Preliminary LA-ICP-MS trace element data for ilmenite and apatite from Fedorivka, Stremyhorodske and Nosachiv Ti-P deposits of the Ukrainian Shield

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Abstract. Proterozoic massif-type anorthosites of the Ukrainian Shield host a number of intrusions with economic concentrations of ilmenite-apatite ores. Among them are Fedorivka and Stremyhorodske deposits within the central part of the Korosten pluton and Nosachiv deposit in the Korsun-Novomyrhorod complex. LA-ICP-MS trace elements analyses of apatite revealed similarities and differences between these deposits, partially attributed to fractional crystallization such as strongly negative europium anomaly Eu/Eu* (0.09-0.11) in sample from the Nosachiv deposit. Application of trace elements in cumulus apatite as petrological indicators suggest potential crustal contamination by a silicic component in the case of Nosachiv and Stremyhorodske ores, clearly distinct from more primitive melt composition revealed for the Fedorivka deposit. Sample from Fedorivka has also the highest content of scandium (111 ppm on average) and lowest of REE which could indicate useful application of petrological data in mineral exploration focused on potential by-products such as scandium or REE.

1 Introduction

Ukraine holds the largest titanium reserves in Europe hosted in both primary and alluvial deposits and remains an important titanium producer, even though only placer ores are currently being mined. Proterozoic massif-type anorthosites and related rocks contain economic concentrations of not only titanium and phosphorus but can be also considered as a potential source of other raw materials such as vanadium, scandium or REE occurring as substitutions in major ore minerals. The aim of this study was to analyse trace element content of ilmenite and apatite from three orthomagmatic titanium deposits of the Ukrainian Shield to gain a better insight into the ore forming processes and examine the potential for additional by-products.

2 Geological settings

There are two Paleoproterozoic anorthosite-mangerite-charnockite-granite (AMCG) complexes within the Ukrainian Shield: the Korosten and Korsun-Novomyrhorod plutons (Shumlyanskyy et al. 2017). The Korosten AMCG complex consist of a number of granitic rocks that belong to the rapakivi group, and a suite of basic rocks that includes predominantly anorthosite and leucogabbronorite, with subordinate gabbro-noritic rocks which host Fedorivka and Stremyhorodske deposits (Fig. 1). Similarly, The Korsun-Novomyrhorod AMCG complex constituents (Fig.1) are also mainly rapakivi granites, anorthosite, leuconorite, with less abundant mesocratic norite, gabbro-norite and gabbro (Shumlyanskyy et al. 2017).

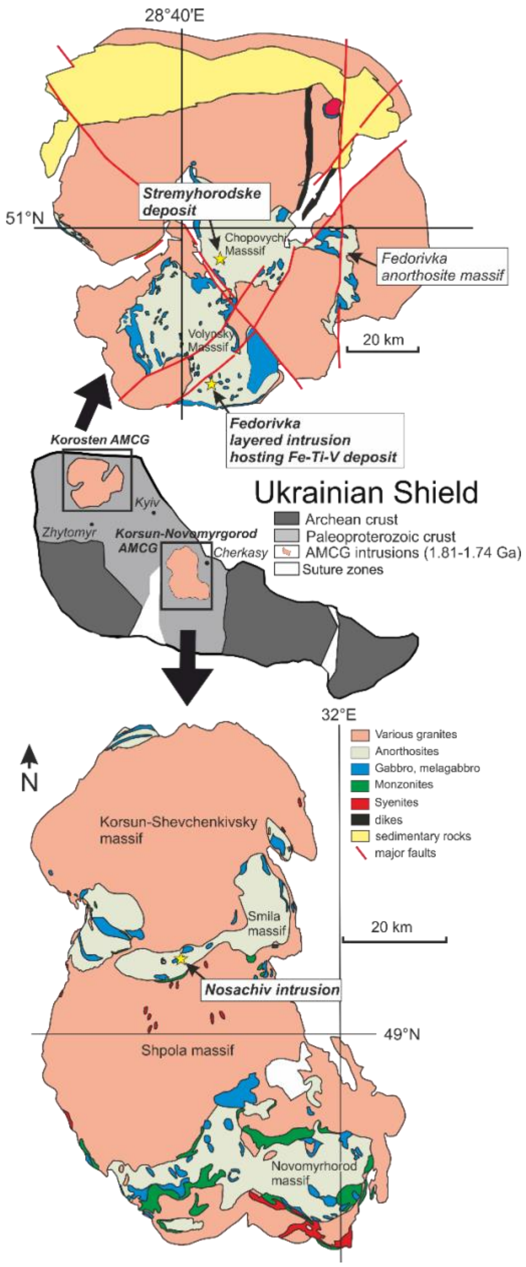

Figure 1. Geological map of the Korosten and Korsun-Novomyrhorod plutons of the Ukrainian Shield with the location of studied Ti-P ore deposits.

