МІНЕРАЛОГІЯ, ГЕОХІМІЯ ТА ПЕТРОГРАФІЯ

UDC 548.549.5 (477)
DOI: http://doi.org/10.17721/1728-2713.111.05

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RUTILE FROM THE CRYSTALLINE ROCKS OF THE SOUTHWESTERN PART OF THE UKRAINIAN SHIELD

(*Представлено членом редакційної колегії д-ром геол.-мін. наук, проф., Василем ЗАГНІТКОМ*)

Background. ***Rutile is a widespread accessory mineral in crystalline rocks of the Ukrainian Shield, notable for its geochemical stability and capacity to incorporate trace elements like Nb, Fe, V, Zr, Al and a wide range of other trace elements. The aim of this study is to analyze the color, morphology, and chemical composition of rutile from indigenous crystalline rocks of the southwestern part of the Ukrainian Shield in order to identify diagnostic features characteristic of different rock types, as well as to enable stratigraphic reconstructions and track the migration of sedimentary rutile.***

Methods, ***Samples and Analytical details. The study is based on the analysis of 363 rutile crystals extracted from 57 heavy mineral concentrate samples, as well as textual archival materials from 11 geological surveys conducted by the Right-Bank Geological Expedition between 1972 and 2009. The samples represent rutile from various lithotypes, including granites, gneisses, pegmatites, enderbites, ultrabasic rocks, and other crystalline formations of the southwestern part of the Ukrainian Shield. Binocular microscopy and SEM-EDS analysis were used to examine rutile morphology and chemical composition.***

Results. ***Rutile content ranges from 0.8 g/t in enderbites to 109.4 g/t in sillimanite-biotite gneisses. Most crystals are black or dark brown and acicular in form, often included in quartz or biotite. The majority (72 %) of rutile samples contain trace impurities, with V, Nb, Cr, and Fe being most common. Impurity patterns vary with rock type, metamorphic grade, and regional distribution. Northern rocks (e.g., Fastiv area) show Nb–V–Fe associations; southern samples often contain isolated V. Chromium-bearing rutile was discovered in migmatized metabasites in the Berdychiv area.***

Conclusions. ***Rutile preserves the geochemical signature of its host rocks and reflects both lithological and metamorphic conditions. It can serve as a reliable indicator mineral for reconstructing the provenance of sedimentary rutile, and Nb–Cr trace element associations may assist in identifying potentially diamond-bearing source rocks.***

Keywords: ***Rutile, southwestern part of the Ukrainian Shield, crystalline rocks, chemical composition.***

Background

Rutile is a widely distributed mineral in both crystalline and sedimentary rocks of the Ukrainian Shield (USh) and its slopes. Due to its high stability and the presence of impurities such as Nb, Ta, and other highly charged elements, it can be used in prospecting, genetic mineralogy, studies of geochemical processes in the crust and mantle, as well as a mineralogical geothermobarometer, among other geochemical studies (Baldwin, & Brown, 2008; Banfield, & Veblen, 1991; Bangaku Naidu et al., 2019; Foley, Barth, & Jenner, 2000; Luvizotto, & Zack, 2009; Malkov, 2008; Meinhold, 2010; Meinhold et al., 2008; Preston et al., 2002; Rudnick et al., 2000; Tomkins, Powell, & Ellis, 2007; Triebold et al., 2012; Watson, Wark, & Thomas, 2006; Xiao et al., 2006; Zack et al., 2002; Zack, Moraes, & Kronz, 2004; Zack et al., 2011). In Ukraine, most scientific works are focused on the study of rutile from sedimentary rocks (Tsymbal, 2014; Tsymbal, Shumlyanskyy, & Tsymbal, 2018; Vyshnevskyi, 2023). In previous works (Pavliuk, & Pavliuk, 2018; Pavliuk, 2019a; 2019b), we also studied rutile from many placers of the southwestern part of the Ukrainian Shield. However, to accurately determine the origin of this mineral from specific indigenous sources and trace the directions of its transport to the placer, we lacked information about the peculiarities of its chemical composition in the 'local' host rocks forming the crystalline basement. Therefore, we have dedicated this study to examining the color, morphology and chemical composition of rutile from native rocks and identifying markers characteristic of different rock types and regions within the southwestern part of the Ukrainian Shield. Our findings provide important information for a more precise determination of the origin of sedimentary rutile.

Methods

For analytical purposes, mineralogical duplicates and textual archival materials from 11 geological surveys of the Right-Bank Geological Expedition were used for the period from 1972 to 2009 on the territory of the Dnister-Buh and Ros-Tikych megablocks and their framing areas. Samples for mineralogical analysis were taken from the core of crystalline rocks. The sampling interval ranged from 1.0 to 3.0 m, with each sample weighing up to 5 kg. Mineralogical sample processing included grinding to 1 mm, washing on a concentration table, finishing to a "gray concentrate" on a tray, separation of the mineral concentrate in bromoform into light and heavy fractions, and then separation of the heavy fraction into magnetic and electromagnetic fractions. Mineralogical analysis was carried out under a binocular microscope.

To study the morphology and chemical composition of rutile, 363 crystals were handpicked from 57 heavy mineral concentrates of rock samples. Specifically, the study included 2 samples from vein quartz, 4 from Zhytomyr and Zvenyhorodka granites, 2 from pegmatites, 4 from metasomatites, 10 from gneisses, 2 from quartzites, 8 from Berdychiv granites, 3 from migmatites, 2 from charnockites, 5 from enderbites, 1 from basalt, 4 from gabbroids, 2 from diabases, 6 from crystalline schists, and 1 from ultrabasite. The heterogeneity of our samples is due to the varying distribution of the represented rock types within the study area and the availability of their samples, as well as the variable rutile content within them. In some rocks, the rutile content reaches up to grams per ton, while in others, only a few grains are present in the entire sample. Rutile crystals were selected and their color evaluated using a binocular microscope equipped with a cold-light LED lamp. The selected crystals were then fixed in epoxy, polished, carbon-coated to ensure conductivity, and analyzed using a GSM-6700F scanning electron microscope with a JE-2300 energy-dispersive system. All analyses were conducted using a 20 kV accelerating voltage, a beam current of 0.75 nA, a beam size of 1 µm, and a counting time of 60 seconds per analysis. The theoretical detection limits in SEM-EDS measurements are approximately 0.1 wt%: ~0.5–1.0 wt% for light elements, ~0.1–0.5 wt% for transition metals, and ~0.1 wt% for heavy metals (Z>30).

