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Distribution of Technology-Critical Elements in the Trepça Mine (Kosovo): Insights from Mineralogical, Geochemical and Microstructural Analyses

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Abstract

This study investigates the presence of Technology-Critical Elements in the Trepça mine (Stan Tërg, Mitrovicë), representing the first assessment of their distribution within this mining district. Samples were collected in all ore bodies (three samples per ore body) in horizons VIII-XI. Mineralogical, geochemical and microstructural characterization was performed using X-ray diffraction (XRD), Inductively Coupled Plasma Mass-Spectrometry (ICP-MS), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX). The analyses confirmed the presence of several Technology-Critical Elements, especially Bi, Co, Ge, W, Ga, In, Te and Sb, whose distribution, correlation with mineral phases and structure were also identified. XRD enabled the identification of mineral phases while SEM-EDX provided structural and morphological characteristics of these mineral phases. The ICP-MS results indicate significant variability in the distribution of these elements. Bi reached extremely high concentrations (up to 2570.68 ppm in ore body 136), well above the method detection limit (MDL = 0.01 ppm), whereas Co exhibited elevated yet moderate concentrations that increased with depth, indicating a depth-dependent rise in concentration. V, W, Sb and Sn also exhibited elevated concentrations. Peak enrichment levels were observed for Bi (up to 2750 ppm) in Horizon IX, Sb (up to 504 ppm) in Horizon XI, W (up to 308 ppm) in Horizon VIII, and In (up to 34,730 ppm) within selected ore bodies, indicating pronounced vertical geochemical zonation. The results demonstrate that selected ore bodies represent significant potential sources of Technology-Critical Elements, supporting future resources and strategic raw material assessment within the Trepça mining district.

Keywords: Trepça; mine; Technology-Critical Elements; distribution; ICP-MS; XRD; SEM-EDX

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1. Introduction

Based on COST action TD1407, gallium (Ga), germanium (Ge), niobium (Nb), indium (In), tellurium (Te), tantalum (Ta), thallium (Tl), the Platinum Group Elements, as well as some Rare Earth Elements that are grouped into what are called Technologically Critical

Elements [1]. Technological development and innovation increasingly depend on secure access to Technology-Critical Elements, which have been intensively investigated only in recent decades [2]. These elements play a key and indispensable role in technology components such as electronics, renewable energy, transportation, agriculture, healthcare, and the military [3,4]. Raw materials are considered 'critical' due to supply shortages, which significantly affect both technological development and the economy. There are currently over thirty such elements defined by the European Commission [3,4].

The concentration of these elements in the Earth's crust ranges from ultra-trace concentrations, as in the case of the Platinum Group Elements (<ng/g), to µg/g for other critical elements. However, the high demand for these elements requires extensive geological exploration and exploitation for their utilization [5]. Technology-Critical Elements such as Ga, Ge, Nb, In, Ta and Rare Earth Elements have experienced a substantial increase in demand, particularly in high-technology and renewable energy application.

These elements have found application in a large number of fields, especially in technology and industry [6]. The demand for the extraction of these critical technological elements in the last 2–3 decades has increased by 2 times for the element Te, 3 to 4 times for the Platinum Group Elements, 5 times for Nb, 15 times for Ga, and approximately 20 times for In [5].

The area of Trepça, despite its long-term potential for the exploitation of Pb-Zn-Ag, has not been evaluated and studied for the Technology-Critical Elements, which are today more than required for technological advancements. This has created a gap regarding the occurrence, location, distribution and host mineral phases for these elements.

Given the importance in the research of these elements, Trepça represents a very important objective for the research and evaluation of the distribution of these elements. This study presents an evaluation by integrating techniques such as ICP-MS, XRD and SEM-EDX of Technology-Critical Elements, thus providing new data and a focus on the Technology-Critical Elements in the Trepça mine.

The purpose of this study was based on a large number of Pb-Zn hydrothermal deposits, which have yielded results on the occurrence and distribution of Technology-Critical Elements such as the deposits presented below:

Nanmushu Pb-Zn polymetallic deposit, China [7]
Hehuashan Pb-Zn polymetallic deposit [8]
Yangtze Pb-Zn polymetallic deposit, China [9]
Pb-Zn hydrothermal deposit, Zhenzigou, Diannan, Xiquegou and Erdao in Qingchengzi [10]

Why Trepça Mine?

The Trepça mine is characterized by a complex range of geological and geochemical processes; therefore, research on Technology-Critical Elements in this mine is essential in order to identify their occurrence, concentration and spatial distribution within the Trepça mine. In recent decades, there has been an increased global demand for certain elements that have not been studied or adequately addressed before [1]. The same situation applies to the Trepça mine, where Au, Ag, Pb and Zn were exploited, while Technology-Critical Elements were not investigated.

The purpose of this study is to identify the occurrence and distribution of these elements and the areas with the highest concentration. Ge, In and Ga are Technology-Critical Elements that numerous studies have proven can be extracted from Pb-Zn deposits [11]. Hydrothermal Pb-Zn deposits commonly show enrichment in Cd, Ga, Ge and In, reflecting metal mobilization during hydrothermal ore-forming processes [11,12]. Accurate sampling and proper sample handling are as crucial as the sample quality itself [13]. Sampling was done directly in ore bodies dominated mainly by Galena and Sphalerite but with a large occurrence of other mineral phases which will be presented in XRD analyses. A sampling plan was developed, which included all ore bodies in Trepça mine from horizon VIII to XI. Samples were collected directly from the ore body, ground, and then sent for chemical, mineralogical and structural analysis. Inductively Coupled Plasma Mass-Spectrometry (ICP-MS) is a fundamental method for the determination of trace elements and has a very low detection limit of the concentration of these elements and a wide field of application of this instrumental method [5]. The chemical composition was determined with ICP-MS, the mineral phases were identified by X-ray diffraction and their microstructure was examined using Scanning Electron Microscope. Also, based on recent versions of software and statistical interpretation we are able to determine the spatial and trend distribution of these elements. Hydrothermal Pb-Zn deposits such as the Trepça mine are recognized as prime targets for the concentration of Technology-Critical Elements because the crystal structures of the major sulfide minerals, such as Sphalerite (ZnS), Galena (PbS), and Pyrite (FeS_2), readily accommodate a wide range of trace elements through isomorphic substitution and lattice defects. Elements such as Ge, Ga, In, Cd, Sb, Bi, and Sn commonly replace Zn or Pb in the sulfide lattices or occur as nano- to micro-scale inclusions within these minerals. This study fills the research gap by providing assessment of Technology-Critical Elements in horizons VIII to XI, offering new insights into their concentration, mineralogical association and spatial distribution.

2. Geological Setting

Based on several documents from the Kosovo Archives, Trepça began its mining activity in 1927 and is still in active today [14].

The Pb and Zn reserves have been studied in three main regions:

- **Stan Tërg Region**-the ore reserves are located in a number of locations-Trepça, Zijaça, Melenica, Maja e Madhe, Maxhera, Rashani and Vidishiqi. The total reserves are 31.47 Mt in Trepça region, with the average concentration Pb = 3.5%, Zn = 2.87% and Ag = 67 g/t [15].
- **Kishnica Region**-the reserves are located in Hajvalia, Badovc; the total reserves in the Kishnica region are 14.21 Mt with average concentration of Pb = 3.76%, Zn = 4.87%, Ag = 128 g/t and Au = 1.1 g/t [15].
- **Kopaonik Region**-the reserves are concentrated in the locations of Bellobrdo, Crnac, Plakonica, Kalogjer, and Zuta Prlina, amounting to 8.12 Mt in total, with average concentration of Pb = 7.55%, Zn = 3.6% and Ag = 107 g/t [15].

The concentrations of selected elements in the Trepça mine, based on previously conducted studies, are presented in Table 1.

Table 1. Distribution of chemical elements in the Trepça mines [16].

Element (ppm)	Stan Terg	Artana	Kizhnica	Drazhnje
Zn	524,100	543,380	544,690	645,600
Fe	95,234	76,359	115,454	23,947
Mn	699	22,879	1337	260
Cd	921	1331	1313	1428
Sn	519	5936	663	2787
Cu	728	6288	973	2215
In	71	40	730	8.40
Co	3.40	<0.29	2.10	32.30
Hg	3.80	26.00	13.00	62.00
Ga	2.40	101.00	0.78	4.80
Ag	2.00	23.00	2.50	0.97

Table 1 demonstrates the importance of and need for more detailed studies on the distribution of Technology-Critical Elements. From Table 1 it can be observed that Pb-Zn deposits contain measurable concentrations of several Technology-Critical Elements and based on these results this study was focused particularly on active horizons VIII to XI in all ore bodies.

The history of the exploitation of Ag, Pb, and Zn in Kosovo is closely linked to the history of Kosovo itself [17]. Trepça has played a key role in the development of the economy of Kosovo and the former Yugoslavia [18].

Trepça is located in the village of Stan Tërg, 10 km northeast of the city of Mitrovica. This region lies within the Shala e Bajgorës area, with all mines located in its vicinity (Figure 1). Mitrovica is a north-eastern city of Kosovo [19]. It has a long history of Pb and Zn metallurgy production [18]. Trepça is located in the north-eastern part of Kosovo in the Mitrovica region, approximately 38 km from the capital of Kosovo. It is located in a geographical area where the landscape is dominated by the mountains of the Shala e Bajgorës region. In terms of communication, it has a strategic advantage due to its location along cross-border transportation corridors between Serbia–Kosovo–North Macedonia–Montenegro, which constitute a major economic axis. Additionally, the railway line has historically been one of the main routes for mineral transport [20].

