



# Study of Valuable Impurities of Ore-Forming Titanium Minerals in the Ukraine

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## Abstract

Titanium ore is a critical raw material for the EU. Ukraine has significant titanium ore reserves, which are represented by several genetic types and have a number of advantages: the possibility of extracting raw materials for various purposes; favorable mining and geological conditions for most placer and residual deposits; complexity of objects. Ilmenite is the most important titanium mineral, most typical for basic and ultrabasic rocks of the crystalline basement and sedimentary rocks. The value of titanium ores is enhanced by the presence of valuable impurities (V, Sc, Ta, Nb). The quality of titanium ores is related to their degree of alteration. The degree of alteration of ilmenite influences on the industry where the concentrates are used and the development of their processing technologies. The authors have developed approaches to assessing this parameter and have shown the dynamics of changes in the chemical composition of ilmenite in the weathered crust and sedimentary rocks. Based on the statistical processing of data from the chemical analysis of titanium ores, it is shown that Sc has the highest concentrations in the ilmenite of the Korosten complex compared to other geological bodies of the Ukrainian Shield, which provokes the need to improve the relevant technologies.

**Keywords:** titanium ores, alteration of ilmenite, impurities, leucoxenization

## 1. Introduction

### 1.1 Titanium deposits in the world and in the Ukraine

Titanium is one of the most important structural metals today. Its use is an indicator of the technical level of an industrially developed country in the world. Titanium deposits of Ukraine are represented by several genetic types and have a number of advantages: the possibility of extracting raw materials for various purposes; high potential of titanium resources and reserves; favorable mining and geological conditions for most placer and residual deposits; complexity of objects. Reserves of primary deposits of Ukraine constitute 53.6% of all reserves, coastal marine zircon-rutile-ilmenite placers – 27.2%, ilmenite alluvial placers – 8.9% and mantle of weathering – 10.3% (Galetskyi, 2009). Placers and partially residual deposits represent the basis of modern extraction of titanium-zirconium minerals in Ukraine. Today Mining is carried out directly from buried coastal and alluvial placers. Ilmenite is the most important titanium mineral of magmatic origin, most typical for basic and ultrabasic rocks of the crystalline foundation. Often, the development of continental ilmenite deposits occurs together with its ore-bearing weathering mantle.

The TiO<sub>2</sub> content of primary ores in Ukrainian deposits varies from 4–5% in poor ores to 34.2% in massive ores (Nosachivka deposit). Ilmenite in these ores is unaltered and is a high-quality raw material for both pigment production and metallurgy. Titanium-magnetite concentrate can also be used for metallurgy, which is likely to be extracted from some deposits (Kropyvenka, Davydky). Ores from magmatic depos-

its are complex and contain V<sub>2</sub>O<sub>5</sub> up to 0.042% (Fedorivske deposit). The content of this component exceeds that of ores from the Bjorkreim-Sogndal massif (Norway) and even the Bushveld massif. V<sub>2</sub>O<sub>5</sub> is also found in ores from the primary Stremihorod, Kropyvenka, Torchynske residual and other deposits.

The Ukrainian subprovince of titanium and titanium-zirconium placer deposits was actively studied after the Second World War. At that time, geologists of production organizations determined the chemical composition of ilmenite and other titanium minerals from these placers for the first time. In the works of E. Dudrovych (1977), M. Dyadchenko (1954, 1975), Komliev (2022), V. Ovcharenko (1977), G. Proskurin (1981), S. Tsymbal & Yu. Polkanov (1975) S. Shvaiberov (1989), substance composition, physical and chemical features of individual placer minerals, including impurities in titanium minerals. Impurities in titanium ores of Ukraine have not been sufficiently studied, yet. During the exploration of placers of the Volyn titanium district, the content of vanadium and scandium in ilmenite has been determined only selectively (60–80's of the 20th century).