Results

The average content of rutile in crystalline rocks. To estimate the rutile content in the crystalline rocks of the southwestern part of the USh, relevant information from geological reports of previous years was collected and processed (Dovgan et al., 1985; Dovgan et al., 1989; Kulyk, 1996; Lyashko et al., 1986; Slynko, & Bondar, 1972; Zabiyaka et al., 1974; Yangicher et al., 1982 and other reports). It was found that the average content of rutile varies within quite wide limits: from 0.8 g/t in enderbites to 36.8 g/t in gneisses. The highest amount was found in sillimanite-biotite gneisses enriched with garnet and graphite – 109.4 g/t, and abnormally high content was recorded in some rocks (Tab. 1).

Table 1

Abnormally high rutile content in the crystalline rocks of the southwestern part of the Ukrainian Shield, g/t

Area	Sample No.	Rock types	Rutile content, g/t	Author
Fastiv	2CT-215	Silimanite-biotite gneiss	1530	Slynko, Bondar, 1972
Fastiv	409-36	Two-mica granite	1870	Dovgan et al., 1985
Skvyra	96K-17	Biotite migmatite	4900	Kulyk, 1996
Berdychiv	1631-39	Pegmatite	2230	Zabiyaka et al., 1974
Vinnytsia	728-124	Skarn	2193	Liashko et al., 1986
Haivoron	445-1	Sillimanite-garnet-biotite gneiss	3300	Dovgan et al.,1989
Haivoron	15783-1	Garnet-graphite-biotite gneiss	1770	Yangicher et al., 1982

The average content of rutile, ilmenite, and titanite in the main rock types of the southwestern part of the USh was calculated based on the database we collected, consisting of 8,129 mineralogical analyses (Table 2).

Table 2

Average content of titanium minerals in main rock varieties of the southwestern part of the Ukrainian Shield

Rock types	No. of samples	Average content, g/t			Sum, g/t	Percentage of total titanium mineral content			Percentage of accessory minerals*
		Rutile	Ilmenite	Titanite		Rutile	Ilmenite	Titanite	
Igneous rocks									
Granites	1452	8.5	546.4	100.5	655.4	1.3	83.4	15.3	12.4
Pegmatites	500	15.5	184.1	58.2	258.1	6.0	71.4	22.6	7.7
Gabbroids	348	1.2	1993.5	123.5	2118.2	0.1	94.1	5.8	29.3
Diabases**	29	2.4	4743.4	166.9	4912.7	0.01	96.59	3.4	36.3
Pyroxenites	229	1.2	1515.1	61.6	1557.9	0.1	96.0	3.9	23.6
Ultrabasites	301	4.3	341.6	7.1	353.0	1.2	96.8	2.0	8.6
Metamorphic rocks									
Gneisses	1140	36.8	780.1	110.3	927.2	4.0	84.1	11.9	15.9
Crystalline schists	1095	2.9	1308.1	247.5	1558.5	0.2	83.9	15.9	35.1
Migmatites	417	23.4	460.9	160.0	644.3	3.6	71.6	24.8	11.5
Charnockites	65	10.3	1795.6	37.7	1843.6	0.6	97.4	2.0	27.4
Enderbites	166	0.8	2257.6	86.5	2344.9	0.03	96.3	3.7	33.2
Amphibolites	345	5.1	461.4	934.8	1401.3	0.4	32.9	66.7	22.0
Magnetite quartzites	217	0.9	161.2	0.8	162.9	0.55	98.95	0.5	0.8
Calciphyres	900	6.1	382.5	514.3	902.9	0.6	42.4	57.0	24.2
Metasomatites	392	4.1	412.9	294.9	711.9	0.6	58.0	41.4	16.5

Note: * Percentage of total accessory minerals in the given set; ** titanomagnetite predominates in diabases.

A significant number of rutile analyses allow us to substantiate conclusions regarding the distribution patterns of titanium minerals, namely:

1. Rutile is least common among Ti minerals.
2. Rutile is most common in sub-acidic (gneisses, migmatites, charnockites) and acidic (granites, pegmatites) rocks of the southwestern part of the USh.
3. The specific content of rutile in the total mass of titanium minerals is maximum in pegmatites, and somewhat lower in migmatites and gneisses. Note that the real content of rutile in pegmatites is underestimated due to the impossibility of fixing its small inclusions in quartz by standard mineralogical analysis.
4. In the group of rocks of basic-ultrabasic composition, the highest percentage of rutile was found in ultrabasites (1.2 %).
5. In calcium-enriched parasedimentary rocks: amphibolites, calciphyres, as well as various metasomatites, there is a predominance of titanite over ilmenite.
6. In intrusive and volcano-sedimentary rocks of subbasic-basic composition, such as enderbites, crystalline schists, gabbroids, and diabases, titanium minerals constitute one-third of all accessory minerals.

The color range of rutiles. 234 crystals approximately 0.05 mm in size were selected for color assessment. Statistical data on the color of rutile are provided in Table 3.

As we can see from the Table, the absolute majority of rutile grains are black (68.2 %), much less – dark brown (18.4 %). Crystals of these colors absolutely dominates even in acidic rocks: granites, pegmatites, and vein quartz. Rutile of gabbro-amphibolites is mainly characterized by light brown varieties. Greenish rutiles make up 50 % of all rutiles of magnetite quartzites. Rutiles of this color contain an extremely large number of inclusions, which probably cause this color. Rutiles of other colors are quite rare.

Table 3

Color of rutile in the crystalline rocks

Rock types	No. of crystals	Black	Dark brown	Reddish	Light brown	Yellow	Greenish
Igneous rocks							
Granites, pegmatites	48	32	16				
Gabro-amphibolites	6				6		
Diabases	3	2			1		
Basalts	10	4	2		2	1	1
Ultrabasites	4		3		1		
Metamorphic rocks							
Vein quartz	11	9			2		
Magnetite quartzites	2		1				1
Gneisses	89	69	7	2	7	2	2
Crystalline schists	21	19	2				
Migmatites	8	1	7				
Charnockites	14	10	1		3		
Enderbites	11	9	2				
Metasomatites	7	5	2				
Total., No. crystals	234	160	43	2	22	3	4
Total, %	100	68,2	18,4	0,9	9,4	1,3	1,7

Morphology of rutile. Rutile, extracted from the heavy fractions of crystalline rocks, is predominantly represented by angular fragments, with a significantly smaller proportion of better preserved crystals of elongated prismatic form, measuring 0.05–0.3 mm (Fig. 1).