Figure 1. Satellite view of study area.

As can be seen in Figure 1, Mitrovica is one of the northern cities in Kosovo; it is a city with a developed mining activity and metallurgical complex. From the satellite view, it can be observed that this area is densely populated due to the large number of activities and employees in the Trepça mine. Initially, the Trepça mine was accessed through the gallery in the First Tunnel, located between the city of Mitrovica and the village of Stan Tërg, and later through the central shaft toward Horizon XI, which was opened at a vertical depth of 60 m.

Kosovo, particularly the Mitrovica region, is an area of great geological interest which is characterized by a variety of geological and geochemical formations [21]. The Trepça Pb-Zn-Ag belt is located in NNW-SSE direction of the Vardar Zone. This belt extends over approximately 80 km [17]. The Pb-Zn-Ag mineralization is of Oligocene to Miocene age and is of hydrothermal origin and is associated with post-collision of magmatic activity [22].

The geological structure of Trepça includes integrated volcanic rocks and sedimentary units that play a key role in controlling economically significant mineralization. Ore bodies, formed through metasomatic processes in limestone, are typically found at the following contacts:

- ➢ between limestone and breccias;
- ➢ between limestone and shales [21].

This zone is characterized by complex geological formation as presented in Figure 2 in the geological map of the study area.

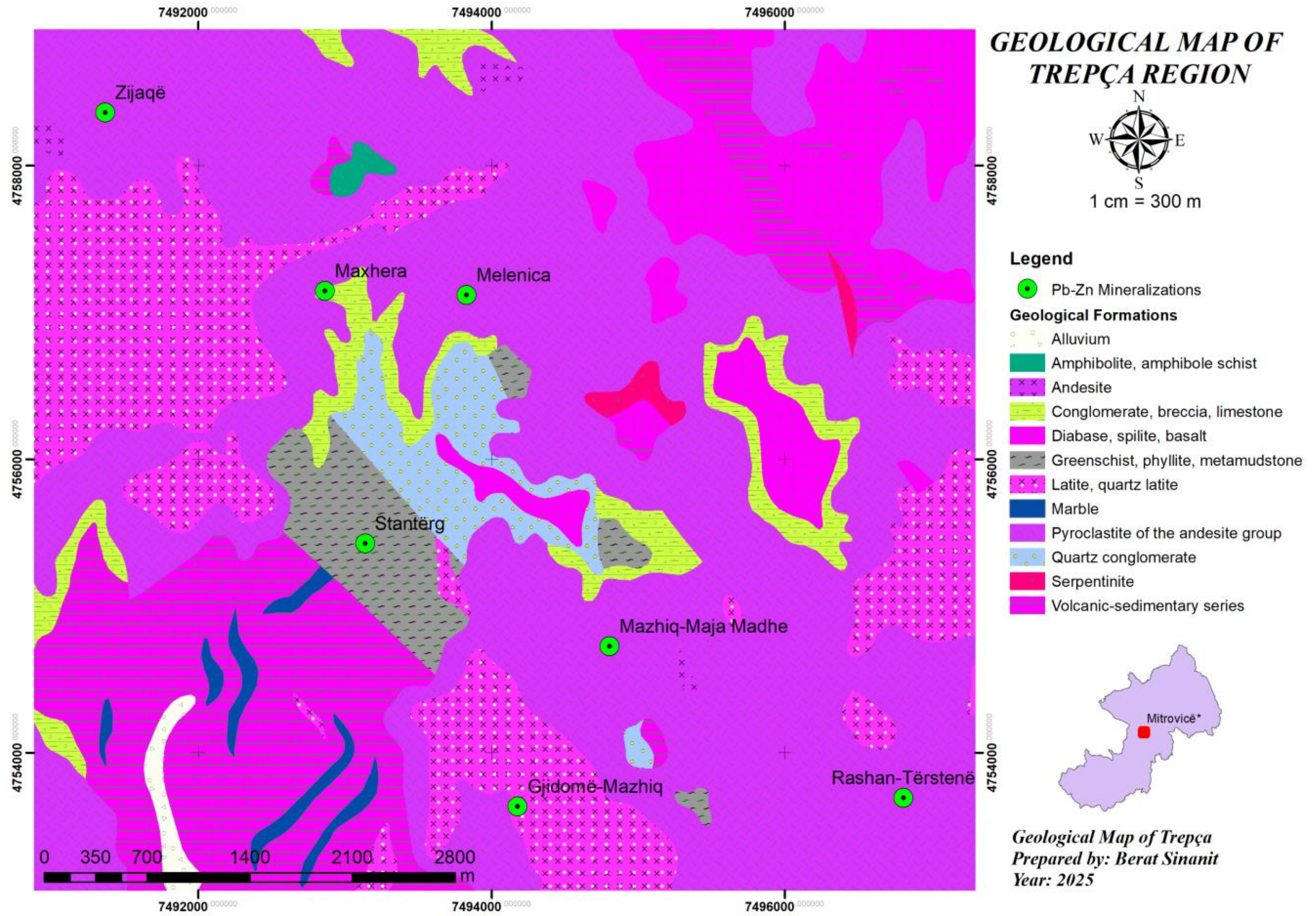

Figure 2. Geological map of study area.

Figure 2 shows a geological map reflecting the lithological and tectonic structure of the study area, where the various geological formations are presented. Extension of the ore bodies dips at 45°. The geological structure of Trepça includes volcanic rocks and sedimentary units that play a key role in the distribution of mineralization.

Metallogenic characterization of the Trepça mine

The Trepça metallogenic region includes the Stan Tërg-Kishnica-Artana triangle, which represents a complex geological area containing numerous Pb-Zn deposits. The Trepça series is particularly important due to its numerous Pb-Zn deposits [15]. The position of the ore fields is controlled by the tectonic system, with the Vardar zone os characterized by faults trending of 340–035°.

Magmatic processes, mainly granitoids, have played a key role in the formation of Pb-Zn deposits in the Trepça mine in Stan Tërg and in the entire Trepça metal complex [21]. Therefore, fractures, faults, and tectonic zones functioned as pathways for metal-bearing fluids, resulting in the formation of ore bodies.

From the lithological perspective, the genesis of the Pb-Zn deposit in Stan Tërg is mainly hosted in limestone formations which have mainly formed columnar ore bodies through the metasomatic processes, whereas the schist rocks, which have not interacted with mineral-bearing fluids, and the ore bodies have been built only in vein form through hydrothermal processes.

Mineralizations in this area formed during two major tectonic cycles:

1. Mesozoic;
2. Tertiary [21].

During these two periods, four main types of mineral deposits were formed, the most important of which is the Endogenous type, which includes Pb-Zn deposits formed in three main phases:

1. Skarn;
2. Skarn-Hydrothermal;
3. Hydrothermal [21], which also serves as a prerequisite for the occurrence of Technology-Critical Elements.

3. Materials and Methods

3.1. Sampling Strategy

This research on the distribution of Technology-Critical Elements in horizons VIII–XI of the Trepça mine is structured in two main phases.

- ➢ Identification of the occurrence of Technology-Critical Elements in the Trepça mine using ICP-MS;
- ➢ Determination of the concentration and spatial distribution of Technology-Critical Elements in horizons VIII-XI and all ore bodies.

The following methodology was used to conduct this study:

- ➢ Three samples were taken from each ore body to consider the heterogeneous distribution of hydrothermal Pb-Zn mineralization, in order to best characterize a geochemical and mineralogical representation.

3.2. Sampling Strategy

Rock samples were dried at 105 °C, crushed using a jaw crusher, and pulverized in an agate mill to <75 µm. Approximately 0.1 g of powdered sample was digested using a mixed acid solution (HF-HNO_3-$HClO_4$) in Teflon vessels.

Digestion was carried out on a hot plate until complete dissolution, followed by evaporation and final dilution to 50 mL with ultrapure deionized water.

The ICP-MS analyses were conducted at the Institute "Artmer" of Bülent Ecevit University in Zonguldag, Turkey.

The samples were divided into three subsamples:

- Samples for ICP-MS analysis;
- Samples for SEM analysis;
- Samples for XRD analysis.

Samples were prepared by diluting 1000 mg/L solutions or Sample solutions were prepared from 1000 mg/L multi-element standards (11355-ICP Multi-Element Standard, Merck, Darmstadt, Germany). High-quality and certified geological reference material was used: soil sample JSAC 0401. The samples for ICP-MS analysis were digested and subsequently analyzed.

3.3. ICP-MS Analysis

To conduct this study, three advanced analytical techniques were employed:

ICP-MS analyses were carried out using a PerkinElmer NexION 300D instrument at the Artmer Institute, Bülent Ecevit University (Zonguldak, Turkey). The instrument was operated at an RF power of 1600 W, with plasma, auxiliary, and nebulizer gas flow rates of 15 L/min, 1.2 L/min, and 0.95 L/min, respectively. Residence times ranged from 20 to 50 ms per isotope. Rh and In were employed as internal standards to correct for instrumental drift and matrix effects, and method detection limits (MDLs) for the investigated Technology-Critical Elements ranged between 0.01 and 0.1 ppm.

ICP-MS was used to determine the occurrence and concentrations of Technology-Critical Elements in ore bodies within horizons VIII–XI. This technique enables rapid, accurate, and highly sensitive multi-element analysis, allowing the simultaneous determination of up to 76 elements at trace to ultra-trace levels (ng/L to pg/L). The method is based on sample atomization and ionization in an argon plasma, followed by mass-to-charge separation and detection of positively charged ions by a mass spectrometer.