### 1.2 The content of impurities in titanium minerals

Summary data on the content of impurities in titanium minerals in placers of the world are given by Elsner H. (2010). In this work, it is stated that the content of Nb<sub>2</sub>O<sub>5</sub> in ilmenite concentrates can reach 0.2 wt.% (Capel, Western Australia) and 0.26 wt.% (Madagascar), V<sub>2</sub>O<sub>5</sub> – at the level of 0.09 wt.% (Pulmoddai, Sri Lanka) to 0.25 wt.% (Egypt). In general, el-

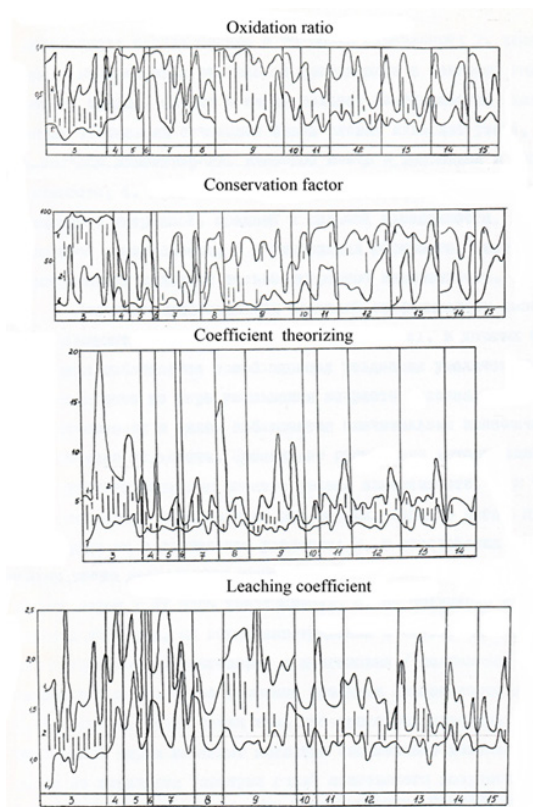


Fig. 1. Dynamics of changes in the chemical composition of ilmenite in sedimentary rocks of placer areas. 1 – intervals of values; 2 – prevailing values; 3 – mantle of weathering; age of sedimentary rocks: 4 – J2; 5 – K1 6 – K2; 7 – Pg2; 8 – Pg 2-3; 9 – Pg3-N1; 10 – N1-2; 11 – aI; 12 – fII; 13 – gII; 14 – aIII-IV; 15 – dIV

Rys. 1. Dynamika zmian składu chemicznego ilmenitu w skałach osadowych w rejonie złóż 1 – przedziały wartości; 2 – dominujące wartości; 3 – płaszcz wietrzenia; wiek skał osadowych: 4 – J2; 5 – K1 6 – K2; 7 – Pg2; 8 – Pg 2-3; 9 – Pg3-N1; 10 – N1-2; 11 – aI; 12 – fII; 13 – gII; 14 – aIII-IV; 15 – dIV

evated concentrations at the level of 0.1–0.2 wt.%  $V_2O_5$  are characteristic of many alluvial-deluvial placers and residual deposits genetically related to weathering of the main rocks. Placers with this  $V_2O_5$  content in titanomagnetites are known in the Philippines, New Zealand, and Japan, and some of them are being developed.

Currently, the demand for titanium minerals and valuable impurities in their composition is substantially increasing. The main reasons for the optimistic forecasts are that only Norway and Finland have their own sources of raw materials for titanium chemistry in Europe, the reserves of which are very limited and represented by primary deposits that require significantly greater capital investment in their development compared to placers. Unlike the chemistry of titanium, its metallurgy requires higher-quality ore raw materials, and with the exception of large deposits in Ukraine, there is no high-quality raw material base for titanium metallurgy in Europe at all. Therefore, there is a prospect of attracting investments of transnational companies to Ukraine.

It has to be mentioned that under current circumstances of the need to increase the defense capability of Ukraine and the transition to a new functional system of the Armed Forces of Ukraine in accordance with NATO standards (STANAG), there is an urgent need for strategic types of mineral raw materials, such as titanium and rare metals. Later, in the post-war recovery, Ukraine will need replenishment of the ore base of existing enterprises, which means development of new deposits. The value of Ti ores, however, increases even more due

to the ability of titanium ore minerals to concentrate some extremely deficient metals as impurities. The latter primarily include Sc, Nb, Ta and V in ilmenite and leucocene.

### 1.3 Methods

To estimate the levels of impurity elements in rocks and ores, the results of chemical analyzes of rocks and ores were statistically processed using Excel, MathCad. The study uses chemical analyzes of different years made in the laboratories of geological enterprises (Prockurin G.P., 1981; Schvaiberov S.K. 1989, 2002) and cited in numerous reports and papers (Kononov Yu.V., 1966; Korneliussen, A., 2000; Dushene J.-C., 1970; Jose C. Gespar, 1983; Valvasori, A.A., 2020; Vlad-Victor Ene, 2014; Silvio José Elias, 2016). The method of processing analyzes of granulometry and chemical composition of ilmenite, calculation of quantitative indicators that parameterize the granulometric field and the field of variability of ilmenite, integrating the root rocks-weathering crust—mesozoic-cenozoic sedimentary deposits within the placers is used for placers of Irshansk ore field (Komliev O., 2022). Interpretations of the obtained results were carried out on a broad paleogeographical basis, taking into account tectonics, paleorelief, and paleoclimates. This methods allow to estimate quality of ilmenite ores.

