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Unlocking Critical Raw Materials from Copper Waste Dumps at Roșia Poieni: Implications for Sustainable Resource Recovery

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Abstract

Valorising mining waste is critical for sustainable resource management and reduced reliance on primary raw materials. Waste dumps from large-scale porphyry systems are potential secondary sources of critical raw materials (CRMs) as listed in Regulation (EU) 2024/1252. This study investigates mineralogical and microchemical heterogeneity in wastes from the Roșia Poieni porphyry copper district, Romania, testing the hypothesis that this heterogeneity governs both their secondary-resource potential and their environmental behaviour. Samples from the Geamăna and Halda Veche waste dumps were characterised by powder X-ray diffraction (PXRD), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and Raman spectroscopy. PXRD of five selected samples revealed marked inter-sample variability: chalcopyrite ranged from 12.88% to 13.48%, bornite and rutile reached 7.84% and 7.60%, and cuprite reached 15.78%. SEM-EDS confirmed Cu-rich bornite (55.25 wt.% Cu), while Raman spectroscopy identified melanterite alongside calcite and dolomite. The identification of pyrite, melanterite, and carbonate minerals suggests potential acid-generating and acid-neutralising processes, although validation by leaching tests and acid-base accounting is required. These findings establish a mineralogical basis for evaluating targeted recovery of critical and strategic raw materials alongside environmentally responsible mine waste management within a circular-resource framework; representative bulk geochemical analyses and recovery tests are still required to establish recoverable resources.

Keywords: critical raw materials (CRM); mining waste; circular economy; mineralogical characterization; secondary resource recovery; Roșia Poieni; potentially toxic elements (PTE); environmental stewardship

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1. Introduction

The sustainable management of natural resources has become a strategic priority for all EU countries. As the demand for mineral resources grows—particularly for those considered critical to industrial and technological development—the need for circular economic models is increasingly recognised. Circularity, through promoting reuse, recycling, and the

valorisation of secondary raw materials, helps reduce dependence on primary resources and minimise the environmental footprint of extractive industries [1–3].

The strategic importance of these materials is not confined to Europe: securing critical mineral supply has become a shared global priority. The International Energy Agency projects that demand for key energy transition minerals will almost triple by 2030 under its Net Zero Emissions scenario, and major economies beyond the EU—including the United States, China, Japan, Australia, Canada, and South Korea—each maintain their own critical or strategic minerals lists and dedicated national strategies to secure supply [4]. This global race to secure critical raw materials, driven by clean-energy, digital, and defence-related demand, underscores that reprocessing mine waste for secondary CRM/PTE recovery, as investigated here for Roșia Poieni, addresses a challenge of worldwide, not merely regional, significance.

The accelerating demand for critical raw materials (CRMs), driven by the global energy transition, has exposed supply chain vulnerabilities, as these materials are predominantly sourced from a limited number of geopolitical regions [5]. Copper, molybdenum, and associated trace elements in porphyry-type deposits such as those at Roșia Poieni [6,7] are increasingly strategically important, particularly because of their critical role in modern technologies and infrastructure. As one of Romania's most significant active copper mining operations, Roșia Poieni has substantial potential not only as a primary resource base but also as a secondary source of critical raw materials (CRMs) recoverable from mining waste. Elements such as copper and molybdenum are essential for electrical systems, renewable energy infrastructure, and industrial catalysts, while trace concentrations of selenium, tellurium, and rare earth elements—often associated with sulphide mineral assemblages—are increasingly valued in green technologies and defence applications. Given the geopolitical concentration of CRM supply and the related vulnerabilities in European value chains, the European Union has prioritised secure and sustainable sourcing through the recently adopted Critical Raw Materials Act [8,9]. This legislative initiative mandates that by 2030, at least 10% of the CRMs consumed in the EU must originate from domestic extraction, while 25% must come from recycling and the valorisation of secondary sources [8]. In this global context, reprocessing mining waste stored in waste dumps offers a major circular economy opportunity, reducing the extractive sector's carbon footprint while lowering long-term storage risks [10,11]. Recent European-level assessments show that waste dumps from porphyry copper systems have underestimated polymetallic potential, with associated elements such as molybdenum, tellurium, and cobalt recoverable through modern selective leaching or bio-extraction technologies. Consequently, reintegrating these massive volumes of waste dumps into the direct economic circuit can mitigate the EU's industrial supply deficit [10,11]. In this context, a comprehensive assessment of CRM potential in mining waste and marginal ore at Roșia Poieni contributes directly to national and European strategies to reduce import dependency and promote circular economy practices in the extractive sector.

Mining wastes, particularly dumps, represent an underexplored yet potentially valuable secondary source of CRMs. These repositories often contain substantial concentrations of economically significant metals, making them attractive for recovery via innovative and sustainable technologies [12]. Their valorisation not only mitigates environmental risks but also diversifies supply and aligns with circular economy principles.

Thus, this study tests the hypothesis that the mineralogical heterogeneity of the Roșia Poieni copper waste dumps simultaneously determines their potential as a secondary source of valuable raw materials and their environmental behaviour, providing a scientific basis for integrated resource recovery and environmental stewardship. The specific objectives are to: (i) identify and quantify the principal mineral phases in representative waste samples;

(ii) characterise selected mineral grains and their elemental composition using SEM-EDS; (iii) identify alteration-related and environmentally relevant phases using Raman spectroscopy; and (iv) integrate the three datasets to distinguish resource-bearing phases from phases relevant to acid generation, buffering, and future remediation. Climate resilience and assisted phyto-mining are considered downstream applications of this baseline characterisation and are not experimentally tested here.

Research on climate-driven mobilisation, predictive risk modelling, or assisted phyto-mining is reserved for subsequent experimental work that requires dedicated leaching, speciation, field monitoring, and plant-uptake data.

2. Materials and Methods

2.1. Study Area and Sampling Strategy

2.1.1. Geographical Description

Roșia Poieni is located in the Metaliferi Mountains—named for their historically rich metalliferous mineralisation—about 90 km northwest of Alba Iulia and 7 km south of the Arieș River, in the commune of Lupșa. The area is characterised by mountainous relief, with altitudes ranging from 800 to 1200 m, and is predominantly composed of volcanic and sedimentary rocks favourable to metalliferous mineralisation. The Metaliferi Mountains are known for their lithological complexity, including ophiolites, Mesozoic limestones, and Neogene magmatic formations, which have concentrated important reserves of precious and non-ferrous metals. The area has a moderate climate, with average annual temperatures of 4–6 °C at high altitudes and rainfall of around 800–1000 mm/year. The Roșia Poieni mine, opened in 1978, is Romania's largest disseminated copper and gold deposit and accounts for about 65% of the country's copper reserves [6]. Long-term exploitation and processing have generated substantial volumes of mine waste and waste dumps, making the area particularly relevant for studies on secondary-resource recovery and environmentally sustainable mine waste management.

2.1.2. Geological Features

The Roșia Poieni perimeter, located in the Metaliferi Mountains (Apuseni Mountains), is characterised by a complex geological composition, dominated by ophiolitic formations, intrusive and effusive magmatic rocks (microdiorites, andesites) and Mesozoic sedimentary rocks (limestones, marls, sandstones). The Roșia Poieni deposit is a porphyry copper deposit, consisting mainly of fine disseminations and pylons of pyrite, chalcopyrite, and magnetite, with secondary minerals such as bornite, molybdenite, and sphalerite; gold is included in chalcopyrite and pyrite. The mineralised body, known as Fundoaia, is a porphyritic Miocene subvolcanic body characterised by intense hydrothermal alteration and concentric zoning: a potassic core, a phyllic zone, a propylitic halo, and a zone of advanced argillaceous alteration [6]. Copper mineralisation is concentrated in the potassic zone (>0.6% Cu) and decreases towards the periphery. The estimated reserves are about 350 million tons of ore, with an average grade of 0.36% Cu and 0.29 g/t Au [13]. The geological structure and distribution of mineralisation make Rosia Poieni Romania's largest copper deposit and one of the most relevant for studies on recovering critical mineral resources.

2.1.3. Sampling Methodology

The selection of the investigated perimeters was based on critical criteria such as terrain accessibility, historical mining activity, and the estimated potential content of critical raw materials (CRMs) and potential toxic elements (PTEs). Samples consisting of rocks

and waste dumps (with various grain sizes) were collected from both active (new) and decommissioned (old) waste dumps within the quarry perimeter.

To ensure strict standardisation and representative sampling from highly heterogeneous waste repositories—where particle size variability, stratification, segregation, and random mineral distribution pose significant challenges—a dedicated Sampling and Characterisation Protocol was developed. This framework integrates the guidelines of European Standard EN 14899:2005 (*Characterisation of waste—Sampling of waste materials*) [14] and Technical Report CEN/TR 16376:2012 (*Characterisation of waste—Overall guidance document for characterisation of waste from the extractive industries*) [15].

On-site adaptation of the protocol involved mapping the waste dumps into a systematic sampling grid. To ensure geographical and compositional representativeness, each primary sample comprised five composite sub-samples. Sample selection was further refined by excluding non-representative areas, such as access roads or partially greened zones. Preliminary in situ portable X-ray fluorescence (pXRF) screening was employed to improve sample representativeness by identifying sampling locations exhibiting similar elemental profiles and to minimise redundant sampling, as previous studies showed [16]. The objective of the protocol was to identify samples with contrasting elemental compositions, resulting in the collection of ten samples, labelled RP1-RP10 (Figure 1). PXRF screening therefore guided where the samples were collected in the field; it was not used to select the subset of samples for which quantitative PXRD results are reported (Section 3.1).

