–02	31.42	37.78	1.40	1.39	0.17	27.83	n.d.
02–03	31.04	38.71	1.36	0.77	n.d.	28.13	n.d.
02–04	30.76	40.18	0.98	n.d.	n.d.	28.08	n.d.
02–05	31.44	38.95	1.47	n.d.	n.d.	28.14	n.d.
02–06	30.28	38.23	1.65	1.35	n.d.	27.67	n.d.
02–07	31.09	40.21	0.85	n.d.	n.d.	27.85	n.d.
02–08	31.34	40.39	0.86	n.d.	n.d.	27.41	n.d.
02–09	31.19	40.03	1.14	n.d.	n.d.	27.65	n.d.
02–10	31.25	40.23	0.81	n.d.	n.d.	27.70	n.d.
02–11	31.19	40.32	0.73	n.d.	n.d.	27.76	n.d.
02–12	30.92	39.85	0.91	n.d.	n.d.	28.32	n.d.
01–01	30.87	41.07	0.73	n.d.	n.d.	27.33	n.d.
01–02	30.88	40.09	1.24	n.d.	n.d.	27.78	n.d.
01–03	31.09	40.10	0.70	n.d.	n.d.	28.11	n.d.
01–04	31.35	40.14	0.71	n.d.	n.d.	27.80	n.d.
01–05	30.79	41.27	0.83	n.d.	0.02	27.09	n.d.
01–06	30.56	41.07	0.60	n.d.	n.d.	27.77	n.d.
01–08	31.16	40.27	1.02	n.d.	n.d.	27.55	n.d.
01–09	30.82	39.89	1.05	n.d.	n.d.	28.24	n.d.
01–10	31.35	40.01	1.11	n.d.	n.d.	27.53	n.d.
03–01	31.58	38.86	1.35	n.d.	n.d.	28.21	n.d.
03–02	31.37	39.50	1.94	n.d.	n.d.	27.19	n.d.
03–03	31.16	38.51	1.44	0.97	n.d.	27.92	n.d.
03–06	30.70	39.89	0.73	n.d.	n.d.	27.86	0.82
03–07	31.05	40.69	0.66	n.d.	n.d.	27.59	n.d.
03–10	31.37	38.16	1.24	1.22	n.d.	28.01	n.d.
04–02	32.20	38.80	1.54	n.d.	n.d.	27.45	n.d.
04–03	31.72	39.65	0.91	n.d.	n.d.	27.72	n.d.
04–06	31.28	40.16	1.24	n.d.	n.d.	27.33	n.d.
04–07	31.19	40.18	0.87	n.d.	n.d.	27.75	n.d.
04–09	30.03	41.48	0.78	n.d.	n.d.	27.03	0.68

Table 4. Titanite chemical composition, wt. %.



Text-fig. 2. Chondrite-normalised plot of REE in titanite from hornblende schist.