The Fedorivka Ti-P deposit is located 30 km north of Zhytomyr and 125 km west of Kyiv. It is hosted by the Fedorivka Layered Intrusion (FLI), and consist of ilmenite, apatite and titanomagnetite accumulations within layers of oxide-rich olivine gabbro. It's worth to point out that the Fedorivka Layered Intrusion which hosts the deposit should be confused with the Fedorivka Anorthosite Massif. The gutter- or banana-shaped gabbroid intrusion is 240-450 m wide and 3,5 km long in northeast direction with ore-bearing gabbro found a the depth up to 322 m (Gurskiy 2002). Available resource estimation amount to 129.776 Mt of ore with 3 wt% P_2O_5 (Syvyi et al. 2019) but the information about the reserves of titanium are limited. Average grade has been reported as 6.5 wt% TiO_2, 2.9 wt% P_2O_5 and 0.042 wt% V_2O_5 (Scherbak and Bobrov 2005). Some ilmenites have been mentioned as carriers of isomorphic admixtures of Sc and V.

The Stremyhorodske Ti-P deposit is located 20 km south-east of Korosten and 130 km north-west from Kyiv. Ore mineralization consist of ilmenite, apatite and minor titanomagnetite hosted by predominantly troctolites of the oval-shaped, 2.3 x 1 km in size, igneous body which appears conical in cross sections (Gursky et al. 2003). Resources are estimated as 886.344 Mt of ore with 2.4 wt% P_2O_5 (Syvyi et al. 2019). Access to data on reserves of titanium ores and scandium ores is limited, available sources report the average content of 6.91% TiO_2, 2.42% P_2O_5, 0.2% vanadium and 80 g/t of scandium.

The Nosachiv Ti-P deposit is located 45 km south-west of Cherkasy, 160 km south-east of Kyiv. Hosted by 2250 m long and 200-780 m wide gabbroid intrusion, the ilmenite-apatite deposit is drilled up to 600-650 m and opened at depth (Kryvdik et al. 2009). The ore in Nosachiv deposit is related to two separate intrusive phases: first stage is represented by fine-to medium grained olivine and olivine-containing, apatite rich and ilmenite-poor gabbroids while the second one is the main ore stage characterized by an almost complete absence of olivine and apatite in ilmenite-rich, coarse to medium-grained norites (Gursky et al. 2003). Access to data on reserves of titanium ores and scandium ores is limited, available sources report average grade to be 7.44% TiO_2 and 0.75% P_2O_5.

3 Samples and methods

One apatite-ilmenite bearing samples were chosen from each deposit based on overall abundance of ore minerals and bulk rock geochemical assays (1.5-2.5 wt. % P_2O_5 and 4-5 % TiO_2). Sample from the Stremyhorodske deposit come from the drillcore C80 (sample depth 66 m), Nosachiv material come from the drill core 2004 (depth 84 m). Ilmenite and cumulus apatite are the main ore minerals in each sample, in Stremyhorodske deposit they are accompanied by minor magnetite with trellis ilmenite exsolutions while in Fedorivka sample by magnetite with very fine ulvöspinel exsolutions forming cloth texture.

After petrographic observations in reflected light, samples were analyzed with JEOL JXA-8230 electron microprobe as well as ESL213 Nd:YAG laser ablation system coupled to an Thermo Scientific iCAP TQe ICP-MS in the Laboratory of Critical Elements AGH-KGHM at AGH University of Krakow. For apatite, the laser was fired at a frequency of 20 Hz and fluence of 4 J/cm2 with 40 µm laser spot size. In case of ilmenite, fluence of 5 J/cm2 and a 50 µm laser spot size was used. Helium was used as carrier gas with a flow rate of 0.70 L/min. Typical acquisition consisted of 40 s of spot measurement followed by 30 s of wash time between each analysis. For apatite, NIST 612 glass standard was used as the external standard for quantification of the element content while NIST 610 and Loliondo Arusha apatite nanopellet (myStandards GmbH) were also monitored for QAQC. In case of ilmenite, Kennedy Ridge magnetite nanopellet (MAKR-NP, myStandards GmbH) was used for quantification of trace elements while BHVO-2-NP nano-pellet was used for quality control of the analyses.