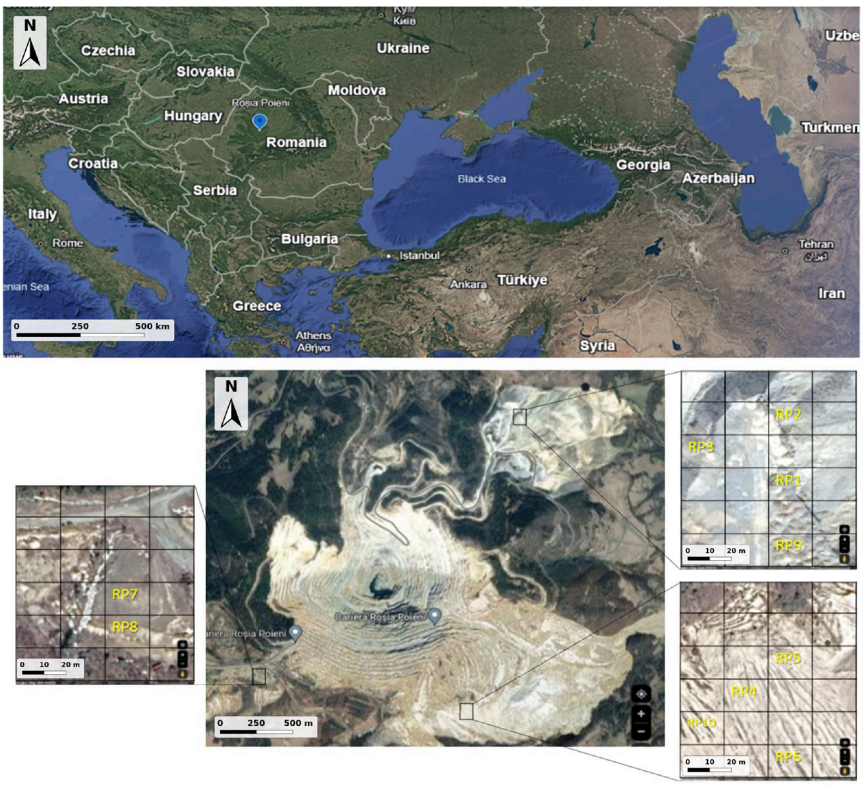


Figure 1. Map with sampling areas on the waste dumps in the Roșia Poieni mining area (Basemap and satellite imagery: © Google Earth; Imagery © 2023 Airbus, Landsat/Copernicus, Maxar Technologies).

2.2. Sample Preparation

Following field sampling, ten samples were separated and labelled RP1 to RP10. Processing employed cold preparation methods to prevent thermal degradation or phase alterations of sensitive mineral species (drying, sieving and grinding in an agate mortar and pestle to a fine powder with a grain size < 0.063 mm). This processing is required for PXRD

analysis because finer powder reduces background noise and improves analysis quality. Before grinding, all samples were examined macroscopically, and selected rock fragments were set aside for polished-section preparation and SEM-EDS and Raman analyses.

2.3. Analytical Framework and Instrumentation

A complementary analytical framework was used to relate bulk mineralogy to grain-scale chemistry and alteration products for the selected samples. Powder X-ray diffraction (PXRD) was used for bulk phase identification and quantitative phase analysis; SEM-EDS was used to examine selected mineral grains and obtain spot elemental compositions; and Raman spectroscopy was used as an independent structural method for identifying selected crystalline and secondary alteration phases. The methods were interpreted jointly because each addresses a different scale of heterogeneity relevant to resource assessment and environmental behaviour.

2.3.1. Powder X-Ray Diffraction (PXRD)

Phase identification and quantification were performed on a Bruker D8 Advance automatic diffractometer (Bruker AXS GmbH, Karlsruhe, Germany), equipped with a vertical goniometer, θ–2θ configuration, Cu radiation (CuKα with λ = 1.54056 Å), and a Ni filter. The operating voltage was 40 kV, and the beam current was 40 mA. Diffraction patterns were recorded from 5 to 150° 2θ, with a 0.02° 2θ step scan at 1 s per step. The receiving slit was 0.6 mm in a 1-0.1-1 slit system. The PDF-2/Release 2007 database was updated to the PDF-2/Release 2013 database for data analysis, and the EVA 13 software (ICDD database) was employed to identify the different mineral phases. Quantitative phase analysis and specimen purity assessment were performed using the quantitative phase analysis tools of DIFFRAC.SUITE (version 02) software package, maintaining statistical errors below 2%. Phase abundances are reported as wt.% of the crystalline fraction; the refinement normalises the identified crystalline phases to 100 wt.%, but X-ray amorphous material was not quantified.

2.3.2. Raman Spectroscopy

Raman spectroscopic analyses were performed using a Renishaw inVia micro-Raman spectrometer (Renishaw plc, Wotton-under-Edge, UK) equipped with 532 and 785 nm excitation lasers and a CCD detector. For the analyses reported in this study, excitation was provided by the 532 nm laser at 5% of the maximum laser power. The system used an 1800 lines/mm grating (VIS), and spectra were acquired with Leica microscope (Leica Microsystems, Wetzlar, Germany) objectives ranging from 5× to 50× magnification. Both static and continuous scanning modes were used, with exposure times of 10–20 s depending on the analysed mineral phase and a spectral range of approximately 100–4000 cm^{-1}. Raman peak intensities were used for phase identification rather than quantitative estimation of mineral abundance, because signal intensity depends on instrumental settings, focusing, crystal orientation, and Raman scattering efficiency. No visible laser-induced degradation was observed in the analysed mineral phases.

2.3.3. Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS)

Morphological observations and micro-chemical quantifications of complex sulphides were carried out using a Hitachi TM 3030 Plus Tabletop scanning electron microscope (Hitachi High-Tech Corporation, Tokyo, Japan), equipped with a Bruker Quantax XFlash® 6/10 energy dispersive X-ray spectrometer (EDS; Bruker Nano GmbH, Berlin, Germany). Before analysis, the polished sections underwent a rigorous carbon-coating procedure

to eliminate electrostatic charging effects, maximise the signal-to-noise ratio, and ensure accurate elemental quantification of the target mineral phases.

2.4. Use of Generative AI in the Preparation of Graphical Materials

The graphical abstract and Figures 5, 6, 8 and 10 were prepared with the assistance of a generative artificial intelligence (GenAI) tool, Claude Opus 5.5 (Anthropic, San Francisco, CA, USA; accessed October 2026). For the data figures (Figures 5, 6 and 8), the tool was used to generate the plotting code (heatmaps and PCA biplot), including the data standardisation and principal component analysis underlying Figure 6; the input values were the quantitative PXRD and SEM-EDS results obtained in this study (Section 3), supplied by the authors, and every resulting figure was checked against the original data tables. For the graphical abstract and the conceptual framework (Figure 10), the tool was used to draft the layout and graphic elements on the basis of the authors' interpretation of the results. GenAI was not used to acquire, process or interpret the analytical data (PXRD patterns, SEM-EDS spectra and Raman spectra). All AI-assisted materials were reviewed, corrected where necessary and approved by the authors, who take full responsibility for their content.

3. Results

The combined analyses identified a heterogeneous assemblage of primary ore minerals, gangue minerals, and secondary alteration products. In the context of Regulation (EU) 2024/1252, it is important to distinguish raw materials from their host minerals: copper is a critical and strategic raw material and phosphorus/phosphate rock are critical raw materials, whereas chalcopyrite, bornite, cuprite, and apatite are mineral hosts rather than CRMs themselves [8]. Therefore, the results below describe mineral phases and then interpret the raw material relevance of the elements they contain.

The principal phases identified across the investigated material include chalcopyrite, cuprite, bornite, rutile, kaolinite, montmorillonite, illite, muscovite, biotite, galena, magnetite, pyrite, sericite, albite, anorthite, quartz, melanterite, dolomite, apatite, calcite, augite, meionite, moganite, cristobalite, sanidine, orthoclase, adularia, labradorite, andesine, clinochlore, chamosite, and titanite (sphene). Their occurrence varies among samples, demonstrating the mineralogical heterogeneity that is central to the working hypothesis.

Table 1 groups the principal identified phases according to mineral class. Their relevance is considered in terms of (i) hosting EU-listed critical/strategic raw materials, where applicable, and (ii) environmental functions such as sulphide oxidation, acid buffering, or sorption. This distinction avoids treating every identified mineral as a CRM-bearing phase.

Table 1. Classification of the main identified mineral phases.

Class	Mineral Phases Identified
oxides and sulphides	cuprite, chalcopyrite, pyrite, hematite, magnetite, bornite, rutile, anatase
carbonates	calcite, dolomite
phyllosilicates and clay minerals	kaolinite, illite—montmorillonite (mixed layer), muscovite, biotite, phlogopite, chamosite, sericite, clinochlore
quartz and other silicates	quartz, albite, anorthite, augite, meionite, moganite, cristobalite, sanidine, orthoclase, adularia, labradorite, andesine, titanite (sphene)
phosphates	apatite, monazite

The analytical results are presented in three complementary groups:

(a) XRD analysis of the selected samples representing contrasting mineralogical assemblages from Roșia Poieni.

(b) SEM-EDS analysis of the selected samples representing contrasting mineralogical assemblages from Roșia Poieni.
(c) Raman analysis of the selected samples representing contrasting mineralogical assemblages from Roșia Poieni.

3.1. XRD Analyses of Selected Samples from Roșia Poieni

Within this study, XRD was used to characterise bulk mineral assemblages in powdered samples. Because the measurements represent mixed bulk material rather than hand-picked individual grains, the resulting patterns integrate ore minerals, silicates, clay minerals, carbonates, and alteration products present within each analysed sample (Figures 2 and 3).

Among the ten collected samples (RP1–RP10), five samples (RP1, RP2, RP7, RP8, and RP9) were selected for detailed presentation of quantitative PXRD results because they illustrate contrasting mineralogical assemblages relevant to the study objectives. The selected samples cover different mineralogical characteristics, including oxidised Cu-bearing phases (RP7), Cu-bearing sulphide assemblages (RP8 and RP9), silicate- and clay-rich material (RP1), and clay and silica rich material (RP2). This selection was intended to demonstrate compositional variability within the investigated waste materials rather than to provide a statistically representative characterisation of the entire deposits. Consequently, the quantitative mineralogical results are interpreted exclusively at the level of the five selected samples, without extrapolation to the complete Geamăna and Halda Veche waste dumps.

Table 2 summarises the dominant resource and environment relevant phases in the five samples. Resource potential is interpreted cautiously from the occurrence and abundance of Cu-bearing minerals and rutile.