3.4. XRD Analysis

Analyses to identify mineral phases were performed through X-ray diffraction. This research was carried out at the BEU ARTIMER X-Ray Laboratory utilizing a Panalytical Empyrean model instrument (Malvern Panalytical, Almelo, The Netherlands). The measurements were performed under conditions of 45 k and 45 mA power, employing a reflection–transmission spinner stage, with a scan range of 10–90° and an incremental step size of 0.0013°. This study was conducted only in horizons VIII to XI, where all ore bodies within these horizons are included. The above horizons have been fully exploited, while the continuity of these ore bodies at depth has not been studied.

3.5. SEM-EDX Analysis

A Scanning Electron Microscope was used to examine the microstructural features of the collected samples. Elemental composition was determined using the integrated EDX (energy-dispersive X-ray spectroscopy) detector.

SEM/EDX analyses were performed at the Center for Scientific and Technological Research and Applications (ARTMER) of Bülent Ecevit University in Zonguldak, using an FEI Quanta FEG 450 model. Measurements were performed in BSE (back scattered electron) mode under LFD low-vacuum conditions, with an accelerating voltage ranging between 15 and 20 kV. A conductive gold (Au) layer was used to prepare the samples for SEM/EDX analysis, while carbon (C) was used to bond the samples to polymers for mounting.

4. Results

Laboratory analyses by ICP-MS show the occurrence of numerous Technology-Critical Elements, including Bi, Co, Ge, W, Ga, In, Te and Sb.

In Horizon VIII, relatively high concentrations of Bi (570 ppm) and W (308 ppm) were observed.

In Horizon IX, Bi shows strong variability, ranging from 9 ppm to 2750 ppm in ore body 136, with a mean concentration of 578 ppm and a high standard deviation, indicative of heterogeneous distribution. Co is nearly homogeneous at 29 ppm, whereas Ge and Li occur at minimal concentrations in this horizon. Sb concentrations are heterogeneous in this horizon from 0 to 297 ppm, with an average of 87 ppm.

In Horizon X, Bi concentrations are the lowest (mean 133 ppm). Co remains homogeneous (28 ppm). Sb concentration increases compared to Horizon IX, reaching an average of 234 ppm and a maximum of 427 ppm.

In Horizon XI, Bi decreases with increasing depth, whereas Co increases. Likewise, Sb reaches its highest average concentration (270 ppm) and a maximum value of 504 ppm in this horizon. Sn concentration also decreases with increasing depth.

Figure 3 shows the distribution of Technology-Critical Elements for all ore bodies. Bars progress from left to right with increasing depth, and the yellow line denotes the depth-dependent trend.

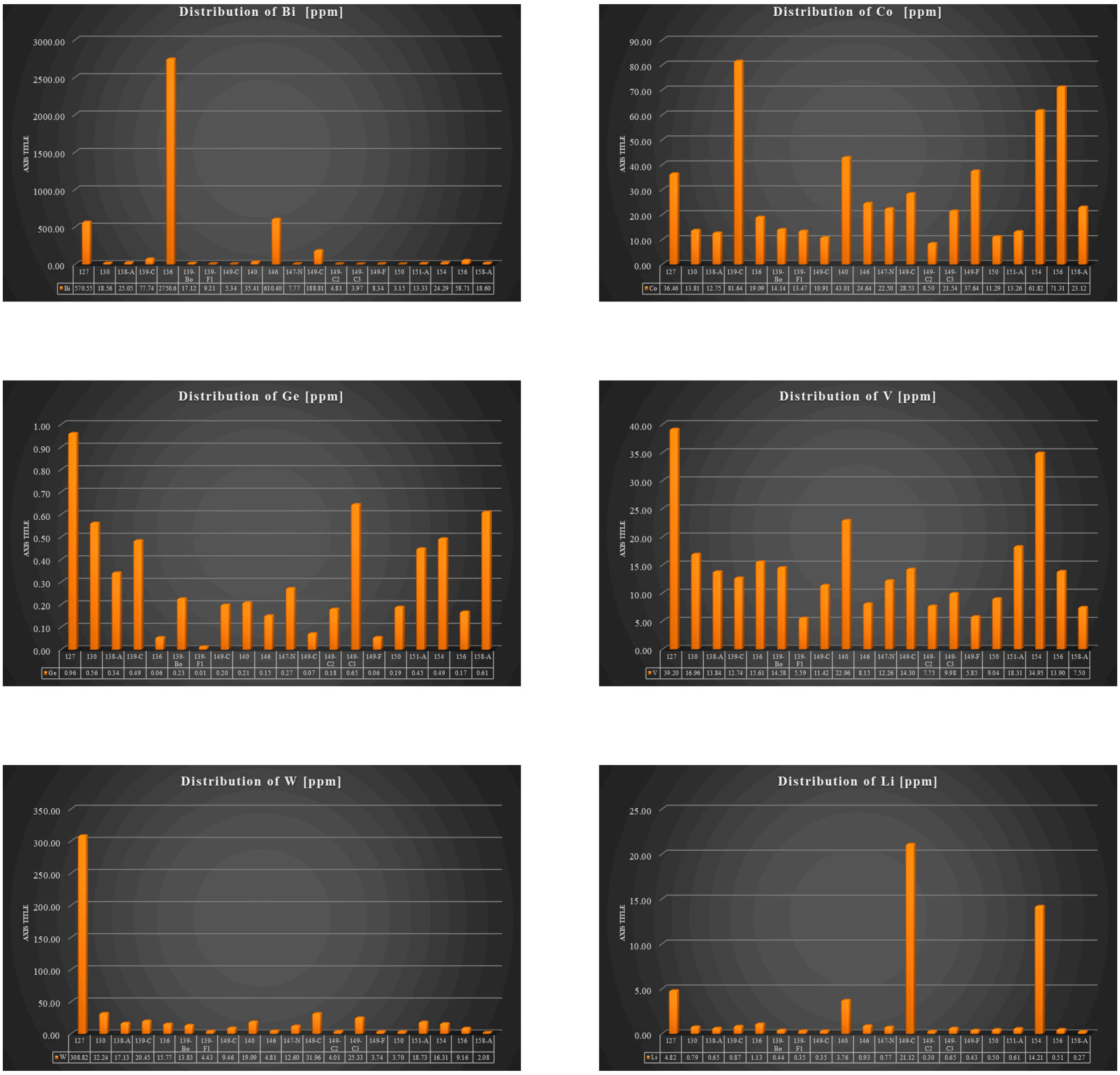

Figure 3. Distribution of critical elements as a function of depth.

This horizon is characterized by elevated Sn, reaching 714 ppm in ore body 149-F, indicative of advanced hydrothermal mineralization. Now, we will present a mineralogical description of the samples taken, first by presenting a description of the mineral phases present in the Trepça mine and then looking at the mineralogical correlation between these phases and Technology-Critical Elements.

4.1. Sample 126

Figure 4 presents the XRPD diffractogram for sample 126, giving the results as below.

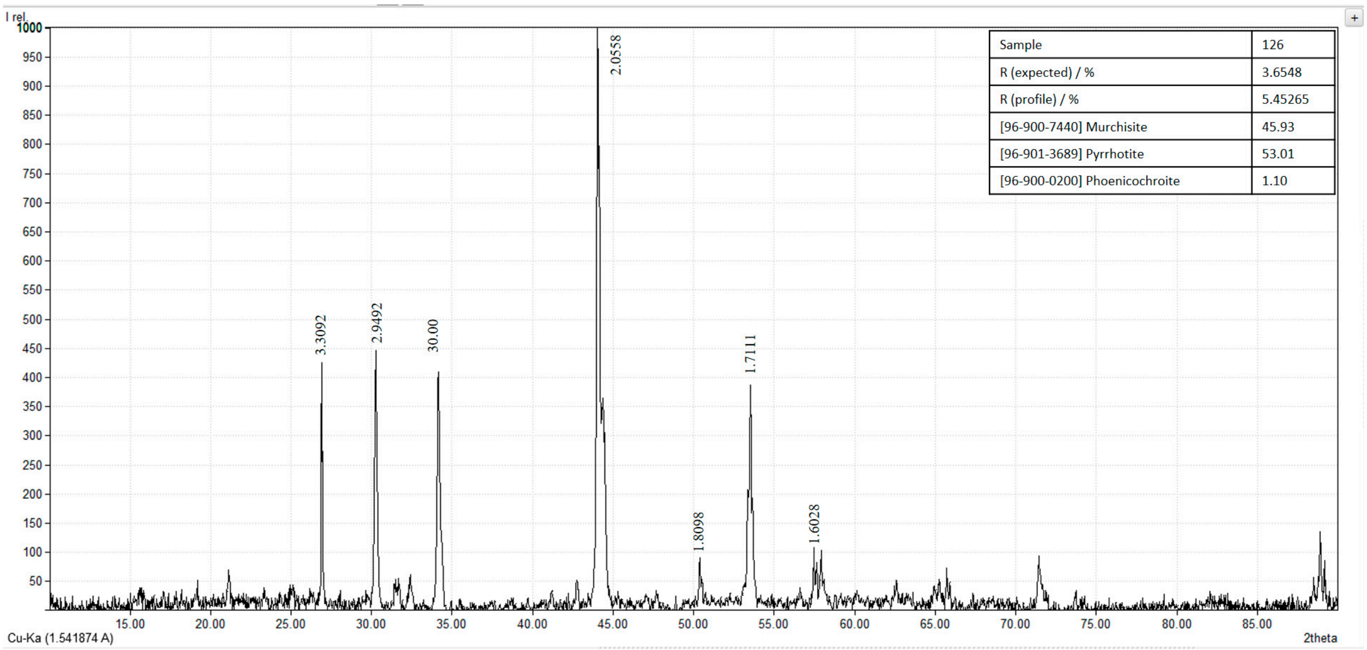

Figure 4. XRD diffractogram for sample 126.