Spot #	P	V	Mn	Sr	Y	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U	Pb
1	1124	2301	1018	173	368	1210	498.9	1099.6	135.7	580.3	125.4	49.5	110.8	15.6	84.7	15.2	37.0	4.7	28.0	3.7	40	63	3.4
2	1220	3032	1000	148	346	687	640.3	1168.8	125.2	488.4	101.4	49.5	89.7	12.9	73.0	13.3	34.3	4.6	30.0	4.1	39	86	3.6
3	588	2589	914	190	413	670	443.1	950.4	114.1	484.6	110.2	42.6	101.3	14.7	83.9	15.6	40.4	5.3	33.9	4.5	40	50	3.1
4	1262	2049	935	156	443	716	441.4	1065.1	141.9	638.0	150.6	45.4	138.6	19.3	104.5	17.7	43.6	5.1	30.1	3.9	48	42	3.2
5	1256	2137	915	153	451	6793	632.3	1630.5	199.8	825.7	174.4	46.0	148.2	20.4	109.2	18.7	45.8	5.5	33.7	4.3	243	81	6.7
6	409	2553	970	141	305	1046	354.1	830.4	101.8	417.5	93.5	29.8	83.3	11.9	65.7	11.9	30.1	4.0	26.1	3.5	35	36	3.0
7	255	2895	986	154	303	622	318.2	655.2	76.3	319.4	71.4	28.0	65.0	10.4	59.7	11.2	30.8	4.2	28.3	4.0	34	38	2.8
8	1364	2687	999	176	367	756	536.8	1113.0	127.9	504.8	106.2	43.7	92.1	13.3	77.5	14.0	36.7	4.9	32.2	4.4	49	65	3.6
9	1084	3205	1082	116	247	3134	380.8	755.0	82.6	346.4	75.9	37.5	68.8	9.6	53.1	9.4	24.1	3.2	21.0	3.0	27	88	4.2
10	596	2270	1045	118	364	1206	545.8	1293.2	145.3	586.1	125.9	43.8	110.9	15.2	82.3	14.3	34.7	4.3	25.7	3.2	36	48	3.4
11	298	2883	1076	122	290	1059	446.9	963.5	104.2	410.7	85.8	38.8	81.8	11.4	63.6	11.2	29.1	3.7	23.8	3.3	27	37	2.8
12	437	2470	989	405	288	1211	503.9	1204.3	136.8	518.4	97.8	43.9	81.6	11.4	61.6	10.9	27.4	3.6	23.7	3.3	41	43	4.6
13	1949	2763	1037	72	414	1998	1764.2	3498.9	331.0	1047.9	167.2	55.7	125.8	16.8	89.2	15.7	40.0	5.2	32.2	3.9	265	188	9.2
14	1449	4267	2133	123	233	925	779.1	1343.4	126.0	405.4	71.6	41.8	59.6	8.2	46.3	8.4	23.0	3.2	22.0	3.2	30	110	4.2
15	730	2417	1176	178	409	557	446.5	1108.1	141.0	614.2	145.0	45.6	127.0	17.8	94.3	16.4	38.7	4.6	27.0	3.5	51	43	3.5
16	295	3182	1084	121	249	712	273.2	653.6	80.6	340.0	80.0	29.1	71.0	10.0	55.3	10.0	25.0	3.1	20.3	2.7	32	26	2.9
17	724	2599	929	168	317	1063	1000.0	1940.2	177.3	578.5	97.7	46.5	79.6	11.3	63.2	11.8	31.3	4.2	27.6	3.8	72	95	4.4
18	733	2604	995	194	316	678	369.6	798.2	92.9	379.7	81.6	34.8	76.0	11.1	63.4	11.8	31.0	4.1	26.3	3.8	48	52	3.4
19	557	2182	990	236	369	521	486.7	1089.2	131.9	553.4	118.8	45.9	103.7	14.4	79.6	14.2	36.4	4.4	27.3	3.8	42	40	3.6

Table 5. Trace element composition of titanite, ppm.

ing up to 265 ppm), U – 26–88 ppm (with anomalous values up to 188 ppm). REEs are relatively poorly fractionated – the (La/Yb)N ratio ranges from 8.1 to 25.5, increasing in one instance to 39.4. Titanites exhibit a weak positive europium anomaly (Text-fig. 2).