Table 2. Minerals identified in relevant samples and CRM potential.

Sample	Minerals	Interpretation
RP7	cuprite	oxidised Cu-bearing assemblage
RP8	chalcopyrite, bornite, rutile	Cu-bearing sulphides; Ti-bearing rutile
RP1	feldspars (albite, sanidine, orthoclase, anorthite), galena, kaolinite	silicate/clay-rich assemblage
RP2	illite–montmorillonite, moganite, labradorite	clay- and silica (moganite)-rich assemblage
RP9	chalcopyrite, pyrite	Cu-bearing sulphide with pyrite

Quantitative phase analysis (Table 3) showed pronounced differences among the selected samples. RP8 contained 12.88% chalcopyrite, 7.84% bornite and 7.60% rutile, whereas RP9 contained 13.48% chalcopyrite together with 5.95% pyrite. Together with RP7 (cuprite), RP8 and RP9 are the Cu-bearing samples among the five analysed by PXRD.

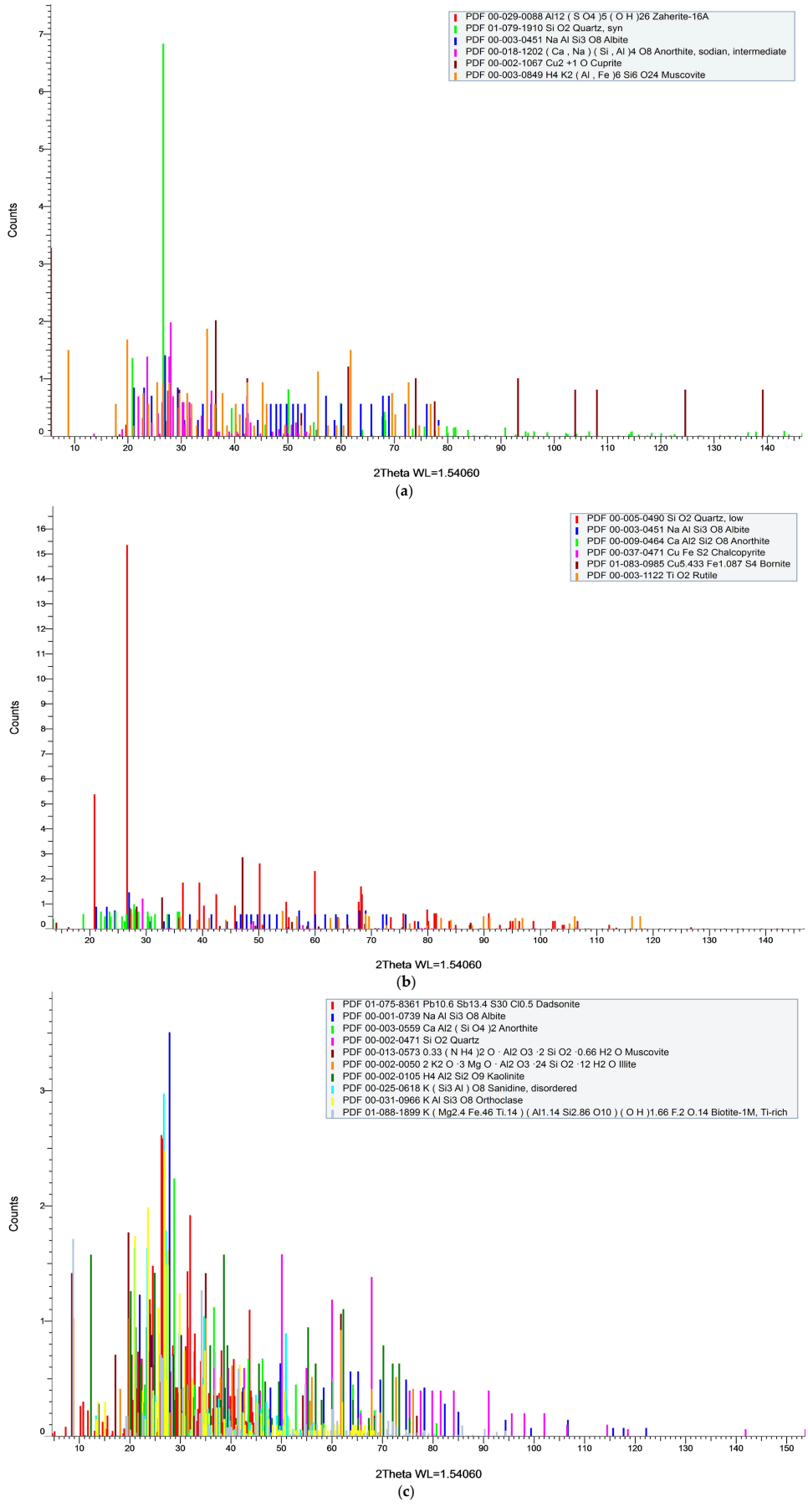


Figure 2. *Cont*.

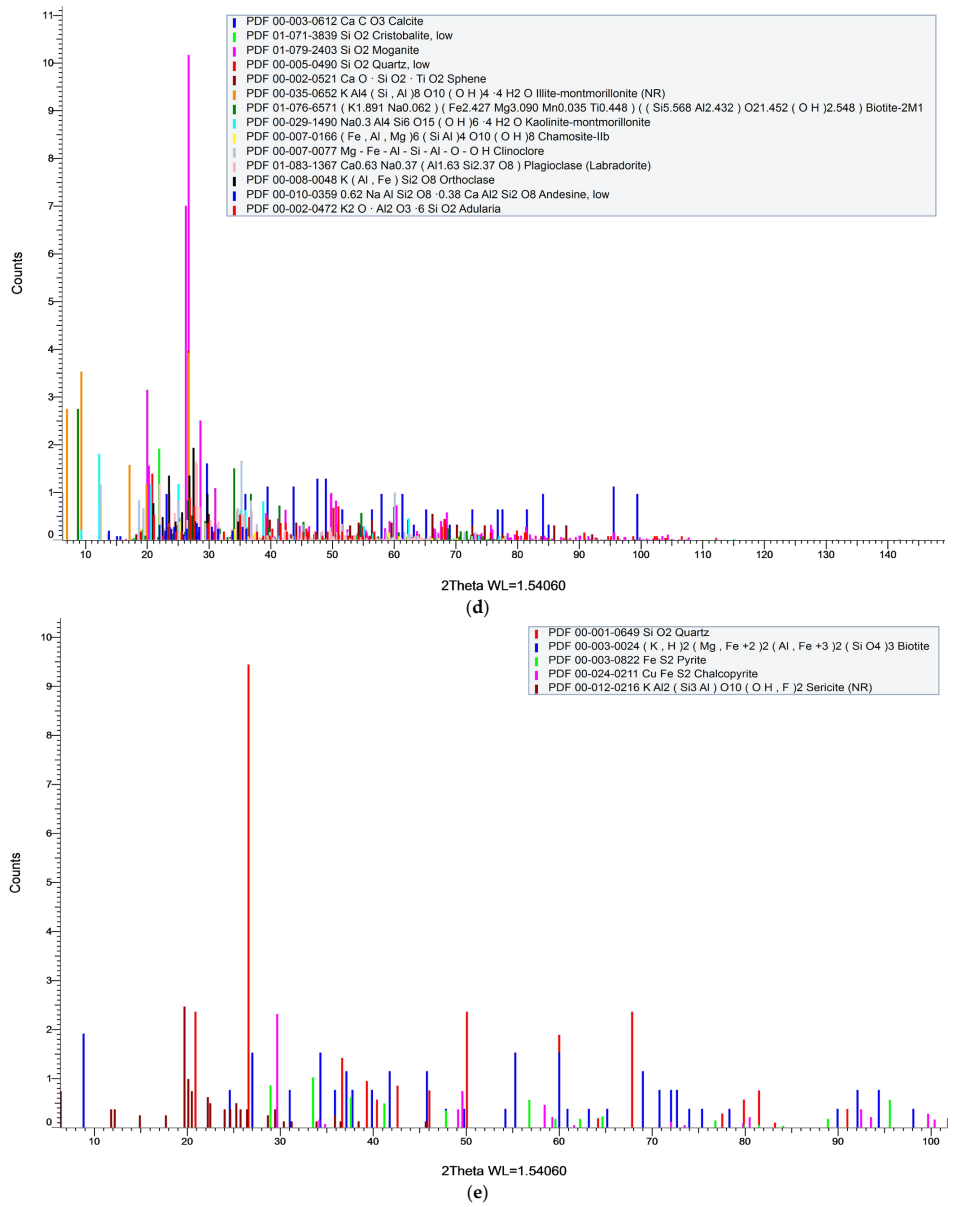


Figure 2. Diffractograms of samples: (**a**) RP7 Halda Veche; (**b**) RP8 Halda Veche; (**c**) RP1 Geamăna; (**d**) RP2 Geamăna; (**e**) RP9 Geamăna.

RP7 contained 15.78% cuprite and 26.00% kaolinite. This cuprite content indicates a distinct oxidised Cu-bearing assemblage compared with the sulphide-dominated RP8 and RP9 samples. RP2 was dominated by mixed-layer illite–montmorillonite (29.49%) and moganite (23.52%), together with labradorite (8.99%), and contained calcite (4.62%) and minor cristobalite, chamosite, and titanite. RP1 was dominated by feldspars (albite 16.87%, sanidine 14.30%, orthoclase 11.93%, and anorthite 10.78%), with galena (7.90%), quartz, muscovite, biotite, kaolinite, and illite (Figures 4 and 5). These contrasts demonstrate that the waste material cannot be treated as a mineralogically uniform feedstock and that any future recovery or remediation strategy would require sample- or domain-specific targeting.