The X-ray diffraction diffractogram for sample 126 presents a mineralogical composition typical of hydrothermal polymetallic mineralization with Pyrite (36.2%), Calcite (34.6%), Sphalerite (18.6%), and Galena (6.0%). This analysis clearly shows that hydrothermal processes present a clear association between sulfides and carbonate minerals. While the concentration of Technology-Critical Elements in this sample is presented in Table 2.

Table 2. Concentrations of selected elements (Bi, Co, Ge, V, W, Li, Ga, In, Te, Nb, Y, Zr, Mo, Sn, Sb) in the ore body 126.

Ore Body	Bi	Co	Ge	V	W	Li	Ga	In	Te	Nb	Y	Zr	Mo	Sn	Sb
126	570.55	36.46	0.96	39.2	308.82	4.82	5.72	1.52	1.15	0.93	0	0	16	0	0

Now we will present the images and structure of these mineral phases shown in Figure 5.

4.2. Sample 136

Figure 6 presents the diffractogram for sample 136 which presents identified mineral phases of ore body 136 in horizon IX.

X-ray diffraction analysis for sample 136 shows a composition dominated by Quartz and Wollastonite, but with a low occurrence of Galena as well as some mineral phases such as Miersite, Fluorocronite and Bismuthinite. After identifying the mineral phases of sample 136, Table 3 presents the ICP-MS concentrations of the selected elements.

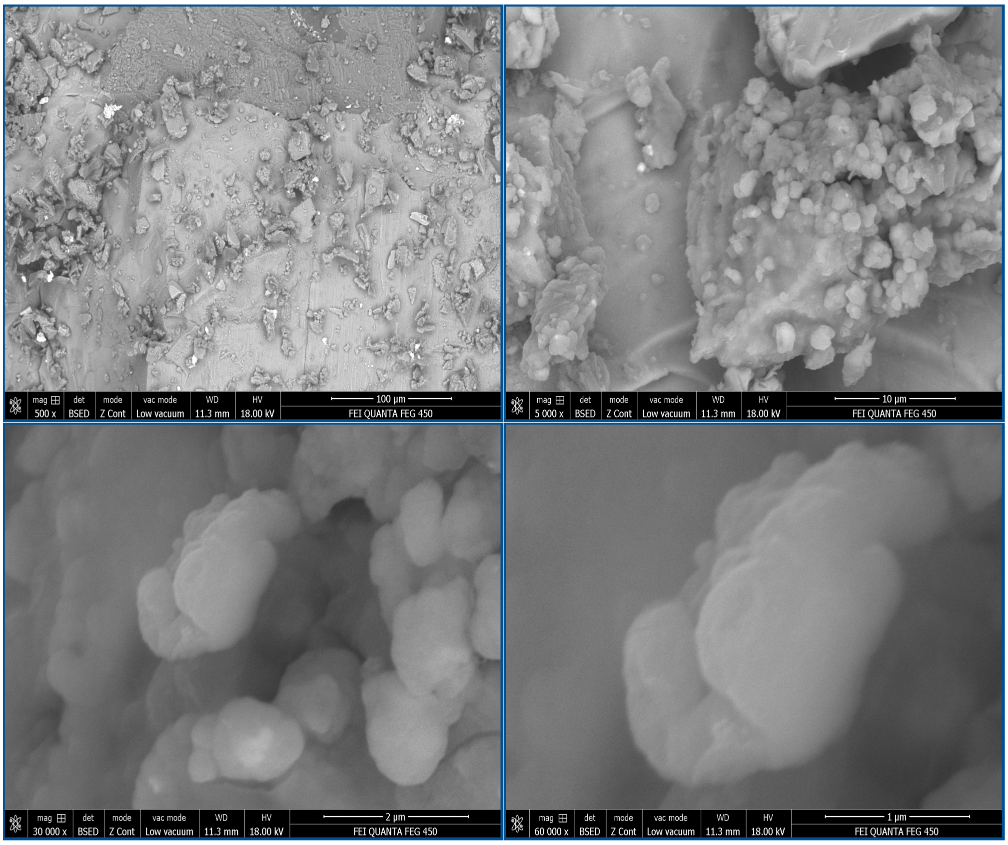

Figure 5. SEM micrographs showing the morphology of ore body 126.

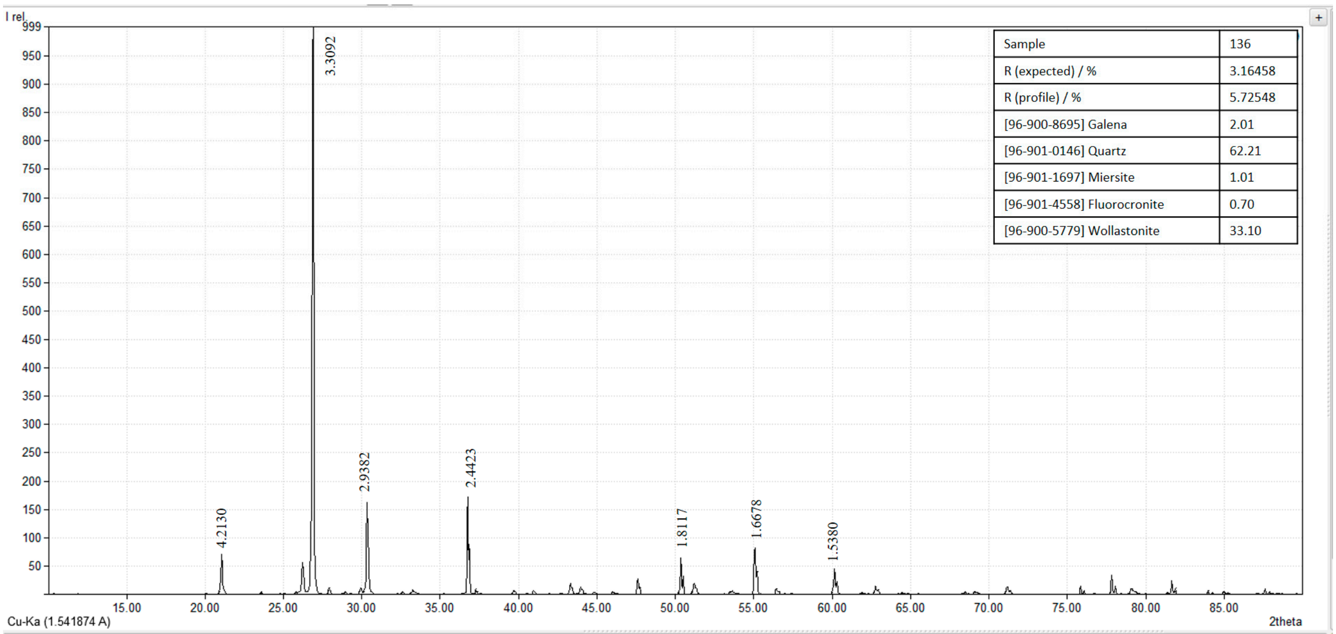

Figure 6. XRD diffractogram for sample 136.

Table 3. Concentration of chemical elements (Bi, Co, Ge, V, W, Li, Ga, In, Te, Nb, Y, Zr, Mo, Sn, Sb) in the ore body 136.

Ore Body	Bi	Co	Ge	V	W	Li	Ga	In	Te	Nb	Y	Zr	Mo	Sn	Sb
136	2750.68	19.09	0.06	15.61	15.77	1.13	1.38	0.31	41.8	0.51	0	0	22.3	0	126

Concentration of Bi in this sample is also with Galena, especially for Bi and Sb. Wollastonite and Quartz are directly related to elements such as V, W and Co. Thus, the mineralogy identified by XRD is consistent with the distribution of chemical elements. The figures bellow presents the images and structure of these mineral phases shown in Figure 7.

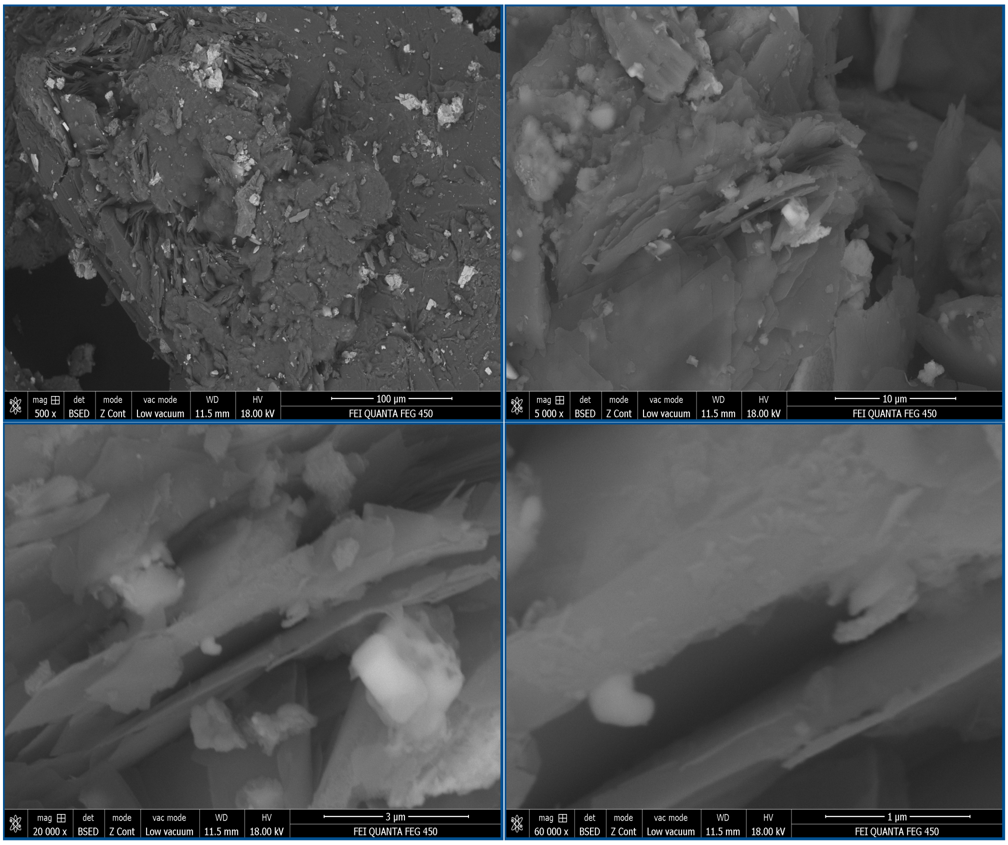

Figure 7. SEM micrographs showing the morphology of ore body 136.

