

Article



Vanadium and Cobalt Occurrence in the Fe-Ti-V Oxide Deposits Related to Mesoproterozoic AMCG Complex in NE Poland

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Abstract: On the basis of geochemical whole-rock and mineralogical point analyses, the concentrations of V and Co were determined in magnetite-ilmenite oxide ores, associated with sulphides, at the Krzemianka and Udryn deposits in the Mesoproterozoic Suwałki Anorthosite Massif (SAM) in NE Poland. EPMA analyses showed that the main carrier of vanadium was magnetite (mean = 0.42wt%) and, to a lesser extent, ilmenite (mean = 0.14 wt%) and minor Al-spinels (mean = 0.04 wt%). In turn, cobalt was found mainly in the form of isomorphic substitutions in magmatic sulphides such as pentlandite (mean = 4.41 wt% Co), pyrrhotite (mean = 0.16 wt%), and chalcopyrite (mean = 0.11 wt%). Moreover, Co-enrichments were also recognized in the secondary sulphides, such as pyrite and bravoite, replacing pyrrhotite (means = 1.6 and 2.7 wt% Co, respectively), and in the form of different thiospinels ((Fe, Ni) (Co, Ni)2S4), mainly siegenite (mean = 22.0 wt% Co), replacing pyrrhotite and pentlandite. Vanadium cations were substituted in Fe, Ti oxide minerals in place of Fe⁺³ cations, and in the case of cobalt, Fe⁺² cations were substituted in sulphides and thiospinels. Vanadium and cobalt showed high Person's correlation coefficients (r = 0.70), indicating their close spatial coexistence and a common source, which was parental anorthosite-norite magma of the SAM suites. The common magma genesis of magnetite-ilmenite and sulphide mineralization was also confirmed by the very similar shapes of the curves of REE content in the oxide-sulphide ores in relation to chondrite, in which negative Eu anomalies and positive Sm anomalies are clearly visible. Although the average contents of vanadium and cobalt were low (arithmetic means = 960 ppm, and 122 ppm, respectively), the resources of these metals were estimated to be large due to the enormous reserves of magnetite-ilmenite ores hosted by the SAM. However, the Fe-Ti-V ores associated with Fe, Ni, Co, and Cu sulphides were considered to be sub-economic because of their depth of occurrence (mainly 1.0 km below the surface level); their metal contents, which were usually too low; and additionally the fact that the location is in a highly environmentally protected landscape and lake area.

Keywords: trace elements; strategic elements; vanadium; cobalt; Fe-Ti-V deposits; anorthosites; norites; Mesoproterozoic AMCG; Poland

1. Introduction

The development of modern green technologies and the pursuit of a zero-emissions economy have necessitated the use of critical elements on a much larger scale than before [1,2]. These elements which are defined as critical generally do not form independent deposits but accompany another major metallic element in the ores, in the form of isomorphic substitution in other major minerals. The most recent list of elements considered critical for the European Union includes vanadium and cobalt [3]. Cobalt is used in numerous metallurgical and chemical applications, mainly in cathode materials for re-

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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https://creativecommons.org/license s/by/4.0/). chargeable batteries and as super alloys that exhibit outstanding strength and surface stability at high temperatures [4,5].

The land-based cobalt resources identified worldwide constitute about 25 million tons [6]. Three main types of metal deposits supply almost 90% of cobalt to world markets; these are sediment-hosted stratiform Cu deposits, Ni-bearing laterite deposits, and magmatic Ni-Cu-Co sulphide deposits hosted in mafic and ultramafic rocks [6]. During magma crystallization, cobalt behaves similarly to nickel, crystallizing in sulphides. The main carrier of cobalt is pentlandite (*Ni*, *Fe*, *Co*)₉*S*₈, in which the Co content ranges from below one to several percent by weight. The average content of cobalt in igneous rocks is 23 ppm [7]. The rocks that are richest in Co are ultrabasic rocks, dunites, and peridotites (127–148 ppm Co), whereas norites and gabbros contain on average 50 to 60 ppm Co, and granites contain approximately 5 ppm [7]. In the hydrothermal stage, a large group of cobalt sulphides, arsenides, antimonides and arsenic, and antimony sulphides are formed. The most common among these are cobaltite (up to 36 wt% Co), glaucodot (up to 31 wt% Co), danaite (3–10 wt% Co), safflorite (~28 wt% Co), skutterudite (up to 30 wt% Co), siegenite (20–30 wt% Co), bravoite (up to 6 wt% Co), and costibite (~27 wt% Co).

Vanadium is one of the most important alloying additives in the production of full-alloy and high-strength low-alloy steels. The average vanadium content in the continental crust is high, at approximately 150 ppm [8]. Vanadium occurs through isomorphic substitution in numerous minerals, but these minerals are disseminated as accessory minerals in rocks. Among the orthomagmatic deposits, which are genetically related to ultrabasic (dunite) and basic rocks (gabbro, norite, and anorthosite), the content of V_2O_5 ranges from 0.2 to 2 wt%, respectively. The main V carriers in these deposits are generally titanium-rich magnetite ($Fe^{2+}(Fe^{3+}, Ti)_2O_4$) and ulvöspinel ($TiFe_2O_4$) and ilmenite ($FeTiO_3$). Vanadium (V^{3+}) forms a spinel-coulsonite (V_2FeO_4) an isomorphic series with other spinels, such as magnetite and chromite, and therefore Fe^{3+} may be substituted by V^{3+} in these minerals. Considerable admixtures of V^{3*} or V^{4*} are present in dark rock-forming minerals [8]. In orthomagmatic Fe-Ti(-V) deposits, a typical grade of titanomagnetite ore is 0.2-1 wt% V₂O₅ (max. 1-2 wt%) [8]. The world's resources of vanadium exceed 63 million tons [6]. Additional sources of vanadium are titaniferous magnetite, phosphate rock, uraniferous sandstone and siltstone, bituminous sands, and heavy crude oil [6]. One of the main types of vanadium-supplying deposits is orthomagmatic Fe-Ti-V oxide, which is accompanied by sulphide mineralization. The presence of polymetallic sulphides (Fe, Cu, Co, and Ni) in this type of deposit can also be a source of cobalt, which can be present in the form of its own sulphides and isomorphic substitutions in other sulphides.

This type of Fe-Ti-V deposit was documented in NE Poland in the 1960s up to the 1980s. However, detailed data on the economic potential of these deposits for critical elements were poorly provided during exploration. Hence, the aim of this study was to determine the whole rock contents of V and Co in mineralized samples from the Krzemianka and Udryn Fe-Ti-V deposits in the Suwałki Anorthosite Massif (SAM) in Poland. The results of electron microprobe analyses of selected minerals are also presented in order to show the residence sites of these elements.

2. Geological Setting

2.1. Regional Geology

The Krzemianka and Udryn Fe-Ti-V ore deposits are located in the Mesoproterozoic Suwałki Anorthosite Massif (SAM) in the NE part of Poland [9–13], within the Mesoproterozoic beltiform magmatic AMCG (Anorthosite–Mangerite–Charnockite-Granite rapakivi) suite known as the Mazury Complex (Figure 1) [9]. This is a belt of granitoids and associated mafic and intermediate igneous rocks following an E–W-trending lineament extending from the Baltic Sea through northern Poland and southern Lithuania to western Belarus [14]. Anorthosite occurs at three autonomous massifs: Sejny, Suwałki, and Kętrzyn. The SAM has an oval shape and occupies an area of 250 km². Most of the crys-

talline basement of NE Poland is represented by late Svecofennian (1.84-1.80 Ga) orogenic granitoids and supracrustal succession [15]. All the abovementioned units were intruded by plutons of the Mesoproterozoic AMCG suite around 1.5 Ga [15]. This suite is dominated by A-type granitoids with a rapakivi-like texture. The subsequent intrusions are gabbro-norite, anorthosite, and locally mangerite and charnockite rocks. The central part of the SAM consists of anorthosites surrounded by rings of norites, gabbronorites, diorites, and granites (Figure 1). The formation of the AMCG suite was a complex process with multiple magma batches sequentially differentiating and probably undergoing mixing and crustal assimilation [16]. A network of fractures and fault zones cutting the SAM rock sequences was filled by low-temperature S-type granite and pegmatite veins, emplaced between 1495 ± 15 Ma (Udryn, Jeleniewo) and 1488 ± 5 Ma (Udryn) [15]. These younger tectonic structures, which are widespread within the SAM, postdate the last episode within the SAM. New insights also allowed for the description of the occurrence of even later jotunite and nelsonite dikes within the massif [17,18]. Nelsonites are ore-bearing apatite rocks formed through a liquid immiscibility mechanism [19,20]. They were encountered as small dikes or veins in the SAM, as the final stage of ore mineralization. All these crystalline basement rocks are covered by 750-1200 m of sedimentary Phanerozoic rock complexes that dip towards the SW border of the East European Craton [21]. The sedimentary cover is dominated by sandstones, shales, and mudstones deposited in the Ediacaran to early Cambrian and in the early Triassic. The Cretaceous unit is built up mostly of chalk-type facies carbonates. The Cenozoic rock s are composed of unconsolidated, clastic sediments [12].



Figure 1. Schematic geological map (without Palaeozoic–Cenozoic sedimentary rock cover) of the Suwałki Anorthosite Massif (modified after [9]) with the location of the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland.

2.2. Geology of Fe-Ti-V Oxide Deposits

The Fe-Ti-V deposits were discovered in the NE part of Poland within the crystalline basement mafic rocks through an intense drilling exploration program launched in the 1960s–1980s. Two large Fe-Ti-V deposits, the Krzemianka and Udryn deposits, were documented within the eastern part of the Mesoproterozoic SAM of the AMCG affinity (Figure 1). The AMCG suite is unconformable, covered by Mesozoic-Cenozoic sedimentary rocks of thicknesses varying from 500 m on the east to 1000 m on the north-west [9,12]. Anorthosite and norite intrusions compose the core part of the massif and are surrounded by diorites and gabbronorites [9,12]. The SAM is divided by major faults of variable direction into three tectonic blocks [22]. The western one, with the Krzemianka and Udryn Fe-Ti-V deposits, is uplifted.

The ilmenite-magnetite ores are located in tectonic nodes and fill tectonic fractures at the gabbronorite-diorite-anorthosite contacts [21,22]. The deposits under consideration here are made of titanium-and vanadium-bearing magnetite, containing ilmenite and hematite-ilmenite, occurring in various proportions from 1:1 to 1:10 [23]. Hematite-ilmenite series can be found, disseminated in the host rocks. Ilmenite grains or aggregates contain two systems of hematite exsolutions [23–27]. Five types of Fe-Ti ores were distinguished: norite ore and poor pyroxene ores (15–25% Fe), pyroxene ores (22–25% Fe), plagioclase ores (25–35% Fe), spinel ores (35–48% Fe), and brecciated ores [28]. The richest parts of orebodies, called "ferrolites", are characterized by Fe-Ti oxide concentrations exceeding 40% of the rock volume. The ore-oxides represent two solid solution series: magnetite-ulvöspinel and ilmenite-hematite, depending on the P-T and oxidation conditions in Fe-Ti-V ores and their host rocks [23,24,29].

In total, the Krzemianka and Udryn deposits have resources estimated at about 1.34 billion tons of Fe-Ti-V ore, containing approximately 388.2 million tons of iron (Fe₂O₃), approx. 98 million tons of titanium (TiO₂), and approximately 4.1 million tons of vanadium (V₂O₅), [30]. They are classified as sub-economic on account of their low metal contents, especially of vanadium (0.26–0.31% V₂O₅ on average) and because of their occurrence at a depth exceeding 300 m [31]. However, the Fe-Ti-V mineralization contains lower contents of Fe-Cu-Ni-Co sulphides (1–3% by rock volume) and some amounts of REE carbonates and other trace elements [32–36]. The obtained Re-Os model age for pyrite, pyrrhotite and magnetite is 1536 ± 67 million years [37,38]. The Krzemianka and Udryn deposits belong genetically to the iron deposits of the Allard Lake type [23]. In addition, sub-economic Fe-Ti-V mineralization has also been identified at the Jezioro Okragłe and Jeleniewo prospects [28].

2.2.1. The Krzemianka Fe-Ti-V Oxide Deposit

The Krzemianka deposit has an arcuate shape (2.5 km wide and 5 km long), with an area of approximately 13.2 km², and is located in the western part of SAM, close to its contact with granite and dioritoide rock cover (Figure 1) [28]. The deposit lies under the Cambrian, Permian, Triassic, Jurassic, Cretaceous, and Cenozoic sediments; the sedimentary cover may reach a total thickness of about 900 m. The Fe-Ti-V oxide ores in the deposit lie at depths of 850 to 2300 m; however, the majority of ore lies at a depth of 1100– 1700 m [28]. The largest orebody is hosted by anorthosite. The orebodies are in the form of lenses, schlieren, pseudo-seams, and veins dipping generally at an angle of about 45° towards the SE (Figure 2), [28,39]. Their orebodies are variable in size. Their thicknesses vary from a few centimetres to 150 m. The contacts of orebodies with anorthosites and diorites are sharp [28]. The construction of the south-western ore zone in the upper part is made of norites and anorthosites which gradually turn downwards from rich ores to poor mineralization. The lower part consists of plagioclase-type ore, the ore bodies having sharp boundaries with the anorthosites. Plagioclase-type ore has been distinguished for macroscopic classification, e.g., a massive titanomagnetite ore mixture with anorthosite of labradore-andesine composition [23,28].





Figure 2. Schematic geological cross section (without Cenozoic sedimentary rock cover) of the Krzemianka Fe-Ti-V ore deposit in NE Poland (modified after [39]). Abbreviations: 1—anorthosite; 2—norite; 3—ilmenite-magnetite ore; T1—Lower Triassic; P—Permian; Cm—Cambrian.

The deposit is made up of titanium- and vanadium-bearing magnetite, containing ilmenite and hematite-ilmenite, occurring in various proportions from 1:1 to 5:1 and even 10:1 [28,39]. Magnetite contains many decomposition products, including ulvöspinels, ilmenite, and Al-spinel solid solutions [23,39]. The Fe-Ti-V mineralization is accompanied by Fe and Cu sulphides: pyrrhotite, chalcopyrite, pyrite, marcasite, cubanite, chalcocite, and Ni and Co sulphides such as pentlandite, bravoite, millerite, linnaeite, and violarite [23,26–28]. Sulphides may form up to 1–3% of the volume of the Fe-Ti-V ores. In the Krzemianka deposit, about 1.07 billion tons of ilmenite-magnetite ore containing vanadium have been documented. This Fe-Ti-V mineralization has an average grade of 27% Fe₂O₃, 7% TiO₂, and 0.3% V₂O₅ [30].

2.2.2. The Udryn Fe-Ti-V Oxide Deposit and Other Prospects

The Udryn deposit is located in the central part of the Suwałki Anorthosite Massif, approximately 4 km east of the Krzemianka deposit (Figure 1). Twelve boreholes were drilled in this region down to 2300 m [28]. The total area of the Udryn deposit is approximately 0.8 km². Magnetite-ilmenite mineralizations with a content of >15% Fe are considered ore materials. The shapes of the bodies of magnetite-ilmenite mineralization are similar to those found in the Krzemianka deposit, e.g., major lenses and schlieren, dipping generally towards the SE (Figure 3) [28]. The ore bodies in the Udryn deposit are variable in size, with lengths up to 0.8 km and widths up to 0.4 km. Their thicknesses vary from a few centimetres to 100 m. The ore bodies have sharp boundaries, and the boundary reaction zone is defined by the occurrence of volatile-rich minerals such as brown mica, apatite, and cummingtonite [10]. The deposit is also cut by faults and small fissures and the ore bodies have a complicated internal structure, with variations in their

texture and composition, but they can be easily traced in the drills because of their large size [28]. This deposit has a similar composition to that of Krzemianka but contains more spinel minerals. In the Udryn deposit, massive ores account for approximately 7–8% of the Fe-Ti-V type mineralization and sub-economic resources are estimated at approximately 263 million tons of Fe-Ti-V ore [39].



Figure 3. Geological cross section (without Cenozoic sedimentary rock cover) of the Udryn Fe-Ti-V ore deposit (modified after [39]). Abbreviations: 1–anorthosite; 2–norite; 3–ilmenite-magnetite ore; 4–fault. T1–Lower Triassic; P–Permian; Cm–Cambrian.

The Jeleniewo prospect was recognized at the SW side of the SAM (Figure 1). This Fe-Ti mineralization was emplaced under leucogabbronorites and anorthosites in the 1115–2300 m depth interval. Mineralizations occur in parallel lenses, running in a NW-SE direction and dipping to the SW. Massive Fe-Ti ores represent about 7–8% in volume of the boreholes' materials and their sub-economic resources are estimated at approximately 116 million tons [28].

On the western margin of the SAM, in the Łopuchowo IG-1 borehole (Figure 1), interesting sulphide-oxide mineralizations containing REE-bearing fluorapatite in nelsonite dikes, were described for the first time in Poland [17].