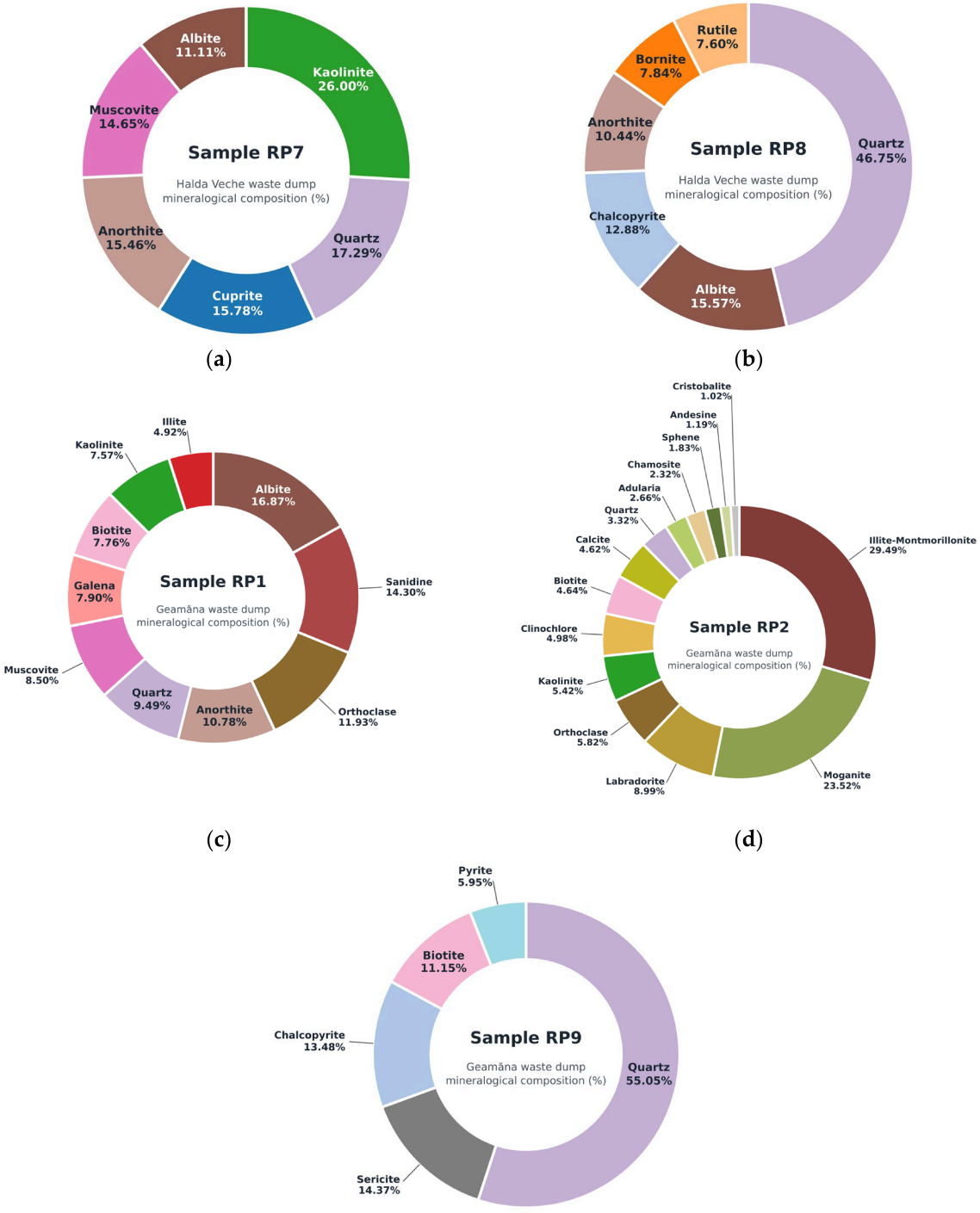


Figure 3. Mineralogical composition in percentages of samples: (**a**) RP7 Halda Veche; (**b**) RP8 Halda Veche; (**c**) RP1 Geamăna; (**d**) RP2 Geamăna; (**e**) RP9 Geamăna.

Table 3. Quantitative phase composition (wt.%, Rietveld refinement) of the five selected PXRD samples.

Mineral	RP7 (%)	RP8 (%)	RP1 (%)	RP2 (%)	RP9 (%)
cuprite	15.78	0.0	0.0	0.0	0.0
chalcopyrite	0.0	12.88	0.0	0.0	13.48
bornite	0.0	7.84	0.0	0.0	0.0

Table 3. *Cont.*

Mineral	RP7 (%)	RP8 (%)	RP1 (%)	RP2 (%)	RP9 (%)
rutile	0.0	7.6	0.0	0.0	0.0
kaolinite	26.0	0.0	7.57	5.42	0.0
illite–montmorillonite	0.0	0.0	0.0	29.49	0.0
illite	0.0	0.0	4.92	0.0	0.0
galena	0.0	0.0	7.9	0.0	0.0
moganite (SiO_2)	0.0	0.0	0.0	23.52	0.0
quartz	17.29	46.75	9.49	3.32	55.05
albite	11.11	15.57	16.87	0.0	0.0
anorthite	15.46	10.44	10.78	0.0	0.0
muscovite	14.65	0.0	8.5	0.0	0.0
biotite	0.0	0.0	7.76	4.64	11.15
sericite	0.0	0.0	0.0	0.0	14.37
calcite	0.0	0.0	0.0	4.62	0.0
pyrite	0.0	0.0	0.0	0.0	5.95
cristobalite	0.0	0.0	0.0	1.02	0.0
labradorite	0.0	0.0	0.0	8.99	0.0
andesine	0.0	0.0	0.0	1.19	0.0
sanidine	0.0	0.0	14.30	0.0	0.0
orthoclase	0.0	0.0	11.93	5.82	0.0
adularia	0.0	0.0	0.0	2.66	0.0
clinochlore	0.0	0.0	0.0	4.98	0.0
chamosite	0.0	0.0	0.0	2.32	0.0
titanite (sphene)	0.0	0.0	0.0	1.83	0.0

Values are wt.% of the crystalline fraction obtained by Rietveld refinement (DIFFRAC.SUITE); all refined phases are listed. 0.0 = not detected. Totals deviate slightly from 100% because of rounding. Amorphous material was not quantified. Moganite and cristobalite are SiO_2 polymorphs; titanite = sphene.

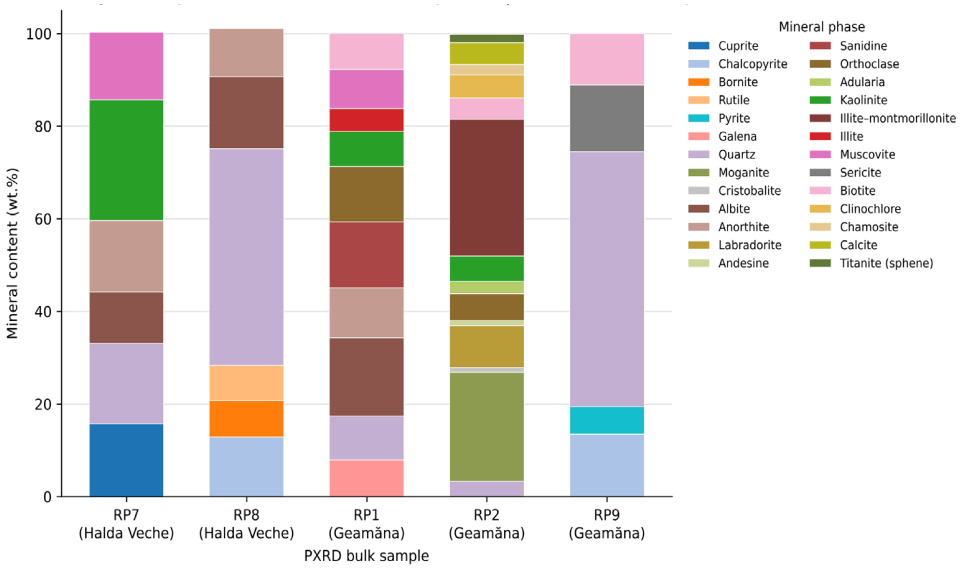


Figure 4. Mineralogical composition (%) of the XRD bulk samples from the Roșia Poieni waste dump (stacked bar chart by sample).