4 Results

4.1 Trace element composition of ilmenite

	STR (n=7)	FED (n=9)	NOS (n=9)
	ppm		
Sc	**91.7** (79.7-105)	**111** (103-117)	**66.8** (64.2-70)
V	**620** (347-963)	**111** (84.3-129)	**1723** (1309-2028)
Cr	0.89 (0.75-1.12)	2.39 (1.84-2.7)	269 (210-297)
Mn	6372 (5962-7515)	5693 (5560-5946)	4654 (4488-4771)
Co	28.9 (20.7-38.6)	53.1 (47.9-56.5)	58.8 (47.1-67.7)
Ni	0.49 (0.28-0.85)	0.78 (0.57-1.11)	3.06 (1.8-3.79)
Cu	10.5 (9.6-11.2)	11.4 (9.99-17.7)	10.5 (10.1-10.8)
Zn	141 (61.9-210)	105 (79-205)	141 (118-189)
Nb	131 (39.6-173)	38.5 (36.4-40.3)	240 (233-251)
Mo	28.5 (22.7-33.5)	1.79 (1.29-2.74)	13.6 (13.2-14.4)
Sn	4.54 (3.37-8)	0.14 (0.11-0.18)	8.95 (8.22-9.72)
Hf	9.10 (2.18-21)	3.68 (3.54-3.76)	12.9 (0.95-21.1)
Ta	6.28 (1.17-8.88)	2.73 (2.49-2.96)	14.7 (14.18-15.3)
W	0.86 (0.46-1.02)	0.03 (0.02-0.04)	4.58 (3.99-5.37)

Table 1. Selected LA-ICP-MS trace element composition of ilmenite. Average content in ppm, minimum-maximum content in brackets, n=number of analytical spots.

Ilmenite trace element composition has been summarized in Table 1. Ilmenite from Nosachiv is enriched in vanadium which can be attributed to the lack of magnetite (typical host of vanadium) in comparison to Fedorivka and Stremyhorodske deposits. It is also characterized by higher content of Cr, Ni but also Ta and W. Ilmenite from Fedorivka contains the highest content of scandium (on average 111 ppm of Sc), followed by Stremyhorodske (on average 91.7 ppm Sc) and Nosachiv (on average 66.8 ppm of Sc).

4.1 Trace element composition of apatite

Among analyzed samples, apatite from the Fedorivka deposit is clearly distinct from Nosachiv and Stremyhorodske deposits, which are more similar to each other and are characterized by higher content of Y, REE, Th, U and lower Sr (Fig. 2).

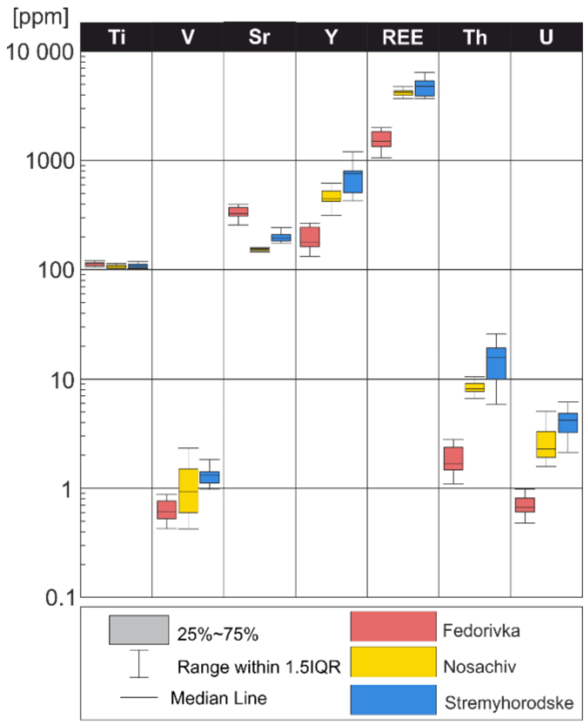

Figure 2. Box-and-whisker plot for selected trace element composition of analyzed apatites from Ti-P deposits of the Ukrainian Shlied.

Rare earth elements content is the highest in Stremyhorodske sample (∑REE 3700-6411 ppm), followed by Nosachiv (∑REE 3748-4800 ppm), distinctly lower in Fedorivka (∑REE 1058-2008 ppm) and in all cases chondrite normalized REE patterns exhibit negative Eu anomaly (Fig. 3). Eu/Eu* (calculated as EuN/(SmN*GdN)$^{0.5}$) range from 0.47-0.53 for Fedorivka, 0.24-0.27 for Stremyhorodske to 0.09-0.11 for Nosachiv. Negative Eu anomaly is typically attributed to fractional crystallization of plagioclase and strongly negative Eu anomaly in Nosachiv samples might be linked with the K-feldspars known to occur within the intrusion. Different degree of fractional crystallization is also suggested by ternary discrimination diagram (Kieffer et al. 2023, 2024a) where each deposit form separate field with Fedorivka standing out with more primitive melt composition (Fig. 4, however a relatively wide spread of data collected within a single sample is noteworthy).