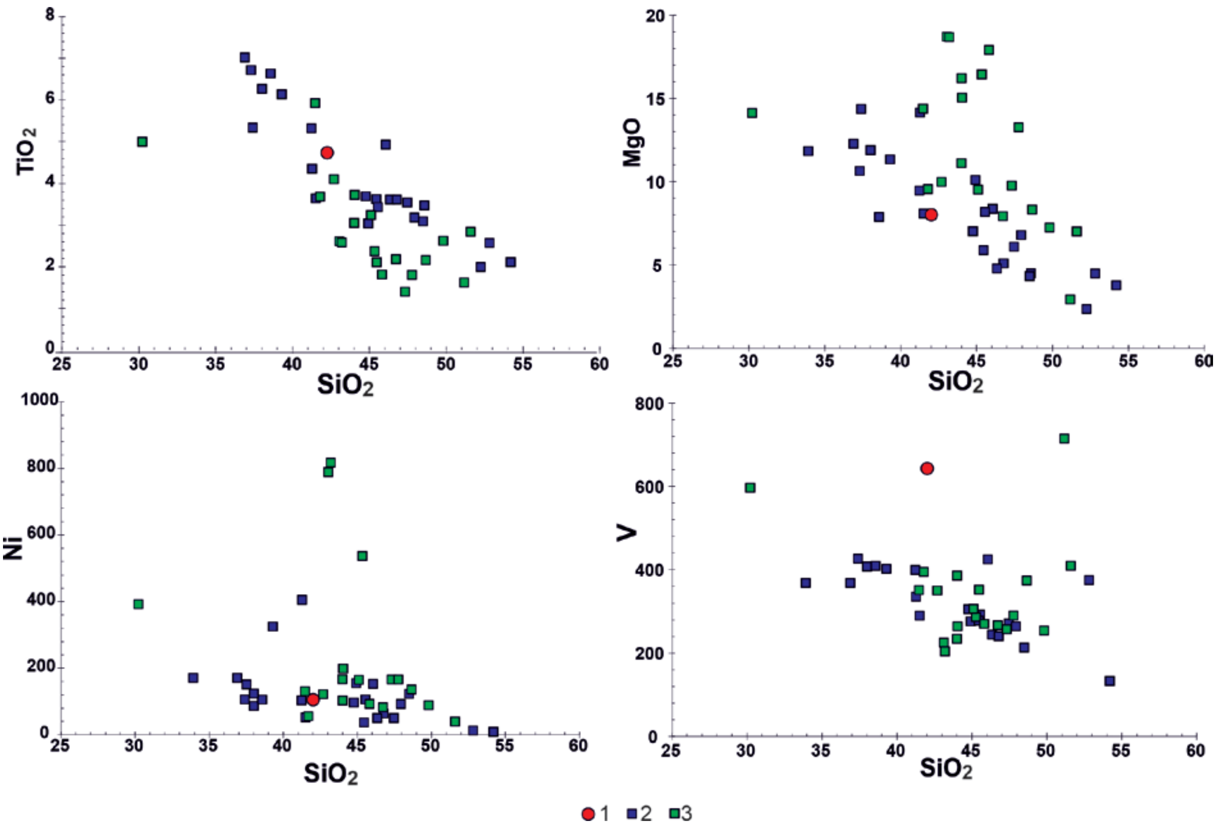
Whole-rock chemical composition of the hornblende schist

With 42.02% SiO_2 and 8.01% MgO (Table 6), the rock plots within the picritic basalt field in the classification diagrams of Cox *et al.* (1979) and LeBas *et al.* (1986). Other features include high concentrations of TiO_2 (4.66%), Fe_2O_3 (18.44%), and alkalis (Na_2O = 2.27%, K_2O = 0.55%). Consequently, the diagrams of Irvine and Baragar (1971), Winchester and Floyd (1977), and Pearce (1996) classify the studied schist as part of the alkaline basalt or alkaline series. The Ni concentration (105 ppm) is moderate, while the Cu concentration (292 ppm) is elevated, and the V concentration (643 ppm) is high. In the diagrams used to determine the tectonic setting, the hornblende schist plots within the fields of either intraplate basalts (Pearce 1982; Wood 1980) or oceanic island basalts (Pearce 2008; Hollocher 2012).