Figure 7 presents SEM micrographs of ore body 136 showing Quartz–Wollastonite matrix with lamellar and plate-like textures and disseminated sulfide minerals, including Galena and Bismuthinite. Bright micro-domains correspond to Bi-bearing phases, supporting strong Bi–Te enrichment and hydrothermal telluride-related mineralization. Scale bars are shown on each image. The nodules and contrasting zones represent metallic phases such as Galena and indicate high concentrations of Bi, Te, and Mo, as confirmed by chemical analyses. This confirms the idea of a polymetallic hydrothermal system where subsequent crystallization processes have deposited some of these Technology-Critical Elements considered and the morphology analyzed in the electron microscope matches the mineral phases identified in XRD giving us an interpretation on the genetic process of the ore body.

4.3. Sample 146

Figure 8 presents XRPD analyses of sample 146 which presents identified mineral phases of ore body 146.

X-ray diffraction analysis for sample 146 shows a dominance of Quartz (76%), Stannoidite (11.3%), Anglesite (6.8%), and Sphalerite (5.9%). While in Table 4, we present the concentration of selected chemical elements analyzed. Phase percentages obtained by XRD represent normalized quantitative results. Minor or amorphous phases, if present below the detection limit of the method, may not be reflected in the reported values.

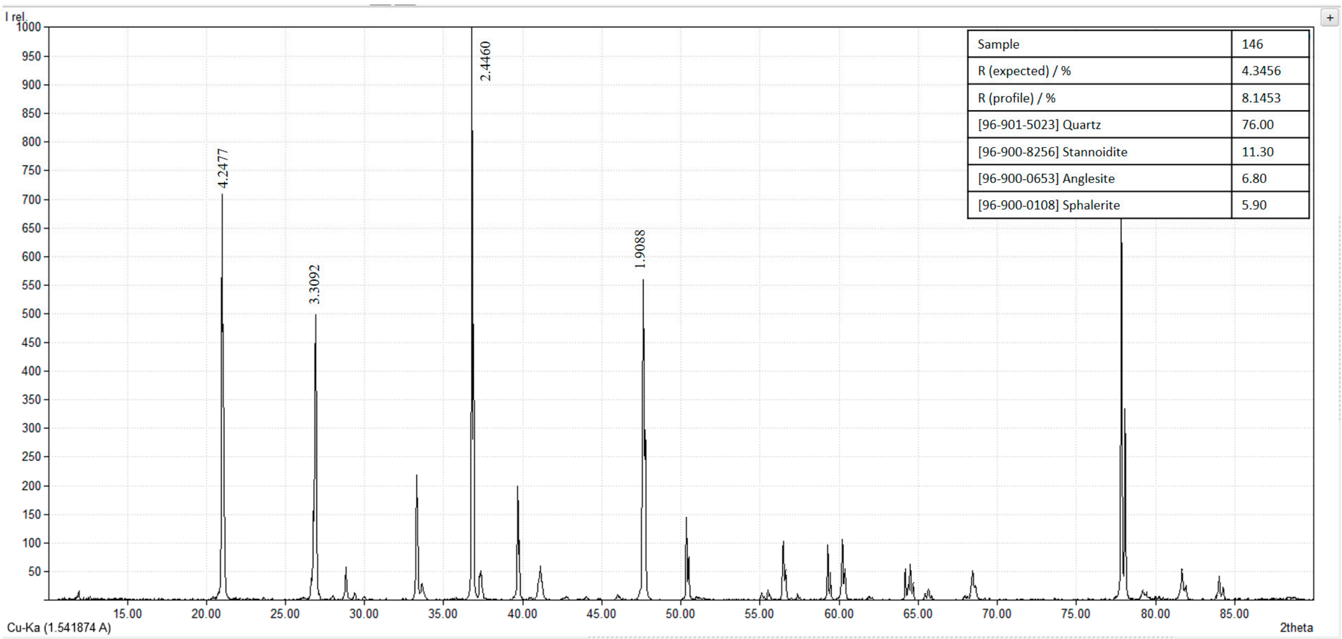

Figure 8. XRD diffractogram for sample 146.

Table 4. Concentration of chemical elements (Bi, Co, Ge, V, W, Li, Ga, In, Te, Nb, Y, Zr, Mo, Sn, Sb) in the ore body 146.

Ore Body	Bi	Co	Ge	V	W	Li	Ga	In	Te	Nb	Y	Zr	Mo	Sn	Sb
146	610.4	24.64	0.15	8.15	4.81	0.93	0.37	0.5	4.16	0.16	12	4.6	11.4	0	117

Below, we present the images and structure of mineral phases of sample 146 in Figure 9.

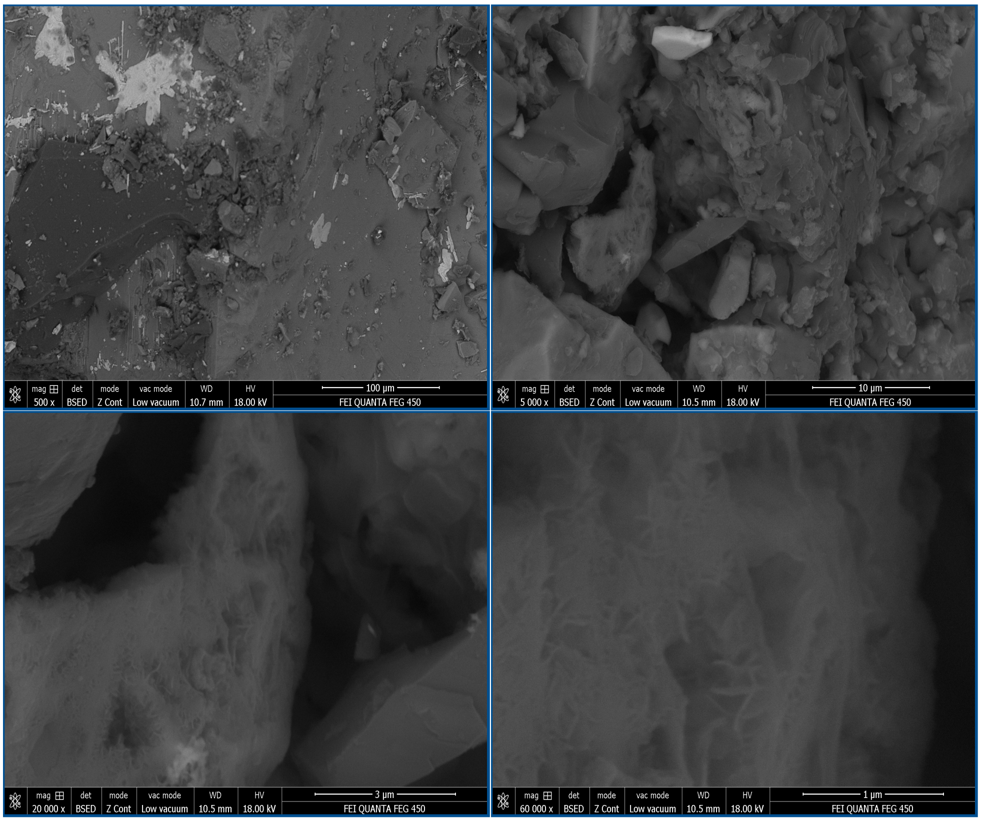

Figure 9. SEM micrographs showing the morphology of ore body 146.

Figure 9 presents SEM images of ore body 146 illustrating Quartz matrix with disseminated sulfide minerals and heterogeneous hydrothermal textures. Scale bars are shown on each image.

4.4. Sample 149-F

Figure 10 shows the XRD diffractogram for sample 149-F, respectively for ore body 149-F, one of the most promising ore bodies in this horizon.