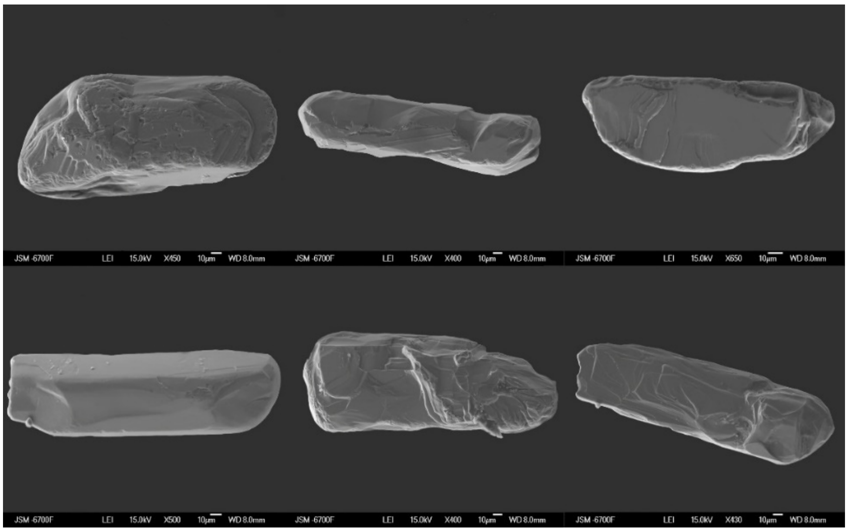

Fig. 1. Representative rutile crystals of elongated prismatic form

Significant damage to the crystals during rock crushing and washing on the concentration table prevents a reliable assessment of their morphology. Therefore, for a more comprehensive assessment of its forms and the characteristics of its presence in various minerals, we used data from descriptions of 144 thin sections of the most common varieties of crystalline rocks in the studied area (Tab. 4).

Table 4

Features of rutile occurrence in the crystalline rocks based on petrographic research (frequency of occurrence, %)

Rock types	Inclusions of rutile in minerals				Percentage of "large" crystals >0.07 mm
	Quartz	Biotite	Microcline	Plagioclase	
Granites	26	32	33	0	0
Pegmatites	7	5	56	67	0
Gneisses	20	21	0	0	40
Crystalline schists	4	5	0	0	20
Migmatites	19	37	11	33	20
Quartzites and vein quartz	24	0	0	0	20
All rocks, %	54	19	9	3	16

The absolute majority of rutile is in the form of acicular crystals and their intergrowths, which are found mainly in quartz and less in biotite. Rutile inclusions in feldspars are characteristic of rocks of acidic composition: granites, pegmatites, and migmatites. In skarns, rutile is recorded only in two cases: as acicular crystals in scapolite and in dolomite.

Relatively large grains of rutile, up to 0.7 mm, in the form of prisms and irregular crystals, are quite rare and have only been found in rock samples from 10 boreholes. The majority of these boreholes are located in the Pervomaisk area of the Middle Buh region on sections composed of rock formations of the Buh series. This area includes the Kosharo-Oleksandrivka, Mohylne, and Hrushka sites in Pervomaisk area, where rock formations belong to the Buh series. In some thin sections of gneisses and quartzites from these sites, the rutile content typically ranges from 1 to 2 %. In the Kosharo-Oleksandrivka site, dark brown coarse-grained rutile is predominantly found in the garnet-sillimanite-biotite quartzites of the Kosharo-Oleksandrivka suite of the Buh series. In other sites, besides quartzites, rutile has also been identified in garnet-biotite gneisses and migmatites.

According to the petrographic studies, rutile is closely related to the processes of quartzization, greisenization, and chloritization (it is often found in chloritized biotite).

As shown in Table 4, only 16 % of rutile in crystalline rocks is non-acicular and exceeds the dimensions of 0.05–0.07 mm. This allows it to be identified through ordinary mineralogical analysis. In addition, most of the rutile is enclosed within the quartz crystals. As a result, it remains with the quartz in the "waste" during the washing of mineralogical samples. This rutile can be extracted from the quartz shell only in the case of long-term hydrodynamic separation when quartz grains are crushed along microcracks. Such separation occurs, for example, in thoroughly washed fine-grained sands of Neogene titanium-zirconium placers. Consequently, a significant amount of fine rutile goes undetected by mineralogical analysis.

Chemical composition of rutile. To study the chemical composition of rutile, we selected samples from the prevalent rock varieties within the southwestern part of the Ukrainian Shield (Fig. 2).