Wt. %	9365/694	ppm	9365/694	ppm	9365/694
SiO_2	42.02	Ni	105	Gd	6.4
TiO_2	4.66	V	643	Tb	0.97
Al_2O_3	10.08	Sc	41	Dy	4.85
Fe_2O_3	18.44	Cu	292	Ho	0.84
MnO	0.17	Zn	39	Er	2.12
MgO	8.01	Sr	430	Tm	0.30
CaO	11.08	Rb	5.8	Yb	1.53
Na_2O	2.27	Ba	103	Lu	0.21
K_2O	0.55	Zr	180	U	0.6
P_2O_5	0.34	Nb	24.8	Pb	2.1
Cr_2O_3	0.04	Th	2.2	Co	73
LOI	1.90	Y	22.3	Ga	24
Total	99.63	La	22.9	Mo	0.7
C	0.22	Ce	52.2	Cs	0.2
S	0.42	Pr	7.11	Hf	5.3
		Nd	31.0	Ta	1.5
		Sm	7.2	W	0.7
		Eu	2.25	Sn	2.0

Table 6. Chemical composition of the hornblende schist.

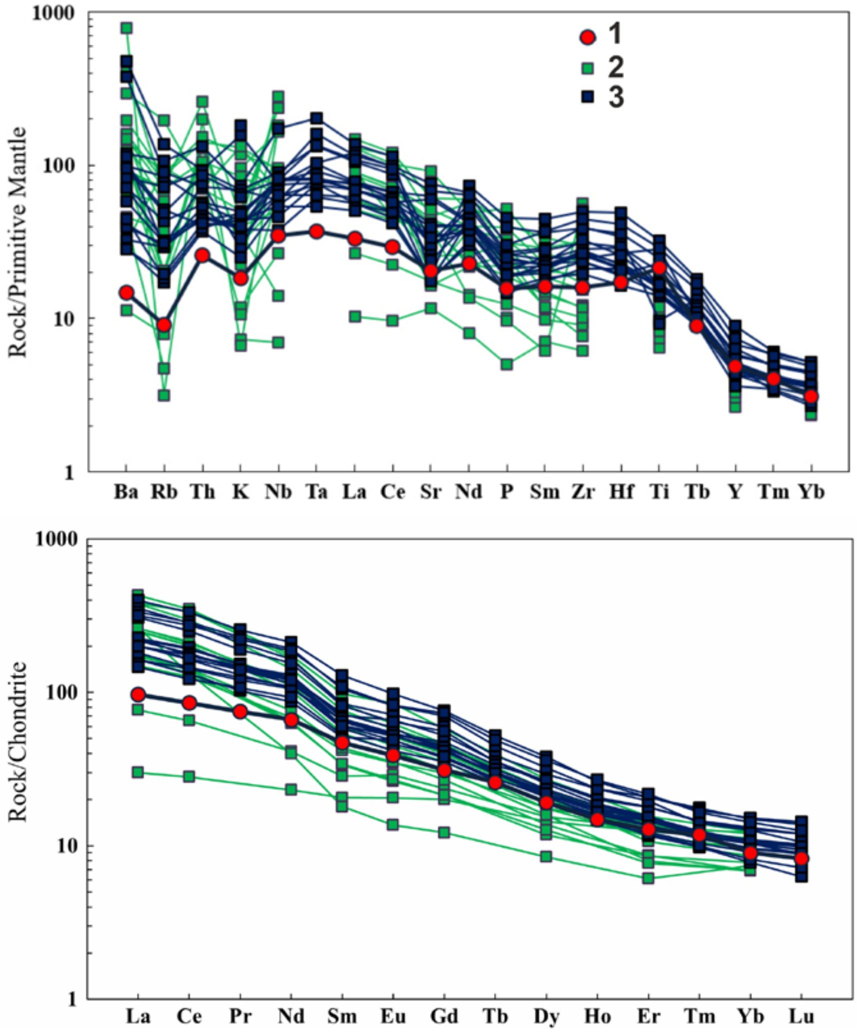
Compared with other Devonian rocks associated with the Prypyat-Dnieper-Donets Rift, the studied sample plots within the field of Devonian dykes in the Azov region of the Ukrainian Shield, as well as



Text-fig. 3. Selected plots of the chemical composition variations in mafic and ultramafic rocks related to the Prypyat-Dnieper-Donets Rift. 1 – hornblende schist; 2 – Devonian dykes of the Azov Domain of the Ukrainian Shield (Yutkina *et al*. 2017); 3 – basalts of the Dnieper-Donets basin (Wilson and Lyashkevich 1996).