3. Analytical Methods

3.1. The Whole-Rock Geochemistry

In total, 39 samples, representing a variety of Fe-Ti-V oxide and sulphide mineralizations, were the subject of the whole-rock geochemistry and point analyses. Samples were collected from the archive core materials of boreholes drilled during the 1970s and 1980s. Twenty-three samples were collected from the Krzemianka deposit (boreholes: Krzemianka –24, –50, –56, –63) and 16 samples came from the Udryn deposit boreholes (Udryn –7, –10, –11) (Figure 4). The ore-grade economic intervals of the drill cores were analyzed for their metallic element contents using a portable pXRF spectrometer (Olympus Delta Premium Model DP-4000-CC) before sampling to select suitable samples for geochemical analysis (Figure 5) [33].



Figure 4. Location of boreholes sampled and studied in the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland. Note: the boundaries of the deposits are projected onto the ground surface.



Figure 5. Schematic geological profile of the Krzemianka 63 drill hole, together with the results of analyses carried out with a portable XRF spectrometer to assess the content of Cr, V, Ti, and Fe (as a percentage) in the selected ore interval.

The geochemical analyses were performed at the Polish Geological Institute-National Research Institute, using international and internal standards, and included duplicate analyses. The contents of trace elements were determined in pressed powder samples (As, Ba, Bi, Br, Cd, Ce, Co, Cr, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sn, Sr, Th, U, V, Y, Zn, and Zr) and the major element oxides were determined in fused samples (SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, P₂O₅, SO₃, Cl, and F), (Table 1). All analyses were performed using the wavelength dispersive spectrometry (WDS-XRF) X-ray fluorescence method, using a Philips PW-2400 spectrometer. Additionally, the contents of the rare earth elements (REEs: Sc, Y, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) and trace elements (Ag, As, Bi, Cd, Co, Cu, Hf, In, Mn, Mo, Ni, Nb, Re, Sb, Se, Sn, Ta, Te, Th, Tl, W, and V) were determined after decomposition with a full mixture of HCl, HNO₃, HF, and HClO₄ acids using a Perkin Elmer ICP-MS Elan DRC II mass spectrometer by means of inductively-coupled plasma mass spectrometry (ICP-MS). Au, Pd, and Pt were measured using a Perkin Elmer model 4100 ZL spectrometer and the graphite furnace atomic absorption spectrometry (GF AAS) method. In the case of gold analyses, samples were preroasted and reconstituted with a mixture of HCl and HNO₃ acids. Liquid–liquid extraction to methyl isobutyl ketone (MIBK) was performed to separate the matrix and concentrate the test solution. The platinum and palladium samples were digested with aqua regia, and then they were isolated on activated carbon using formic acid. The basic statistical parameters (arithmetic mean, geometric mean, median, and standard deviation) of the content of elements in bulk-rock samples from Fe-Ti-V deposits were determined, as well as the correlation matrices between elements in the considering deposits. The degree of correlation of parameters was interpreted as follows. $r \le 0.5$: no correlation, r > 0.5 to 0.7: weak correlation, r > 0.7 to 0.9: strong correlation, and r > 0.9: very strong correlation.

Datasets containing values below the limit of detection (LD) can lead to underestimates or overestimates of both the mean value and standard deviation, and therefore to correct this influence statistical substitution methods are commonly used to replace a value below the minimum limit of detection with a value equal to half the limit of detection (LD/2). In our bulk-rock geochemistry statistics, we considered the sample population of a specific element only in cases when the numbers of samples with values above the low detection limit constituted at least 75%, and other values were treated as LD/2.

	WDS-XRF [ppm]											
As	Ba	Bi	Br	Cd	Ce	Co	Cr	Cu	Ga	Hf	La	Мо
3	10	3	1	3	5	3	5	5	3	3	5	2
Nb	Ni	Pb	Rb	Sn	Sr	Th	U	V	Y	Zn	Zr	
2	3	3	3	2	2	3	2	5	3	2	3	
			ICP-MS [ppm]							GF AAS [ppm]		
Sc	Y	La	Ce	Pr	Nd	Eu	Sm		Au	Pd	Pt	
0.5	0.5	0.5	0.5	0.5	0.5	0.05	0.05		0.001	0.005	0.01	
Gd	Tb	Dy	Но	Er	Tm	Yb	Lu					
0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05					
					ICP-	MS [p]	pm]					
Ag	Cd	In	Mn	Re	Sb	Se	Sn	Та	V	Те	T1	W
0.1	0.5	0.05	1	0.05	0.5	2	1	0.05	5	0.5	0.05	0.1
As	Bi	Co	Cu	Hf	Ni	Nb	Mo	Th				
2	0.05	0.5	0.5	0.05	0.5	0.5	0.5	0.05				
					WD	S-XRF	[%]					
SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P2O5	SO ₃	Cl	F
0.1	0.01	0.05	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.01	0.001	0.01

Table 1. The minimum detection limits of element measurements via the applied methods.

3.2. The Ore Microscope and Microprobe Studies

Mineralogical and petrographic examinations, together with photo-micrographic documentation, were carried out on a NIKON ECLIPSE LV100 POL microscope with NIS-Elements software (Version 3.0). The quantitative examination of ore minerals on the electron microprobe was preceded by a preliminary investigation using a ZEISS LEO-1430 scanning electron microscope with an EDS (energy-dispersive spectrometry) detector. Electron microprobe analysis (EPMA) was performed using a Cameca SX-100 microprobe equipped with five WDS detectors. The following parameters were used during the EPMA analyses: HV accelerating voltage: 15 kV, beam current: 20 nA, a focused beam (<1 μ m in diameter), acquisition time at the peak position: 20 s, at the background position: 10 s, and carbon sputtering. International (commercial) standards from the SPI-53 set from SPI and from the sulf-16 set from P&H were used for instrument calibration.

The determination of low concentrations in small phases with an electron microprobe is not straightforward and uncertainties differ according to the acceleration voltage, counting statistics, background subtraction, sample heterogeneity, beam drift, and other analytical factors (e.g., stray X-rays and surface contamination). Although the precision of each single measurement for a given element was different due to the specificity of the method, it was possible to determine the variability of measurement precision. In the case of trace elements, such as V in magnetite and ilmenite, the variations in measurement precisions ranged from 450 to 650 ppm (with an average of approximately 550 ppm) and from 200 to 300 ppm (with an average of approximately 250 ppm), respectively. In the case of cobalt and nickel, the variations in measurement precision ranged from 800 to 1000 ppm (with an average of approximately 900 ppm) in pentlandite, pyrrhotite, chalcopyrite, and pyrite. The statistics of the elements presented in this article include values above or close to the level of precision of a single measurement.

4. Results

4.1. Metallic Mineralization in Light of the Microscopic and EPMA Studies

All samples were collected from Fe-Ti-rich mineralizations from archival drill cores in the area of the Krzemianka and Udryn Fe-Ti-V deposits, hosted by the SAM. They were dark gray or black, massive or semi-massive rocks, with a characteristic metallic luster and a different ratio of ore mineralization to host rock minerals (Figure 6). They were mainly anorthosites and norites, and less frequently pyroxenites or gabbros, and mineralized nelsonite dikes were also found. Opaque minerals constituted 45-90% of the rock volume and they were massive, xenomorphic, and in most cases they formed a sideronite texture. Transparent minerals were plagioclases and various amounts of orthoand clinopyroxenes, and small amounts of phlogopite were observed in most of the samples. Plagioclase was characterized by a striped structure, whereas irregular, wormy myrmekites occurred in places on the edges of plagioclase grains. As a result of the equilibrium between orthopyroxene and plagioclase, the grains of plagioclase tended to be rounded. The pyroxenes were partially biotitized and chloritized. Pleochroic fields could be observed in brown micas. These tiny mica laminas often surrounded the grains of pyroxenes; they were the product of the reaction between magnetite and plagioclase and pyroxenes. The analysis of brown micas flakes from the SAM leuco-and gabbro-norite cumulates showed a titanium phlogopite composition. The degree of Ti enrichment in the brown micas ranged from 2.59 to 9.41 wt% TiO₂ [40].



Figure 6. Typical massive and semi-massive magnetite-ilmenite (mgt-ilm) ores hosted by anorthosite or norite from the Udryn (**A**) and Krzemianka (**B–F**) deposits. Note: Krzem 63–Krzemianka 63 borehole, 1784 m—an approximate depth of sampling. Abbreviations: mgt-ilm—magnetite-ilmenite; pl—plagioclase; px—pyroxene; sul—sulphides.

The main ore minerals were magnetite and ilmenite, which constituted more than 90% of the massive ores, and were commonly accompanied by sulphides, mainly pyrrhotite, pentlandite, and chalcopyrite (Figure 7A–H). These sulphides may constitute up to 3–5% of the ore's volume. In addition, Al-spinels (with diverse molecular contents of Al, Fe, Mg, and Cr from the hercynite and chromite terms, Table 2) and minor sulphides such as pyrite, siegenite, millerite, bravoite, cubanite, galena, sphalerite, and rare inclusions of greenockite, talnakhite, hessite, or native bismuth were identified.



Figure 7. Microphotographs of characteristic oxide and sulphide ore mineralization from the Krzemianka and Udryn Fe-Ti-V deposits. (**A**–**G**) are reflected-light photomicrographs with crossed nicoles and (**H**) is a backscattered electron (BSE) image. (**A**) typical ilmenite-magnetite ore in the Krzemianka and Udryn deposits. Magnetite with exsolution of ulvöspinel, in association with ilmenite (ilm) and Al-spinels (spinel); (**B**) front of ilmenitization process on the border of magnetite (ilm), and Al-spinels (spinel) in magnetite (mgt); (**D**) exsolutions of ulvöspinel in magnetite, and ilmenite laths; (**E**) ilmenite with hematite exsolutions; (**F**) typical sulphide (pyrrhotite—po, chalcopyrite—cp) aggregates in magnetite-ilmenite ore; (**G**) the pyrrhotite (po) is gradually replaced from the outer edges towards the center by pyrite (py); (**H**) millerite (mlr) replaces chalcopyrite (cp) in the pseudomorphs of pyrite (py) after pyrrhotite.

Mineral	Value	Fe	Al	Mn	V	Cr	Mg	Ti	Zn	0
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
magnetite	magnetite arithmetic mean		0.38	0.03	0.42	0.26	0.08	0.59	0.03	21.29
$Fe^{2+}Fe^{3+2}O_4$	standard deviation	1.25	0.33	0.03	0.14	0.25	0.09	0.68	0.02	0.43
	geometric mean	70.33	0.30	0.02	0.37	0.14	0.06	0.29	0.02	21.29
	median	70.59	0.29	0.02	0.48	0.14	0.06	0.26	0.02	21.26
	minimum content	66.20	0.01	b.d.l.	0.01	b.d.l.	0.01	0.02	b.d.l.	20.46
	maximum content	72.20	2.06	0.13	0.59	1.26	0.53	2.65	0.08	22.54
	number of analyses a.d.l.	81	81	69	81	80	80	81	45	81
ilmenite	arithmetic mean	35.44	0.25	0.81	0.14	0.04	0.87	30.59	0.04	31.72
FeTiO ₃	standard deviation	1.47	0.77	0.14	0.04	0.08	0.37	1.22	0.03	0.45
	geometric mean	35.41	0.04	0.80	0.13	0.03	0.79	30.56	0.02	31.72
	median	35.19	0.03	0.80	0.14	0.03	0.80	31.10	0.03	31.78
	minimum content	33.15	b.d.l.	0.59	0.05	b.d.l.	0.16	26.68	b.d.l.	30.17
	maximum content	39.91	4.39	1.18	0.24	0.59	1.66	31.89	0.12	32.89
	number of analyses a.d.l.	59	57	59	59	47	59	59	31	59
Al-spinels	arithmetic mean	19.24	32.08	0.13	0.04	0.36	7.05	0.17	1.26	39.35
$M^{2+}M^{3+2}O_4$	standard deviation	2.99	1.06	0.03	0.02	0.37	1.43	0.17	0.64	0.90
	geometric mean	19.01	32.07	0.13	0.04	0.25	6.91	0.09	1.09	39.34
	median	18.35	32.13	0.13	0.05	0.17	7.37	0.09	1.03	39.35
	minimum content	14.82	29.76	0.08	b.d.l.	0.09	4.85	0.01	0.36	37.70
	maximum content	24.02	34.10	0.20	0.07	1.45	9.44	0.61	2.25	41.08
	number of analyses a.d.l.	30	30	30	30	30	30	30	30	30

Table 2. The basic statistical parameters of the chemical composition of magnetite, ilmenite, and Al-spinels from the Krzemianka and Udryn Fe-Ti-V deposits in Poland.

a.d.l. – above low detection limit; b.d.l. – below low detection limit; s.d. – standard deviation; $*M^{2+}$ is Mg, Fe, Zn, and Mn and M³⁺ is Fe, Al, V, and Cr.

Magnetite and ilmenite form hipautomorphic crystals up to several mm in diameter. Magnetite contains several generations of exsolutions of ulvöspinel, ilmenite, and Al-spinels (Figure 7A–F). The chemical composition of magnetite includes, on average, 70.3 wt% Fe (range 66.2–72.2 wt%), 21.3 wt% O (range 20.5–22.5 wt%) and substitutions of Al (mean 0.38 wt%), Cr (0.26 wt%), Mg (0.08 wt%), Ti (0.59 wt%), and V (0.42 wt%) (Table 2, Figures 8 and 9A, Table A1).



Figure 8. The composition of Fe-Ti oxides plotted in a TiO₂-FeO-0.5Fe₂O₃ ternary diagram in ore samples from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland. Explanation of calculation (in atomic proportions): TiO₂-Ti (IV); FeO = Fe (II) + Mg (II) + Mn (II) + 2O (II); Fe₂O₃ = Fe (III) + Cr (III) + Al (III) + V (III) + 3O (II).

Ilmenite formed wide lamellae in which Al-spinel nodules forming a palisade structure were observed (Figure 7C). Exsolutions of ulvöspinel in magnetite formed two generations of nets, usually occurring at some distance from the ilmenite lamellae (Figure 7D). A characteristic feature of Ti-rich mineralization is the reaction zone between ilmenite and magnetite. It is composed of Al-spinel inserts with magnetite relics that indicate the outline of the primary original magnetite shape (Figure 7B). Fe-Ti oxides have an interstitial habit as a result of subsolidus grain boundary readjustment [23]. The textures of Fe-Ti oxides result from subsolidus re-equilibration [25]. We observed cloth and trellis textures in magnetite. The primary cloth texture of ulvöspinel is oxidized to trellis ilmenite lamellae and granules [23,24]. We also observed Al-spinel fine lenses exsolutions from magnetite and fine granules in ilmenite. The ilmenite grains or aggregates contain exsolution intergrowths with hematite, mostly in dispersed mineralizations (Figure 7E).

Ilmenite's chemical composition showed an average of 35.4 wt% Fe, 30.6 wt% Ti, and 31.7 wt% O (Table 2). Ilmenite contained substitutions of Mg (mean = 0.87 wt%, range 0.16–1.66 wt%), Mn (mean = 0.81 wt%), and V (mean = 0.14 wt%), (Figure 9B). Several measurements showed Al contents of a few percentage points in terms of weight, up to a maximum of 4.4 wt% (Table A2).



Figure 9. Variation in the content of elements in the chemical composition of magnetite (**A**), ilmenite (**B**), and Al-spinels (**C**) from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland.

Al-spinels commonly occur with magnetite-ilmenite mineralization. The variability of Al-spinels in terms of the content of Al, Fe, Mg, Cr, Mn, and Zn cations is presented in Figure 10A,B. The chemical composition of Al-spinels ranged from 29.8 to 34.1 wt% Al, 14.8–24.0 wt% Fe, 4.9-9.4 wt% Mg, 0.1–1.5 wt% Cr, 0.4–2.3 wt% Zn and of trace substitutions of Mn and V (Table 2, Figures 9C and 10A,B, Table A3).



Figure 10. Ternary diagrams of the chemical composition of Al-spinels in the Fe₃O₄-Al₂O₃-Cr₂O₃ (**A**) and Fe₃O₄-MgO-Al₂O₃ (**B**) from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland.