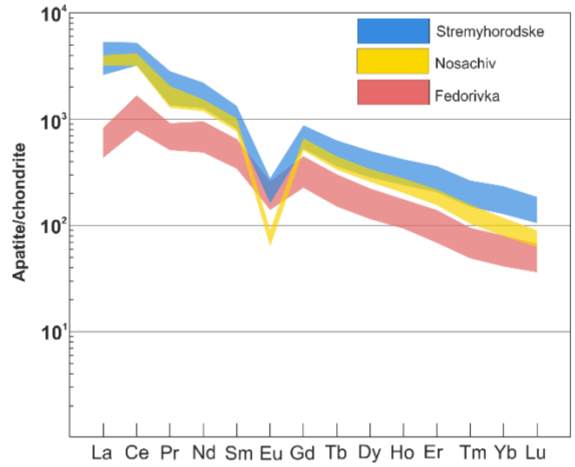

Figure 3. Chondrite normalized REE patterns for apatites from Ti-V deposits of the Ukrainian Shield.

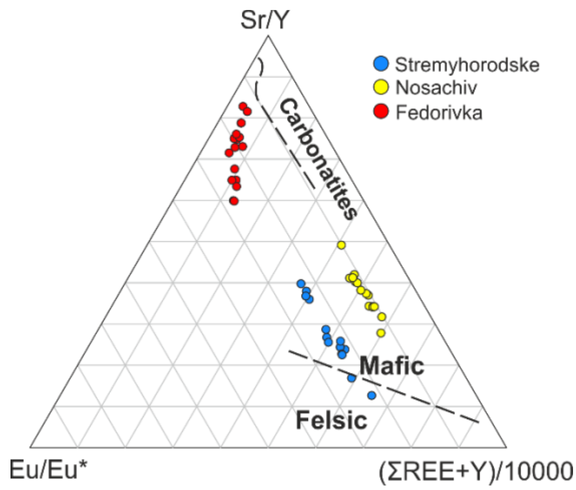

Figure 4. Ternary discrimination diagram for apatite (after Kieffer et al. 2023, Kieffer et al. 2024a).

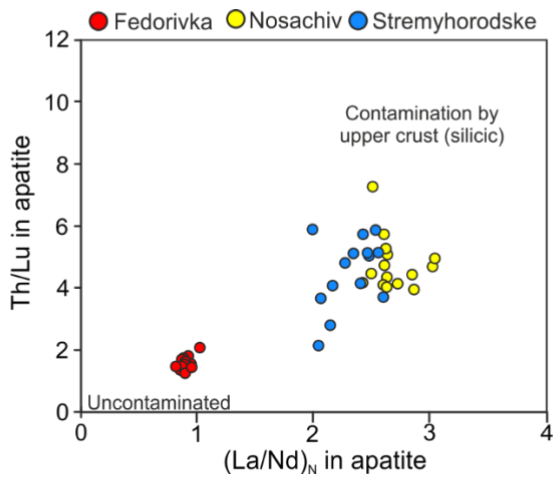

Figure 5. Th/Lu as a function of $(La/Nd)_N$ used as tracker of crustal contamination (after Kieffer et al. 2024b).

Kieffer et al. (2024b) showed that trace elements composition of cumulus apatite has a potential to be a tracer of crustal contamination and position of Nosachiv and Stremyhorodske samples on Th/Lu vs. $(La/Nd)_N$ diagram might be seen as a result of contamination by a silicic component.

5 Conclusions

LA-ICP-MS trace elements study revealed several similarities and differences between Ti-P deposits hosted by AMCG complexes of the Ukrainian Shield. Some of them can be attributed to fractional crystallization and potential crustal contamination by a silicic component but interestingly, these processes might be also linked to the enrichment in potential by-products such as scandium or REE. Samples from Nosachiv and Stremyhorodske deposits, exhibiting signatures of higher degree of fractional crystallization and crustal contamination juxtaposed with more primitive melt composition of Fedorivka deposit, exhibit both higher content of REE in apatite and lower content of Sc in ilmenite. Further studies will examine whether information obtained from petrological indicators can be applied to mineral exploration focused on potential by-products associated with Ti-P mineralization.

Acknowledgements

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