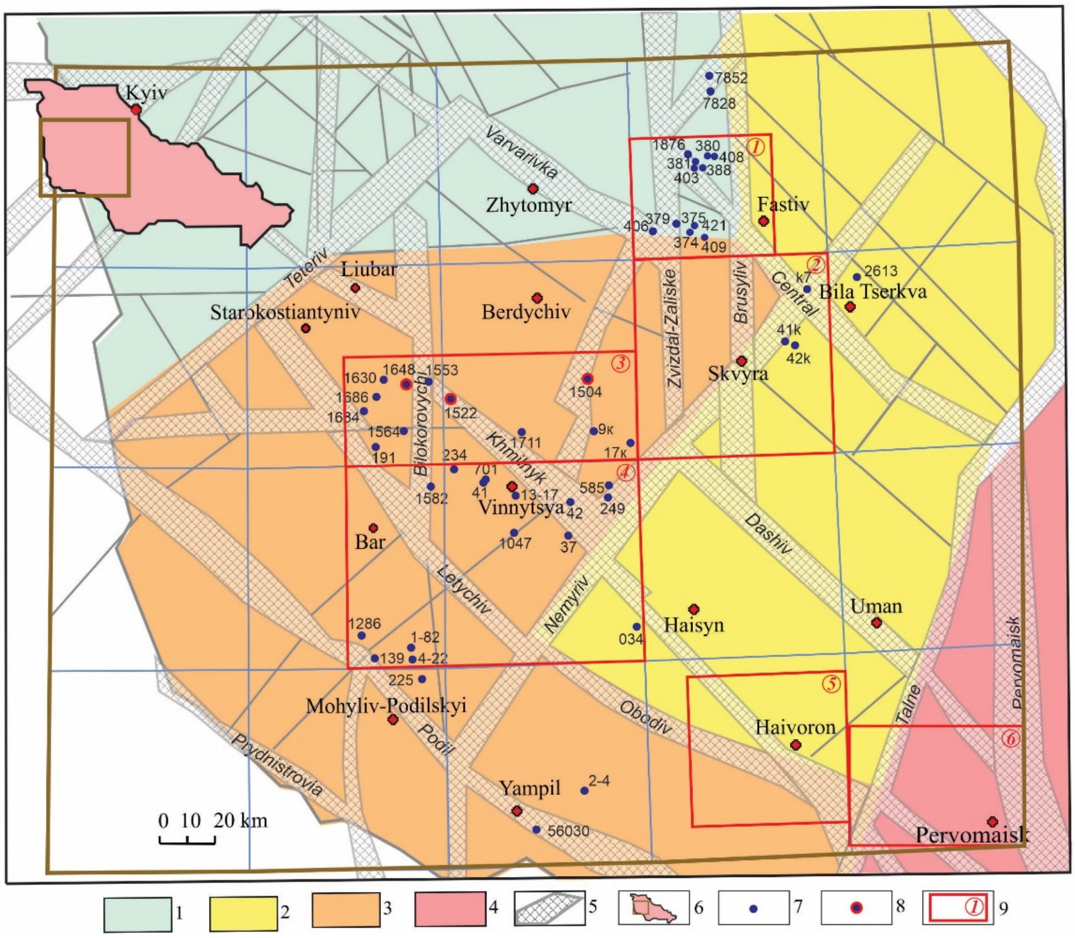

Fig. 2. The scheme depicting the locations of sample collection points containing rutile.
Megablocks: *1* – Volyn, *2* – Ros-Tikych, *3* – Dnister-Buh; *4* – Holovaniv suture zone, *5* – main and secondary tectonic zones, *6* – rutile study region within the Ukrainian Shield, *7* – sampling points, *8* – rutile with Cr and Nb impurities, *9* – contours of areas: 1 – Fastiv, 2 – Skvyra, 3 – Berdychiv, 4 – Vinnytsia, 5 – Haivoron, 6 – Pervomaisk

In Table 5, we present the average chemical composition of rutile for different rock types of the Dnister-Buh, and Ros-Tikych megablocks, as well as, for comparison, part of the Volyn megablock. Additionally, we used data on the rutile composition from kimberlites and crustal eclogites of the Alps, gathered from literary sources, for comparison (Evdokimov, & Bagdasarov, 1981; Garanin, Kudriavtseva, & Kharkiv, 1980; Gurney et al., 1995; Kaminskiy, 1988; Kvasnytsia, & Vyshnevskyi, 2017; Sobolev et al., 1971; Tollo, & Haggerty, 1987; Zack et al., 2002).

Table 5

Chemical composition of rutile from the crystalline rocks of the southwestern part of the Ukrainian Shield (average/min-max), wt%