The most common sulphide was pyrrhotite, coexisting with pentlandite and chalcopyrite (Figures 7F and 11A-H). However, pyrrhotite was predominant among them (ca. 80% of total sulphides), but pentlandite and chalcopyrite contents were similar. These represented the common magmatic sulphides. They formed aggregates that often showed overgrowth of magnetite and ilmenite. Two types of pyrrhotite were recognized [23,25,41]. Our metal-rich ore samples mainly contained the hexagonal form of pyrrhotite, accompanied by chalcopyrite and pentlandite. The pyrrhotite grains were most often xenomorphic in size, ranging from 0.005 to 0.05 mm in diameter. They usually made up polycrystalline aggregates of up to 2-3 mm in diameter. Some pyrrhotite exhibited lamellar structures, resulting from decomposition products of a high-temperature pyrrhotite. EPMA showed that pyrrhotite had a low Fe content (mean = 59.5 wt%) and a high S (mean = 39.1 wt%) content, as well as constant substitution of Ni and Co (Table 3, Table A4). In pyrrhotite, there were oval or lenticular exsolutions-products of pentlandite or chalcopyrite-with diameters from a few to several hundred micrometres (Figure 11A,B,D,F). They arranged themselves parallel to the planes of separation in pyrrhotite (001). Moreover, star-shaped exsolution products of pentlandite in pyrrhotite were observed. Pentlandite and chalcopyrite were also found in the form of intergranular fillings between the pyrrhotite grains. They exhibited xenomorphic crystals with distinctive cleavage, which were up to 0.5 mm in length. The decomposition of pentlandite in pyrrhotite showed a variable chemical composition, on average 34.9 wt% Ni, 27.2 wt% Fe, and 33.3 wt% S, as well as the constant substitution of Co (Table 4, Table A5). The other secondary sulphides were also observed crystallizing along the fractures or cleavage of primary minerals (e.g., pyrrhotite and pentlandite). They formed as a result of the decomposition of high-temperature pentlandite-pyrrhotite solid solutions into their low-temperature products. They were represented mostly by thiospinels from the (Fe, Ni) (Co, Ni)₂S₄ terms [41]. EPMA showed that the proportions of metal contents indicated the presence of diadochid substitutions and/or micro-overgrowths of several transition phases in these minerals. Siegenite $((Ni,Co)_3S_4)$, bravoite $((Fe,Ni,Co)S_2)$, mackinawite $((Fe,Ni)S_{0.9})$, and probably smithite ((*Fe*,*Ni*)₉*S*₁₁) were identified. The average composition of siegenite was 26.3 wt% Ni, 22.0 wt% Co, 10.8 wt% Fe, and 41.1 wt% S (Table 4, Table A6). Bravoite had much higher Fe and lower Co contents, compared to siegenite (Table 4). Bravoite occurred inside pentlandite along its cleavage, in the form of veinlets or lattices up to approx. 30 µm thick. Moreover, lenticular or lanceolate exsolutions of mackinawite were also observed in pentlandite. Chalcopyrite accounted for about 10% of the sulphide contents in the investigated magnetite-ilmenite ores. It created small overgrowths with pyrrhotite or pentlandite, up to several hundred μ m in diameter. The adhesive desorption of these sulphides by gangue minerals was visible. Chalcopyrite was more commonly observed as a thin (30–100 μ m thick) lamellae exsolution in pyrrhotite. The chemical composition of chalcopyrite contained, on average, 34.5 wt% Cu, 30.5 wt% Fe, and 34.4 wt% S and the constant substitution of Co, Ni, and Zn (Table A7). Exsolutions of regular cubanite lamellae or sporadically millerite were also observed in the decomposition product of chalcopyrite in the pentlandite (Figure 7H). Cubanite was also found in the form of tiny xenomorphic crystals associated with pyrrhotite. The chemical composition of cubanite included 41.0 wt% Fe, 23.2 wt% Co, and 35.0 wt% S (Table 3, Table A8).



Figure 11. BSE images of characteristic sulphide mineralization hosted by magnetite-ilmenite ores from the Krzemianka and Udryn Fe-Ti-V deposits. (**A**) a typical sulphide aggregate in magnetite

(mgt)-ilmenite (ilm) ore, in which the primary pyrrhotite (po) and pentlandite (pn) were subject to secondary mineralization processes. They were replaced by sulphide associations with chalcopyrite (cp), siegenite (sie), bravoite (brv), and pyrite with smythite (smy) and by thiospinels (spl). (**B**) pyrrhotite (po) grain subject to pyritization (py) within the magnetite (mgt)-ilmenite (ilm) aggregate; galena (gn) insert is present at the border of pyrite and pyrrhotite, cp—chalcopyrite; (**C**) siegenite (sie) replacement of pyrrhotite (cp) along the cracks. Greenockite and galena (gn) grains associated with low-temperature minerals of the chlorite group (chl); py—pyrite; mgt—magnetite; gck—greenockite; (**D**) sulphide aggregate consisting of pyrrhotite (po), chalcopyrite (cp), siegenite (sie), pentlandite (pn), and Co-bearing pyrite (Co-py), BSEI false colors; (**E**) sphalerite (sp), surrounded by chlorites (chl) in the ilmenite-magnetite ore; (**F**) native bismuth (Bi) inclusion in magnetite (mgt); the aggregate consists of pyrrhotite (po), chalcopyrite (cp) and pyrrhotite (po) aggregate hosted by magnetite (mg). Greenockite can be a secondary product of the supergene alteration of Cd-rich sphalerite; (**H**) hessite (hes) inclusion in chalcopyrite (cp) and pyrrhotite (po) aggregate hosted by magnetite-ilmenite ore, BSE.

Table 3. The b	asic statistical	parameters of th	e chemical	composition of	of pyrrhotite,	chalcopyrite,
cubanite, talna	khite, and pyrit	e from the Krzer	nianka and	Udryn Fe-Ti-V	' deposits.	

Mineral	Value	Fe	S	Ni	Со	Cu	Zn
		wt%	wt%	wt%	wt%	wt%	wt%
pyrrhotite	arithmetic mean	59.53	39.06	0.61	0.16	0.04	0.03
(FeS)	standard deviation	0.56	0.34	0.54	0.05	0.03	0.04
	geometric mean	59.53	39.06	0.48	0.15	0.51(<i>n</i> = 46)	0.38 (<i>n</i> = 42)
	median	59.56	39.03	0.55	0.15	0.04	0.03
(n = 61)	minimum content	56.13	38.34	0.19	0.05	b.d.l.	b.d.l.
	maximum content	60.53	39.75	4.00	0.28	0.14	0.16
pyrite	arithmetic mean	44.13	53.00	1.05	1.60	0.06	0.04
FeS ₂	standard deviation	2.49	0.50	1.90	2.36	0.06	0.03
	geometric mean	44.06	52.99	0.20	0.49	0.03	0.03
	median	45.44	53.07	0.11	0.25	0.04	0.03
(n = 37)	minimum content	38.02	51.96	0.01	0.06	b.d.l.	b.d.l.
	maximum content	47.12	53.98	8.72	8.61	0.21	0.13
Mineral	Value	Cu	Fe	S	Ni	Со	Zn
		wt%	wt%	wt%	wt%	wt%	wt%
chalcopyrite	arithmetic mean	34.52	30.50	34.36	0.11	0.11	0.08
CuFeS ₂	standard deviation	0.37	0.31	0.26	0.13	0.10	0.14
	geometric mean	34.52	30.50	34.36	0.06	0.09	0.06 (n = 42)
	median	34.52	30.46	34.36	0.06	0.08	0.06
(n = 50)	minimum content	33.65	29.88	33.83	0.01	0.02	b.d.l.
	maximum content	35.37	31.35	34.87	0.56	0.55	1.01
cubanite	arithmetic mean	23.19	40.97	35.01	0.05	0.08	0.04
CuFe ₂ S ₃	standard deviation	0.40	0.41	0.21	0.04	0.035	0.04
	geometric mean	23.18	40.97	35.01	0.03	0.07	0.02
	median	23.24	40.92	34.98	0.05	0.08	0.02
(n = 10)	minimum content	22.24	40.34	34.72	0.01	0.04	0.01
	maximum content	23.63	41.98	35.44	0.14	0.14	0.13
talnakhite	arithmetic mean	27.09	29.05	35.00	4.20	3.94	0.30
$Cu_{9}(Fe Ni)_{8}S_{3}$	standard	0.47	0.80	0 71	0.93	1 20	0.16

	deviation						
	geometric mean	27.09	29.04	35.00	4.15	3.84	0.27
	median	27.09	29.05	35.00	4.20	3.94	0.30
(n = 3)	minimum content	26.76	28.48	34.50	3.54	3.09	0.18
	maximum content	27.42	29.61	35.50	4.86	4.78	0.41
	a i ai i						

b.d.l.-below detection limit.

Table 4. The basic statistical parameters of the chemical composition of pentlandite, siegenite, and bravoite from the Krzemianka and Udryn Fe-Ti-V deposits.

Mineral	Value	Ni	Fe	Со	Cu	Zn	S
		wt%	wt%	wt%	wt%	wt%	wt%
pentlandite	arithmetic mean	34.89	27.21	4.41	0.35	0.05	33.30
(Fe,Ni)9S8	standard deviation	3.58	2.15	3.09	0.85	0.04	1.59
	geometric mean	34.69	27.13	3.63	0.12 (<i>n</i> = 42)	0.04	33.27
	median	36.33	27.10	3.19	0.11	0.05	32.96
(n = 45)	minimum content	23.70	22.26	1.12	b.d.l.	b.d.l.	32.14
	maximum content	39.23	37.35	15.30	4.38	0.15	41.19
siegenite	arithmetic mean	26.31	10.75	22.03	0.09	0.04 (<i>n</i> = 16)	41.14
(Ni,Co) ₃ S ₄	standard deviation	2.61	2.80	3.29	0.06	0.03	1.04
	geometric mean	26.19	10.35	21.79	0.07	0.03	41.13
	median	25.50	10.84	22.14	0.08	0.04	41.54
(n = 18)	minimum content	22.89	4.33	13.84	b.d.l.	b.d.l.	37.71
	maximum content	33.22	17.21	29.67	0.20	0.12	42.10
bravoite	arithmetic mean	28.10	28.26	2.66	0.45	-	39.38
$(Fe,Ni,Co)S_2$	standard deviation	2.19	2.24	1.14	0.74	-	0.48
	geometric mean	28.04	28.20	2.45	-	-	39.38
	median	27.94	28.29	3.22	0.05	-	39.12
(n = 7)	minimum content	25.99	26.01	1.35	b.d.l.	b.d.l.	39.09
	maximum content	30.36	30.48	3.40	1.31	0.04	39.94

b.d.l.—below detection limit.

Igneous pyrrhotite is a hexagonal polymorph that changes along the grain edges into a monoclinic polymorph, which is usually highlighted during the oxidation of polished sections. Monoclinic pyrrhotite was most often replaced by secondary pyrite (Figures 7G, 11A,B). Pyrite was formed in late processes as a monoclinic pyrrhotite replacement. The characteristic bird's-eye textures, as a result of oxidative conditions during increasing sulphur fugacity fS2, were observed (Figure 7G). The chemical composition of pyrite was, on average, 44.1 wt% Fe and 53.0 wt% S and a constant substitution of Co and Ni (Table 3, Table A9). Another product of pyrrhotite transformations was smithite, which was probably formed as a product of the low-temperature decomposition of strongly magnetic monoclinic pyrrhotite (Figure 11A) [41]. Sphalerite, up to a few µm in diameter, is present in the form of inclusions within the younger generation of chalcopyrite, and next to chlorite, as a filling of cracks in pyroxenes and Al-spinels. Moreover, irregular, amoebic single grains of sphalerite with diameters up to 50 µm were found in the vicinity of chlorites forming massive clusters (Figure 11E). They had a chemical composition of 64.5-65.2 wt% Zn, 32.4-32.7 wt% S, and 1.9-2.3 wt% Fe. Galena was identified in the form of small grains, not exceeding 2–3 µm in diameter. This occurred in a dispersed form within rock-forming silicates, siegenite, and also in ilmenite admixing lamellae, and within pseudomorphoses of pyrite after pyrrhotite (Figure 11C). Single ingrowths or micro-grains of native bismuth, greenockite (CdS), and hessite (Ag_2Te) were identified for the first time in this area. Native bismuth ingrowths were observed in magnetite and pyrrhotite (Figure 11F). Greenockite was found in the form of ingrowths and veins in chalcopyrite (Figure 11G). The chemical composition of greenockite was 53–60 wt% Cd and 23–26 wt% S, with substitutions of Fe, Zn, and Cu (from 5.5 to 8.3 wt%). Additionally, accessory hessite micro-grains with a diameter of 1–5 μ m were identified at the edges of chalcopyrite (Figure 11H).

4.2. Trace Element Distribution in Fe-Ti-Oxides and Sulphides Mineralization Determined by EPMA

EPMA analyses revealed that the most abundant trace elements in the sulphide mineralization were cobalt and nickel (Figure 12). These elements occurred mainly as substitutions in pentlandite, pyrrhotite, chalcopyrite, and pyrite, and as secondary minerals—thiospinels ((*Fe*,*Ni*) (*Co*,*Ni*)₂*S*₄), which formed as a result of pentlandite decomposition [41]. Cobalt and nickel substitutions in sulphides and thiospinels ranged from 0.1 to 40 wt% (Figure 12). The highest contents of Co were found in siegenite (29.7 wt%), and those of Ni were found in pentlandite (39.2 wt%) (Table 4). The contents of Co and Ni in siegenite averaged 22.0 wt% and 26.3 wt%, respectively. On the other hand, Co substitution in pentlandite was, in the vast majority of analyses, in the range of 2 to 7 wt% (Table A5). The remaining, definitely higher Co impurities in pentlandite (>14 wt%) should be interpreted as the presence of other thiospinels, most often identified as siegenite. The association of cobaltiferous-pentlandite with thiospinels (Fe, Co, Ni) showing lower Co substitution, such as bravoite or talnakhite, was confirmed via EPMA.



Figure 12. Bivariate diagram of Ni vs. Co in sulphides and thiospinels from the Udryn and Krzemianka Fe-Ti-V deposits. Zero values and values below low-precision limits are not presented on the logarithmic axis. Note: gray dashed lines indicate the range of precision of measurements in the entire population for a given element and sulphide.

Bravoite showed nickel contents in the range of 26 to 30.4 wt% (mean = 28.1 wt%) and Co substitution from 1.4 to 3.4 wt% (mean = 2.7 wt%), (Table 4). In talnakhite, the mean values of Ni and Co substitutions were about 4 wt%. The presence of pentlandite

and its decomposition products (thiospinels) was subordinate to that of pyrrhotite (approximately 1:10); therefore, much larger resources of Co and Ni should be associated with the presence of pyrrhotite, despite the fact that it contained much lower concentrations of these metals. The mean values of Co and Ni substitution in pyrrhotite were 0.16 and 0.61 wt%, respectively. The range of nickel substitution (0.2 to 4.0 wt%) in pyrrhotite was much higher than that of cobalt (0.05 to 0.3 wt%). In turn, the substitutions of Co and Ni in chalcopyrite were present at a similar level (mean = 0.11 wt%). The variability of Co and Ni substitution ranged from trace amounts up to 0.56 wt% (Table 3). Cubanite, which was formed as a result of the decomposition of a solid solution of magmatic chalcopyrite, contained traces of Co and Ni substitutions in pyrite. Pyrite was of secondary origin and replaced pyrrhotite. Co and Ni substitutions in pyrite ranged from trace amounts up to about 9 wt%, respectively. The mean value of the Co and Ni contents was 1.6 and 1.1 wt% (n = 37), respectively. It was possible to recognize a Co-rich pyrite with Co substitution >1 wt%.

Cobalt showed a variable correlation with the Ni distribution in sulphides and thiospinels. A strong positive correlation of Co with Ni was observed in chalcopyrite and cubanite (r = 0.73, and r = 0.62, respectively) but no correlations occurred in other sulphides (Table 5). As an example, there were no correlation between distributions of Co with Fe in pyrrhotite and pentlandite, which indicates the possibility of mutual substitution by both elements (Figure 13A,B).



Figure 13. Bivariate diagrams of trace elements in sulphides from the magnetite-ilmenite ores in the Udryn and Krzemianka Fe-Ti-V deposits. (**A**) Fe vs. Co in pentlandite; (**B**) Fe vs. Co in pyrrhotite.

Mineral	Element	S	Cu	Ni	Со	Fe	Mineral
e	S	1.00	0.08	-0.34	0.08	-0.01	
dit	Cu	-0.03	1.00	-0.12	-0.04	0.13	tite
llan	Ni	-0.62	-0.13	1.00	-0.31	-0.76	rho
ent	Co	-0.02	-0.09	-0.54	1.00	0.10	pyr
<u></u>	Fe	0.30	-0.02	-0.29	-0.50	1.00	
e	S	1.00	0.11	-0.22	-0.19	0.22	
yril	Cu	-0.08	1.00	0.18	-0.20	0.01	e
doc	Ni	-0.14	-0.08	1.00	-0.27	-0.46	yril
nalc	Co	0.14	-0.18	0.73	1.00	-0.71	d.
cl	Fe	-0.31	-0.28	-0.31	-0.41	1.00	
ite	S	1.00	-0.39	-0.78	0.16	0.73	uite
oan	Cu	0.26	1.00	0.38	-0.36	-0.31	gen
cut	Ni	-0.15	-0.33	1.00	-0.42	-0.62	sie

Table 5. Pearson's correlation coefficients of selected elements for the sulphides from magnetite-ilmenite ores in the Fe-Ti-V deposits in Poland.

Co	-0.08	-0.13	0.62	1.00	-0.34	
Fe	-0.09	-0.83	0.12	0.25	1.00	

Note: Pearson's correlation was based on EPMA in pentlandite (n = 45 measurements), pyrrhotite (n = 61), chalcopyrite (n = 50), pyrite (n = 37), cubanite (n = 10), and siegenite (n = 16). Coefficients with absolute values greater than 0.28 are statistically significant at the 95% level.