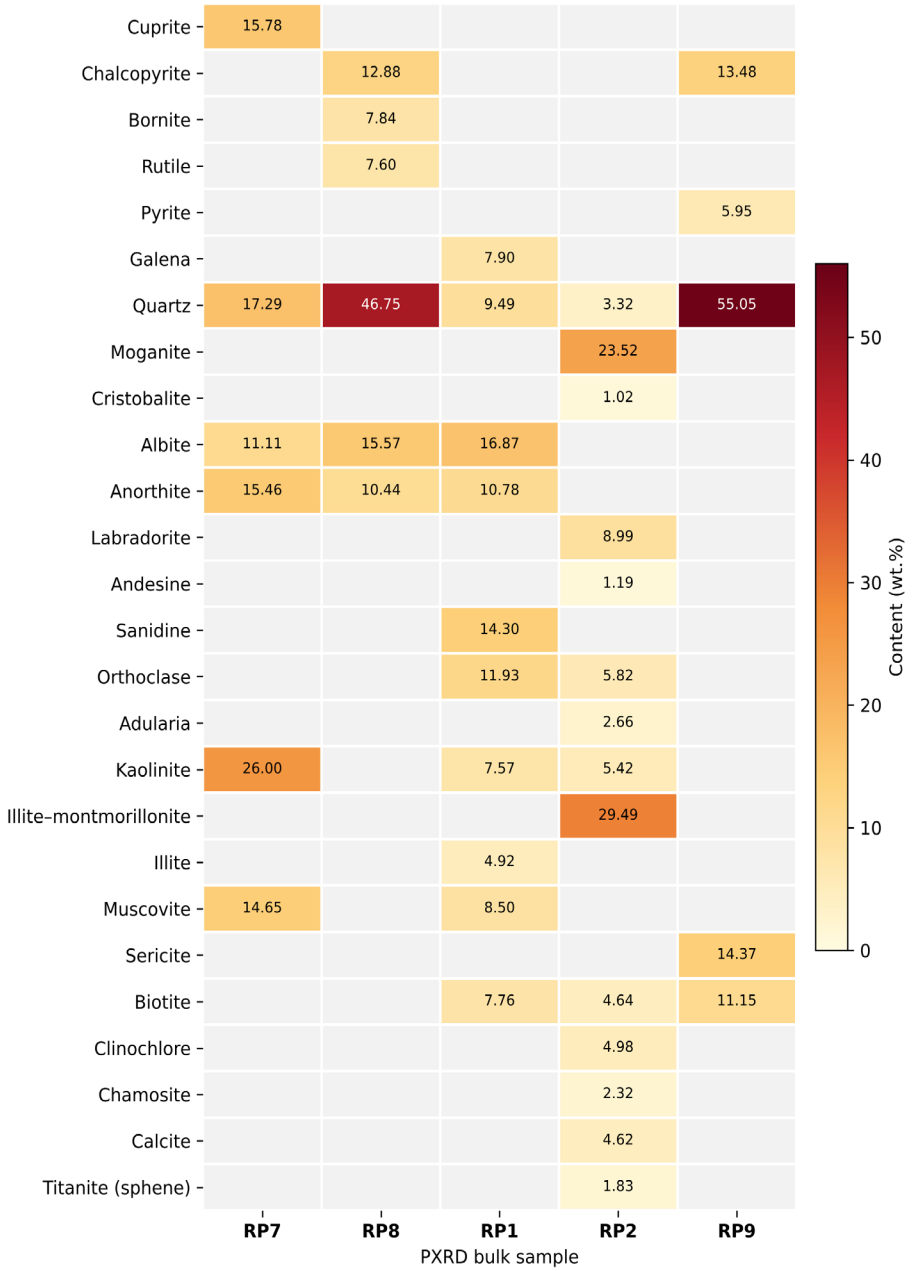


Figure 5. Heatmap of mineral phase distribution (%) across the XRD bulk samples from the Roșia Poieni waste dump.

While the presence of Cu-bearing mineral phases in RP7, RP8, and RP9 suggests that these materials may warrant further assessment for Cu recovery, the observed abundances are specific to the analysed samples (Figure 6). They cannot be used to infer the spatial distribution, average Cu concentration, or total recoverable Cu resources of the waste dumps. Additional systematic sampling and quantitative elemental analyses would be required to establish the extent and economic significance of Cu-bearing material across the deposits.

PCA was used as an exploratory visualisation of compositional contrasts among the five selected PXRD samples (Figure 6). Given the limited number of samples, the analysis is descriptive and is not intended to support statistical inference or population-level generalisation. In Figure 6, PC1 and PC2 jointly explain 70.9% of the total variance (PC1 45.9%, PC2 24.9%) (blue = Halda Veche samples; orange = Geamăna samples; the arrows show the mineral loading vectors with the strongest contribution to the first two components).

Phases detected only in RP2 have identical loadings and are therefore shown as a single grouped vector.

The PXRD dataset therefore supports the first component of the hypothesis: the Roșia Poieni waste is mineralogically heterogeneous and contains Cu-bearing phases concentrated in specific samples, particularly RP7, RP8, and RP9. At the same time, the occurrence of pyrite, clay minerals, and carbonates provides mineralogical information relevant to environmental behaviour.

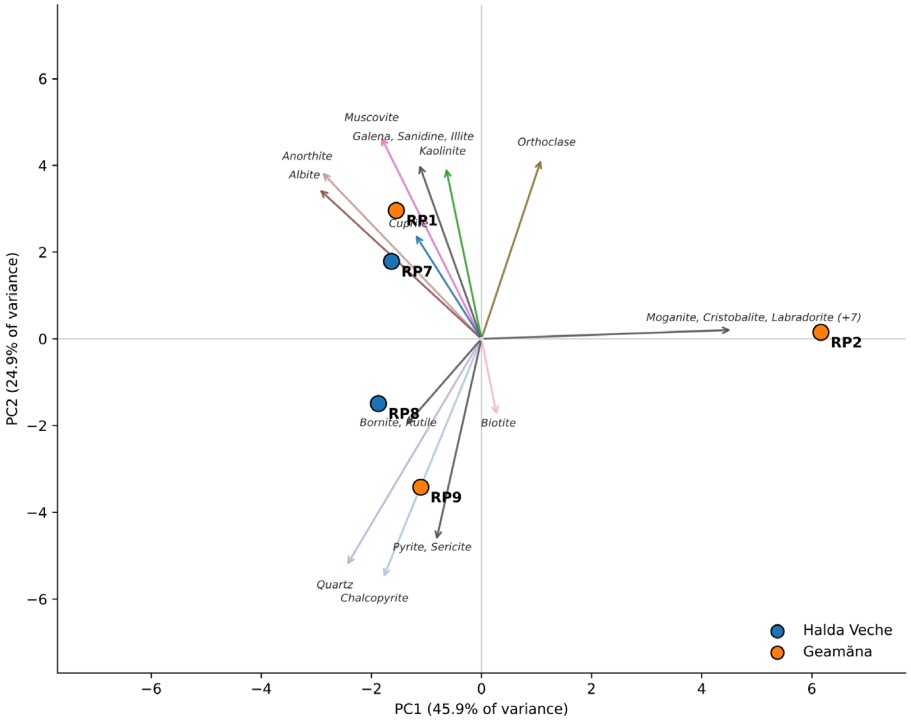


Figure 6. Principal component analysis (PCA) biplot of the five XRD bulk samples, based on standardised mineralogical composition.

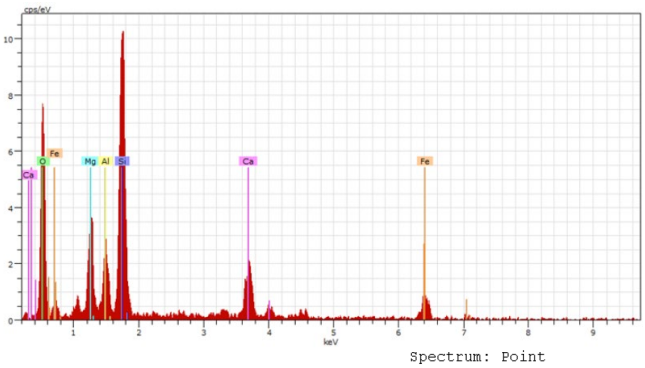
3.2. SEM-EDS Analyses of Selected Samples from Roșia Poieni

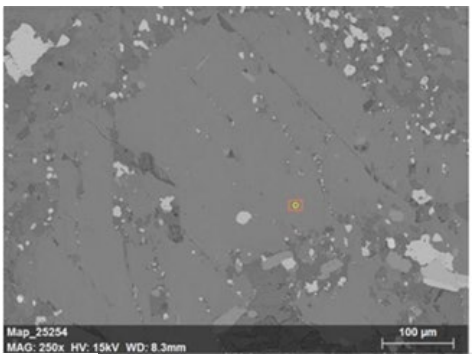
SEM-EDS analyses were performed on rock samples collected from Geamăna and Halda Veche perimeters from Roșia Poieni. These rocks were analysed macroscopically, then sliced and processed to obtain polished sections. Analysis of the polished sections confirmed many of the minerals identified by XRD, as well as some new ones briefly described in this paper. Figure 7 shows analyses of augite, bornite, phlogopite, apatite, and meionite.

SEM-EDS analyses (Figure 7) provided grain-scale compositional information for selected minerals and complemented the bulk XRD results. The reported spectra correspond to individual analysed spots and should therefore be interpreted as mineral-scale compositions rather than bulk waste dump concentrations (Table 4).

Augite contained Mg, Ca, Fe, Si, and Al in the analysed spot. Its main significance in this dataset is petrological: it records the silicate component of the waste matrix.

Bornite showed 55.25 wt.% Cu in the analysed EDS spot, together with Fe and S. This confirms the occurrence of a Cu-rich sulphide phase at grain scale and supports the XRD evidence for residual Cu-bearing minerals. Regulation (EU) 2024/1252 lists copper as both a critical and a strategic raw material, as it is essential for the energy industry and for the manufacture of electronic equipment and batteries.

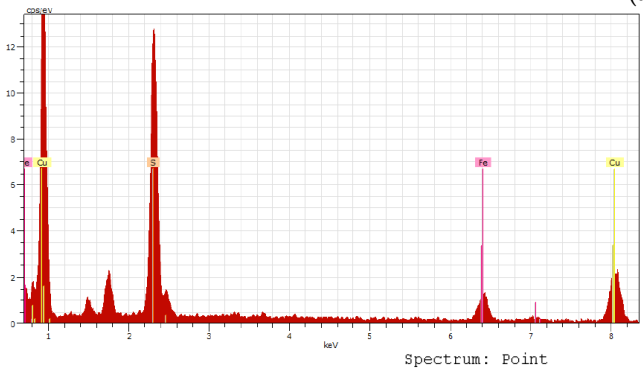


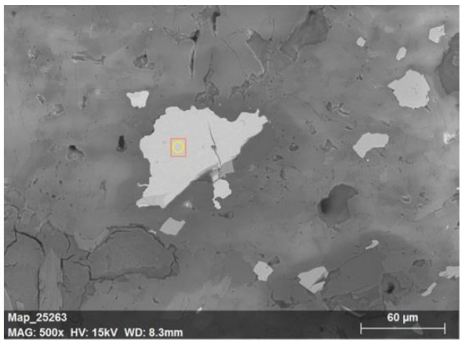


Spectrum: Point

Element	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Oxygen	8	K-series	43.17	45.46	62.20	7.2
Silicon	14	K-series	21.67	22.81	17.78	0.9
Magnesium	12	K-series	7.46	7.86	7.08	0.4
Calcium	20	K-series	8.31	8.75	4.78	0.3
Aluminium	13	K-series	5.07	5.34	4.33	0.3
Iron	26	K-series	9.29	9.79	3.84	0.3
Total:			94.98	100.00	100.00	

(**a**)