Rock types	No. of crystals	TiO_2	SiO_2	Al_2O_3	FeO	Cr_2O_3	V_2O_3	Nb_2O_5	Ta_2O_5	ZrO_2	WO_3
Volyn megablock, Fastiv area											
Zhytomyr granites	13	97.28 96.2–100	bdl	bdl	bdl	0.03 bdl–0.4	0.75 bdl–1.52	1.38 bdl–2	bdl	bdl	0.34 bdl–1.14
Pegmatites	8	99.26 98.18–100	bdl	bdl	bdl	bdl	0.39 bdl–1.52	0.20 bdl–0.84	bdl	bdl	0.07 bdl–0.56
Garnet-biotite gneisses	16	97.81 95–100	bdl	bdl	0.04 bdl–0.64	0.08 bdl–0.48	0.31 bdl–1.44	1.50 bdl–2.81	bdl	bdl	0.15 bdl–1.13
Graphite-biotite gneisses	20	98.00 93.93–100	bdl	bdl	0.13 bdl–1.57	0.05 bdl–0.71	0.51 bdl–1.77	0.98 bdl–3.79	bdl	bdl	0.16 bdl–1.24
Biotite gneisses	13	98.15 97.02–99.23	bdl	bdl	bdl	bdl	1.09 bdl–1.8	0.53 bdl–1.79	bdl	bdl	bdl
Amphibole gneisses	6	97.71 95.39–100	bdl	bdl	0.37 bdl–2.2	0.05 bdl–0.3	0.95 bdl–1.84	0.25 bdl–0.76	bdl	0.19 bdl–1.11	bdl
Metasomatites	6	99.21 98.76–100	bdl	bdl	0.09 bdl–0.55	bdl	0.32 bdl–0.99	0.31 bdl–1.19	bdl	bdl	bdl
Vein quartz	11	98.85 97.24–100	bdl	bdl	0.07 bdl–0.82	0.06 bdl–0.61	0.42 bdl–2.14	0.45 bdl–1.83	bdl	bdl	bdl
Dnister-Buh megablock, Vinnytsia area											
Gabbroids	19	99.09 97.48–100	bdl	bdl	0.03 bdl–0.57	bdl	0.42 bdl–2.08	0.13 bdl–1.66	0.02 bdl–0.37	0.12 bdl–0.88	0.10 bdl–0.66
Khmilnyk diabases	4	99.07 97.93–100	bdl	bdl	bdl	bdl	0.54 bdl–0.92	bdl	bdl	0.27 bdl–1.09	bdl
Basalts, Vendian system	10	98.75 96.72–100	0.07 bdl–0.71	bdl	bdl	bdl	0.74 bdl–1.82	0.15 bdl–0.8	bdl	0.14 bdl–0.79	bdl
Ultrabasites, Zhdanivsky massif	5	99.43 98.66–100	bdl	bdl	0.14 bdl–0.69	bdl	0.22 bdl–1.1	0.16 bdl–0.8	bdl	bdl	bdl
Garnet-biotite gneisses	19	98.49 94.44–100	0.02 bdl–0.4	0.20 bdl–1.05	0.06 bdl–0.65	0.06 bdl–0.79	0.69 bdl–1.62	0.33 bdl–1.07	bdl	bdl	0.04 bdl–0.75
Dniester-Buh crystalline schists	8	99.08 96.98–100	0.05 bdl–0.37	0.06 bdl–0.48	0.25 bdl–1.96	0.05 bdl–0.4	0.32 bdl–0.28	0.13 bdl–1.07	bdl	bdl	bdl
Diopside-amphibole crystalline schists	7	98.92 96.35–100	0.15 bdl–1.02	0.12 bdl–0.86	0.13 bdl–0.91	bdl	0.25 bdl–0.88	0.13 bdl–0.93	bdl	0.24 bdl–1.65	bdl
Berdychiv migmatites	35	97.92 92.96–100	bdl	0.01 bdl–0.43	0.04 bdl–0.8	0.79 bdl–1.89	0.19 bdl–1.21	0.90 bdl–4.35	bdl	bdl	0.08 bdl–1.24
Berdychiv granites	52	98.64 89–100	0.09 bdl–1.83	0.19 bdl–7.29	0.13 bdl–2.64	0.04 bdl–1.76	0.32 bdl–1.38	0.42 bdl–8.36	bdl	0.04 bdl–0.96	0.02 bdl–0.78
Charnockites	15	99.47 98.71–100	bdl	bdl	bdl	bdl	0.36 bdl–1.06	bdl	bdl	0.08 bdl–1.27	bdl
Enderbites	22	99.06 93.83–100	0.02 bdl–0.44	0.08 bdl–1.60	0.19 bdl–1.51	0.12 bdl–1.9	0.26 bdl–1.55	0.12 bdl–1.02	bdl	0.07 bdl–0.72	0.03 bdl–0.66
Magnetite quartzites	2	99.01 98.74–99.27	bdl	bdl	0.37 bdl–0.73	bdl	0.52 bdl–1.04	bdl	bdl	bdl	bdl
Metasomatites	11	99.87 99.19–100	bdl	bdl	0.06 bdl–0.65	bdl	bdl	0.07 bdl–0.81	bdl	bdl	bdl
Ros-Tikych megablock, Skvyra area											
Zvenyhorodka granites	38	98.72 93.44–100	0.12 bdl–4.54	0.09 bdl–1.69	0.13 bdl–1.93	0.05 bdl–1.02	0.40 bdl–1.71	0.25 bdl–1.84	bdl	0.11 bdl–0.91	0.06 bdl–1.1
Crystalline schists	22	98.71 97.49–100	0.01 bdl–0.31	bdl	0.04 bdl–0.94	bdl	0.80 bdl–1.8	0.19 bdl–1.03	bdl	bdl	0.04 bdl–0.81
Magnetite quartzites	1	98.93	bdl	bdl	bdl	bdl	1.07	bdl	bdl	bdl	bdl
Data from the literature											
Kimberlites (ultrabasic)	118	88.43 64.3–98.24	0.07 bdl–0.45	0.33 bdl–1.75	1.70 0.07–9.99	4.88 0.64–9.75	0.22 bdl–0.98	3.58 bdl–20.90	0.28 bdl–1.82	0.36 bdl–1.46	n.a.
Kimberlites (eclogitic)	32	97.83 95.00–99.67	0.01 bdl–0.08	0.43 bdl–1.60	0.81 bdl–3.14	0.05 bdl–0.20	0.03 bdl–0.27	0.15 bdl–1.30	0.26 bdl–8.06	0.03 bdl–0.29	n.a.
Crustal eclogites (Alps)	11	99.01 96.96–99.99	0.03 bdl–0.08	0.02 bdl–0.06	0.29 bdl–0.44	0.44 bdl–2.40	0.08 bdl–0.27	0.07 bdl–0.23	>0.01 bdl–0.01	0.01 bdl–0.02	0.01 bdl–0.04

Note: bdl – below detection limit.

As can be seen from the Table, the average content of impurities in rutile varies in a wide range from 0 to 3 %, which is comparable to the average content of impurities in rutile from sedimentary rocks of the territory. Variations in the total content of impurities in rutile are observed depending on its location within different megablocks (Fig. 3). The highest content was recorded in the rutile of the Volyn megablock (1.53 %), slightly lower (1.15 %) in the rutile of the Ros-Tikych megablock, and the lowest (0.94 %) in the rutile of the Dnister-Buh megablock. This difference in the total impurities content of rutile in crystalline rocks is probably related to the degree of their metamorphism. For instance, the rocks of the Volyn megablock underwent epidote-amphibolite facies metamorphism, those of the Ros-Tikych megablock – amphibolite facies, and those of the Dnister-Buh megablock – granulite facies.

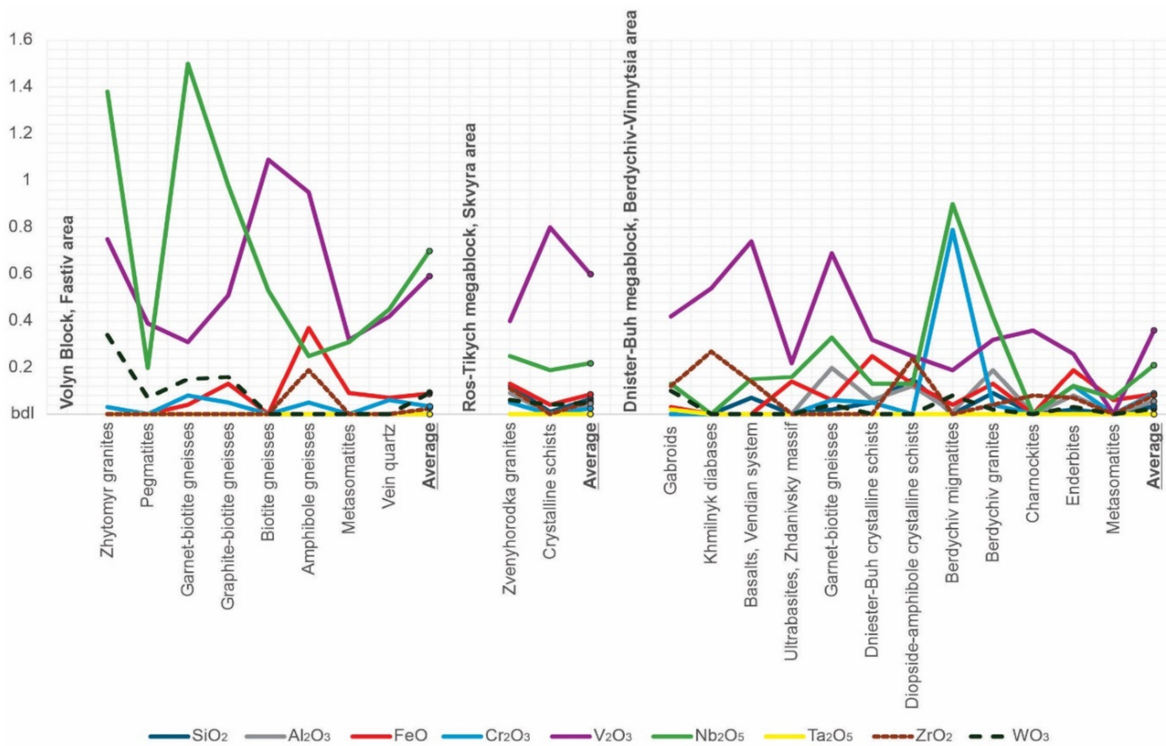

Fig. 3. Diagram of the fluctuations in the content of impurities in rutile of the crystalline rocks within the megablocks of the southwestern part of the Ukrainian Shield