Magnetite is the major carrier of the critical element vanadium. The vanadium content in magnetite was in the range of 0.01 to 0.59 wt%, mean = 0.42 wt.% (Table 2, n = 81, Figure 14A). Magnetite commonly contained an admixture of Ti (range from 0.02 to 2.7 wt%, mean = 0.60 wt% for n = 81) which was substituted for Fe ²⁺(Figure 14B). Figure 14C,D shows the vanadium to titanium and vanadium to chromium ratios observed in magnetite, revealing a weak correlation with the Ti and Cr distribution.



Figure 14. Bivariate diagrams of iron vs. vanadium (**A**), iron vs. titanium (**B**), vanadium vs. titanium (**C**), and chromium (**D**) in magnetite from the Udryn and Krzemianka Fe-Ti-V deposits. Trend lines represent correlations between elements. All plots represent the same set of samples; 0 values and samples with values below the level of precision of a single measurement are not presented on the axis.

Ilmenite contained vanadium from 0.05 to 0.24 wt% V (mean = 0.14 wt% V, n = 59), (Figure 15A,B). Massive ilmenites had the highest V contents, in the range of 0.18–0.24 wt%m with an increase in iron content ranging from 36 to 40 wt%. There was a slight enrichment of massive ilmenites with vanadium (>0.18 wt%) when compared to ilmenite lamellae exsolutions in magnetite or to ilmenite pseudomorphs after magnetite (Figure 15A).



Figure 15. Bivariate diagrams of vanadium vs. iron (**A**) and vanadium vs. titanium (**B**) in ilmenite depending on crystal form in the Krzemianka and Udryn Fe-Ti-V deposits. All plots represent the same set of samples; 0 values and samples with values below the level of precision of a single measurement are not presented on the axis.

4.3. Bulk-Rock Geochemical Investigation of Fe-Ti-V Oxide and Sulphide Ores

The subject of the research was to determine the concentration of elements in the magnetite-ilmenite ores, along with the locally co-occurring polymetallic sulphides from the Krzemianka and Udryn deposits located in the SAM. Twenty-three ore-bearing samples were collected from the Krzemianka deposit and 16 samples from the Udryn deposit. The rocks hosting magnetite-ilmenite mineralization with sulphides were mainly rich in Fe₃O₄ and TiO₂ anorthosites, norites, and jotunites, and to a lesser extent pyroxenites and gabbros. In the studied bulk-rock samples, the iron contents ranged from 6.4 to 76.2% Fe₂O₃t (n = 39; Tables 6 and 7). Most of the Fe-Ti rich ores showed massive and semi-massive textures and they were classified as "ferrolites" (Figure 6). The "ferrolites" showed concentrations in the range of 50–70% (n = 19) and 30–40% Fe₂O₃t (n =10), with samples containing 40–50% Fe₂O₃t constituting approximately 10% of the population (n = 5). Only a few samples had a poorer Fe-Ti mineralization and showed impregnation-veinlet textures. The arithmetic mean of the total iron concentration Fe₂O₃t was higher, at 48.6% (n = 39; Table 6). Fe₂O₃t showed a very strong correlation with Zn (r= 0.94; Table 8) and a strong correlation with TiO_2 (r = 0.89; Figure 16C), Ga (r = 0.86), and Ni (r = 0.72) and a weak correlation with Co (r = 0.69) and Cd (r = 0.64) and no correlation, e.g., with V (r = 0.42; Figure 16B). The arithmetic mean content of TiO₂ was 7.6% (n = 39). TiO₂ showed a strong correlation with Fe₂O₃t (r = 0.89), Zn (r = 0.88), and Ga (r = 0.75) and a weaker correlation with Co, Ni, Cd, and U (r = 0.6), and no correlation with V (Figure 16D). Vanadium concentrations ranged from 104 to 2208 ppm and in 40% of the population the vanadium concentration was above 1000 ppm (0.1%). The arithmetic mean for vanadium = 960.2 ppm (n = 39). Vanadium showed a good correlation with cobalt (r = 0.70, Figure 16D) and no correlation with Fe_2O_3t (r = 0.42; Figure 16E), Ga, or TiO₂.



22 of 46



Figure 16. Bivariate diagrams of trace elements with trend lines in magnetite-ilmenite ores from the Krzemianka and Udryn Fe-Ti-V deposits on the Suwałki Anorthosite Massif in NE Poland. (**A**) TiO₂ vs. Fe₂O₃t; (**B**) V vs. Fe₂O₃t; (**C**) Co *vs*.Fe₂O₃t; (**D**) Co vs. V; (**E**) V vs. TiO₂; (**F**) Co vs. Ni; (**G**) Co vs. Ga; (**H**) Co vs. Zn; (**I**) Ga vs. Ni. Note: the line of best fit is shown as the red line.

Table 6 Representative whole-rock chemistry of mineralized samples from the Fe-Ti-V deposits in Poland.

Sample	K24/01	K50/05	K56/06	U11/05	K63/06	U10/04	K24/03	U7/03	K56/05
	Anorthosite	No	rite	Jotunite		Ferrolite			
SiO ₂ (%)	45.39	28.37	31.32	26.72	8.27	7.27	13.53	16.34	24.16
TiO ₂	1.573	6.037	5.153	6.269	7.221	10.78	9.562	9.372	6.838
Al ₂ O ₃	27.28	13.88	12.2	7.53	5.74	7.87	8.94	8.95	11.3
Fe ₂ O ₃	6.4	39.34	37.1	36.64	76.23	69.78	62.47	56.38	47.38
MnO	0.061	0.217	0.296	0.52	0.394	0.269	0.276	0.271	0.278
MgO	1.25	4.43	5.1	8.03	1.25	2.33	2.48	4.07	3.79
CaO	11.98	5.02	5.11	9.77	1.29	1.57	2.55	2.77	4.47
Na ₂ O	4.58	2.28	1.84	1.47	0.62	0.69	0.97	0.89	1.51
K ₂ O	0.72	0.4	0.56	0.27	0.97	0.19	0.19	0.22	0.55
P_2O_5	0.332	0.054	0.177	2.388	0.027	0.028	0.009	0.022	0.364
SO ₃	0.06	0.44	0.03	1.49	0.2	< 0.01	< 0.01	0.03	< 0.01
Cl	0.082	0.144	0.085	0.089	0.127	0.129	0.091	0.115	0.087
LOI	0.3	0.5	1	0.9	2	1.3	1.1	0.2	0.9
SUM	99.71	99.17	99.21	99.29	98.91	98.14	99.02	98.08	99.17
Ag ppm	0.6	0.5	0.9	0.7	0.3	0.6	0.6	< 0.3	1.2

Au ppb	<1	6	7	2	1	5	4	1	7
Ba	272	171	259	106	<10	<10	<10	<10	706
Cd	3	14	9	15	17	17	11	14	8
Ce	26.8	12.6	38.1	285,0	6.5	6.3	2.9	4.8	35.4
Co	15	138	205	65	128	144	135	143	161
Cr	2.5	362	34	<5	133	2159	218	3777	217
Cu	38	325	604	117	247	94	231	61	658
Dy	1.89	0.64	2.79	23.56	0.3	0.38	0.15	0.29	2.19
Er	0.86	0.37	1.46	11.44	0.17	0.25	0.11	0.19	1.11
Eu	2.9	0.91	3.81	36.85	0.59	0.52	0.19	0.31	3.32
Ga	23	38	31	23	48	70	50	54	43
Gd	2.63	0.76	3.4	32.5	0.47	0.46	0.17	0.28	3,00
Ge	0.05	0.2	0.3	0.7	0.4	0.4	0.4	0.3	0.3
Hf	<3	<3	6	14	5	12	5	8	<3
Ho	0.35	0.13	0.55	4.52	0.05	0.08	< 0.05	0.06	0.43
In	0.025	0.08	0.11	0.3	0.23	0.13	0.16	0.11	0.15
La	12.7	6.8	19.1	114.4	3.2	3,0	1.7	2.7	18.3
Lu	0.08	< 0.05	0.18	1.1	< 0.05	< 0.05	< 0.05	< 0.05	0.13
Nb	5	6	9	31	14	7	7	9	8
Nd	14.9	5.5	19.1	182.7	2.8	2.9	1.2	2,0	17.9
Ni	16	398	570	56	401	664	326	646	426
Pb	13	4	8	6	<3	<3	<3	<3	8
Pd ppb	<5	<5	<5	<5	12	5	5	<5	<5
Pr	3.6	1.5	4.8	41.3	0.8	0.8	0.25	0.6	4.5
Pt ppb	<10	<10	<10	<10	<10	<10	12	12	<10
Rb	6	9	20	11	181	9	7	7	20
Sc	11.7	16.9	24.2	74.9	14.6	17.8	23.8	21.9	21.3
Sm	1.62	0.62	1.29	5.08	0.14	0.22	0.29	0.38	1.39
Sn	2	2	3	5	10	3	4	3	3
Sr	678	383	339	234	86	129	204	198	285
Та	0.16	0.12	0.39	1.77	0.6	0.2	0.18	0.18	0.25
Tb	0.34	0.1	0.48	4.35	0.06	0.06	< 0.05	< 0.05	0.38
Th	0.56	0.77	1.36	2.59	1.31	0.27	0.07	0.18	1.05
Tm	0.1	0.05	0.2	1.41	< 0.05	< 0.05	< 0.05	< 0.05	0.15
V	104	1242	860	456	767	1099	915	980	2009
W	0.3	0.3	0.5	0.3	2.2	0.1	0.5	0.3	1.3
Y	8.3	3.2	13,00	105.6	1.4	1.8	0.8	1.5	10.3
Yb	0.57	0.33	1.21	7.79	0.24	0.23	0.14	0.27	0.89
Zn	62	324	271	481	641	701	630	519	448
Zr	86	51	99	595	28	46	54	53	110

Table 7. Basic statistical parameters for trace elements (in ppm, and in ppb for Au, Pt, and Pd) and major oxides (as a percentage) of the bulk-rock samples (n = 39) from the Fe-Ti-V oxide deposits (the Krzemianka deposit, n = 23 samples; the Udryn deposit, n = 16 samples) in NE Poland.

Element/	Arithmetic	Geometric	Modian	Minimum Con-	Maximum	Standard Devi-
Compound	Mean	Mean	wieulali	tent	Content	ation
Fe ₂ O ₃ total (%)	48.61	44.99	51.43	6.4	76.23	15.69
TiO2 (%)	7.56	7.11	8.05	1.57	11.44	2.26
V (ppm)	960.23	861.84	977	104	2208	403.57
Co	122.33	111.75	137	15	205	40.44
Ga	44.33	41.98	45	21	84	14.46

Ge	0.29	0.27	0.3	0.05	0.7	0.12
Hf	0.95	0.87	0.93	0.38	2.09	0.4
In	0.13	0.12	0.12	0.03	0.3	0.06
Nb	9.38	8.27	8	5	32	6.42
Sc	24.29	21.63	19.8	10.8	74.9	15
W	3.59	0.46	0.3	0.1	101	16.17
Y	11.38	3.98	3.8	0.25	105.6	25.4
La	15.13	7.07	6.8	0.8	118.3	28.69
Ce	33.93	13.8	12.6	1.3	285	71.17
Pr	4.59	1.63	1.7	0.25	41.3	10.27
Nd	19.36	6.51	6.8	0.5	182.7	45.06
Eu	3.76	1.16	1.23	0.07	36.85	8.94
Sm	0.97	0.61	0.62	0.09	5.27	1.27
Gd	3.3	1.03	0.92	0.07	32.5	7.8
Tb	0.44	0.14	0.13	0.03	4.35	1.03
Dy	2.48	0.83	0.83	0.06	23.56	5.63
Но	0.48	0.16	0.16	0.03	4.52	1.07
Er	1.25	0.47	0.44	0.03	11.44	2.71
Yb	0.94	0.42	0.38	0.03	7.79	1.83
Cr	678.22	219.58	171	2.5	5705	1164.87
Cu	328.54	226.55	231	38	1756	323.94
Ni	436.36	302.06	421	16	1370	301.16
Zn (ppm)	453	415.65	481	62	701	152.79
Au (ppb)	6.62	3.46	4	<1	37	8.32
Ag (ppm)	0.66	0.5	0.6	< 0.30	2.5	0.54
Cd	13.77	12.9	14	3	24	4.37
Br	4.64	4.55	5	3	7	0.93
Rb	16.97	11.55	9	6	181	29.56
Sr	271.49	247.15	254	86	678	123.62
Sn	3.15	2.96	3	2	10	1.41
Та	0.34	0.24	0.23	0.08	1.77	0.4
Th	0.75	0.52	0.5	0.07	2.83	0.68
U	2.9	2.55	3	1	5	1.29
Zr	105	72.31	66	25	737	142.92
SiO ₂ (%)	21.47	19.1	18.44	6.27	45.39	10.15
Al ₂ O ₃	11.27	10.72	10.35	5.74	27.28	4.14
MnO	0.26	0.25	0.26	0.06	0.52	0.08
MgO	3.88	3.47	3.43	1.25	8.97	1.9
CaO	4.46	3.77	3.69	1.29	11.98	2.75
Na2O	1.62	1.45	1.51	0.62	4.58	0.84
K2O	0.38	0.34	0.34	0.11	1.11	0.21
P_2O_5	0.23	0.07	0.05	0.01	2.39	0.54
(SO3)	0.33	0.09	0.21	0.01	1.7	0.47
(Cl)	0.11	0.11	0.12	0.08	0.17	0.02

The base metals that appeared with magnetite ilmenite ores were mainly related to the presence of magmatic sulphides, e.g., pyrrhotite, pentlandite, and chalcopyrite. The cobalt concentration ranged from 15 to 205 ppm. Samples with cobalt contents from 120 ppm to 180 (n = 23) were the most abundant. The average arithmetic content of Co was 122.3 ppm (n = 39). Cobalt showed a good correlation with V (r = 0.70), (Figure 16D), Fe₂O₃t, and Ni (r = 0.69; Figure 16F) and a weaker correlation with TiO₂, Ga (r = 0.6, Figure

16G), and Zn (r = 0.56; Figure 16H). The contents of Cu and Ni in bulk-rock samples ranged from 0.18% to 0.14%, respectively. Copper was present in elevated concentrations, ranging from 38 to 1756 ppm. The Cu concentration was <400 ppm in most of the samples (n = 30), and only nine samples had contents >400 ppm. The arithmetic mean was 329 ppm (n = 39). Copper showed a strong positive correlation with Au (r = 0.85) and a very weak correlation with Ag, Ni, and Co (r = 0.65-0.50). Nickel concentrations above 0.06%, which were found in 25% of the population, can also be taken into account. Nickel contents ranged from 16 to 1370 ppm, and the arithmetic mean = 436.4 ppm (Table 7). Nickel showed a strong correlation with Ga (r = 0.82) and Fe₂O₃ and a weaker correlation with Co, TiO₂, Zn, and Cu. Zinc contents ranged from 62 to 701 ppm, with an arithmetic mean of 453 ppm. Zinc showed a positive correlation with a few elements (Table 6). The occurrence of ore mineralization was also associated with an increase in the concentration of chromium, up to 0.57%. In 25% of the sample population, the Cr content ranged from >0.1% to 0.571%. The arithmetic mean for Cr was 678.2 ppm. Chromium showed no correlation with other metals (Table 8).

Elements defined as critical (e.g., Co, Ga, Ge, and In) were associated mainly with sulphide mineralization. Gallium contents ranged from 21 to 84 ppm. Most samples had Ga contents in the range of 30 to 60 ppm (n = 26). The arithmetic mean for Ga was 44.3 ppm (n = 39) and it showed a strong correlation with Fe₂O₃t (r = 0.87), Ni (r = 0.82, Figure 16I), Zn (r = 0.80), and TiO₂ (r = 0.75), and a weaker one with Co and Cd (r = 0.57). Indium concentrations ranged from 0.03 to 0.30 ppm. Most of the samples showed contents from 0.1 to 0.15 ppm of In. The arithmetic mean was 0.13 ppm (n = 39). Indium showed a very strong correlation with Ge and MnO (r = 0.92). Germanium was present in the range of <0.1–0.5 ppm. About 50% of the sample population was between 0.2 and 0.3 ppm (n = 20). The arithmetic mean for Ge was 0.29 ppm (n = 39). Germanium showed a very strong correlation with In (r = 0.92), and a strong correlation with Nb (r = 0.84) and Ta (r = 0.83). Antimony and tellurium concentrations were mostly below detection levels (e.g., 0.5 ppm). Gold concentrations ranged from <1 ppb to 37 ppb. Platinum was present in very low concentrations; only 30% of the sample population showed Pt contents in the range of 10–22 ppb. Likewise, trace concentrations were also present for Pd (>5 ppb), Ag (<0.3 to 2.5 ppm), Nb (5–32 ppm), and Hf (0.38 to 2.09 ppm). Scandium contents ranged from 11 to 75 ppm. The arithmetic mean for scandium was 24.3 ppm.

Table 8. Pearson's correlation coefficients of selected elements for the bulk-rock samples from Fe-Ti-V deposits in Poland.