Analysis #	$^{207}Pb/^{235}U$	2σ	$^{206}Pb/^{238}U$	2σ	ρ	$^{238}U/^{206}Pb$	2σ	$^{207}Pb/^{206}Pb$	2σ	ρ
1	4.7564	0.2475	0.0950	0.0021	0.07	10.5611	0.4264	0.3603	0.0117	0.47
2	3.7041	0.2644	0.0839	0.0025	0.15	11.7784	0.7142	0.3174	0.0150	0.34
3	5.8464	0.2782	0.1044	0.0037	0.72	9.6722	0.4350	0.4130	0.0175	0.12
4	6.5693	0.3920	0.1110	0.0033	0.10	9.0010	0.3422	0.4300	0.0190	0.47
5	4.0697	0.3643	0.0904	0.0042	0.54	11.2908	0.6606	0.3227	0.0152	0.87
6	7.5459	0.3993	0.1224	0.0062	0.76	8.3104	0.3838	0.4540	0.0164	0.21
7	7.1071	0.3684	0.1155	0.0030	0.22	8.7044	0.3739	0.4474	0.0167	0.43
8	4.6642	0.2582	0.0960	0.0028	0.25	10.4864	0.4762	0.3552	0.0159	0.33
9	5.2925	0.5984	0.1030	0.0046	0.72	9.8838	0.5505	0.3641	0.0267	0.87
10	8.2340	0.9801	0.1287	0.0083	0.18	7.9964	0.6698	0.4429	0.0320	0.19
11	7.7329	0.4656	0.1262	0.0033	0.03	7.9677	0.3514	0.4445	0.0190	0.52
12	10.9630	0.7328	0.1566	0.0067	0.26	6.5038	0.3912	0.5064	0.0183	0.78
13	3.9466	0.9072	0.0872	0.0068	0.90	11.8963	0.9117	0.2896	0.0417	0.96
14	3.4190	0.2862	0.0872	0.0025	0.51	11.5387	0.5205	0.2819	0.0179	0.72
15	7.0721	0.4466	0.1189	0.0073	0.42	8.4666	0.3959	0.4382	0.0205	0.87
16	10.9047	0.5628	0.1491	0.0053	0.22	6.7091	0.2806	0.5366	0.0220	0.43
17	3.3500	0.1754	0.0868	0.0018	0.03	11.5419	0.4527	0.2798	0.0097	0.52
18	5.7024	0.4196	0.1025	0.0025	0.08	9.7325	0.3614	0.4034	0.0240	0.06
19	8.2775	0.4777	0.1228	0.0041	0.02	8.1370	0.4470	0.4767	0.0171	0.66

Table 7. Results of the U-Pb dating of titanite.