## 2. Characteristics of Ukrainian titanium ores

### 2.1. Ilmenite alteration

Titanium ores of Ukraine are noted for their quality and large reserves, so they represent considerable value. Today in

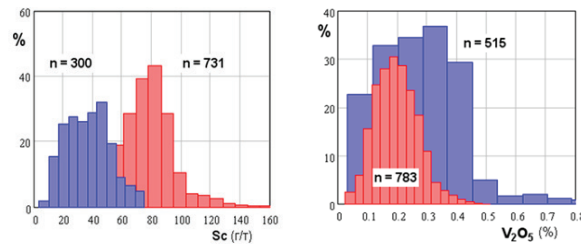


Fig. 2. Distributions of scandium and vanadium oxide in ilmenites and leucoxenes:

- 1) Korosten complex (Korosten and Korsun-Novomyrhorod plutons), in mantle of weathering and alluvium within the plutons – red histograms;
- 2) from other areas of the world (see Table 1) – blue histograms. Content of Sc is given in g/t

Rys. 2. Rozkłady tlenku skandiu i wanadu w ilmenitach i leukoksenach:

- 1) Kompleks Korosteń (pluton Korosteń i Korsun-Nowomyrhorod), w strefie wietrzenia i aluwium w obrębie plutonów – histogramy czerwone;
- 2) z innych obszarów świata (patrz tabela 1) – histogramy niebieskie. Zawartość Sc podano w g/t

Tab. 1. Oxides of Ti, Fe, V in %; Sc, Nb, Ta in g/t. KST and KSN are Korosten and Korsun-Novomyrhorod plutons, respectively [\* placers in the Middle Dnipro region: Samotkansky, Vovchansky, Krasnokutsky; \*\* – various coastal placers – Australia, Hindustan, Indochina, Africa, South and North America; GN, G, GA, A – gabbro-norites, gabbro, gabbro-anorthosites, anorthosites, respectively]

Tab. 1. Tlenki Ti, Fe, V w %; Sc, Nb, Ta w g/t. KST i KSN to odpowiednio plutony Korosteń i Korsun-Nowomyrhorod [\* placery w regionie środkowego Dniepru: Samotkansky, Vovchansky, Krasnokutsky; \*\* – różne place przybrzeżne – Australia, Hindustan, Indochiny, Afryka, Ameryka Południowa i Północna; GN, G, GA, A – odpowiednio gabro-noryty, gabro, gabro-anortozyty, anortozyty]

Object (region, rocks, minerals)	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	Sc	Nb	Ta	V <sub>2</sub> O <sub>5</sub>
KST– G,GA,A	49.21	3.36	43.18	81	109	22	0.206
KST – mantle of weathering	51.66	11.48	33.72	72	163	12	0.196
KST – placers	56.96	17.60	20.56	85	229	15	0.237
KSN – G,GA,A	50.71	3.41	42.99	69	373		0.181
KSN – mantle of weathering	52.40	8.42	36.72		455		0.138
KSN – placers	58.02	18.65	18.37	129	509		0.221
Bilokorovychi dyke (Ukraine)	50.67	2.95	44.04				0.30
Tarasivka placer (Kyiv region, Ukraine)	64.42			50		123	
Middle Dnipro * – placers	68.48	24.14	0.89		1245	558	0.141
Mokro-Yalynsky (Приазов'я) – placers	64.96	28.56	0.46		1679	1583	0.118
Water areas of the Black and Azov seas(Ukraine) (Укр.)	53.14	19.85	23.96			53	0.163
Norway. <b>Ilm</b> , G,GA,A	47.84	7.92	38.55				0.183
Norway. <b>Hemo-Ilm</b> , G,GA,A	32.84	33.37	26.56				0.407
Grenville (Canada) – <b>Hemo-Ilm</b> , G,GA,A	39.25	26.35	30.37	37	25	1	0.367
Labrador (Canada) – <b>Ilm</b> , G,GA,A	50.55	4.72	42.17	39			0.23
Kunene ( Namibia ) – G,GA	51.42	2.49	43.70	37	191	14	0.162
Mozambique – placers	48.80	25.02	15.78		662		0.11
Coastal sea placers **	79.34				2212	188	0.162
Panchzihua ( Southeast China ) – G	52.63	3.71	38.40	43	79		0.156
South Africa – Ultramafic rocks	53.00	7.54	24.02	21	1312	124	0.186
Lyakhovych V.V., 1979. Gabbroids.					560	262	0.196
Lyakhovych V.V., 1979. Granitoids.					2214	820	
Industrial contents in ores					700–2800	200–800	≥ 0.2