	SiO ₂ TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgOC	CaO Na	12O F	K2O P20	D5 SO3	Ag	Au	Br	Cd	Ce	Со	Cr	Cu	Ga	Ge	Hf	In	La	Nb	Ni	Rb	Sc	Sr	Та	Th	U	V	Y	Zn	Zr
SiO ₂	1.00																																	
TiO ₂	0.90 1.00																																	
Al ₂ O	3 0.71 -0.74	1.00																																
Fe ₂ O	3 -0.98 0.89	-0.75	1.00																															
MnC	-0.14 0.16	-0.67	0.17	1.00																														
MgO	0.45 -0.34	-0.14	-0.42	0.47	1.00																													
CaO	0.83 -0.81	0.61	-0.89	0.07	0.31 1	.00																												
Na ₂ C	0.86 -0.84	0.94	-0.90	-0.46	0.06 0	.78 1.	00																											
K ₂ O	0.32 -0.39	0.31	-0.27	-0.10	-0.21 0	0.22 0.	35 1	1.00																										
P2O5	0.33 -0.29	-0.10	-0.34	0.73	0.46 0	0.58 0.	09 -(0.03 1.0	0																									
SO3	0.02 0.00	-0.11	-0.05	0.30	0.20 0	.11 -0	.01 -0	0.14 0.2	6 1.00																									
Ag	-0.11 0.17	-0.06	0.07	0.02	-0.11 -(0.08 -0.	.05 ().06 -0.0	04 0.50	1.00																								
Au	-0.35 0.36	-0.23	0.35	-0.07	-0.27 -0).33 -0.	.27 -(0.13 -0.1	18 0.32	0.54	1.00																							
Br	-0.59 0.56	-0.44	0.56	0.09	-0.21 -().46 -0.	.51 -(0.26 -0.1	12 -0.04	0.18	0.53	1.00																						
Cd	-0.65 0.61	-0.59	0.64	0.28	-0.05 -0).54 -0.	.64 -0	0.36 -0.0	08 0.20	-0.11	0.19	0.50	1.00																					
Ce	0.35 -0.30	-0.10	-0.36	0.72	0.46 0	0.58 0.	10 -0	0.01 0.9	9 0.22	-0.05	-0.19	-0.13	-0.08	3 1.00																				
Со	-0.64 0.61	-0.53	0.69	0.00	-0.21 -0).75 -0.	.67 -0	0.21 -0.5	50 -0.05	5 0.14	0.39	0.41	0.42	-0.50	1.00																			
Cr	-0.25 0.29	-0.08	0.23	-0.13	-0.14 -0).25 -0.	.21 -(0.25 -0.1	18 -0.28	8-0.23	-0.12	0.18	0.20	-0.18	0.21	1.00																		
Cu	-0.28 0.29	-0.25	0.30	-0.02	-0.20 -0).33 -0	.28 (0.01 -0.1	18 0.41	0.65	0.85	0.41	0.14	-0.19	0.48	-0.28	1.00																	
Ga	-0.87 0.75	-0.41	0.86	-0.17	-0.58 -0).78 -0.	.67 -0	0.34 -0.4	42 -0.16	5-0.01	0.28	0.50	0.57	-0.43	0.57	0.39	0.16	1.00																
Ge	-0.21 0.23	-0.58	0.24	0.86	0.25 0	.02 -0	.47 -(0.17 0.7	8 0.17	-0.04	-0.01	0.21	0.26	0.78	-0.06	0.04	-0.03	0.05	1.00															
Hf	-0.04 0.23	-0.38	0.03	0.49	0.23 0	.06 -0.	.23 -(0.05 0.4	5 0.09	0.26	0.13	0.17	0.01	0.47	-0.11	0.00	0.05	-0.13	0.55	1.00														
In	-0.15 0.17	-0.61	0.19	0.92	0.29 0	.06 -0	.42 -(0.02 0.7	7 0.29	0.10	-0.02	0.08	0.21	0.77	-0.14	-0.14	0.02	-0.10	0.92	0.56	1.00													
La	0.35 -0.29	-0.03	-0.35	0.58	0.41 0	0.50 0.	15 ($0.01 \ 0.8$	3 0.18	-0.11	-0.18	-0.15	-0.06	0.84	-0.38	-0.12	-0.19	-0.40	0.63	0.36	0.59	1.00	1 00											
Nb	0.23 -0.17	-0.25	-0.22	0.82	0.41 0	0.45 -0.	.03 (0.05 0.9	4 0.27	0.01	-0.14	-0.06	0.01	0.96	-0.45	-0.14	-0.15	-0.37	0.84	0.54	0.87	0.79	1.00	1 00										
N1	-0.73 0.61	-0.39	0.72	-0.15	-0.39 -0).71 -0.	.62 -0	0.32 -0.4	40 0.04	0.24	0.62	0.64	0.51	-0.41	0.68	0.32	0.55	0.82	0.01	-0.09	-0.13	8-0.35	-0.35	1.00	1 00									
Kb	-0.19 0.01	-0.24	0.28	0.24	-0.24 -0).22 -0.	.21 ().70 -0.0)7 -0.10)-0.04	-0.08	0.06	0.07	-0.06	0.05	-0.13	0.02	0.02	0.13	-0.05	0.30	-0.08	0.12	-0.03	3 1.00	1 00								
Sc	0.37 -0.23	-0.25	-0.36	0.72	0.74 0	0.47 0.	00 -0	$0.12 \ 0.8$	6 0.21	-0.06	-0.25	-0.13	6-0.07	0.86	-0.49	-0.16	-0.23	-0.53	0.68	0.57	0.73	0.69	0.84	-0.48	8-0.10	1.00	1 00							
Sr T	0.85 -0.81	0.94	-0.86	-0.44	0.01 0	1.75 U.	97 (02 (1.28 0.1	2 0.02	-0.03	-0.20	-0.50	0.63	0.13	-0.58	-0.17	-0.20	-0.61	-0.40	-0.24	-0.41	0.19	-0.01	-0.53	5-0.28	0.03	0.01	1 00						
	0.24 -0.18	-0.25	-0.23	0.61	0.41 0	145 -U	.U3 (00 (J.12 U.9	4 0.28	0.04	-0.11	-0.04	0.00	0.95	-0.43	-0.19	-0.10	-0.40	0.83	0.57	0.87	0.79	0.99	-0.35	0.15	0.85	-0.01	. 1.00	1.00					
In	0.27 -0.23	-0.19	-0.24	0.68	0.32 0	$0.40 \ 0.$		0.00 0.0	0.0.12	0.04	-0.18	-0.19	0.11	0.03	-0.33	0.28	-0.08	-0.40	0.01	0.51	0.75	0.72	0.83	-0.38	0.29	0.69	0.00	0.87	1.00	1.00				
U	-0.67 0.63	-0.64	0.65	0.28	-0.15 -0).53 -0.	ו- טט. י פר	0.07 -0.0	17 U.13	0.06	0.06	0.32	0.46	-0.09	0.29	-0.03	0.09	0.47	0.21	0.18	0.30	30.0-	0.03	0.32	0.34	-0.02	-0.73	0.04	0.04	1.00	1.00			
Ta Th U V	0.24 -0.18 0.27 -0.23 -0.67 0.63 -0.43 0.39	-0.25 -0.19 -0.64 -0.28	-0.23 -0.24 0.65 0.42	0.81 0.68 0.28 -0.08	0.41 0 0.32 0 -0.15 -0 -0.13 -0	0.45 -0. 0.40 0. 0.53 -0. 0.44 -0.	.03 () 00 () .66 -() .38 -()).12 0.9).41 0.8 0.09 -0.0 0.21 -0.3	94 0.28 60 0.12 09 0.13 39 -0.09	0.04 0.04 0.06 0.01	-0.11 -0.18 0.06 0.10	-0.04 -0.19 0.32 0.16	0.00 -0.11 0.46 0.39	0.95 0.83 -0.09 -0.40	-0.43 -0.33 0.29 0.70	-0.19 -0.28 -0.03 0.32	-0.10 -0.08 0.09 0.15	-0.40 -0.40 0.47 0.42	0.83 0.68 0.21 -0.18	0.57 0.51 0.18 -0.23	0.87 0.75 0.30 -0.19	0.79 0.72 -0.08 -0.26	0.99 0.83 0.03 -0.40	-0.35 -0.38 0.32 0.37	5 0.15 3 0.29 0.34 -0.08	0.85 0.69 -0.02 -0.39	-0.01 0.00 -0.73 -0.35	1.00 0.87 0.04 5-0.42	1.00 0.04 2-0.35	1.00 0.17	1.00			

 Y
 0.36
 -0.30
 -0.12
 -0.36
 0.73
 0.50
 0.59
 0.09
 -0.02
 0.99
 0.23
 -0.06
 -0.13
 -0.09
 1.00
 -0.51
 -0.18
 -0.21
 -0.45
 0.78
 0.48
 0.77
 0.83
 0.95
 -0.42
 -0.06
 0.89
 0.11
 0.95
 0.82
 -0.09
 -0.41
 1.00

 Zn
 -0.92
 0.88
 -0.79
 0.94
 0.35
 -0.34
 -0.77
 -0.90
 -0.36
 -0.08
 0.64
 -0.18
 0.48
 0.77
 0.83
 0.95
 -0.42
 -0.06
 0.89
 0.11
 0.95
 0.82
 -0.09
 -0.41
 1.00

 Zn
 -0.92
 0.88
 -0.79
 0.94
 0.35
 -0.36
 -0.99
 0.34
 0.53
 0.64
 -0.10
 0.56
 0.17
 0.26
 0.80
 0.46
 0.18
 0.40
 -0.15
 0.03
 0.64
 0.31
 -0.11
 1.00
 0.44
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Note: Pearson's correlation was based on 39 samples with Fe-Ti-V oxide and polymetallic sulphide mineralization. Coefficients with absolute values greater than 0.26 are statistically significant at the 95% level.

Among the REEs, the highest arithmetic mean was found for cerium, at only 34 ppm, with a range from 1.3 to 285 ppm. The sum of the light REEs (La to Gd) ranged from 12.0 to 697.8 ppm, and the arithmetic mean was 97 ppm. On the other hand, the sum of the heavy HREEs (from Tb-Lu + Y) was very low, ranging from approximately 0.05 to 4.35 ppm, and the arithmetic mean was 0.53 ppm. The ratio of LREE to HREE ranged from 0.3 to 23.6 (mean = 3). Yttrium contents were also low, in the range of <0.5 to 105.6 ppm, and the arithmetic mean was 11.4 ppm (n = 39). All of the samples from magnetite-ilmenite ore showed a similar pattern, with a LREE/HREE fractionation and a negative Eu anomaly and a positive Sm anomaly (Figure 17). These are characteristic REE patterns for a magmatic origin of magnetite-apatite ores [42]. The fractionation of Fe-Ti-oxides was important in the ore-bearing rock samples and this indicates that these ores had a common origin. In addition, there was significant (>400×) enrichment in the REE (especially in Ce, La and Nd) in three mineralized samples from the Udryn deposit. The REE concentrations in these three samples were elevated ($\Sigma REE = 0.1\%$) and associated with enrichments in P_2O_5 , CaO, and MgO, as well as to the presence of carbonatites related to Variscan alkaline magmatism [32,34]. REEs spanned a relatively large interval of concentrations, which can be explained partly by fractional crystallization and partly by the varying amounts of apatite crystallized from trapped liquid (these samples had the highest REE and P₂O₅ contents). Anorthosites and norites exhibited compositions typical of cumulate rocks. The contents of elements incompatible with plagioclase and of transition elements were low and were mostly controlled by the mafic mineral content [29].



Figure 17. REE diagram normalized to chondrite data after [43] for the Fe-Ti-V ore samples from the Krzemianka and Udryn deposits in NE Poland.

5. Discussion

5.1. Genetic Implications for Vanadium and Cobalt Occurrence in the SAM

The origin of the Fe-Ti-V oxide mineralization hosted by Proterozoic massif-type anorthosite has been explained through different processes, such as fractional crystallization [44–46], magma mixing [47], immiscibility between silicate and oxide magmas [48], stress-driven melt segregation [49], solid-state remobilization [50,51], and hydro-

thermal remobilization [52]. For the Fe-Ti-V mineralization in the SAM, it was suggested that oxide-silicate melt moved from the deeper parts into the faulted zones of the anorthosite intrusion [16,23]. Moreover, magnetite-ilmenite melt with sulphides followed the same route due to activity of convection flow [29,46]. The Fe-Ti-oxide and sulphide mineralization in SAM was formed from a common parental magma through separate processes [16,53].

In bulk-rock samples, the mean arithmetic content of vanadium and cobalt was 960 ppm (0.17 V₂O₅) and 122 ppm, respectively. The dominant ore minerals were magnetite, ilmenite and Al-spinels with subordinate quantities (1–3% of rock volume) of pyrrhotite (c.a. 80% of total sulphides) and pentlandite and chalcopyrite. These ore minerals were formed in the magnatic stage. The early-magmatic stage included the main concentrations of the oxide minerals of the titanomagnetite–ulvöspinel–ilmenite series (in the temperature range of 575 °C–700 °C), and the late-magmatic stage included sulphides crystallizing at high temperatures (~600 °C), such as pyrrhotite, pentlandite, and chalcopyrite [26]. Various structures of ilmenite and spinel separation in magnetite were common, as well as the structures of these minerals, resulting from the decomposition of solid solutions during differentiation in the primary igneous associations during the change of PT conditions [23,26,27,29,41]. In the post-magmatic stage, in connection with the changes in the primary mineral composition, several processes were recognized, such as oxidation separation (temperature range 700 °C–400 °C); separation (500 °C–200 °C); and deuteric (400 °C), hydrothermal, and hypergenic transformations [23,27,29,41].

Vanadium and cobalt have geochemically different characteristics. Vanadium has oxyphilic properties and has been found to be concentrated during the initial stage of crystallization of metallic minerals in magma. Cobalt is sulphophilic and it crystallizes with other Fe, Cu, and Ni sulphides in the later stages of magma differentiation. However, in our bulk-rock geochemical study, cobalt showed a good correlation with vanadium, Fe₂O₃t, and nickel (r = ~0.70) and a weaker correlation with TiO₂ (r = 0.60). This indicates not only that there was a close spatial coexistence of magnetite-ilmenite mineralization, but also a common source of metals related to the differentiation of anorthosite-norite magma in the AMCG.

Based on the EPMA results, the contents of vanadium in magnetite, ilmenite, and Al-spinels were highly variable. Magnetite, on average, contained 0.42 wt% V ($0.75 V_2O_5$). With progressive oxidation and recrystallization, vanadium moved gradually into magnetite. Vanadium was an isomorphic admixture in magnetite, substituting for Fe⁺³ in its crystal lattice. The vanadium content varied slightly in magnetite, in contrast to the variable Ti content which was a substitution for Fe⁺². Vanadium had a weak positive correlation with Ti and Cr in the magnetite (Figure 14C,D). The redistribution of V and Fe³⁺ substitution ions occurred under variable PT conditions during the evolution of the anorthosite massif [24,44]. Ilmenite contained 0.14 wt% V on average (0.25 V₂O₅). We recognized a slight enrichment of V in massive ilmenites (0.17 to 0.24 wt%) with an increase in the Fe content (36–40 wt%) when compared to ilmenite exsolutions' lamellae in magnetite or to ilmenite pseudomorphs after magnetite. Generally, oxide minerals that have the highest Fe/Ti ratio are the richest in (V + Cr + Al), whereas those with the lowest Fe/Ti ratio are the richest in (Mg + Mn) [29,54–56].

Cobalt was concentrated mainly as isomorphic substitutions in magmatic pentlandite, pyrrhotite, and chalcopyrite and in secondary minerals such as siegenite, pyrite, bravoite, cubanite, and talnakhite. A constant admixture of cobalt in magmatic pentlandite was observed, ranging from 1 to 15.3 wt% (mean = 4.4 wt%). However, higher cobalt contents at the level of 14 to 30 wt% were found in siegenite, and some lower substitution of Co was observed at the level of 3–4 wt% in talnakhite and 1–3 wt% in bravoite. The concentrations of cobalt in pyrrhotite and chalcopyrite were one order lower, in the range of 0.1–0.6 wt% (means = 0.16 and 0.11 wt%, respectively). Pyrrhotite and chalcopyrite also contained nickel substitutions, with mean values of 0.6 and 0.11 wt%, respectively. The low amounts of Co substitutions were also found in cubanite replacing chalcopyrite (maximum 0.14 wt%). The decomposition processes resulted in the disintegration of sulphide solutions such as pyrrhotite \pm pentlandite \pm chalcopyrite and the formation of subsequent generations of Fe, Cu, Ni, and Co sulphides and thiospinels ((*Fe Ni*) (*Co*, *Ni*)₂*S*₄). The proportions of metals indicated the presence of diadochid substitutions and/or micro overgrowths of several transition phases in pentlandite or pyrrhotite. According to [41], the transition phases represent a mixture of different thiospinels ((*FeCo*)₂*S*₄, (*NiCo*)₂*S*₄, and (*FeNi*)₂*S*₄)) exsoluted from pentlandite. They described the decomposition of pentlandite into unidentified thiospinels (Fe,Ni)(Co,Ni)₂*S*₄ and Ni-mackinawite, that may later cause the formation of Co-rich pyrite [41]. The presence of Co-rich pyrite was also recognized during our EPMA, but we additionally identified siegenite, bravoite, cubanite, and talnakhite (Tables 3 and 4, Figure 11). Cobaltiferous pyrite contained from 1 to 8.6 wt% Co (mean = ~2 wt%). In the case of the pyrite replacing pyrrhotite, there was no visible increase in cobalt concentration (<0.1 wt%) compared to primary pyrrhotite.