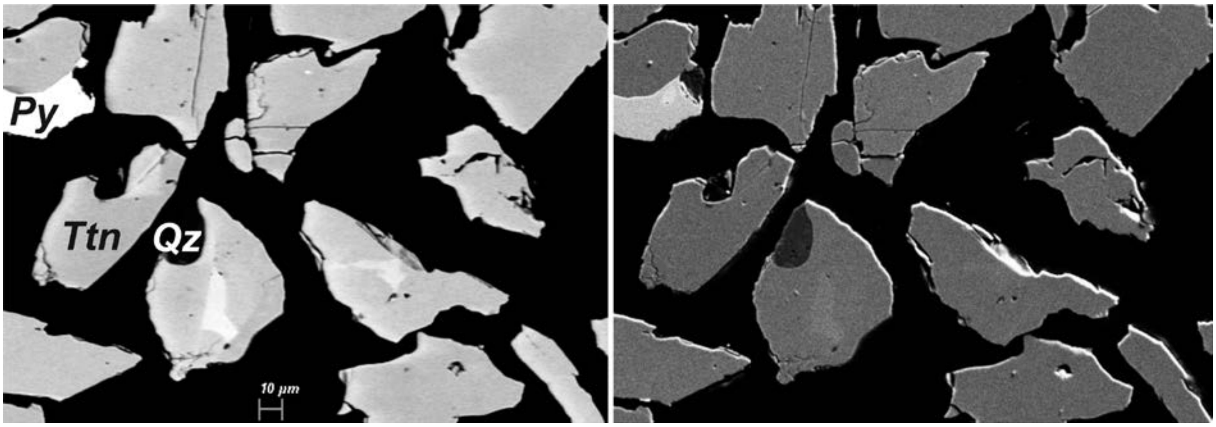
Text-fig. 4. Spidergrams of the trace element and REE composition of mafic and ultramafic rocks related to the Prypyat-Dnieper-Donets Rift. 1 – hornblende schist; 2 – Devonian dykes of the Azov Domain of the Ukrainian Shield (Yutkina *et al*. 2017); 3 – basalts of the Dnieper-Donets basin (Wilson and Lyashkevich 1996).

basalts from the Dnieper-Donets basin (Yutkina *et al.* 2017; Wilson and Lyashkevich 1996). However, the studied schist slightly differs from these rock groups by having higher V, Sc, and Cu contents and lower Zn, Rb, Ba, and REE contents (Text-fig. 3).

In the primitive mantle-normalised trace element spidergram, hornblende schist exhibits relatively low concentrations of the most incompatible elements, with negative anomalies in Rb and K (Text-fig. 4). Moderately incompatible elements form a relatively flat plateau with concentrations around 20–30 primitive mantle norms. The normalised concentrations of HREE and Y decrease sharply, being only 3–5 times higher than in the primitive mantle. The chondrite-normalised REE pattern gradually declines from 100 chondrite norms for La to 10 for Lu. There is no europium anomaly.

The comparison of the normalised graphs for the hornblende schist with those for the Devonian dykes of the Azov Domain of the Ukrainian Shield and basalts of the Dnieper-Donets Basin demonstrates a similarity in their patterns. The primary difference lies in the low content of the most incompatible trace elements in the hornblende schist compared to other rocks. Only some dolerites from the rift (including one found in the Dmytrivka salt dome; Wilson and Lyashkevich 1996) and alkaline basalts have lower trace element concentrations than the studied hornblende schist (Text-fig. 4).

The average oceanic island basalt (OIB, after Sun



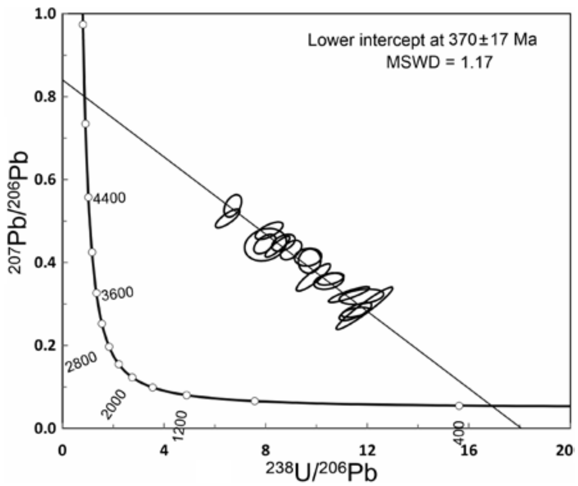
Text-fig. 5. Images of titanite crystals in backscattered (left) and secondary (right) electrons. Mineral symbols: Tnt – titanite, Qz – quartz, Py – pyrite.

and McDonough 1989) normalised patterns occur as gently inclined lines, with a slow increase from 0.1–0.3 OIB norms for the most incompatible elements to 0.7–0.8 OIB norms for the least incompatible elements (not shown). At the same time, there are weak positive anomalies of Th and Ti, and a weak negative anomaly of Rb. The OIB-normalised REE content increases slightly from 0.6 norms for light REEs to 0.8 for heavy REEs.