Vanadium and niobium are the most commonly occurring impurities, often found at relatively high levels, followed by zirconium, chromium, and iron; other impurities occur in 40–60 % of cases with negligible concentrations (Tab. 6).

Table 6

The most important impurities in rutile from the crystalline rocks

Rock types	Complex/series	No. of crystals	Crystals with impurities (as a percentage of the number of grains analyses)								
			Without impurities (bdl)	V_2O_3	Nb_2O_5	Cr_2O_3	FeO	WO_3	ZrO_2	Al_2O_3	SiO_2
The northwestern part of the Ukrainian Shield											
Granites	Zhytomyr	13	7.6	61.5	92.3	0	0	38.5	0	0	0
Pegmatites	Zhytomyr	8	50	37.5	25.0	0	0	12.5	0	0	0
Sillimanite gneisses	Teteriv	49	10.2	48.9	65.3	10.2	6.1	12.2	0	0	0
Amphibole gneisses	Teteriv	6	16.7	66.7	33.3	16.7	16.7	0	16.7	0	0
Crystalline schists	Ros-Tikych	22	13.6	68.2	27.3	0	4.5	4.5	0	0	4.5
Vein quartz	Zhytomyr	11	45.5	27.3	36.4	9.1	9.1	0	0	0	0
The southwestern part of the Ukrainian Shield											
Gabbroids	Kapitanka-Dereniukha	19	36.8	31.6	15.8	0	5.3	15.8	15.8	0	0
Diabases	Khmilnyk	4	25.0	75.0	0	0	0	0	25.0	0	0
Basalts	Vend	10	40.0	50.0	20.0	0	0	0	20.0	0	10.0
Ultrabasites	Zhdanivka	5	40.0	20.0	20.0	0	20.0	0	0	0	0
Gneisses	Dnister-Buh	19	21.0	57.9	36.8	10.5	10.5	5.3	0	15.8	5.3
Crystalline schists	Dnister-Buh	8	62.5	25	12.5	12.5	12.5	0	0	12.5	12.5
Diopside-amphibole crystalline schists	Dnister-Buh	7	28.6	42.9	14.3	0	14.3	0	14.3	14.3	14.3
Migmatites	Berdychiv	35	5.7	22.9	65.7	82.9	5.7	11.4	0	2.9	0
Granites	Zvenyhorodka	38	36.8	36.8	26.3	5.3	10.5	7.9	13.2	5.3	2.6
Granites	Berdychiv	52	36.5	32.7	28.9	3.8	7.7	1.9	5.8	7.7	9.6
Enderbites, Charnokites	Lityn	37	43.2	40.5	8.1	5.4	8.1	2.7	8.1	2.7	2.7
Magnetite quartzites	Buh	3	0	66.7	0	0	33.3	0	0	0	0
Metasomatites	?	17	64.7	11.8	17.7	0	11.8	0	0	0	0
All rocks		363	29.2	40.2	35.0	12.7	7.7	7.2	5.2	3.9	3.3

ISSN 1728-3817

Noticeable fluctuations in impurity content among rocks of the same type are observed. This is evident in Proterozoic gneisses of the Dnister-Buh series in the Fastiv area, where fluctuations in vanadium, niobium, and iron content can reach 2–3 times their average. According to our statistical data, among all the gneisses of the southwestern part of the Ukrainian Shield (6499 spectral analyses), the garnet-biotite varieties contain the highest amount of chromium – 150.3 g/t. According to silicate analysis data, these varieties are also among the most magnesian (MgO content, wt%: pyroxene-bearing – 3.71, amphibole-bearing – 3.76, garnet-biotite – 2.97). Therefore, garnet-biotite varieties of gneisses can be considered the most mafic, and thus the most deep-seated. Among the gneisses, only in the rutile of these varieties does niobium prevail over vanadium among the impurities. A significantly smaller range of impurity content fluctuations in rutile is observed in granites. The granites of the Zhytomyr, Zvenyhorodka, and Berdychiv complexes contain impurities in approximately the same range, although the granites of the older and probably deeper Berdychiv complex have higher niobium and aluminum content and lower vanadium content.

A decrease in impurity content is also observed in the rutiles of granites of the Teteriv, Skvyra, and Berdychiv areas compared to the more ancient formations – gneisses. Rutile in subbasic (enderbites), basic (amphibolites, gabbroids, diabases), and ultrabasic rocks contain significantly fewer impurities, including indicators of deep genesis, such as chromium and niobium, compared to acidic rocks. The content of these impurities is much lower than that found in eclogite and ultramafic nodules of kimberlites.

In comparison with rutile from crystalline rocks of the southwestern part of the USh, rutiles from crustal-mantle rocks (eclogites and ultramafic nodules in kimberlites) are characterized by a high content of iron and a low content of vanadium.

Distribution of impurities and their associations in rutile. Rutile in various crystalline rocks exhibits a unique array of impurity elements, as detailed in Table 6. Out of 363 rutile crystals analyzed, only 106 (29.2 %) do not contain impurities (their quantity does not exceed the analyzer's sensitivity threshold of 0.01 wt%). Among the rocks of the Dniester-Buh megablock, the highest total impurity content (%) is observed in Berdychiv granites (11.0), followed by migmatites (7.04) and enderbites (6.17). Comparable levels have been found only in the Zvenyhorod granites-migmatites of the Ros-Tikych megablock (6.56 %) and the garnet-biotite gneisses of the Fastiv area (5.00 %). A positive correlation is observed between the average rutile content and the total impurities in rutile in both igneous and metamorphic rocks.