the Ukraine, the placers of titanium minerals are exploited. They are also found in crystalline rocks – in gabbroids of the Korosten and Korsun-Novomyrhorod plutons, residual – in the weathering crusts of gabbroids. In alluvial placers, these ores are close to the sources of their formation and connected to the distant transportation. Useful ore mineralization is represented by pure ilmenite (in gabbroid ores), to which in weathering mantle and in the placers, especially abundantly in distant ones, are added leucoxenes and, in some places, rutile. There is currently quite a lot of interest in titanium in the world, and it will undoubtedly grow over time. At the same time, if you look closely at the compositions of ilmenites, the value of titanium ores begins to play out in a new, even brighter light.

The theoretical chemical composition of ilmenite is assumed to be TiO<sub>2</sub> (52.7%) and FeO (47.3%). On the earth's

surface (in hypergenic conditions), the chemical composition of ilmenite changes due to the integrated action of tectonic, paleoclimatic, paleogeomorphological, and paleohydrological factors. They can create favorable conditions for weathering of crystalline rocks and their transformation into chemical weathering crust of kaolin type. Mantle of weathering formation is a necessary condition for the formation of alluvial ilmenite deposits. In the weathering mantle, chemically unchanged ilmenite is released from crystalline rocks and begins to undergo the stages of continental lithogenesis with the participation of the above factors. The "fresh" ilmenite brought to the level of denudation begins to change in the weathering crust and then continues continuously, accelerating with the activation of ancient exogenous processes, when complete or partial destruction of ilmenite placers occurs, slowing down

Tab. 2. Parameters of scandium distribution in the ilmenite deposits of the Korosten complex

Tab. 2. Parametry rozmieszczenia skandiu w utworach ilmenitu kompleksu Korosten

Deposit	Localization environment	N	mean	min	max	moda
Stremyhorod	G,GA,A	161	80	61	100	82
Stremyhorod	mantle of weathering	98	84	15	147	81
Fedorivka	G,GA,A	30	116	90	135	116
Torchyn	G,GA,A	33	66	50	90	60
Torchyn	mantle of weathering	167	64	30	100	70
Hatskivka area of Upper Irsha deposit	mantle of weathering	16	85	47	110	96
Hatskivka area of Upper Irsha deposit	placer	24	84	61	107	85
Valky-Hatskivka deposit	placer	25	62	30	110	50
Valky-Hatskivka deposit	placer	32	71	15	200	60
Trostyanytsya deposit	mantle of weathering	13	84	81	88	81
Trostyanytsya deposit	placer	18	93	88	103	88
Zlobychi deposit	mantle of weathering	29	66	24	94	67
Zlobychi deposit	placer	45	80	38	100	87
Paromivka deposit	mantle of weathering	16	85	62	116	98
Paromivka deposit	placer	14	94	65	134	80
Nosachivka deposit (KSN)	G,GA,A	6	69	48	98	
Southern part of KSN	placer	4	129	76	193	

when they become less active, and even stopping after they become buried. The chemical composition of ilmenite reflects the total result of exogenous processes and, in combination with other methods, provides important information about the paleogeographic development of territories. The main processes that change the chemical composition of ilmenite are oxidation and leaching. At the oxidation stage, unaltered ilmenite from igneous rocks begins to break down under the influence of mainly oxygen. It is oxidized, partially leached, the crystal lattice is destroyed, free titanium and iron oxides are formed, and the ilmenite phase is completely destroyed. The end product of the first stage of ilmenite alteration is leucogenized ilmenite. At the second stage, the main process is iron leaching. At this stage, titanium hydroxides crystallize and end up forming leucoxene, and after complete iron leaching, pseudorutile is formed. Both processes occur simultaneously, but oxidation prevails at the first stage and leaching at the second. Changes in the chemical composition of ilmenite in the hypergene zone can be characterized by various coefficients, which we first proposed to solve various problems during paleogeographic and special paleogeomorphological works in areas promising for ilmenite placer deposits in the territory of the Ukrainian Shield. The results of chemical composition analyses of ilmenite monofractions taken from crystalline rocks of the basement, weathering crust, and Mesozoic and Cenozoic sediments were used. The coefficients were calculated using different methods. However, at the final stage, the oxidation coefficient ( $Fe^{3+}/FeS$ ), leaching coefficient ( $FeS/TiO_2$ ), and thiorization coefficient ( $TiO_2/Fe_2O_3$ ) were used. The disadvantage of these coefficients is the inability to estimate the degree of alteration of ilmenite relative to its theoretical composition. Therefore, in addition to them, we also calculated the degree of preservation of ilmenite using the formula:

$$C_{prs} = 114.4 FeO/TiO_2 \quad (1)$$

This indicator is recommended for the oxidation stage of ilmenite. Based on a large array of data on prospective sites, we studied the dependence of granulometric characteristics and chemical composition of ilmenite monofraction for various elements of the ancient relief of the Late Oligocene-Middle Miocene age. The empirical formula:

$$Md = -aK1 + b/10/K2 - 1/x/ + c \quad (2)$$

was derived. Where: K1 – oxidation coefficient K2 – leaching coefficient, a, b, c – variable coefficients that vary depending on the initial conditions (composition of the source rock, paleorelief slopes, time spent in the hypergenesis zone). Fig. 1 shows the dynamics of changes in the chemical composition of ilmenite in the weathered crust and sedimentary rocks.

## 2.2. Impurities in titanium minerals from Ukrainian deposits

In Table 1 we provide the contents of some trace elements and mineral-forming oxides in ilmenites of a number of their accumulations in Ukraine and some other regions of the world. In many cases, these trace elements are present in ilmenite in such quantities that they definitely acquire industrial importance, especially if we take into account the large size and reserves of titanium deposits. Therefore, the accompanying extraction of trace elements during the processing of the mineral-bearer becomes economically profitable and provokes the need to improve the relevant technologies.

In this paper, which we hope will not be the last, we narrow our report to two rare metals: Sc and V in the ilmenite of numerous titanium deposits and occurrences of the Korosten complex – the Korosten and, to a lesser extent, the Korsun-Novomyrhorod plutons, due to lack of data. It is in the ilmenite of this complex that Sc shows the highest concentrations (at least twice), and this is reflected in Table 1 and the figure below. Moreover, the reserves of ilmenite ores on these plutons are huge.

As for vanadium, its impurities in the Korosten ilmenites are not significant (Table 1 and Figure2). Its highest concen-

Tab. 3. Parameters of vanadium pentoxide distribution in ilmenite deposits of the Korosten complex

Tab. 3. Parametry rozkładu pięciotlenku wanadu w złożach ilmenitu kompleksu Korosten

Deposit	Localization environment	N	mean	min	max	moda
Stremyhorod	G,GA,A	56	0.184	0.060	0.370	0.200
Stremyhorod	mantle of weathering	149	0.168	0.050	0.320	0.140
Fedorivka	G,GA,A	39	0.214	0.024	0.425	0.303
Penyazevychi	G,GA,A	6	0.347	0.060	0.530	
Nosachivka deposit (KSN)	G,GA,A	14	0.215	0.110	0.430	0.200
Hatskivka area of Upper Irsha deposit	mantle of weathering	46	0.195	0.100	0.305	0.230
Valky-Hatskivka deposit	mantle of weathering	37	0.136	0.051	0.400	0.106
Hatskivka area of Upper Irsha deposit	placer	47	0.233	0.060	0.329	0.244
Trostyanytsya deposit	mantle of weathering	40	0.267	0.150	0.460	0.320
Trostyanytsya deposit	placer	67	0.246	0.112	0.355	0.235
Lemna deposit	mantle of weathering	52	0.220	0.140	0.380	0.190
Lemna deposit	placer	83	0.232	0.120	0.310	0.230
Southern part of KSN	mantle of weathering	107	0.138	0.060	0.310	0.160
Southern part of KSN	placer	15	0.221	0.120	0.400	0.190

trations are characteristic of hemi-ilmenites from deposits in Norway and Canada. Titanomagnetites contain even more vanadium, in particular, ores of the Suwalki massif (Poland) with vanadium pentoxide of 0.81% (maximum value 1.2%). Titanium-magnetite clusters are less typical for the Korosten pluton, although they are present in gabbroids at some deposits (Kropyvenka). In any case, we believe that the extraction of vanadium from ilmenite, along with titanium and scandium, is quite profitable.