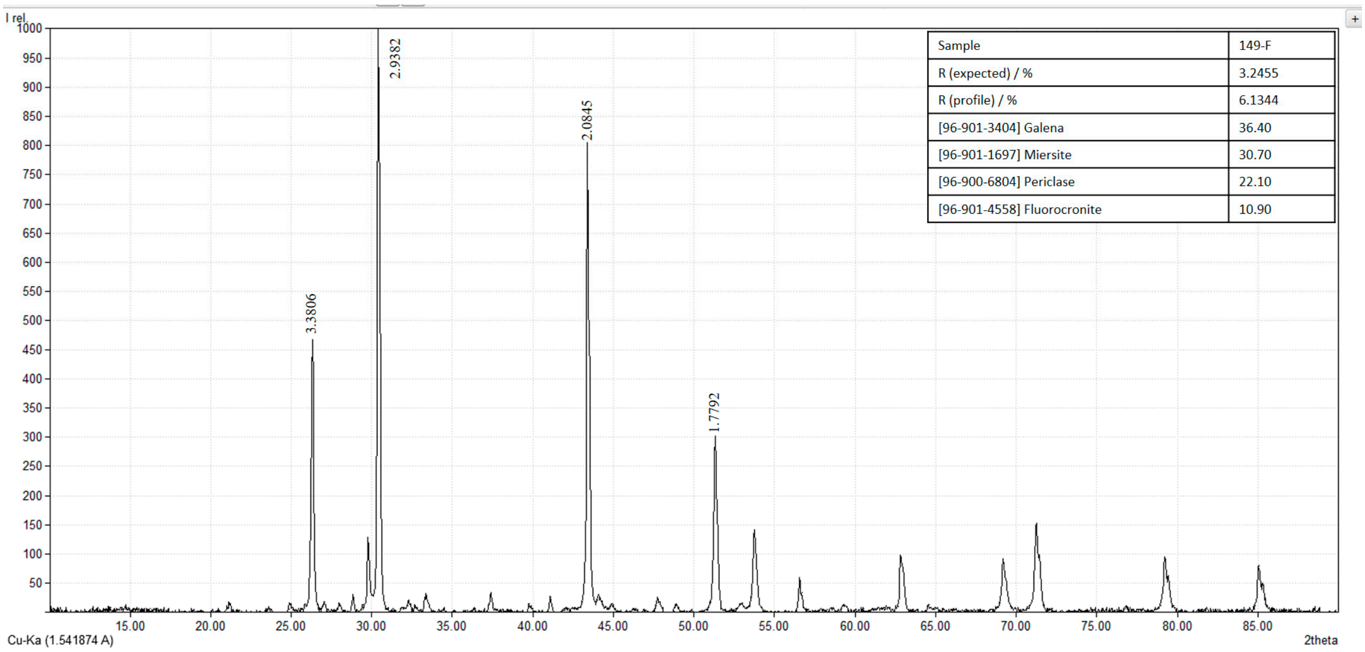

Figure 10. XRPD diffractogram for sample 149-F.

Based on laboratory analysis through X-ray diffraction for the 149-F sample, a dominance of Galena (36.4%), Periclase (22.1%) and Fluorocronite (10.9%) is presented, which has a good correlation with the distribution of chemical elements analyzed through the instrumental technique of ICP-MS and presented in Table 5.

Table 5. Concentration of chemical elements (Bi, Co, Ge, V, W, Li, Ga, In, Te, Nb, Y, Zr, Mo, Sn, Sb) in the ore body 149-F.

Ore Body	Bi	Co	Ge	V	W	Li	Ga	In	Te	Nb	Y	Zr	Mo	Sn	Sb
149-F	8.34	37.64	0.06	5.85	3.74	0.43	0.29	1.23	0.12	0.19	0	0	112	714	415

Now, the Scanning Electron Microscope results for sample 126 as shown in Figure 11 is presented.

Figure 11 presents SEM micrographs of ore body 149-F showing coarse cubic Galena crystals associated with dense sulfide aggregates and subordinate silicate phases. The images illustrate porous and brecciated textures, indicating intense hydrothermal activity and providing microtextural evidence for the association of Sb and Sn with Pb-sulfide mineralization. Scale bars are shown on each image.

4.5. Sample 156

Figure 12 shows the XRD diffractogram for sample 156, respectively for ore body 156.

The distribution of Technology-Critical Elements in this ore body is presented in Table 6.

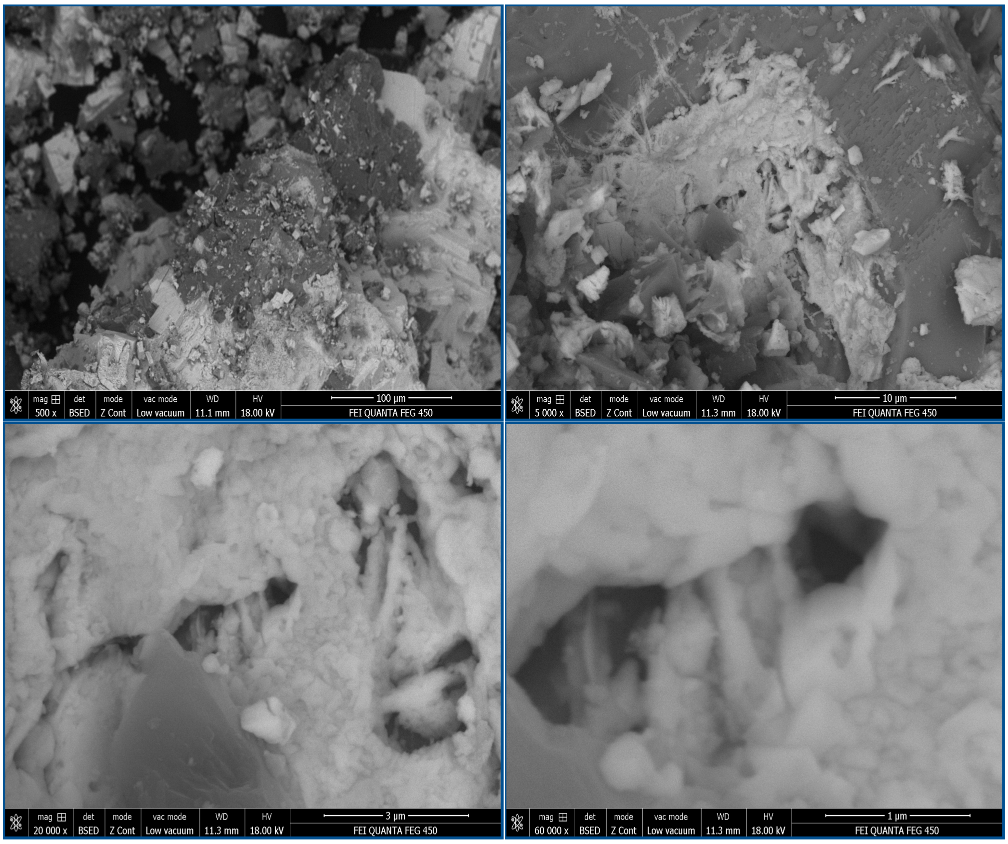

Figure 11. SEM micrographs showing the morphology of ore body 149-F.

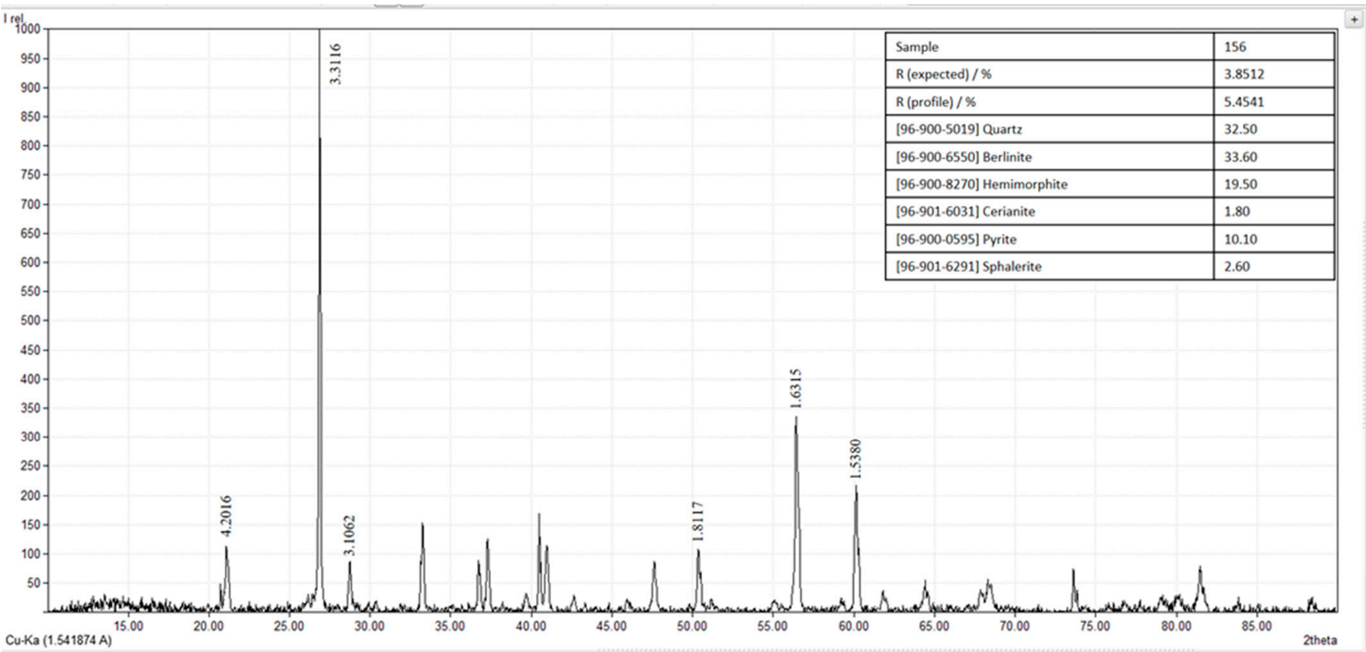

Figure 12. XRD diffractogram for sample 156.

Table 6. Concentration of chemical elements (Bi, Co, Ge, V, W, Li, Ga, In, Te, Nb, Y, Zr, Mo, Sn, Sb) in the ore body 156.