According to [24], during the first stage of accessory or segregation at low contents of interstitial liquid, one can observe high *f*O₂, and gradual cooling metallic minerals crystallized with silicates. During the second process, Fe-Ti-rich anorthosite-norite magma formed and metallic minerals settled at the bottom of the magma chamber at high temperature and an intermediate oxygen partial pressure. The injection of Fe-Ti-rich magma or tectonic introduction of the partially solidified ore chamber into the upper part of the solidified pluton, followed by an immiscible segregation process, explains the concordant character of major Fe-Ti-V ore bodies with disseminated sulphides (Fe, Cu, Co, Ni) [46,56]. Parental ferrodioritic (jotunite) magma of the SAM anorthosite, enriched in plagioclase and orthopyroxene under high-pressure conditions, is saturated in plagioclase and magnetite-ilmenite assemblage at the pressure of crystallization of Fe-Ti oxide emplacement [29]. The REE concentrations in the studied ore samples, normalized to chondrite, had very characteristic clear negative Eu and positive Sm anomalies, indicating the common magmatic origin of Fe-Ti-oxides and sulphide mineralizations hosted by anorthosites and norites.

We suggest that the crystal sorting of Fe-Ti oxide minerals was responsible for the formation of the SAM Fe-Ti-V deposits relative to plagioclase and ferromagnesian silicates [46,57]. Moreover, diapiric uprising of the anorthosite crystal mush favored the sorting during Fe-Ti-enriched cumulate crystallization. Polybaric conditions of mineral crystallization can be shown by the variable Al_2O_3 content in orthopyroxene [46]. These petrological diagnostic features point to a crustal origin, a conclusion supported by Sm-Nd and Re–Os isotopic data [16,46,53]. The Re-Os model age obtained for pyrrhotite and magnetite give an age of 1536 ± 67 million years [29,37,38]. The time range of their crystallization is consistent with the results of U-Pb determination via the zircon SHRIMPIIe method [15] which indicates that the SAM anorthosites are the result of several magmatic pulses, culminating ca. 1515 Ma and 1507 Ma. The development of post-ore tectonics caused the division of Fe-Ti-V ore fields into separate deposits and the network of discontinuities and fault zones were filled by post-ore S-type granites. The crystallization ages of individual granite veins range between 1489 ± 6 Ma and 1475 ± 5 Ma [15]. Hydrothermal processes were probably associated with these granite veins, which were also responsible for magmatic sulphide replacement in the Fe-Ti-V orebodies. The contribution of hydrothermal and pneumatolitic processes in general only locally influenced the major magmatic metallic mineralization. New hydrothermal base metal sulphides formed, such as chalcopyrite, sphalerite and galena, associated with accessory ore minerals (greenockite, hessite, and native bismuth). The enrichment in cadmium of the studied samples—by over 70 times compared to the average Cd content in the earth's crust according to [58]—is also noteworthy. Cadmium is associated with the presence of fine-grained sphalerite that contains substitutions of Cd, as well as the presence of greenockite (CdS) associated with chalcopyrite. They are minerals of hydrothermal origin.

5.2. Economic Potential of Vanadium and Cobalt in the SAM

The Fe-Ti-V mineralization in the Krzemianka and Udryn deposits has been considered to be sub-economic since 1996, despite their large geological resources. Identified resources comprise a total of 1.34 billion tons of Fe-Ti-V ore, containing 388.2 million tons of iron and 98 million tons of titanium [30]. The laboratory tests carried out in the 1970s showed the possibility of obtaining separate concentrates of magnetite, ilmenite, and sulphides from these ores. The main component of the sulphide concentrates was pyrrhotite, which was definitely dominant among sulphides and contained, on average, approx. 0.16 wt% Co and 0.61 wt% Ni. These metals can be recovered from the sulphide concentrate through further technological processing [23]. It should be noted that the vanadium contents obtainable in the magnetite and ilmenite concentrates amounted to approximately 0.75 wt% and 0.2 wt% V2O5, respectively [29]. The vanadium resources were roughly documented at ca. 4.1 million tons, with an average grade of 0.26–0.31% V2O₅. Our geochemical bulk-rock studies of samples from the Krzemianka and Udryn Fe-Ti-V deposits hosted by the Suwałki Anorthosite Massif showed that they were enriched in some elements relative to the respective average elemental contents in the earth's crust [36]. Among them there were also critical elements such as Co and V, and other accompanying metals, represented by Ni, Cu, and Cr, which show only about six times the enrichment in relation to their average content in the earth's crust. The resources of Co were roughly estimated to be greater than 150,000 tons and those of Zn, Ni, Cu, and Cr were up to several hundred thousand tons each [33,59].

It is important to note that, according to the latest estimates—which, however, were made almost two decades ago—the marginal V_2O_5 value in economic ore should be 0.73% V_2O_5 . This means that, according to this criterion, the resources of the two deposits in the SAM would amount to only 1% of the previously documented resources [31].

There are several known examples of this type of magmatic Fe-Ti-V oxide deposits in the world, located in Proterozoic anorthosite massifs and at much more favorable depth conditions and without strong environmental restrictions. They have been discovered in outcrops or shallow sub-surface formations in Africa, Canada, the USA, and Scandinavia [60–65]. The vanadium mean contents in these deposits are typically 0.1–1% V_2O_5 and these vary, for example, in Canada's Charles and Buttercup deposits (0.1 and 0.67% V₂O₅, respectively) [66]. Cobalt is also recognized as a strategic metal which is crucial for the world's development and transition to a low-carbon economy. Orthomagmatic Ni-Cu-Co sulphide deposits are one of the three main sources of cobalt supplied to the world economy [6]. However, the Fe-Ti-V magmatic deposits hosted by anorthosite complexes are impoverished in terms of their concentrations of Ni, Co, and Cu when compared with other orthomagmatic resources, despite the fact that in some cases they may contain local enrichments of these elements in sulphides and are strongly associated with magnetite-ilmenite oxide mineralization. In the SAM they are considered to be sub-economic because of the depth of the occurrence of ores; their insufficient metal contents, and environmental protection aspects.

6. Conclusions

On the basis of detailed geochemical (ICP-MS, WDS-XRF, and GF AAS) and mineralogical (EPMA and SEM) investigations, concentrations of critical elements, such as V and Co, in magnetite-ilmenite and associated sulphide mineralizations from the Krzemianka and Udryn Fe-Ti-V deposits in the Suwałki Anorthosite Massif (NE Poland) were recognized. The mean vanadium and cobalt contents in bulk-rock samples were 0.175% V₂O₅ and 0.012% Co, respectively. The main minerals carrying vanadium were magnetite (mean = 0.75 wt% V₂O₅) and ilmenite (mean = 0.25 wt% V₂O₅). Cobalt occurred mainly as isomorphic substitutions in magmatic pentlandite (mean = 4.4 wt%), pyrrhotite (0.16 wt%), and chalcopyrite (0.11 wt%). Cobalt was also locally present in the form of different thiospinels ((*Fe*, *Ni*) (*Co*, *Ni*)₂S₄) replacing pyrrhotite-pentlandite solid solutions. The most common of these was siegenite. Moreover, the identified secondary pyrite and bravoite also revealed constant enrichments of Co (*ca.* 2 wt%). Magmatic sulphides were the main source of cobalt, which was locally redistributed during the post-magmatic processes (deuteric, hydrothermal, and hypergenic) and incorporated by the secondary minerals.

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Appendix A

Table A1. Chemical composition of magnetite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	Fe	Al	Mn	V	Cr	Mg	Ti	0	Total	Fe/Ti	Al + V + Cr	Mg + Mn
KR-24_03_obsz-01_fot-1.1	70.436	0.285	0.027	0.324	0.16	0.068	1.006	21.394	93.751	70.0	0.769	0.095
KR-24_03_obsz-01_fot-1.2	69.954	0.338	0.015	0.326	0.116	0.104	1.065	21.359	93.349	65.7	0.78	0.119
KR-24_03_obsz-01_fot-1.3	70.587	0.261	0.025	0.43	0.119	0.07	0.303	20.985	92.817	233.0	0.81	0.095
KR-24_03_obsz-01_fot-1.4	69.974	0.402	0.052	0.453	0.175	0.109	0.468	21.108	92.783	149.5	1.03	0.161
KR-24_03_obsz-03_fot-6.6	69.5	0.241	0.026	0.452	0.282	0.056	1.089	21.271	93.042	63.8	0.975	0.082
KR-24_03_obsz-03_fot-6.7	69.64	0.238	0.019	0.377	0.258	0.046	1.055	21.224	92.959	66.0	0.873	0.065
KR-24_03_obsz-03_fot-6.8	70.639	0.334	0.033	0.477	0.112	0.066	0.31	21.1	93.165	227.9	0.923	0.099
KR-24_03_obsz-03_fot-6.9	70.027	0.35	0.014	0.433	0.118	0.077	0.377	20.954	92.398	185.7	0.901	0.091
KR-24_03_obsz-03_fot-6.10	70.611	0.328	0.014	0.494	0.135	0.082	0.527	21.26	93.567	134.0	0.957	0.096
KRZ-56_02_obsz-01_fot-1.1	70.011	0.487	0.033	0.58	0.156	0.06	0.357	21.152	92.935	196.1	1.223	0.093
KRZ-56_02_obsz-01_fot-1.2	70.66	0.276	b.d.l.	0.481	0.125	0.039	0.144	20.912	92.676	490.7	0.882	0.039
KRZ-56_02_obsz-01_fot-1.3	70.883	0.51	0.011	0.498	0.116	0.075	0.162	21.26	93.683	437.5	1.124	0.086
KRZ-56_02_obsz-01_fot-2.6	72.198	0.238	0.005	0.55	0.09	0.021	0.074	21.272	94.483	975.6	0.878	0.026
KRZ-56_02_obsz-01_fot-2.7	72.164	0.186	b.d.l.	0.505	0.125	0.025	0.261	21.373	94.863	276.5	0.816	0.025
KRZ-56_02_obsz-01_fot-2.8	72.002	0.229	0.014	0.515	0.142	0.033	0.145	21.289	94.442	496.6	0.886	0.047
KRZ-56_02_obsz-01_fot-2.9	71.958	0.24	0.035	0.507	0.106	0.03	0.296	21.392	94.734	243.1	0.853	0.065
KRZ-56_02_obsz-01_fot-2.10	71.627	0.48	0.037	0.542	0.091	0.075	0.163	21.443	94.527	439.4	1.113	0.112
KR-63_05_obsz-02_fot-1.3	71.136	0.252	0.018	0.572	0.159	0.053	0.249	21.169	93.675	285.7	0.983	0.071
KR-63_05_obsz-02_fot-1.4	71.634	0.18	0.012	0.584	0.122	0.025	0.116	21.139	93.927	617.5	0.886	0.037
KR-63_05_obsz-03_fot-1.1	71.659	0.161	0.008	0.579	0.147	0.07	0.161	21.179	94.007	445.1	0.887	0.078
KR-63_05_obsz-03_fot-1.2	70.406	0.484	0.016	0.576	0.126	0.157	0.485	21.372	93.649	145.2	1.186	0.173
KR-63_05_obsz-03_fot-1.3	71.237	0.175	0.001	0.557	0.125	0.048	0.238	21.091	93.54	299.3	0.857	0.049
KR-63_05_obsz-04_fot-1.5	68.297	1.903	0.051	0.557	0.145	0.534	0.416	22.244	94.19	164.2	2.605	0.585
KR-63_05_obsz-04_fot-1.6	70.304	0.619	0.019	0.57	0.169	0.219	0.525	21.568	94.126	133.9	1.358	0.238
KR-63_05_obsz-05_fot-1.10	71.631	0.231	0.034	0.583	0.135	0.088	0.15	21.268	94.269	477.5	0.949	0.122
KR-63_05_obsz-05_fot-1.11	70.069	0.573	0.007	0.556	0.129	0.194	0.381	21.309	93.287	183.9	1.258	0.201
KR-63_05_obsz-05_fot-1.12	70.988	0.458	b.d.l.	0.532	0.159	0.154	0.164	21.297	93.789	432.9	1.149	0.154
KR-63_05_obsz-08_fot-1.5	71.235	0.197	0.017	0.588	0.129	0.061	0.185	21.117	93.649	385.1	0.914	0.078

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KR-63_05_obsz-08_fot-1.6	70.437	0.446	0.015	0.569	0.103	0.15	0.263	21.19	93.223	267.8	1.118	0.165
KR-63_05_obsz-08_fot-1.7	71.57	0.266	0.013	0.57	0.154	0.092	0.189	21.318	94.304	378.7	0.99	0.105
UDR-7_01_obsz-01_fot-1.1	69.137	0.465	0.062	0.448	0.451	0.081	1.233	21.564	93.523	56.1	1.364	0.143
UDR-7_01_obsz-01_fot-1.2	69.962	0.294	0.027	0.416	0.456	0.038	1	21.434	93.719	70.0	1.166	0.065
UDR-7_01_obsz-01_fot-1.3	69.586	0.405	0.028	0.498	0.441	0.068	1.036	21.499	93.642	67.2	1.344	0.096
UDR-7_01_obsz-01_fot-1.4	69.769	0.498	0.019	0.523	0.442	0.092	0.916	21.582	93.934	76.2	1.463	0.111
UDR-7_01_obsz-01_fot-1.5	69.595	0.481	0.019	0.485	0.439	0.063	0.829	21.411	93.392	84.0	1.405	0.082
UDR-7_01_obsz-01_fot-1.6	69.702	0.412	0.075	0.471	0.488	0.072	1.216	21.688	94.174	57.3	1.371	0.147
UDR-7_01_obsz-01_fot-1.7	67.557	0.746	0.102	0.52	0.427	0.118	2.31	22.134	93.98	29.2	1.693	0.22
UDR-7_01_obsz-01_fot-1.8	68.033	0.593	0.08	0.495	0.449	0.076	2.268	22.082	94.222	30.0	1.537	0.156
UDR-7_01_obsz-01_fot-1.9	68.621	0.783	0.075	0.48	0.426	0.152	1.767	22.096	94.457	38.8	1.689	0.227
UDR-7_01_obsz-01_fot-1.10	69.937	0.425	0.048	0.465	0.444	0.068	0.892	21.517	93.883	78.4	1.334	0.116
UDR-7_01_obsz-02_fot-1.1	69.115	0.448	0.066	0.452	0.451	0.091	1.432	21.673	93.805	48.3	1.351	0.157
UDR-7_01_obsz-02_fot-1.2	68.396	0.914	0.051	0.516	0.472	0.21	1.627	22.121	94.356	42.0	1.902	0.261
UDR-7_01_obsz-02_fot-1.3	66.203	1.216	0.128	0.512	0.517	0.28	2.652	22.543	94.139	25.0	2.245	0.408
UDR-7_01_obsz-03_fot-1.1	68.706	0.415	0.053	0.475	0.439	0.084	1.484	21.56	93.246	46.3	1.329	0.137
UDR-7_01_obsz-03_fot-1.2	67.921	0.639	0.094	0.497	0.473	0.122	1.86	21.862	93.551	36.5	1.609	0.216
UDR-7_01_obsz-03_fot-1.3	67.283	0.656	0.1	0.462	0.453	0.123	2.297	21.946	93.363	29.3	1.571	0.223
UDR-10_3_obsz-03_fot-2.5	69.72	0.4	0.069	0.412	0.2	0.081	1.717	21.865	94.515	40.6	1.012	0.15
UDR-10_3_obsz-03_fot-2.6	67.932	0.686	0.1	0.459	0.235	0.219	2.552	22.293	94.551	26.6	1.38	0.319
UDR-10_3_obsz-03_fot-2.7	69.483	0.4	0.076	0.392	0.144	0.135	1.586	21.691	93.932	43.8	0.936	0.211
UDR-10_3_obsz-03_fot-2.8	69.964	0.44	0.1	0.458	0.236	0.149	1.426	21.851	94.682	49.1	1.134	0.249
UDR-10_3_obsz-03_fot-2.9	71.984	0.01	b.d.l.	0.006	0.006	b.d.l.	0.387	20.916	93.349	186.0	0.022	b.d.l.
DR-10_4_obsz-03_fot-1.5	69.612	0.272	b.d.l.	0.492	1.262	0.05	0.185	21.183	93.166	376.3	2.026	0.05
UDR-10_4_obsz-03_fot-1.6	69.668	0.428	0.031	0.462	0.744	0.058	0.285	21.156	92.868	244.4	1.634	0.089
UDR-10_4_obsz-04_fot-1.5	70.716	0.336	0.004	0.563	0.712	0.063	0.261	21.378	94.063	270.9	1.611	0.067
UDR-11_05_obsz-04_fot-1.5	71.428	0.198	0.009	0.245	0.016	0.038	0.059	20.856	92.907	1210.6	0.459	0.047
UDR-11_05_obsz-04_fot-1.6	71.334	0.171	0.014	0.22	0.025	0.028	0.22	20.924	93.078	324.2	0.416	0.042
UDR-11_06_obsz-02_fot-1.7	71.689	0.118	b.d.l.	0.153	0.023	0.033	0.094	20.851	93.049	762.6	0.294	0.033
UDR-11_06_obsz-02_fot-1.8	71.301	0.139	0.002	0.211	0.028	0.039	0.059	20.77	92.684	1208.5	0.378	0.041
UDR-11_06_obsz-02_fot-1.9	71.372	0.118	0.026	0.218	0.021	0.038	0.057	20.788	92.786	1252.1	0.357	0.064
$UDK-11_06_0bsz-02_fot-1.10$	/1.554	0.175	b.d.l.	0.188	0.061	0.048	0.066	20.84	92.88	1080.8	0.424	0.048
UDK-11_06_obsz-02_tot-1.11 UDP 11_06_obsz-04_fot 1.1	/0.858	0.232	0.041	0.2	0.034	0.042	0.102	20.766	92.39	094./ 1020 5	0.466	0.083
0.0111_00_0052-04_101-1.1	/1.050	0.231	0.013	0.231	0.042	0.005	0.009	20.701	92.513	1047.3	0.304	0.010

UDR-11_06_obsz-04_fot-1.2	71.3	0.141	b.d.l.	0.225	0.018	0.037	0.026	20.76	92.65	2742.3	0.384	0.037
UDR-11_06_obsz-04_fot-1.3	71.144	0.21	0.006	0.21	0.051	0.041	0.064	20.825	92.697	1111.6	0.471	0.047
UDR-11_06_obsz-04_fot-1.4	71.397	0.123	0.002	0.262	0.033	0.016	0.056	20.791	92.855	1274.9	0.418	0.018
UDR-11_06_obsz-06_fot-1.1	70.791	0.172	0.013	0.214	0.051	0.028	0.062	20.659	92.072	1141.8	0.437	0.041
UDR-11_06_obsz-06_fot-1.2	71.377	0.166	0.023	0.232	0.048	0.011	0.113	20.858	92.937	631.7	0.446	0.034

b.d.l.-below detection limit.