Below is a brief description of the distribution of the most common metal impurities in rutile from various crystalline rocks of the studied area.

Iron is detected in a small number of rutile samples (7.7 %); its content is generally insignificant, averaging 0.09 wt%. The maximum average iron content of 0.37 wt% is found in rutile from magnetite quartzites, supporting the thesis regarding the influence of geochemical background on impurity composition.

Tungsten is encountered rarely, occurring in only 7.2 % of rutile analyses, except for rutile extracted from granites of the Zhytomyr complex from Fastiv area (38.5 %). These granites contain an elevated amount of apatite and sulfides. The rutile of these granites contains from 0 to 1.14 wt% tungsten, with an average of 0.34 wt%. Tungsten is closely associated with vanadium and niobium. The association of these metals is natural, as the granites belong to the Bystriv association of rare-metal granites common in the area of the Teteriv depression (Dovgan et al., 1982).

Zirconium is detected in 19 out of 363 analyses (5.2 %). This impurity is mainly enriched in the rutiles of the Dnister-Buh megablock: granites, migmatites, charnockites, and enderbites of the Berdychiv complex. In four rutile grains from these rocks, the zirconium content exceeds 1 wt%.

Vanadium is the most common impurity in rutile, occurring in 40.2 % of rutile analyses. In the southern part of the territory, vanadium appears as a single impurity in rutile, while in the northern part, in both granites and gneisses, it typically occurs in association with other metals, most often with niobium and iron. This information can be used to establish the likely genesis of rutiles from sedimentary rocks.

Niobium is the second most common impurity in rutile (35 %). It is exceedingly rare in enderbites and charnockites and absent in rutiles of magnetite quartzites and Khmilnyk diabases. Generally, it is more prevalent in rutiles of crystalline rocks in the northwestern part of the Ukrainian Shield. The highest niobium content (on average) is found in rutile of garnet-biotite gneisses and granites of the Zhytomyr complex in the Fastiv area (1.95 wt% and 1.38 wt%, respectively). Slightly lower concentrations are recorded in rutile of gneisses of the Teteriv series in the same area, at 0.98 wt%. Albite-muscovite pegmatites and greisenized granites with tantalum-columbite are widespread in the Fastiv area, in the region of the Teteriv paleo-threshold, and the Brusyliv suture zone (Dovgan et al., 1982). This fact explains the increased geochemical "background" of niobium in this region.

In the rutile from rocks of the southern part of territory, niobium is mainly found as a single impurity and occurs most often in migmatites, gneisses and granites. In the vast majority of rock types, niobium is found in association with vanadium, sometimes additionally with iron. The Nb–V–(±Fe) association is most prevalent in Zhytomyr granites (comprising 61.5 % of all impurities) and Teteriv gneisses (29.3 %) – the predominant rock varieties in the northern part of the region. In other rock types, this association typically does not exceed 19 %. The Nb–Cr association is found exclusively in rutile of the Berdychiv area, in samples of migmatized basic rocks of probably deep origin.

Chromium is the third most common impurity in rutile, occurring in 46 analyses (12.7 %). However, 29 of them are analyses of rutile from 3 samples of migmatites with inclusions of rocks of the basic composition from Berdychiv area. If these are excluded from the statistics, the occurrence of chromium will decrease to 17 cases, amounting to 5.1 %. At the same time, chromium impurities are absent in the rutile of basites-ultrabasites, which may indicate their shallow (crustal) origin. Chromium alone was determined in only 9 analyses of rutile. In other cases, it is found in Cr–Nb associations (most often), as well as Cr–Fe, Cr–Nb–V, Cr–Nb–Fe associations. Regarding the Berdychiv migmatized basites, a deep Cr–Nb association clearly prevails in their rutile.

Tab. 7 below shows the values of the maximum content of impurity elements in rutile from the crystalline rocks of the territory.

As seen from the Tab. 7, only the maximum niobium oxide content exceeds 3 wt%. Other impurities are observed within the range of 0.7–2.64 wt%. Tungsten is found in rutile of subcarbonate rocks with signs of skarn development (presence of diopside, scapolite), while chromium is detected in migmatites of the Berdychiv area, which contain relicts of basites with chromium spinelides.

Table 7

The maximum content of impurity elements in rutile from the crystalline rocks of the western part of the Ukrainian Shield

Max. content of impurities, wt%	Sample No.	Rock types	Area	Other impurities, wt%
V_2O_3 – 2.14	375-72	Vein quartz	Fastiv	–
V_2O_3 – 2.08	249-5	Gabbro-amphibolite	Vinnytsia	–
Nb_2O_5 – 8.36	1286	Garnet-biotite granite	Vinnytsia	FeO — 2.64
Nb_2O_5 – 4.35	1504-7	Garnet-hornblende migmatite	Berdychiv	Cr_2O_3 – 1.89, FeO – 0.8
Nb_2O_5 – 3.79	421-33	Sillimanite-graphite-biotite gneiss	Fastiv	V_2O_3 – 1.04, FeO – 0.96
Cr_2O_3 – 1.90	1047-4	Hypersthene-garnet-biotite enderbite	Vinnytsia	FeO – 1,51, ZrO – 0.72 Al_2O_3 – 1.6, SiO_2 – 0.44
Cr_2O_3 — 1.89	1504-7	Garnet-hornblende migmatite	Berdychiv	Nb_2O_5 – 4.35, FeO – 0.8
Cr_2O_3 — 1.78	1630-9	Hornblende migmatite	Berdychiv	–
FeO — 2.64	1286	Garnet-biotite granite	Vinnytsia	Nb_2O_5 – 8.36
FeO — 2.20	378-25	Hypersthene- hornblende-biotite gneiss	Fastiv	Nb_2O_5 – 0.71
WO_3 — 1.24	421-33	Sillimanite-graphite-biotite gneiss	Fastiv	V_2O_3 – 1.11, Nb_2O_5 – 1.91 FeO – 1.57
WO_3 — 1.24	1504-7	Garnet-hornblende migmatite	Berdychiv	Cr_2O_3 – 0.88, Nb_2O_5 – 0.46, FeO – 0.72
ZrO_2 — 1.65	1630-11	Diopside gneiss	Berdychiv	V_2O_3 – 0.88, Nb_2O_5 – 0.93
ZrO_2 — 1.27	1686-6	Charnockite with diopside	Vinnytsia	—
ZrO_2 — 1.11	406-66	Amphibole-scapolite gneiss	Fastiv	—

Discussion and conclusions

Rutile is a widespread mineral found in almost all types of crystalline rocks within the southwestern part of the Ukrainian Shield and its surrounding areas. However, it is less abundant compared to other titanium-bearing minerals such as ilmenite and titanite. The average rutile content ranges from 0.8 g/t in enderbites to 36.8 g/t in gneisses, reaching up to 4912.7 g/t in diabases. The vast majority of rutile exhibits black (68.2 %) or dark brown (18.4 %) coloration. The size of rutile grains predominantly varies between 0.05 and 0.3 mm. Most rutile occurs as acicular crystal inclusions and their intergrowths, primarily within quartz and, to a lesser extent, in biotite. Relatively large grains of rutile, in the form of prisms and irregularly shaped crystals, are commonly distributed within feldspars and biotite.