Ore Body	Bi	Co	Ge	V	W	Li	Ga	In	Te	Nb	Y	Zr	Mo	Sn	Sb
156	58.71	71.31	0.17	13.9	9.16	0.51	0.5	1.13	0.38	0.48	17	6	16.2	0	504

Now we will present the images and structure of these mineral phases shown in Figure 13.

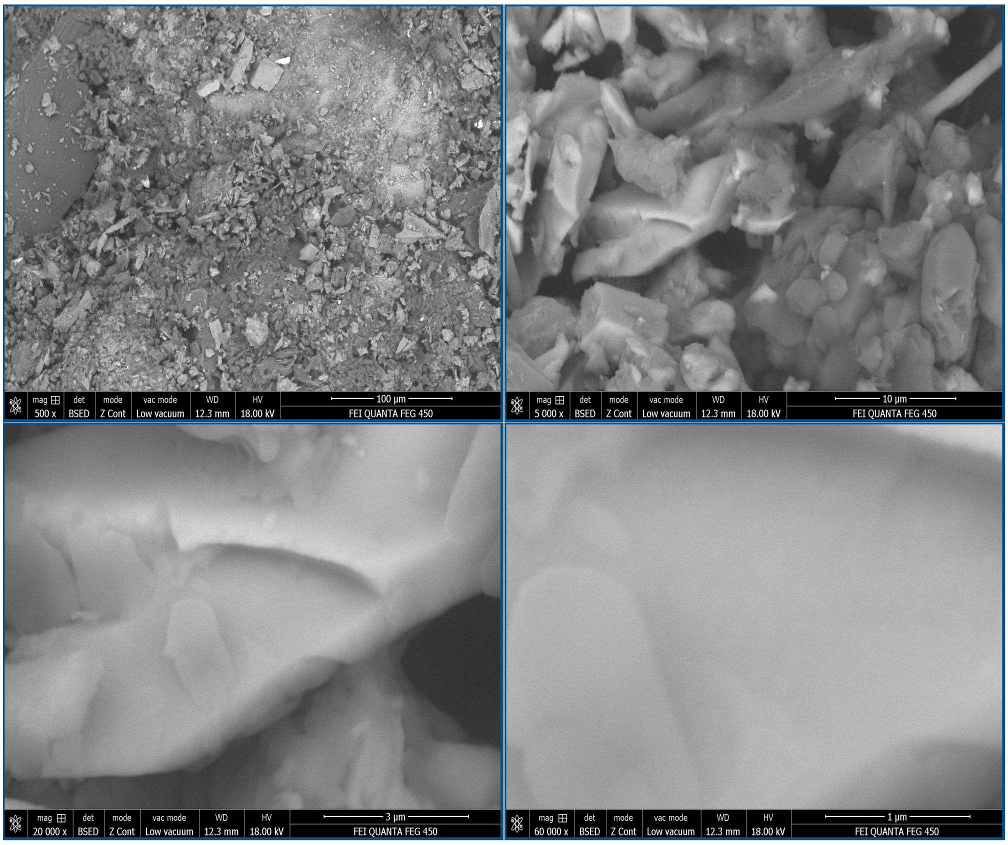

Figure 13. SEM micrographs showing the morphology of ore body 156.

Figure 13 SEM images of ore body 156 illustrating Quartz–Hemimorphite matrix with disseminated Pyrite and Sphalerite and heterogeneous hydrothermal textures. Scale bars are shown on each image.

Correlation analysis of Technology-Critical Elements with mineral phases

One of the best ways to visualize the distribution of Technology-Critical Elements and their correlation with mineral phases is through correlation analysis, is through correlation analysis (Table 7).

Correlation analysis (Table 7) supports the PCA results by showing strong positive correlations between Bi–Te, Mo–Sn–Sb, and Ge–Ga–W.

Principal Component Analysis of Technology-Critical Elements

Geostatistical methods are widely applied in geological research to interpret multivariate datasets and identify controlling factors [23]. Principal Component Analysis (PCA) is a method for reducing data with minimal loss of important information. It was applied to reduce dimensionality and to identify the main factors influencing the distribution of chemical elements. To present the orientation and clustering of these elements, we have constructed the PCA as shown in Figure 13.

Figure 14 shows the relationships between Technology-Critical Elements and their loadings on PC1 (31.8%) and PC2 (21.3%).

Table 7. Pearson correlation matrix between selected Technology-Critical Elements and major mineral phases.

	Bi	Co	Ge	V	W	Li	Ga	In	Te	Nb	Y	Zr	Mo	Sn	Sb	Pyrite	Quartz	Sphalerite	Galena	Fluorocronite	Periclase
Bi	1.00																				
Co	−0.07	1.00																			
Ge	−0.17	0.16	1.00																		
V	0.12	0.35	0.58	1.00																	
W	0.13	0.10	0.65	0.70	1.00																
Li	−0.01	0.26	−0.01	0.45	0.16	1.00															
Ga	−0.06	−0.18	0.25	0.52	0.41	0.12	1.00														
In	−0.19	−0.38	0.03	−0.10	−0.08	−0.22	0.10	1.00													
Te	0.98	−0.10	−0.27	0.02	−0.03	−0.01	−0.11	−0.17	1.00												
Nb	0.13	−0.08	0.51	0.56	0.54	−0.13	0.49	0.26	0.07	1.00											
Y	−0.13	0.09	−0.33	−0.03	−0.16	−0.17	0.09	0.06	−0.13	0.04	1.00										
Zr	−0.14	−0.18	0.13	−0.19	−0.09	−0.20	0.03	−0.03	−0.12	0.21	−0.08	1.00									
Mo	−0.19	0.02	−0.09	−0.41	−0.19	−0.06	−0.17	−0.18	−0.39	−0.46	0.03	0.85	1.00								
Sn	−0.17	0.14	−0.08	−0.35	−0.15	0.01	−0.33	−0.01	−0.13	−0.43	−0.35	−0.19	0.85	1.00							
Sb	0.17	0.00	−0.49	−0.51	−0.33	−0.37	0.02	0.08	−0.11	−0.39	0.13	0.05	0.39	0.26	1.00						
Pyrite	−0.21	−0.03	0.05	0.20	−0.10	0.66	0.23	−0.13	−0.15	0.08	−0.15	0.18	−0.27	−0.20	−0.31	1.00					
Quartz	0.59	−0.03	−0.27	−0.12	−0.12	−0.03	−0.30	−0.28	0.55	−0.07	0.04	−0.14	−0.24	−0.19	−0.10	−0.20	1.00				
Sphalerite	−0.15	0.26	0.15	−0.08	−0.09	−0.19	−0.05	0.08	−0.13	0.12	−0.15	−0.14	0.01	−0.02	−0.01	0.06	−0.25	1.00			
Galena	−0.04	0.07	−0.26	−0.24	−0.10	−0.12	−0.24	−0.10	−0.02	−0.18	−0.17	−0.10	0.48	0.75	0.27	−0.14	−0.13	−0.07	1.00		
Fluorocronite	0.03	−0.26	−0.17	−0.15	−0.09	−0.14	−0.23	−0.14	0.05	−0.01	0.04	0.04	−0.24	−0.20	−0.17	0.13	−0.12	0.17	0.06	1.00	
Periclase	−0.16	0.06	−0.11	0.06	−0.13	0.09	−0.15	0.14	−0.13	−0.05	0.24	−0.23	−0.22	−0.07	−0.04	0.04	−0.28	0.11	0.06	0.27	1.00

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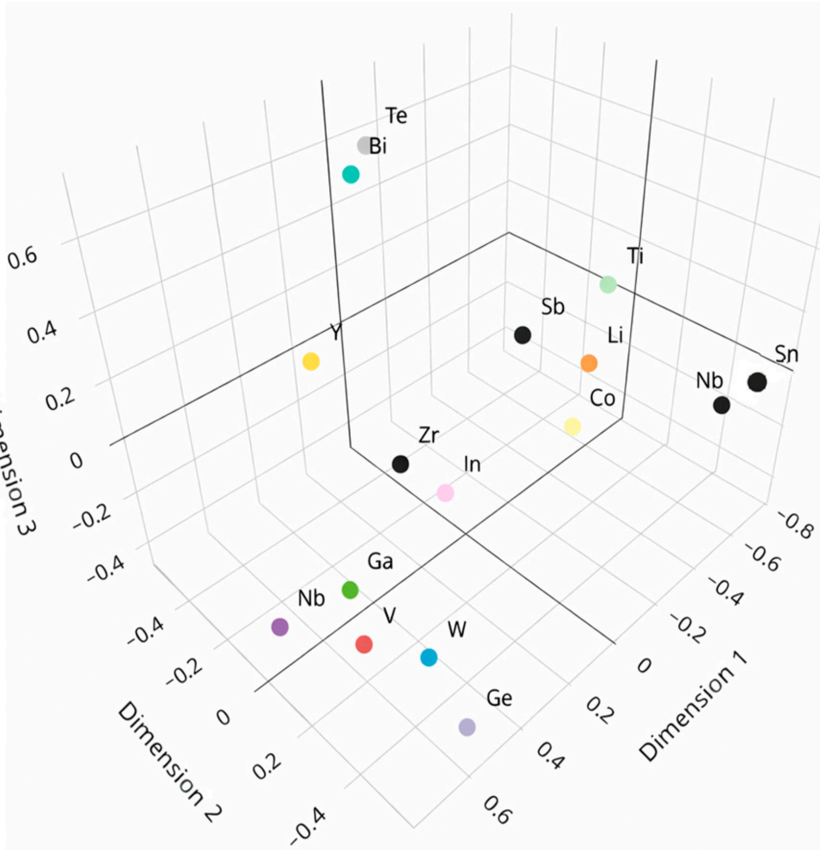

Figure 14. Principal Component Analysis (PCA) for selected elements.