Isotopic age

Titanite in the studied hornblende schist forms isometric or rhombohedral crystals, mostly irregular in shape, which are found in intergrowths with other minerals. The internal structure of titanite is mainly homogeneous, although in some cases lighter areas, apparently enriched in iron, are visible in electron microscopic images (Text-fig. 5).

The results of the U-Pb isotopic dating of titanite are presented in Table 7 and Text-fig. 6. Based on the data obtained, the age of titanite is 370 ± 17 Ma, which corresponds to the time of metamorphic transformation.



Text-fig. 6. Results of the U-Pb dating of titanite from hornblende schist.

DISCUSSION

The development of the Prypyat-Dnieper-Donets Rift began in the Late Frasnian (Wilson and Lyashkevich 1996), which, according to the International Chronostratigraphic Chart (Cohen *et al*. 2013), corresponds to an age of 375–372 Ma. However, the oldest magmatic activity associated with the formation of the rift is represented by kimberlites located in the junction zone of the Donets Basin and Azov Domain of the Ukrainian Shield. These rocks were dated at 383–384 Ma (Yutkina *et al*. 2004; Shumlyanskyy *et al*. 2021a). The kimberlites, in turn, are overlain by the alkaline mafic volcanic rocks of the Middle to Late Devonian Antonivka Formation. Signs of volcanic activity in the Dnieper Basin as early as the Middle Devonian were also observed by Lyashkevych (1987).

Using the K-Ar method, the Prypyat-Dnieper-Donets Rift volcanic rocks were extensively dated in the 1950s to 1970s. The results were summarised by Lyashkevich (1987), who demonstrated that, for the lower effusive-pyroclastic section, the isotopic ages ranged from 414 to 298 Ma, while for the upper section, ages ranged from 399 to 234 Ma. Two age groups were identified among the dyke rocks: the older diabases dated between 600 and 497 Ma, and a younger group with ages varying from 408 to 220 Ma. The Ediacaran K-Ar ages (610–540 Ma) obtained for diabases in the 1950s (Usenko *et al*. 1958) were used to support the idea that the Rift development began at the same time as the formation of the Volyn continental flood basalt province (Semenenko *et al*. 1977). However, given the limitations of the analytical equipment of that period and the shortcomings of the methodology for determining K-Ar isotopic ages using bulk rock samples, these dates cannot be regarded as reliable.

The age of the Rift sediments was determined using faunal data (e.g., Manukalova-Hrebenyuk 1974; Khomenko 1986; Bilyk and Ivanyshyn 2000; Kotlyar 2008; Konstantynenko *et al*. 2013). Volcanogenic formations are confined to two main stratigraphic levels: the Frasnian complex, which developed beneath the salt formation, and the Famennian complex, which overlies the salt formation (e.g., Belyaev *et al.* 1977; Voloshyna 1977). Some researchers (e.g., Halitskyi 1977; Lyashkevich 1987) have noted that the age of the complexes gradually decreases from the Donbas to the Prypyat Basin, indicating a gradual migration of volcanism from east to west. Intrusive diabase bodies are often observed at different levels of the salt formation. According to the stratigraphic position of the volcanic rocks, their age can be defined as 375–360 Ma. Thus, the obtained titanite age of 370 ± 17 Ma is contemporaneous with the age of volcanism in the Prypyat-Dnieper-Donets Rift. However, as mentioned above, it is regarded as a metamorphic age, rather than magmatic emplacement or outpouring. This prompts several questions, which are discussed below.

Rift volcanic rocks are often extensively altered by post-magmatic (or late magmatic) processes, including carbonatization, chloritization, epidotization, albitization, and the formation of actinolite hornblende after clinopyroxene (Bernadskaya 1961; Savchenko 1977). However, amphibolization is poorly developed. According to Bernadskaya (1961), amphibole almost completely replaces clinopyroxene in exceptional cases only. Hydrothermal alteration such as propylitization, argillitization, and sometimes the development of secondary quartzites, was also observed (Savchenko 1977). All researchers noted the presence of accessory titanite. However, in the literature, we could not find evidence of the transformation of volcanic rocks into hornblende schists.