The majority of analyzed rutile samples (72 %) contain impurities of various metals. The average impurity content in rutile from different rocks ranges from 0 to 3 wt%. Impurities in rutile from sedimentary and crystalline rocks of the southwestern part of the Ukrainian Shield are similar in both composition and average content, which indicates their genetic relationship.

Petrographic studies indicate that rutile is closely associated with processes such as silicification, greisenization, and chloritization. Consequently, rutile may form during at least three stages: magmatic, metamorphic (granitization), and low-temperature diaphthoresis. To confirm this hypothesis, absolute age determination of rutile needs to be conducted. A correlation is observed between the total impurity content in rutile and the degree of metamorphism of the host rocks. Rutile appears to be progressively purified from impurities as the grade of regional metamorphism increases.

Based on average content, the predominant impurities in rutile are vanadium, niobium, chromium, and iron. In the southern part of the region, vanadium is a single impurity in rutile, primarily from basic-ultrabasic rocks. In contrast, in the northern part, vanadium is typically found in association with other metals, most frequently niobium and iron, in both granites and gneisses. This pattern can be utilized to infer the probable genesis of rutiles from sedimentary rocks.

The Nb–Cr association is found exclusively in rutile from three boreholes in migmatized metabasites of probable deep origin, located within the Berdychiv area. Rutiles with this impurity association are promising for identifying diamond-bearing rocks. Chromium is absent in rutile from the gabbroids and ultrabasic rocks studied in the area, which may indicate their relatively shallow formation depth.

Rutile from rare-metal (niobium, tantalum, tungsten, molybdenum) – enriched crystalline rocks (niobium, tantalum, tungsten, molybdenum) of the Fastiv area contains impurities of these metals. Such rutile may have industrial significance, and its content should be considered during the exploration of Neogene titanium-zirconium placers located in the Fastiv area.

The highest average FeO content (0.37 wt%) has been detected in rutile from magnetite quartzites. This indicates that rutile accumulates and preserves information about the origin and metallogenic specialization of its host rocks. Impurities of iron, chromium, vanadium, niobium, and zirconium in rutile can be effectively utilized to identify the primary sources of rutile in sedimentary rocks and valuable mineral placers.

Authors' contribution: Oleksandra Pavliuk – conceptualization, methodology, analytics, rutile description, data analysis, map creation; Viacheslav Pavliuk – collection and analysis of archival data, map creation, data analysis; Oleh Semeniv – data validation, data analysis and processing, software, formal analysis.

Sources of funding. The study was carried out under a departmental project of the NAS of Ukraine (project No. 0123U100651).

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Отримано редакцією журналу / Received: 06.07.25
Прорецензовано / Revised: 20.09.25
Схвалено до друку / Accepted: 16.12.25

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РУТИЛ ІЗ КОРІННИХ ПОРІД ПІВДЕННО-ЗАХІДНОЇ ЧАСТИНИ УКРАЇНСЬКОГО ЩИТА

В с т у п . ***Рутил – поширений акцесорний мінерал у кристалічних породах Українського щита. Він вирізняється геохімічною стабільністю та здатністю включати такі елементи, як Nb, Fe, V, Zr, Al, а також широкий спектр інших елементів домішок. Метою цього дослідження є аналіз кольору, морфології та хімічного складу рутилу з корінних кристалічних порід південно-західної частини Українського щита з метою виявлення діагностичних ознак, які характерні для різних породних різновидів, а також для можливості стратиграфічних реконструкцій і відстеження міграції теригенного рутилу.***

М е т о д и . ***Дослідження базується на аналізі 363 кристалів рутилу, виділених із 57 шліхових проб р, а також текстових архівних матеріалах 11 геологічних зйомок Правобережної геологічної експедиції, проведених у 1972–2009 роках. Зразки репрезентують рутил з різних літотипів: гранітів, гнейсів, пегматитів, ендербітів, ультрабазитів та інших порід південно-західної частини Українського щита. Для вивчення морфології та хімічного складу використовували бінокулярну мікроскопію та аналіз SEM-EDS.***

Р е з у л ь т а т и . ***Вміст рутилу коливається від 0,8 г/т в ендербітах до 109,4 г/т у силіманіт-біотитових гнейсах. Більшість кристалів – чорні або темно-коричневі, голчастої форми, часто включені в кварц або біотит. Переважна частина зразків рутилу (72 %) містить домішки, серед яких найпоширенішими є V, Nb, Cr і Fe. Характер домішок варіює залежно від типу породи, ступеня метаморфізму та регіонального положення. Для північних порід (наприклад, район Фастова) характерні асоціації Nb–V–Fe, тоді як у південних зразках переважає ізольований V. Рутил із вмістом хрому виявлено у мігматизованих метабазитах Бердичівського району.***

В и с н о в к и . ***Рутил зберігає геохімічний "відбиток" порід-хазяїнів і відображає як літологічні, так і метаморфічні умови. Він може слугувати надійним індикаторним мінералом для реконструкції джерел осадового рутилу, а асоціації домішок Nb–Cr – для виявлення джерел потенційно алмазоносних порід.***

К л ю ч о в і с л о в а : ***рутил, південно-західна частина Українського щита, кристалічні породи, хімічний склад.***

Автори заявляють про відсутність конфлікту інтересів. Спонсори не брали участі в розробленні дослідження; у зборі, аналізі чи інтерпретації даних; у написанні рукопису; в рішенні про публікацію результатів.

The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses or interpretation of data; in the writing of the manuscript; in the decision to publish the results.