5. Discussion

Since its establishment, Trepça has been known primarily for the exploration and exploitation of Pb-Zn-Ag deposits; this study shifts the focus toward the concentration of Technology-Critical Elements. The heterogeneous distribution of these elements in the Trepça mine shows the complexity of hydrothermal mineralization as well as their correlation with the main mineral phases such as Galena and Sphalerite, indicating a diverse paragenesis.

Elevated concentrations of Bi and Sb in selected ore bodies highlight the metallogenic potential of the Trepça mine for Technology-Critical Elements. The laboratory results are valuable both for characterizing the geochemical distribution of these elements and for providing a basis for the economic reassessment of the Trepça mine with respect to Technology-Critical Elements.

Overall, Bi and W reach their highest concentrations in horizons VIII–IX and decrease with increasing depth. Sb and Sn peak in horizon X. With increasing depth, Co and Sb tend to increase, whereas Bi, W, and Sn show decreasing trends. This study clearly presents the distribution of elements as a function of depth. Co, Li, In, Mo, Sn, and Sb increase with increasing depth, whereas Bi, Ge, V, W, Ga, and Nb show decreasing trends.

This horizon is characterized by elevated Sn, reaching 714 ppm in ore body 149-F, indicative of advanced hydrothermal mineralization.

The high Bi concentration suggests incorporation into the structure of Galena as a mineral known to accommodate Bi and Ag. W, which also reached high concentrations in horizons VIII and IX, is usually associated with hydrothermal systems or skarn-type mineralization. The other elements occurred at lower concentrations compared to those mentioned above, especially Co, V, Ga, In, Te and Nb which are associated with Sphalerite and Pyrite and this related with correlation analysis.

Figure 5 presents SEM images which confirm the X-ray diffraction results, clearly showing that sample 126 is formed through a complex hydrothermal crystallization process where sulfides and carbonates serve as the main minerals for the Technology-Critical Elements identified here (Bi, W, Ga, In and Te). From this we see that we have a good correlation between these elements and the sulfide and carbonate minerals.

Concentration of Bi in this sample is also with Galena, especially for Bi and Sb. Wollastonite and Quartz are directly related to elements such as V, W and Co. Thus, the mineralogy identified by XRD is consistent with the distribution of chemical elements.

This confirms the idea of a polymetallic hydrothermal system where subsequent crystallization processes have deposited some of these Technology-Critical Elements considered and the morphology analyzed in the electron microscope matches the mineral phases identified in XRD giving us an interpretation on the genetic process of the ore body.

This mineralogical composition is also related to the chemical distribution of elements in this ore body, especially with the distribution of Bi and Sb, which is especially related to Stannoidite.

Scanning Electron Microscopic images show a complex morphology with Quartzite lamellae. Quartz appears as the main matrix in these images while small crystals are associated with sulfide mineral phases such as Sphalerite and Stannoidite which are the basis for the occurrence of Bi and Sb. Sb is also associated with mineral phases such as Anglesite which indicate the incorporation of these elements in fine crystalline phases.

The proposed association of Sn and Sb with Pb mineralization is supported by correlation analysis (Table 7). Sn shows a strong positive correlation with Galena ($r = 0.75$), indicating Galena as a major host phase for Sn in the studied samples. Sb displays a weak to moderate positive correlation with Galena ($r = 0.27$), suggesting partial incorporation into Pb-sulfide assemblages.

While the SEM images reveal large cubic crystals and dense aggregates typical of galena and miersite, these phases, in addition to Pb, also exhibit elevated concentrations of Sb and Sn, as confirmed by ICP-MS chemical analysis. Also, what can be mentioned is the occurrence of pores representing hydrothermal fluids which enable the migration of trace elements such as Ga, In and Li. Thus the observed morphology is consistent with XRPD identified mineral phases and with the inferred migration behavior of trace elements.

This distribution corresponds to the distribution of Sb and Co which are associated with Pyrite and Sphalerite.

Scanning Electron Microscope (SEM) images have shown heterogeneous morphologies with fragmentary structures, plate-like crystals and some needle-shaped crystals which are typical of the Hemimorphite mineral identified also through X-ray diffraction. While Pyrite, Sphalerite and Cerianite indicate the occurrence of Sb, Bi, Mo, Te and REE present also in chemical analyses, indicating a complex hydrothermal polymetallic mineralization.

Correlation analysis (Table 7) supports the PCA results by showing strong positive correlations between Bi–Te, Mo–Sn–Sb, and Ge–Ga–W. These associations reflect element partitioning into specific mineralogical hosts within the hydrothermal system.

The very high correlation between Bi and Te indicates their co-precipitation, suggesting the presence of tellurides in the hydrothermal processes. Bi also gave a high correlation with Quartz which represents an intrusion of silicate fluids in the later phase of mineralization.

The association of Bi with Galena and Co with Pyrite is supported by correlation analysis and is consistent with numerous previous studies demonstrating incorporation of these elements into PbS and FeS_2 structures in hydrothermal Pb–Zn systems.

Overall, the correlation data support a multi-phase mineralization model in which Pb–Zn sulfides act as the principal carriers of Ge, In, and Ga.

The PCA results indicate that the distribution of Technology-Critical Elements is controlled by several geochemical associations.

The tight clustering of Ge, Ga, Nb, W, and V indicates a common geogenetic control on their distribution. This association is interpreted to reflect incorporation of these elements during the high-temperature skarn-forming to early hydrothermal stage of mineralization.

The correlation analysis and the alignment with the PCA clearly present the relationship between the critical technological elements and the mineral phases, reflecting also the geochemical and metallogenic processes that have influenced the distribution and concentration of these elements in the Trepça mine.

The significance of the Technology-Critical Elements concentrations studied at the Trepça mine becomes clearer when compared with data from other known hydrothermal Pb-Zn deposits worldwide.

The exceptionally high Bi concentration measured at Trepça places this deposit among the most Bi-enriched Pb-Zn systems reported in the literature.

The Bi–Te association supports their co-precipitation during late-stage hydrothermal mineralization.

The Mo–Sn–Sb grouping reflects incorporation of these elements into sulfide minerals.

The observed depth-related geochemical trends provide important insights into the evolution of the ore-forming hydrothermal system.

Such vertical zonation is typical of many hydrothermal polymetallic systems and indicates a vertically evolving fluid pathway characterized by decreasing temperature and changing fluid chemistry with depth.

From an exploration perspective, these trends can be used as geochemical vectors to guide future exploration and targeting within the Trepça mine.

6. Conclusions

Trepça ore bodies show strong enrichment in Bi, Sb, W, Co, and In, with maximum concentrations of 2750 ppm Bi, 504 ppm Sb, 308 ppm W, 71 ppm Co, and ~730 ppm In. These values are comparable to those reported from globally recognized Technology-Critical-Elements-bearing Pb–Zn deposits, confirming Trepça as a geochemically significant Technology-Critical-Elements-bearing system.

Based on the analyzed samples from the ore bodies, they show a wide chemical and mineralogical variability, confirming a complex hydrothermal polymetallic system. Chemically, the samples show high concentrations of several Technology-Critical Elements: Bi (up to 2750 ppm in sample 136), Sb (up to 504 ppm in sample 156), W (up to 308 ppm in sample 126), and Co (up to 71 ppm in sample 156).

The presence of Ga, In, Te, V, Nb, Mo, REE, and other elements confirms the geological complexity of the ore bodies and mineral phases, as well as the variations in ore genesis under the influence of magmatic and metamorphic processes.

The Trepça ore bodies show notable concentrations of Bi (up to 2750 ppm), Sb (up to 504 ppm), W (up to 308 ppm), Co (up to 71 ppm), and In (up to ~730 ppm), indicating that these elements represent the most promising targets for further economic evaluation. Future work should include mineral-scale quantification of these Technology-Critical Elements using EPMA and LA-ICP-MS, detailed process mineralogy to assess deportment and recoverability, and preliminary resource estimation for the most enriched horizons.

Trepça is a polymetallic deposit comprising several areas that for decades have been explored mainly for Pb-Zn-Ag; current demand justifies systematic assessment for Technology-Critical Elements.

6.1. Most Prospective Horizons/Ore Bodies

Horizons VIII and IX are most prospective for Bi and W, with maximum Bi concentrations reaching 2750 ppm (ore body 136) and W up to 308 ppm. Horizon X is characterized by elevated Sn and Sb, while Horizon XI shows the highest average Sb (up to 504 ppm) and Co (up to 71 ppm). Selected ore bodies (e.g., 136, 149-F, and 156) represent priority targets for Technology-Critical Elements enrichment.

6.2. Primary Mineralogical Controls

The primary mineralogical hosts of Technology-Critical Elements are sulfide minerals, particularly Galena and Sphalerite, which incorporate Bi, Sb, Sn, In, Ge, and Ga through substitution and micro-inclusions. Pyrite is an important host for Co and Mo, whereas Quartz- and Wollastonite-bearing assemblages are associated with W and V enrichment.

6.3. Recommendations

Future exploration should prioritize sulfide-rich ore bodies within horizons VIII–XI and include systematic LA-ICP-MS or EPMA analyses of Sphalerite and Galena to better quantify Technology-Critical Elements distribution at the mineral scale. Additional drilling focused on deeper extensions of Sb- and Co-enriched horizons is recommended. Further research should also evaluate the metallurgical recoverability of selected Technology-Critical Elements.

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