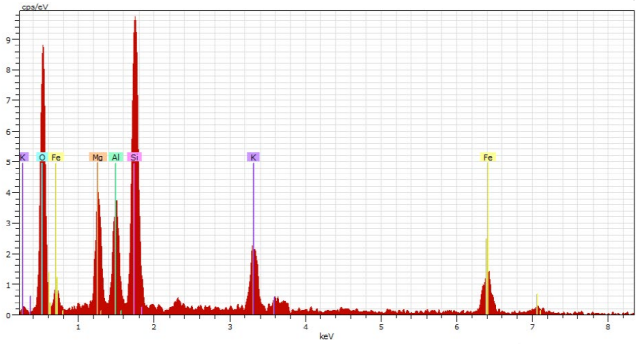


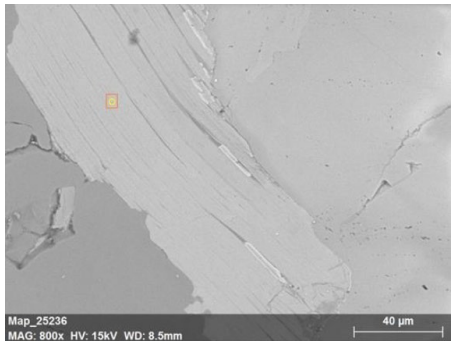


Spectrum: Point

Element	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Copper	29	K-series	47.17	55.25	38.84	1.5
Sulfur	16	K-series	20.54	24.06	33.52	0.7
Oxygen	8	K-series	4.75	5.56	15.54	1.0
Iron	26	K-series	12.92	15.13	12.10	0.4
Total:			85.38	100.00	100.00	

(**b**)



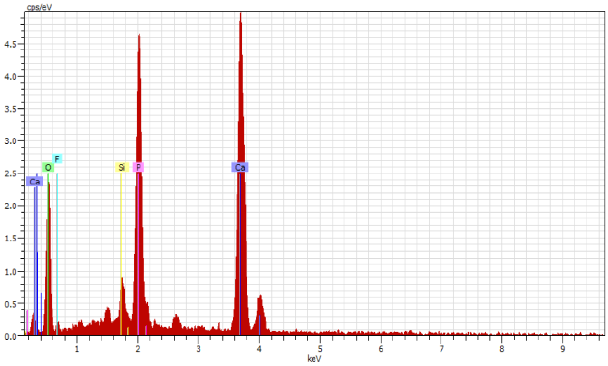


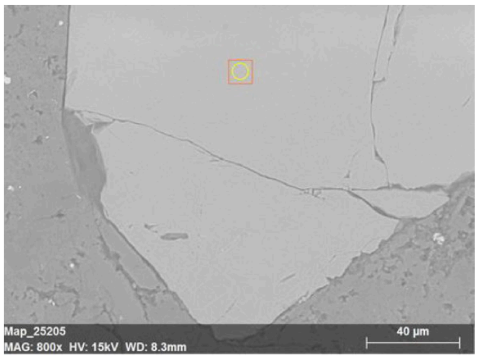
Spectrum: Point

Element	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Oxygen	8	K-series	36.80	43.91	62.56	5.3
Silicon	14	K-series	14.87	17.75	14.40	0.6
Iron	26	K-series	15.25	18.19	7.43	0.5
Magnesium	12	K-series	5.50	6.57	6.16	0.3
Aluminium	13	K-series	4.89	5.84	4.93	0.3
Potassium	19	K-series	6.49	7.74	4.51	0.2
Total:			83.81	100.00	100.00	

(**c**)

Figure 7. *Cont*.

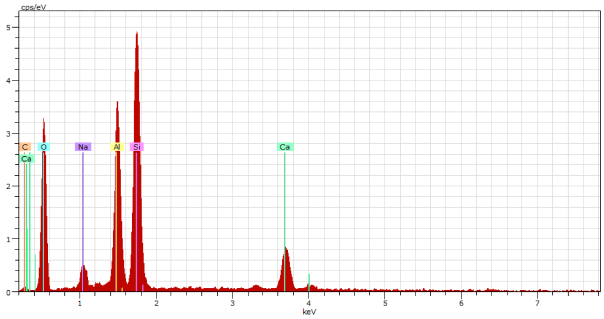




Spectrum: Point

Element	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Oxygen	8	K-series	43.93	45.23	64.34	7.0
Calcium	20	K-series	35.43	36.47	20.71	1.1
Phosphorus	15	K-series	13.08	13.46	9.89	0.5
Fluorine	9	K-series	2.86	2.95	3.53	1.0
Silicon	14	K-series	1.83	1.88	1.53	0.1
		Total:	97.13	100.00	100.00	

(**d**)





Spectrum: Point

Element	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [%]
Oxygen	8	K-series	46.44	47.76	60.15	6.3
Silicon	14	K-series	22.66	23.30	16.72	1.0
Aluminium	13	K-series	13.70	14.08	10.52	0.7
Carbon	6	K-series	3.36	3.46	5.80	1.2
Calcium	20	K-series	8.29	8.52	4.29	0.3
Sodium	11	K-series	2.80	2.88	2.53	0.2
		Total:	97.25	100.00	100.00	

(**e**)

Figure 7. SEM-EDS analysis of: (**a**) augite; (**b**) bornite; (**c**) phlogopite; (**d**) apatite; (**e**) meionite.

Table 4. SEM-EDS spectra on CRM from Roșia Poieni dumps.

Mineral	Key Elements Detected	Raw Material Relevance	Interpretation
bornite	Cu, S, Fe	Cu: critical and strategic	Cu-rich sulphide host
apatite	Ca, P, F	P/phosphate rock: critical	P-bearing mineral; bulk grade not established
phlogopite mica	Mg, Fe, K, Si	no direct CRM assignment	Gangue phyllosilicate (insulators, refractories, ceramics)
augite	Mg, Ca, Fe, Si	no direct CRM assignment	Gangue silicate
meionite	Ca, Al, Si, Na	no direct CRM assignment	Gangue silicate (industrial use—glass, ceramics)

The reported phlogopite spectrum was dominated by O, Fe, Si, K, Mg, and Al. Phlogopite is known for its refractory and insulating properties and is used in the construction industry and in electrical equipment. Phlogopite is not classified as a critical raw material; in the present dataset, its significance is primarily mineralogical.

The analysed apatite spot contained 13.46 wt.% P, 36.47 wt.% Ca, and 2.95 wt.% F. This observation is relevant because phosphorus and phosphate rock are included in the EU critical raw material list. Phosphorus, increasingly cited as a potential CRM, gives apatite a strategic role in agriculture and biotechnology, increasing its economic value considering the current global demand for nutritional resources.

The heatmap in Figure 8 compares the elemental content in SEM-EDS-analysed minerals, highlighting concentrations of critical elements such as Cu, P, Ca, Fe, etc.

SEM-EDS confirms that selected grains host economically relevant elements at the microscale. Most notably, the analysed bornite grain contained 55.25 wt.% Cu, while apatite contained 13.46 wt.% P. These measurements support phase identification and demonstrate mineral-scale element hosting, but they are not representative bulk concentrations and should not be used alone to calculate resource grades.

The augite, phlogopite, and meionite analyses document the chemically diverse silicate matrix surrounding the ore-related phases. This gangue mineralogy is relevant to future processing because it can influence comminution, separation, reagent consumption, and environmental behaviour, although these process effects were not experimentally tested in the present study.

Taken together, SEM-EDS and XRD resolve complementary scales of heterogeneity: XRD quantifies bulk mineral assemblages, whereas SEM-EDS verifies the composition of selected grains. This combination strengthens phase identification without extending interpretation beyond the analytical scale of the measurements.

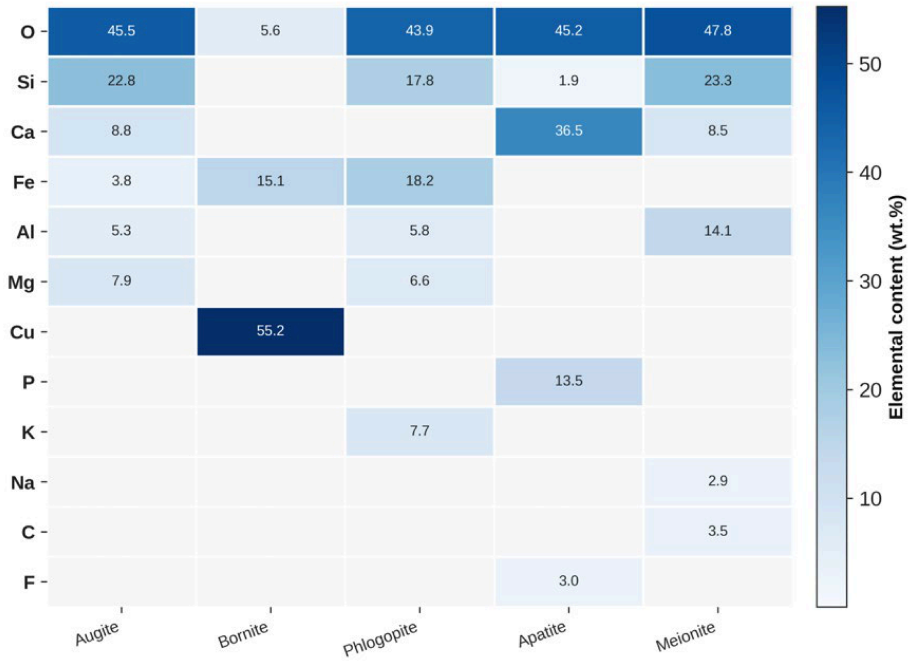


Figure 8. Heatmap of SEM-EDS elemental composition (wt.%) of representative minerals from the Roșia Poieni waste dump.

3.3. Raman Analyses of Selected Samples from Roșia Poieni

Raman spectroscopy was used as a complementary, non-destructive method for identifying selected mineral phases and alteration products. Its principal role in this study

is to structurally confirm phases relevant to sulphide oxidation, acid buffering, and post-depositional mineral transformation.