Appendix B

Table A2. Chemical composition of ilmenite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	Fe	Al	Mn	V	Cr	Mg	Ti	0	Total	Fe/Ti	Al + V + Cr	Mn + Mg
KR-24_03_obsz-01_fot-1.5	34.816	0.023	0.687	0.151	0.027	1.029	31.097	31.771	99.727	1.12	0.201	1.716
KR-24_03_obsz-03_fot-6.11	33.898	0.03	1.179	0.16	0.006	0.897	31.864	32.056	100.191	1.06	0.196	2.076
KR-24_03_obsz-03_fot-6.12	34.182	0.017	0.832	0.147	0.037	1.053	31.891	32.162	100.388	1.07	0.201	1.885
KR-24_03_obsz-03_fot-6.13	34.43	0.026	0.72	0.149	b.d.l.	1.038	31.324	31.782	99.477	1.10	0.175	1.758
KRZ-56_02_obsz-01_fot-1.4	33.751	2.994	0.785	0.111	0.125	1.115	28.613	32.547	100.156	1.18	3.23	1.9
KRZ-56_02_obsz-01_fot-1.5	35.652	0.02	0.87	0.155	0.041	0.234	31.475	31.793	100.391	1.13	0.216	1.104
KRZ-56_02_obsz-01_fot-2.1	35.859	0.025	0.709	0.123	0.043	0.47	29.858	30.845	97.982	1.20	0.191	1.179
KRZ-56_02_obsz-01_fot-2.2	35.583	0.003	0.76	0.118	0.018	0.507	31.219	31.716	100.081	1.14	0.139	1.267
KR-63_05_obsz-02_fot-1.7	33.15	2.163	0.91	0.161	0.067	1.375	29.353	32.331	99.599	1.13	2.391	2.285
KR-63_05_obsz-02_fot-1.8	34.189	1.378	0.866	0.177	0.074	1.075	30.45	32.457	100.688	1.12	1.629	1.941
KR-63_05_obsz-03_fot-1.4	34.242	0.017	0.741	0.117	b.d.l.	1.284	31.416	31.95	99.839	1.09	0.134	2.025
KR-63_05_obsz-03_fot-1.5	35.033	0.027	0.645	0.111	0.022	1.226	31.196	31.984	100.332	1.12	0.16	1.871
KR-63_05_obsz-04_fot-1.4	34.668	0.026	0.719	0.091	0.036	1.194	31.272	31.932	100.062	1.11	0.153	1.913
KR-63_05_obsz-05_fot-1.6	33.937	1.186	0.896	0.166	0.082	1.352	29.661	31.888	99.261	1.14	1.434	2.248
KR-63_05_obsz-05_fot-1.7	34.769	0.038	0.813	0.143	0.042	1.037	30.583	31.45	98.931	1.14	0.223	1.85
KR-63_05_obsz-05_fot-1.8	34.142	0.017	0.727	0.081	0.033	1.366	31.603	32.076	100.058	1.08	0.131	2.093
KR-63_05_obsz-05_fot-1.9	33.966	0.025	0.722	0.113	0.019	1.3	31.214	31.753	99.173	1.09	0.157	2.022
KR-63_05_obsz-08_fot-1.1	35.008	0.024	0.66	0.125	0.003	1.127	30.302	31.318	98.699	1.16	0.152	1.787
KR-63_05_obsz-08_fot-1.2	34.613	0.015	0.718	0.12	0.012	1.168	31.365	31.953	100.038	1.10	0.147	1.886
KR-63_05_obsz-08_fot-1.3	35.232	0.018	0.703	0.141	0.016	1.208	30.875	31.818	100.052	1.14	0.175	1.911
KR-63_05_obsz-08_fot-1.4	35.008	0.032	0.661	0.132	0.019	1.211	30.839	31.755	99.77	1.14	0.183	1.872
UDR-7_01_obsz-02_fot-1.4	35.119	b.d.l.	0.712	0.113	b.d.l	0.803	31.191	31.721	99.782	1.13	0.113	1.515

UDR-7_01_obsz-02_fot-1.5	35.459	0.007	0.592	0.086	0.025	0.737	30.943	31.577	99.564	1.15	0.118	1.329
UDR-7_01_obsz-02_fot-1.6	35.309	b.d.l.	0.654	0.125	b.d.l.	0.651	31.45	31.848	100.177	1.12	0.125	1.305
UDR-7_01_obsz-02_fot-1.7	35.122	0.051	0.639	0.049	0.005	0.689	31.568	31.883	100.1	1.11	0.105	1.328
UDR-7_01_obsz-03_fot-1.4	35.19	0.038	0.974	0.152	0.051	0.373	30.946	31.439	99.259	1.14	0.241	1.347
UDR-7_01_obsz-03_fot-1.5	35.495	0.019	0.951	0.149	0.027	0.336	31.009	31.505	99.582	1.14	0.195	1.287
UDR-7_01_obsz-03_fot-1.6	35.526	0.011	1	0.083	0.028	0.369	31.096	31.561	99.733	1.14	0.122	1.369
UDR-10_3_obsz-03_fot-2.1	34.103	0.025	0.641	0.1	0.04	1.63	31.384	32.11	100.084	1.09	0.165	2.271
UDR-10_3_obsz-03_fot-2.2	33.651	0.017	0.641	0.122	0.007	1.603	31.745	32.176	100.029	1.06	0.146	2.244
UDR-10_3_obsz-03_fot-2.3	34.205	0.045	0.596	0.13	b.d.l.	1.631	31.516	32.21	100.379	1.09	0.175	2.227
UDR-10_3_obsz-03_fot-2.4	33.959	0.02	0.685	0.072	0.015	1.659	31.636	32.245	100.436	1.07	0.107	2.344
UDR-10_4_obsz-03_fot-1.3	35.145	0.026	0.763	0.164	0.033	0.56	31.681	31.941	100.318	1.11	0.223	1.323
UDR-10_4_obsz-03_fot-1.4	34.935	0.202	0.724	0.138	0.082	0.631	31.478	31.96	100.21	1.11	0.422	1.355
UDR-10_4_obsz-04_fot-1.9	35.536	0.119	0.954	0.172	0.073	0.411	31.27	31.854	100.448	1.14	0.364	1.365
UDR-10_4_obsz-04_fot-1.10	34.149	4.388	0.81	0.122	0.586	1.189	26.678	32.885	100.889	1.28	5.096	1.999
UDR-10_4_obsz-01_fot-1.5	35.32	0.01	0.776	0.141	0.027	0.392	31.523	31.764	99.999	1.12	0.178	1.168
UDR-10_4_obsz-01_fot-1.6	35.792	0.018	0.688	0.112	b.d.l.	0.52	31.344	31.822	100.358	1.14	0.13	1.208
UDR-11_04_obsz-02_fot-2.11	36.507	0.03	0.928	0.18	0.027	0.646	30.642	31.789	100.875	1.19	0.237	1.574
UDR-11_04_obsz-01_fot-4.11	37.156	0.02	0.881	0.181	b.d.l.	0.736	30.086	31.624	100.793	1.23	0.201	1.617
UDR-11_04_obsz-01_fot-4.12	38.197	0.03	0.867	0.174	0.016	0.697	28.812	31.05	99.937	1.33	0.22	1.564
UDR-11_05_obsz-01_fot-1.7	37.282	0.026	0.851	0.15	0.026	0.647	29.766	31.396	100.29	1.25	0.202	1.498
UDR-11_05_obsz-01_fot-1.8	36.302	0.011	0.798	0.114	b.d.l.	0.797	30.146	31.38	99.615	1.20	0.125	1.595
UDR-11_06_obsz-02_fot-1.2	36.005	0.027	0.941	0.177	0	0.845	30.63	31.787	100.611	1.18	0.204	1.786
UDR-11_06_obsz-02_fot-1.3	36.247	0.026	0.935	0.075	0.028	0.804	30.118	31.434	99.863	1.20	0.129	1.739
UDR-11_06_obsz-02_fot-1.4	38.566	0.025	0.811	0.141	0.003	0.786	28.496	30.989	99.985	1.35	0.169	1.597
UDR-11_06_obsz-02_fot-1.5	39.905	0.031	0.663	0.176	0.037	0.717	26.826	30.172	98.608	1.49	0.244	1.38
UDR-11_06_obsz-02_fot-1.6	39.352	0.023	0.762	0.103	0.061	0.743	28.445	31.145	100.82	1.38	0.187	1.505
UDR-11_06_obsz-04_fot-1.5	36.368	0.017	0.89	0.183	0.035	0.821	30.057	31.46	99.967	1.21	0.235	1.711
UDR-11_06_obsz-04_fot-1.6	36.796	0.024	0.858	0.171	b.d.l.	0.808	29.522	31.206	99.514	1.25	0.195	1.666
UDR-11_06_obsz-04_fot-1.7	36.502	0.023	0.858	0.229	b.d.l.	0.806	30.188	31.606	100.415	1.21	0.252	1.664
UDR-11_06_obsz-06_fot-1.3	35.281	0.093	1.009	0.117	0.024	0.295	31.791	32.033	100.78	1.11	0.234	1.304
UDR-11_05_obsz-03_fot-1.7	36.408	0.029	0.889	0.147	0.031	0.745	30.365	31.612	100.376	1.20	0.207	1.634
UDR-11_05_obsz-03_fot-1.8	37.015	0.021	0.878	0.179	b.d.l.	0.818	29.643	31.372	100.097	1.25	0.2	1.696
UDR-11_05_obsz-04_fot-1.7	34.846	0.017	1.045	0.161	0.039	0.703	31.466	31.913	100.3	1.11	0.217	1.748

UDR-11_05_obsz-04_fot-1.8	34.359	0.02	0.999	0.149	0.011	0.771	31.327	31.705	99.431	1.10	0.18	1.77
UDR-11_05_obsz-04_fot-1.9	33.303	0.348	1.117	0.113	0.001	0.853	31.636	31.976	99.537	1.05	0.462	1.97
UDR-11_06_obsz-02_fot-1.1	39.206	0.071	0.759	0.225	0.019	0.772	27.528	30.563	99.24	1.42	0.315	1.531

Appendix C

Table A3. Chemical composition of Al-spinels from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	Fe	Al	Mn	V	Cr	Mg	Ti	Zn O	Total	Fe/Ti	Al + V + Cr	Mn + Mg
KR-24_03_obsz-01_fot-1.6	17.956	32.652	0.128	0.029	0.172	7.44	0.179	2.254 39.93	3 100.782	100.3	32.853	7.568
KR-24_03_obsz-01_fot-1.7	17.446	32.675	0.157	0.031	0.199	7.301	0.244	2.163 39.73	7 100.031	71.5	32.905	7.458
KR-24_03_obsz-03_fot-6.1	15.136	33.091	0.131	0.023	0.274	8.223	0.317	2.217 40.12	99.559	47.7	33.388	8.354
KR-24_03_obsz-03_fot-6.2	15.922	32.714	0.127	0.046	0.294	7.955	0.427	2.084 39.89	6 99.479	37.3	33.054	8.082
KR-24_03_obsz-03_fot-6.3	15.281	33.157	0.113	0.001	0.242	8.111	0.313	2.197 40.12	99.605	48.8	33.4	8.224
KR-24_03_obsz-03_fot-6.4	16.837	32.689	0.116	0.033	0.143	7.717	0.069	2.246 39.7	1 99.617	244.0	32.865	7.833
KR-24_03_obsz-03_fot-6.5	17.716	32.332	0.136	0.041	0.157	7.119	0.026	2.141 39.20	98.9	681.4	32.53	7.255
KRZ-56_02_obsz-01_fot-1.6	22.707	31.653	0.157	0.041	0.094	5.144	0.02	1.69 38.62	2 100.184	1135.4	31.788	5.301
KRZ-56_02_obsz-01_fot-1.7	22.74	31.296	0.196	0.065	0.088	4.852	0.009	1.467 38.04	5 98.775	2526.7	31.449	5.048
KRZ-56_02_obsz-01_fot-2.3	21.653	32.146	0.132	0.028	0.13	5.584	0.519	1.42 39.28	88 100.916	41.7	32.304	5.716
KRZ-56_02_obsz-01_fot-2.4	21.852	31.73	0.172	0.038	0.13	5.556	0.61	1.286 38.99	08 100.39	35.8	31.898	5.728
KRZ-56_02_obsz-01_fot-2.5	22.833	31.003	0.136	0.06	0.109	5.18	0.023	1.773 38.09	99.225	992.7	31.172	5.316
KR-63_05_obsz-02_fot-1.5	18.734	31.2	0.131	0.063	0.137	7.849	0.029	0.946 38.62	78 97.781	646.0	31.4	7.98
KR-63_05_obsz-04_fot-1.2	17.419	32.533	0.079	0.017	0.166	8.368	0.179	0.95 39.92	7 99.719	97.3	32.716	8.447
KR-63_05_obsz-04_fot-1.3	16.769	32.971	0.111	0.054	0.15	8.439	0.28	0.855 40.23	99.901	59.9	33.175	8.55
KR-63_05_obsz-05_fot-1.1	15.522	33.757	0.076	0.057	0.186	9.205	0.078	0.387 40.82	6 100.185	199.0	34	9.281
KR-63_05_obsz-05_fot-1.2	15.406	33.842	0.098	0.052	0.204	9.352	0.092	0.413 40.99	3 100.513	167.5	34.098	9.45
KR-63_05_obsz-05_fot-1.3	14.822	34.099	0.075	0.055	0.16	9.441	0.066	0.431 41.08	32 100.288	224.6	34.314	9.516
KR-63_05_obsz-05_fot-1.4	18.37	32.113	0.12	0.042	0.131	7.931	0.019	0.902 39.40	6 99.051	966.8	32.286	8.051
KR-63_05_obsz-05_fot-1.5	18.331	31.976	0.117	0.072	0.118	8.062	0.032	0.941 39.39	9 99.131	572.8	32.166	8.179
KR-63_05_obsz-08_fot-1.8	17.23	32.582	0.124	0.032	0.17	8.36	0.244	0.859 39.95	99.667	70.6	32.784	8.484
KR-63_05_obsz-08_fot-1.9	17.483	32.697	0.113	0.054	0.138	8.264	0.213	0.916 40.02	8 99.93	82.1	32.889	8.377
UDR-7_01_obsz-01_fot-1.11	21.062	31.72	0.139	0.05	0.585	6.315	0.035	1.432 39.1	3 100.516	601.8	32.355	6.454
UDR-7_01_obsz-01_fot-1.12	20.479	32.037	0.145	0.043	0.561	6.419	0.024	1.461 39.30	2 100.523	853.3	32.641	6.564
UDR-10_4_obsz-03_fot-1.1	23.269	30.323	0.142	0.055	1.206	5.678	0.342	0.865 38.46	51 100.443	68.0	31.584	5.82