As for vanadium, its impurities in the Korosten ilmenites are not significant (Table 1 and Figure 2). Its highest concentrations are characteristic of hemi-ilmenites from deposits in Norway and Canada. Titanomagnetites contain even more vanadium, in particular, ores of the Suwalki massif (Poland) with vanadium pentoxide of 0.81% (maximum value 1.2%). Titanium-magnetite clusters are less typical for the Korosten pluton, although they are present in gabbroids at some deposits (Kropyvenka). In any case, we believe that the extraction of vanadium from ilmenite, along with titanium and scandium, is quite profitable.

In Tables 2 and 3, we present statistical characteristics for Sc and V<sub>2</sub>O<sub>5</sub> in some deposits mainly on the Korosten pluton (we have a small amount of such data for the Korsun-Novomyrhorod pluton).

The following is noteworthy:

1. In most cases, in the same deposits, ilmenite from placers is significantly richer in scandium than in the underlying residual environments (in mantle of weathering). The explanation for this is the greater stability of Sc compared to Fe in the process of leucoxenization. It is known that during weathering, the ferrous iron in ilmenite is gradually oxidized and leaves ilmenite in the form of Fe<sup>3+</sup>. At least partially. Titanium and scandium remain on site and are enriched in leucoxene. Therefore, placers that have been exposed to weathering for a longer and/or more active period of time (for example, due to a longer transportation profile from the

source of erosion) may be characterized by ilmenite richer in scandium. This may be the case with ilmenite in the southern Korsun-Novomyrhorod pluton placers, up to 190 g/t, for which we do not have sufficient data (on Sc).

2. Significantly elevated scandium contents were found in 30 analyzes of ilmenites from gabbroids of the Fedorivka deposit. We do not have an explanation for this.

3. As for vanadium, it seems that it is removed from ilmenite under the influence of weathering, but obviously weaker than iron.

### 3. Conclusion

Ukraine's titanium ores are distinguished by their quality and large reserves, which allows them to be used both to produce a range of chemical products and in metallurgy. Different applications require the ores of the appropriate quality. The main processes that change the chemical composition of ilmenite are oxidation and leaching. Changes in the chemical composition of ilmenite in the hypergene zone can be characterized by various coefficients, which we first proposed to solve various problems when conducting paleogeographic and special paleogeomorphological works in areas with prospects for ilmenite placer deposits in the Ukraine. The authors characterized ilmenites from different ages and conditions of placer formation. Based on these studies, it is possible to create models of ilmenite zonation in placers and further geometrization of deposits. An important problem is the content of useful impurities in ilmenites, in particular vanadium and scandium. In this case, placers that have been exposed to weathering for a longer and/or more active period of time (i.e., the above-mentioned processes of chemical composition changes) may be richer in scandium. Vanadium is removed from ilmenite by weathering, but this process is weaker than iron removal, and therefore may also be a valuable impurity, which should be taken into account when developing technologies for its extraction.

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### *Badanie cennych domieszek rudnych mineralow tytanu na Ukrainie*

*Ruda tytanu jest surowcem o krytycznym znaczeniu dla UE. Ukraina posiada znaczne zasoby rud tytanu, które są reprezentowane przez kilka typów genetycznych i mają szereg zalet: możliwość wydobywania surowców do różnych celów; korzystne warunki górniczo-geologiczne dla większości złóż rezydualnych. Ilmenit jest najważniejszym minerałem tytanu, najbardziej typowym dla skał zasadowych i ultrazasadowych podłoża krystalicznego oraz skał osadowych. Wartość rud tytanu podnosi obecność cennych domieszek (V, Sc, Ta, Nb). Jakość rud tytanu jest związana ze stopniem ich przeobrażenia. Stopień przemiany ilmenitu wpływa na przemysł, w którym stosowane są koncentraty oraz rozwój technologii ich przetwórstwa. Autorzy opracowali podejście do oceny tego parametru oraz pokazali dynamikę zmian składu chemicznego ilmenitu w zwietrzalej skorupie i skałach osadowych. Na podstawie statystycznego opracowania danych z analizy chemicznej rud tytanu wykazano, że Sc ma najwyższe stężenia w ilmenicie kompleksu Korosteń w porównaniu z innymi utworami geologicznymi Tarczy Ukraińskiej, co rodzi potrzebę udoskonalenia odpowiednich technologii.*

**Słowa kluczowe:** rudy tytanu, odmiany ilmenitu, domieszki, leukoksynizacja