Raman spectroscopy identified several minerals with geochemical relevance or potential environmental impact. The spectral characteristics and importance of each mineral are briefly presented in Figure 9 and detailed below:

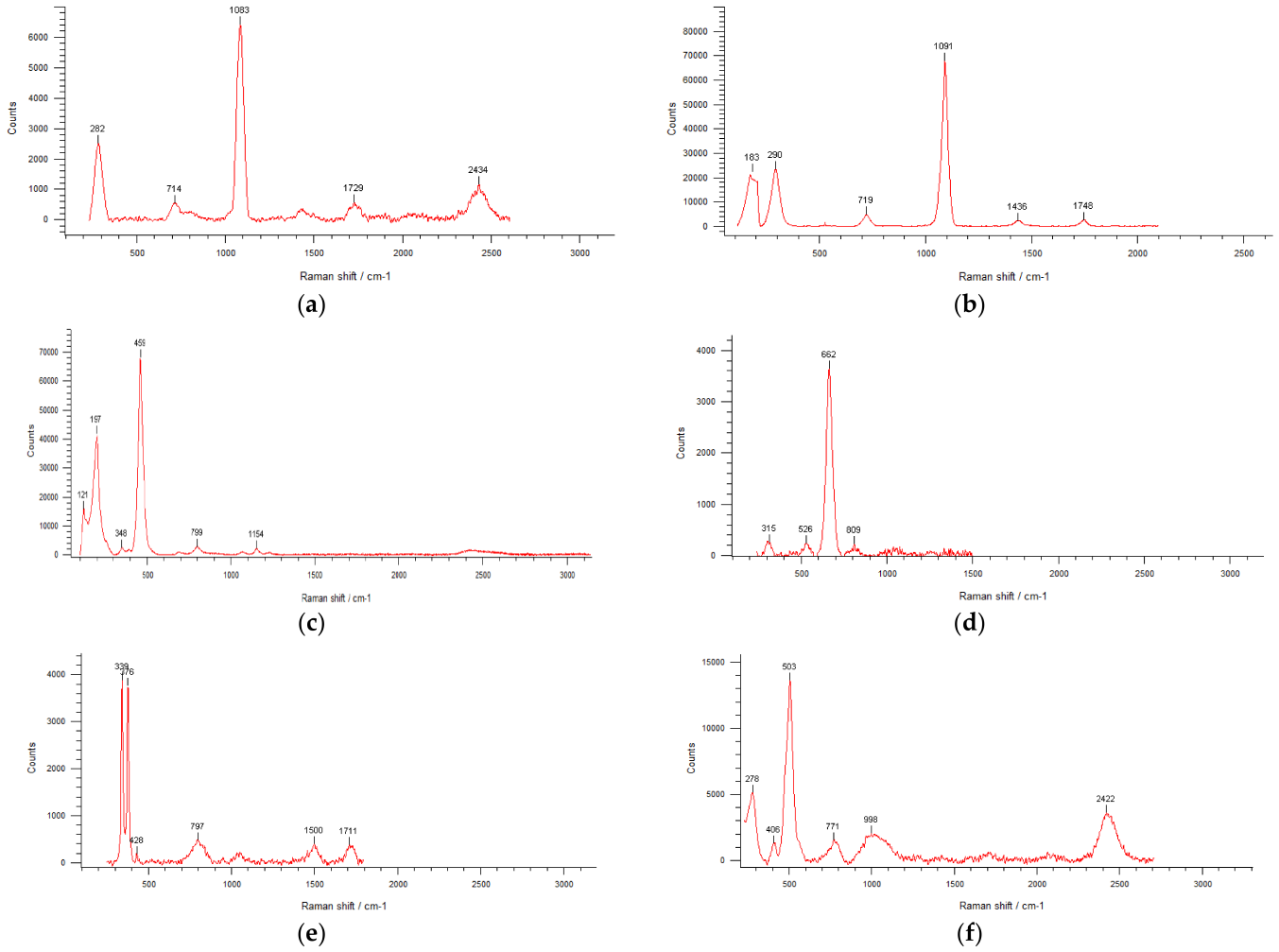


Figure 9. Raman spectrum for: (**a**) calcite; (**b**) dolomite; (**c**) melanterite; (**d**) magnetite; (**e**) pyrite; (**f**) anorthite.

Calcite shows characteristic bands at 282, 714, 1083, 1729, and 2434 cm^{-1}, with the 1083 cm^{-1} band representing the specific signature of calcium carbonate. Although it is not considered a critical mineral (CRM), calcite has an important role in neutralising acids and can act as a geochemical buffer in acidic environments.

Dolomite is distinguished by bands at 183, 290, 719, 1091, 1436, and 1748 cm^{-1}, and bands below 300 cm^{-1} allow it to be differentiated from calcite. It is a geochemically stable mineral that plays an important role in maintaining pH balance and can be used in environmental remediation processes.

Melanterite has a characteristic spectrum with bands at 121, 197, 348, 459, 799, and 1154 cm^{-1}, specific to hydrated ferrous sulphate ($FeSO_4 \cdot 7H_2O$). This mineral is a clear indicator of sulphur mineral oxidation and can contribute to acid mine drainage (AMD), making it important for assessing contamination risks.

Magnetite is identified by bands at 315, 526, 682, and 809 cm^{-1}, with the intense band at 682 cm^{-1} typical of Fe_3O_4. Although it is not a CRM, magnetite can contain valuable

metallic impurities such as titanium or vanadium and has industrial applications due to its ferromagnetic properties.

Pyrite has bands at 328, 339, 797, 1500, and 1711 cm^{-1}, with bands below 400 cm^{-1} corresponding to Fe–S bond vibrations. Although it is not a critical mineral, pyrite plays an essential role in the oxidation, leaching, and mobilisation processes of metals from mining wastes.

Anorthite, specific to the calcium-rich plagioclase feldspars, has bands at 278, 406, 503, 771, 998, and 2422 cm^{-1}. This mineral is widely used in industries such as ceramics and glass but has no value from a critical-resources perspective.

The Raman-identified phases (Table 5) provide complementary information on the potential environmental behaviour of the investigated waste material. Melanterite is a secondary Fe sulphate associated with sulphide oxidation and therefore provides mineralogical evidence of oxidative alteration. Pyrite is environmentally relevant because its oxidation is a major contributor to acid mine drainage in sulphidic mine wastes [17–19]. In contrast, calcite and dolomite can contribute to acid neutralisation through carbonate dissolution. The coexistence of sulphides, secondary sulphates, and carbonate minerals therefore indicates the potential for competing acid-generating and acid-neutralising processes within the waste dumps. Magnetite and anorthite are interpreted primarily as components of the mineralogical matrix, and their identification alone does not demonstrate contaminant release or resource recoverability. These mineralogical observations provide a basis for subsequent kinetic leaching, acid-base accounting, speciation, and remediation studies.

Table 5. The relevance of minerals in the context of CRM.

Mineral	EU Raw Material Relevance	Environmental/Mineralogical Relevance	Interpretation
pyrite	no direct CRM designation	principal sulphide relevant to AMD	environmental indicator/acid-generating phase
chalcopyrite	hosts Cu (critical and strategic)	principal Cu-bearing sulphide	resource-relevant host mineral
bornite	hosts Cu (critical and strategic)	Cu-rich sulphide	resource-relevant host mineral
apatite	hosts P/phosphate (critical)	P-bearing phosphate mineral	potential resource indicator; bulk grade needed
melanterite	no direct CRM designation	secondary Fe sulphate; oxidation indicator	environmental alteration phase
magnetite	no direct CRM designation	Fe oxide; may host trace elements	matrix phase; trace hosting not quantified

The Raman results therefore complement the XRD and SEM-EDS observations by structurally confirming mineral phases associated with sulphide alteration and geochemical buffering in the Roșia Poieni waste dumps. Together, these observations support the environmental component of the working hypothesis by showing that mineralogical heterogeneity encompasses both potentially acid-generating phases and acid-neutralising phases. Figure 10 summarises the relationships between the identified mineral groups, their principal geochemical processes, and their implications for resource recovery and environmental behaviour.