UDR-10_4_obsz-03_fot-1.2	22.083	31.074	0.155	0.047	1.449	5.378	0.459	0.705 38.732 100.121	48.1	32.57	5.533
UDR-10_4_obsz-04_fot-1.1	24.015	29.755	0.147	0.064	0.761	5.562	0.035	0.957 37.696 99.007	686.1	30.58	5.709
UDR-10_4_obsz-04_fot-1.2	22.769	30.63	0.121	0.04	0.851	5.761	0.016	1.109 38.298 99.621	1423.1	31.521	5.882
UDR-10_4_obsz-04_fot-1.3	22.656	31.383	0.137	0.06	0.924	5.501	0.049	0.369 38.661 99.8	462.4	32.367	5.638
UDR-10_4_obsz-04_fot-1.4	22.583	30.658	0.173	0.052	0.871	5.478	0.121	0.362 38.037 98.486	186.6	31.581	5.651

Appendix D

Table A4. Chemical composition of pyrrhotite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	S	Ni	Со	Fe	Total	Analytical Point	S	Ni	Со	Fe	Total
10/1	39.45	0.55	0.23	59.12	99.35	4/1	38.87	0.79	0.17	59.82	99.65
11/1	39.5	0.46	0.21	58.85	99.02	6/1	39.3	1.01	0.16	59.32	99.79
11/1	39	0.66	0.18	59.53	99.37	8/1	38.55	1.02	0.2	59.33	99.1
12/1	39.27	0.76	0.12	59.22	99.37	9/1	38.61	0.99	0.14	59.4	99.14
6/1	38.72	0.67	0.12	59.68	99.19	10/1	38.99	0.97	0.08	59.12	99.16
7/1	38.72	0.75	0.13	59.57	99.17	8/1	38.82	1	0.14	59.48	99.44
8/1	38.65	0.72	0.13	59.37	98.87	12/1	39.1	1	0.13	59.25	99.48
3/1	39.41	0.62	0.1	59.74	99.87	1/1	39.052	0.223	0.115	60.038	99.428
4/1	39.74	0.62	0.11	59.69	100.16	2/1	38.991	0.249	0.136	59.738	99.114
9/1	38.58	0.76	0.16	59.61	99.11	7/1	39.117	0.258	0.099	59.08	98.554
10/1	39.36	0.77	0.13	59.56	99.82	5/1	38.627	0.392	0.178	60.288	99.485
11/1	39.21	0.37	0.05	59.58	99.21	6/1	38.742	0.347	0.134	60.183	99.406
6/1	39.23	0.6	0.16	59.56	99.55	7/1	38.883	0.303	0.171	60.215	99.572
7/1	39.34	0.6	0.18	59.79	99.91	3/1	39.73	0.275	0.098	59.715	99.818
7/1	38.55	0.87	0.18	59.6	99.2	4/1	39.42	0.246	0.186	59.794	99.646
3/1	39.02	0.65	0.12	59.36	99.15	3/1	39.685	0.635	0.109	59.315	99.744
4/1	39.29	0.61	0.15	59.74	99.79	1/1	39.028	0.227	0.185	59.493	98.933
10/1	38.49	1	0.13	59.94	99.56	2/1	39.093	0.277	0.221	59.403	98.994
11/1	38.75	1.03	0.16	59.9	99.84	3/1	38.891	0.272	0.193	59.794	99.15
2/1	38.34	1.6	0.15	59.02	99.11	1/1	39.478	0.26	0.179	59.396	99.313
3/1	38.76	4	0.09	56.13	98.98	2/1	39.542	0.225	0.264	59.564	99.595
10/1	38.77	0.6	0.14	59.71	99.22	1/1	39.459	0.201	0.266	59.151	99.077
6/1	39.25	0.44	0.13	59.44	99.26	2/1	39.054	0.196	0.245	59.589	99.084

7/1	39.22	0.31	0.11	59.75	99.39	1/1	38.969	0.243	0.116	60.198	99.526
9/1	39.01	0.23	0.15	59.56	98.95	2/1	38.689	0.232	0.179	60.526	99.626
10/1	39.14	0.24	0.12	59.76	99.26	1/1	39.699	0.19	0.201	59.761	99.851
1/1	39.04	0.46	0.15	59.26	98.91	2/1	39.751	0.213	0.21	59.684	99.858
2/1	39.04	0.39	0.13	59.48	99.04	9/1	38.914	0.214	0.237	60.323	99.688
5/1	38.97	0.94	0.19	59.41	99.51	5/1	38.952	0.202	0.239	59.41	98.803
6/1	38.76	0.94	0.16	59.26	99.12	6/1	38.996	0.217	0.278	59.065	98.556
3/1	39.11	0.97	0.14	59.62	99.84						

Appendix E

Table A5. Chemical composition of pentlandite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	S	Cu	Ni	Со	Fe	Total	Analytical Point	S	Cu	Ni	Со	Fe	Total
5/1	33.51	0.07	26.06	6.93	32.57	99.14	3/1	33.22	0.09	34.45	6.71	26.1	100.57
6/1	32.15	0.09	29.24	15.3	22.74	99.52	4/1	33.44	4.38	30.33	5.97	26.62	100.74
7/1	32.95	0.09	29.08	15.23	22.26	99.61	5/1	33.61	0.21	33.94	7.04	25.86	100.66
5/1	32.96	0.21	35.78	2.57	28.2	99.72	2/1	32.74	0.12	37.4	2.18	27.58	100.02
6/1	33.21	3.2	33.01	2.44	27.95	99.81	3/1	32.73	0.07	36.95	3.38	26.99	100.12
1/1	32.8	0.11	36.76	1.4	28.54	99.61	4/1	32.91	0.05	36.79	3.02	26.99	99.76
2/1	33.09	0.06	37.19	1.39	28.9	100.63	1/1	33.08	0.11	35.92	2.65	26.37	98.13
3/1	33.2	0.11	36.33	1.22	28.19	99.05	2/1	33.25	0.01	36.11	2.74	27.1	99.21
4/1	35.26	0.23	26.59	1.12	37.35	100.55	3/1	33.41	0.41	36.41	2.56	27.11	99.9
8/1	33.82	0.06	33.58	6.89	26.7	101.05	4/1	33.22	0.05	36.58	3.32	26.96	100.13
9/1	33.5	0.03	33.49	6.94	26.64	100.6	3/1	33.03	0.19	39.22	2.82	27.12	102.38
1/1	32.24	0.13	33.92	7.15	26.73	100.17	4/1	33.02	0.05	38.35	3.67	27.37	102.46
4/1	32.89	0.11	36.33	3.16	27.23	99.72	12/1	32.93	0.05	38.08	3.72	27.28	102.06
5/1	32.7	0.07	36.42	3.09	27.14	99.42	13/1	32.72	0.07	38.42	3.73	26.95	101.89
6/1	32.43	0.05	36.65	2.96	27.27	99.36	5/1	33.01	0.11	36.14	3.6	27.06	99.92
1/1	33.01	0.36	39.23	1.43	26.47	100.5	6/1	33.09	0.11	36.36	3.19	27.57	100.32
2/1	32.74	1.05	38.06	1.55	26.28	99.68	7/1	41.19	0.08	27.63	3.6	27.22	99.72
3/1	32.96	2.5	36.54	1.56	26.57	100.13	3/1	32.88	0.11	36.89	2.76	27.29	99.93
1/1	32.54	0.07	35.25	6.86	25.88	100.6	4/1	32.83	0.03	36.73	3.16	27.3	100.05
2/1	32.5	0.16	35.14	6.8	25.77	100.37	5/1	32.81	0.04	36.71	2.99	27.33	99.88

3/1	32.59	0.13	35.78	5.67	26.22	100.39	6/1	33	0.09	36.67	3.11	27.31	100.18
6/1	32.32	0.11	35.25	6.31	26.34	100.33	7/1	39.03	0	23.7	7.67	29.29	99.69
7/1	32.14	0.12	34.71	6.94	25.7	99.61							

Appendix F

Table A6. Chemical composition of siegenite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	S	Cu	Ni	Со	Fe	Total
2/1	42.1	0.19	25.05	20.82	12.52	100.68
3/1	41.59	0.03	25.1	20.9	12.77	100.39
4/1	41.57	0.17	25.51	19.57	14.34	101.16
3/1	37.71	0.2	33.22	19.63	4.33	95.09
4/1	40.37	0.16	32.13	18.84	7.28	98.78
1/1	40.72	0.09	25.15	23.2	10.39	99.55
2/1	40.88	0.09	25.4	22.4	10.84	99.61
3/1	40.86	0.05	25.47	23.04	10.23	99.65
1/1	41.87	0.08	25.89	21.6	10.65	100.09
2/1	42.09	0.15	25.67	21.54	10.75	100.2
5/1	41.44	b.d.l.	27.05	23.61	10.84	102.94
6/1	41.54	b.d.l.	26.64	23.29	11.37	102.84
7/1	41.84	0.05	26.63	23.31	11.39	103.22
1/1	42.04	0.04	25.49	21.94	11.05	100.56
2/1	41.56	0.13	25.2	22.34	11.05	100.28
8/1	41.53	0.07	27.85	13.84	17.21	100.5
8/1	40.61	0.07	22.89	29.67	6.75	99.99
9/1	40.19	0.02	23.15	27.03	9.78	100.17

Appendix G

Table A7. Chemical composition of chalcopyrite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	S	Zn	Cu	Ni	Со	Fe	Total	Analytical Point	S	Zn	Cu	Ni	Со	Fe	Total
4/1	34.65	0.08	34.24	0.45	0.51	30.05	99.98	2/1	34.54	0.03	34.49	0.15	0.13	30.42	99.76
7/1	34.52	0.1	34.26	0.24	0.2	30.26	99.58	1/1	34.6	0.05	34.96	0.05	0.05	30.24	99.95
8/1	34.57	b.d.l.	34.65	0.08	0.09	30.25	99.64	2/1	34.57	0.16	34.7	0.04	0.04	30.43	99.94
9/1	34.8	b.d.l.	34.38	0.04	0.09	30.85	100.16	4/1	34.34	0.05	34.66	0.01	0.1	30.38	99.54
9/1	33.83	0.06	33.73	0.12	0.08	31.17	98.99	5/1	34.32	1.01	33.92	0.11	0.24	30.46	100.06
10/1	33.89	0.11	34.5	0.01	0.06	30.75	99.32	5/1	34.71	0.08	34.53	0.01	0.08	30.32	99.73
1/1	34.43	0.09	34.87	0.01	0.06	30.95	100.41	6/1	34.61	0.13	34.63	0.01	0.07	30.38	99.83
2/1	34.32	0.15	34.22	0.03	0.08	30.83	99.63	7/1	34.55	b.d.l.	34.71	0.01	0.08	30.52	99.87
10/1	34.38	0.07	34.75	0.08	0.07	30.6	99.95	5/1	34.31	0.02	34.6	0.14	0.19	30.46	99.72
11/1	34.58	0.02	35.11	0.1	0.12	30.31	100.24	1/1	34.19	0.13	35.37	0.05	0.07	30.46	100.27
2/1	34.28	0.02	34.37	0.25	0.17	30.68	99.77	2/1	34.22	0.01	35.12	0.04	0.15	30.27	99.81
6/1	34.74	0.03	34.69	0.04	0.12	30.05	99.67	11/1	34.15	0.01	35.17	0.16	0.17	30.09	99.75
7/1	34.54	0.06	34.05	0.39	0.55	30.05	99.64	3/1	34.27	0.12	34.64	0.33	0.14	30.71	100.21
7/1	34.07	0.05	34.23	0.02	0.03	30.65	99.05	4/1	34.22	0.02	34.47	0.14	0.08	30.96	99.89
8/1	34.15	0.1	34.37	0.02	0.05	30.5	99.19	1/1	34.2	0.05	34.61	0.42	0.16	30.44	99.88
9/1	34.56	0.01	34.97	0.04	0.08	30.36	100.02	2/1	34.05	0.1	34.59	0.56	0.26	30.07	99.63
1/1	33.87	0.13	34.38	0.07	0.06	31.35	99.86	4/1	33.995	0.055	34.321	0.006	0.047	30.455	98.879
4/1	34.03	0.03	34.94	0.19	0.03	30.47	99.69	6/1	34.265	0.031	34.158	0.047	0.074	30.76	99.335
5/1	34.13	0.11	35.22	0.07	0.07	30.4	100	8/1	34.443	0.114	34.55	0.01	0.071	30.491	99.679
4/1	33.97	0.06	34.83	0.18	0.07	30.4	99.51	9/1	34.692	0.011	34.194	0.01	0.117	30.724	99.748
5/1	34.01	b.d.l.	34.7	0.1	0.09	30.64	99.54	4/1	34.482	b.d.l.	34.051	0.075	0.063	29.875	98.546
6/1	34.17	0.13	34.63	0.08	0.05	30.22	99.28	3/1	34.523	0.125	34.495	0.049	0.065	30.407	99.664
1/1	34.34	b.d.l.	34.34	0.03	0.05	31.18	99.94	3/1	34.698	0.104	34.452	0.018	0.058	30.417	99.747
2/1	34.39	0.1	34.14	0.04	0.05	30.51	99.23	3/1	34.871	b.d.l.	34.3	0.042	0.02	30.705	99.938
1/1	34.59	0.15	34.12	0.17	0.16	30.35	99.54	7/1	34.451	b.d.l.	33.651	0.074	0.053	30.864	99.093

Appendix H

Table A8. Chemical composition of cubanite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	S	Zn	Cu	Ni	Со	Fe	Total
4/1	35.11	0.13	23.22	0.14	0.14	40.79	99.53
5/1	35.19	0.01	23.63	0.06	0.06	40.34	99.29
8/1	34.82	0.01	23.23	0.08	0.1	40.97	99.21
9/1	34.95	0.01	22.24	0.09	0.1	41.98	99.37
3/1	35.1	0.01	23.56	0.01	0.11	41.03	99.82
6/1	34.72	0.01	23.31	0.05	0.05	40.85	98.99
7/1	34.9	0.06	23.21	0.01	0.09	40.96	99.23
8/1	34.89	0.03	22.81	0.04	0.05	40.88	98.7
3/1	35	0.04	23.4	0.01	0.04	40.76	99.25
4/1	35.44	0.06	23.24	0.01	0.04	41.12	99.91

Appendix I

Table A9. Chemical composition of pyrite from the Krzemianka and Udryn Fe-Ti-V deposits in NE Poland identified via EMPA.

Analytical Point	S	Zn	Cu	Ni	Со	Fe	Total	Analytical Point	S	Zn	Cu	Ni	Со	Fe	Total
13/1	52.87	0.07	0.03	1.22	1.95	43.99	100.29	1/1	52.201	b.d.l.	0.01	0.005	1.268	46.165	99.74
14/1	51.96	0.03	0.18	3.45	0.6	42.81	100.35	2/1	52.639	b.d.l.	0.031	0.071	1.902	45.437	100.105
11/1	53.13	0.01	0.1	0.06	0.12	47.12	100.64	3/1	52.292	0.074	0.01	0.01	1.552	45.972	99.964
12/1	52.8	b.d.l.	0.2	5.49	0.22	41.88	100.77	4/1	52.006	0.027	0.01	0.081	1.815	46.01	100.052
5/1	53.11	0.03	0.09	3.61	0.2	43.21	100.37	5/1	53.069	0.039	0.047	1.192	3.314	42.133	99.957
6/1	53.18	b.d.l.	0.02	0.48	0.13	46.83	100.67	6/1	53.099	0.028	0.01	1.23	0.113	45.376	99.897
1/1	52.33	b.d.l.	0.01	4.98	0.37	41.68	99.45	1/1	53.001	0.01	0.074	0.022	1.054	45.853	100.05
2/1	52.79	0.06	0.01	1.96	0.22	44.88	100	2/1	53.492	0.124	0.033	0.28	0.128	45.97	100.085
8/1	52.27	0.03	0.01	1.5	0.25	44.74	99.28	4/1	53.323	b.d.l.	0.056	0.062	7.063	39.434	100.05
12/1	53.09	b.d.l.	0.08	0.01	4.59	42.04	100	5/1	52.962	0.046	0.016	0.049	4.594	42.067	99.93
6/1	53.56	0.05	0.18	0.09	0.13	46.07	100.15	6/1	52.846	0.003	0.03	0.009	8.608	38.347	99.911
7/1	53.46	b.d.l.	0.21	0.1	0.11	46.04	99.96	7/1	52.794	0.045	0.042	0.04	7.059	39.602	99.724
7/1	53.73	0.03	0.13	0.3	0.09	45.84	100.24	3/1	53.136	0.036	0.052	1.215	0.089	45.618	100.283

8/1	53.57	0.02	0.08	0.22	0.08 45.81	99.87	10/1	53.418	0.127 0.003	0.024	0.288	46.37	100.321
9/1	53.17	0.07	0.2	0.86	0.07 45.62	100.17	1/1	53.977	0.01 0.017	0.112	0.123	45.972	100.394
8/1	53	0.06	0.06	8.72	0.14 38.02	100.1	2/1	53.927	0.084 0.001	0.301	0.064	45.56	100.073
9/1	53.21	0.03	0.01	0.78	3.26 43.53	100.91	3/1	53.453	0.073 0.01	0.046	0.127	45.435	99.575
5/1	52.678	b.d.l.	0.066	0.02	1.122 45.388	99.345	4/1	52.871	0.042 0.087	0.062	0.13	45.448	99.253
3/1	52.451	0.038	0.062	0.082	6.373 40.552	99.67							

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