The pronounced schistosity of the studied rock indicates it has undergone moderate dynamic metamorphism, which, however, did not result in the formation of cataclastic structures. According to the Ridolfi (2021) model, the hornblende in the studied rock crystallised under conditions including a temperature of 730–760°C, a pressure of 1.0–1.4 kBar, and an oxygen fugacity of ΔNNO = 1.2–2.0. These conditions correspond to the hornfels facies of metamorphism, characterised by low pressure at high temperature. According to Frost *et al.* (2000), titanite cannot form under such conditions, giving way to ilmenite + plagioclase paragenesis. However, in quartz-undersaturated rocks, plagioclase is unstable, leading to the formation of edenitic amphibole, and excess calcium can stabilise titanite instead of ilmenite. The hornblende in the studied rock contains significant amounts of Na and K, supporting this model. Additionally, the rock is mafic (belonging to picritic basalt) and contains high levels of TiO_2, which should stabilise titanite under high temperatures and low pressures.

The average crystallisation temperatures of the studied titanite, calculated using the Hayden *et al.* (2008) formula, are 775°C at a pressure of 1.5 kBar and 795°C at 3 kBar. Therefore, the studied hornblende schist results from moderate dynamic metamorphism of a volcanic rock with a picritic basalt composition at high temperature and low pressure.

Since the obtained titanite age corresponds to metamorphic transformation rather than primary magmatic crystallisation, the source rock does not necessarily originate in the volcanism associated with the Prypyat-Dnieper-Donets Rift. It may also represent metamorphosed Precambrian rocks of basic to ultrabasic composition or a hypothetical Ediacaran igneous rock, which, according to Semenenko *et al.* (1977), underlies the rift. This possibility is supported by the presence of fragments of granitoids (Fedorchuk 1984) and Givetian limestone (Kyrykylytsya and Laskov 1970) in the diapiric breccia.

The geochemistry of the Ediacaran rocks that form the Volyn continental flood basalt province is now well-documented (Shumlyanskyy 2008, 2012). In terms of chemical composition, intrusive bodies of high-titanium gabbro-dolerites (Tsymbal and Samborska 2006; Shumlyanskyy *et al*. 2011) show the most significant similarity to hornblende schist. However, these rocks differ in the content of the main components and trace elements. Specifically, the studied schist contains significantly less SiO_2, Al_2O_3, and K_2O, as well as the most incompatible trace elements, and more FeO_{tot}, CaO, and V. These differences indicate a more mafic source composition for the schist source rock. There are no direct geochemical equivalents of hornblende schist among the rocks of the Azov Domain of the Ukrainian Shield. Meanwhile, in terms of chemical composition, it is a complete analogue of the Devonian dykes (Yutkina *et al*. 2017) and basalts of the Dnieper Basin (Wilson and Lyashkevich 1996). The effects of metamorphism can account for minor compositional differences.

CONCLUSIONS

The isotopic age and chemical composition of a fragment of hornblende schist from the diapiric breccia in the Bantysheve Dome, Donbas, have been studied. It was found that the U-Pb age of metamorphic crystallisation of titanite from the schist is 370 ± 17 Ma, matching the age of volcanism in the Prypyat-Dnieper-Donets Rift. The schistosity of the rock suggests it experienced moderate dynamic metamorphism. The mineral association that makes up the rock formed at a high temperature of 775–730°C and a relatively low pressure of 1.4–1.0 kBar, indicating the hornfels facies of metamorphism. The oxygen fugacity was ΔNNO 1.2–2.0. The most probable protolith for the studied schist is the Late Devonian picritic basalt or picritic dolerite linked to the development of the Rift.

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