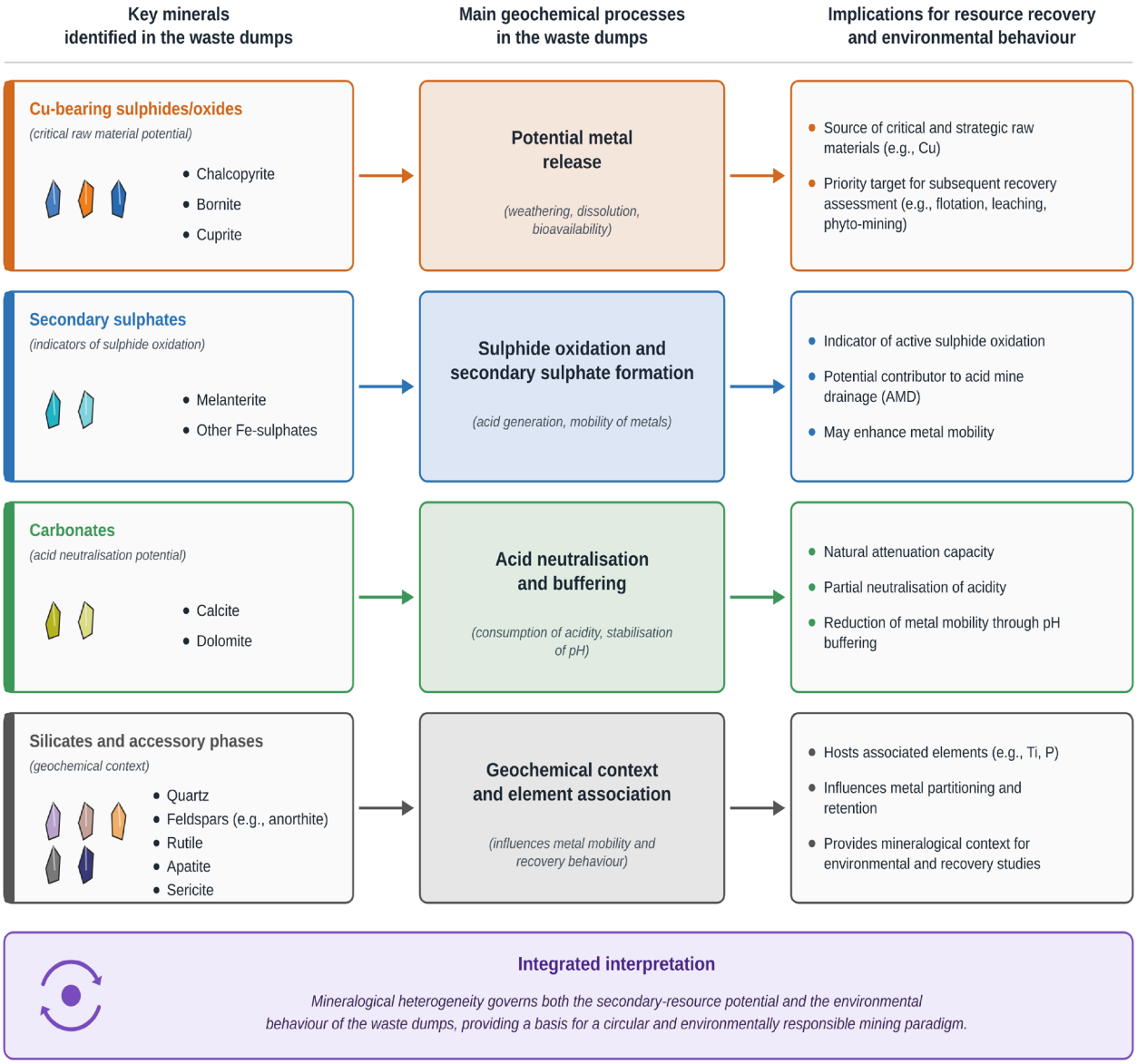


Figure 10. Conceptual framework linking the key mineral groups identified in the Roșia Poieni waste dumps to their main geochemical processes and their implications for resource recovery and environmental behaviour.

4. Discussion

4.1. Mineralogical Heterogeneity and Secondary-Resource Potential

The central hypothesis predicts that mineralogical heterogeneity should control both secondary-resource potential and environmental behaviour. The XRD results support the resource component of this hypothesis by showing that Cu-bearing phases are unevenly distributed among the analysed samples. RP8 contains 12.88% chalcopyrite and 7.84% bornite, RP9 contains 13.48% chalcopyrite, and RP7 contains 15.78% cuprite. These contrasts show that Cu-bearing phases are concentrated in specific samples rather than uniformly distributed in the analysed material; their spatial extent within the waste dumps remains to be established. This heterogeneity is consistent with the broader view that mine waste dumps valorisation requires mineralogical and process-specific characterisation before selecting recovery routes [10,11,20].

The mineralogical assemblage identified in the Roșia Poieni waste dumps includes several phases hosting raw materials classified as critical or strategic under Regulation (EU)

2024/1252 [8]. Copper-bearing phases include chalcopyrite, bornite, and cuprite, while rutile and apatite represent Ti- and P-bearing phases, respectively. Copper and titanium metal are classified as both critical and strategic raw materials, whereas phosphorus and phosphate rock are included among the EU critical raw materials [8]. Accordingly, the occurrence of chalcopyrite, bornite, cuprite, rutile, and apatite identifies mineral hosts associated with raw materials of critical and/or strategic relevance. Their presence and distribution within the waste dumps provide a mineralogical basis for assessing the secondary-resource potential of the investigated material, while mineral occurrence alone does not establish technical or economic recoverability.

SEM-EDS provides independent grain-scale support for this interpretation. The analysed bornite spot contains 55.25 wt.% Cu, confirming a Cu-rich sulphide host, while the apatite spot contains 13.46 wt.% P. Because EDS spot analyses are local measurements, these values cannot be extrapolated to bulk grades. Nevertheless, in combination with XRD, they show why a mineralogy-led approach is necessary: bulk abundance and grain-scale composition answer different questions and together provide a more defensible basis for selecting material for future beneficiation or hydrometallurgical testing [21].

Overall, the mineralogical evidence identifies Cu-bearing phases as clear targets for subsequent resource recovery assessment, while the occurrence of rutile and apatite indicates additional Ti- and P-bearing phases that warrant further geochemical and recovery evaluation (Figure 11).

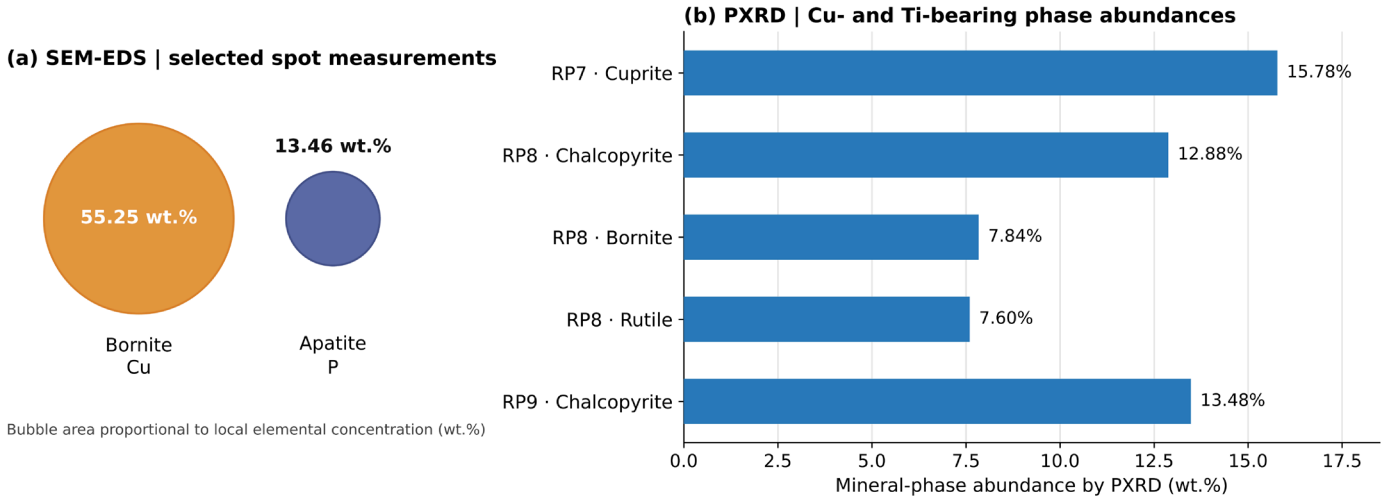


Figure 11. Complementary SEM-EDS and PXRD evidence for selected mineral phases relevant to secondary raw material recovery in the Roșia Poieni mining waste. (**a**) Local elemental concentrations (wt.%) determined by SEM-EDS spot analyses, with bubble areas proportional to the measured values. (**b**) Reported relative abundances (%) of selected Cu- and Ti-bearing mineral phases determined by PXRD. Note: The two datasets are shown separately because they reflect different analytical parameters and spatial scales. SEM-EDS spot concentrations should not be interpreted as bulk elemental grades.

Although the identification of Cu-bearing minerals such as chalcopyrite, bornite, and cuprite indicates the presence of potentially valuable mineral phases in the investigated mining waste, their occurrence alone does not demonstrate the existence of economically recoverable resources. The PXRD results provide information on mineralogical composition, whereas SEM-EDS analyses characterise the local elemental composition of selected mineral grains and cannot be directly extrapolated to the bulk material. Consequently, the results should be interpreted as a preliminary assessment of mineralogical potential rather than evidence of technical or economic recoverability. Further investigations involving representative bulk geochemical analyses, mineral liberation studies, and metallurgical recovery

tests are required to determine metal grades, extraction efficiencies, and the feasibility of secondary-resource valorisation.

4.2. Mineralogical Controls on Environmental Behaviour

The same heterogeneity that creates resource potential also affects environmental behaviour. Pyrite and other sulphides provide an acid-generating component, whereas Raman spectroscopy identified melanterite, indicating oxidative alteration of Fe sulphides. Mineral oxidation, water–rock interaction, and secondary-mineral precipitation govern AMD formation and evolution in sulphidic waste dumps [17,22], and remediation commonly requires strategies that limit sulphide oxidation, neutralise acidity, or manage contaminated drainage [18]. The Roșia Poieni assemblage is therefore environmentally relevant even without inferring metal mobility directly from mineral identification.

The identification of pyrite, melanterite, and carbonate minerals provides important mineralogical indications of potential environmental processes associated with mining waste. Pyrite oxidation may contribute to acid generation, whereas carbonate minerals, particularly calcite and dolomite, may provide acid-neutralising capacity. The occurrence of melanterite may indicate sulphide oxidation and secondary sulphate formation. However, the presence of these mineral phases alone does not demonstrate the actual occurrence, intensity, or environmental consequences of such processes. Without leaching experiments, acid-base accounting, and geochemical monitoring, the environmental behaviour of the investigated materials cannot be quantitatively assessed. Therefore, these findings should be interpreted as preliminary mineralogical indicators of potential environmental reactivity rather than direct evidence of acid mine drainage or contaminant mobilisation.

The environmental significance of the identified mineral phases depends not only on elemental concentrations, but also on the potential mobility and availability of the associated elements. This distinction is particularly relevant in mining-affected environments, where pseudo-total concentrations and labile fractions may provide different perspectives on PTE-related risks, while their spatial distribution can help identify potential dispersion pathways [23]. More broadly, the continued recognition of PTEs such as heavy metals as an important soil threat across Europe highlights the value of combining baseline characterisation with approaches that address contaminant mobility [24,25]. In this context, the mineralogical assemblage identified at Roșia Poieni provides insight into the phases potentially involved in elemental release, retention, and geochemical buffering. However, mineralogical evidence alone cannot quantify elemental mobility or bioavailability; these processes would require complementary approaches such as sequential extraction, porewater analysis and leaching experiments.

4.3. Implications for Sustainable Recovery and Environmental Stewardship

The combined results support an integrated management concept that evaluates resource recovery and environmental stewardship together. Cu-bearing materials represented by samples RP7, RP8, and RP9 merit targeted recovery testing, while pyrite- and melanterite-bearing material merits particular attention in environmental characterisation. Conversely, carbonate- and clay-rich materials may influence buffering, permeability, and sorption. This selective management aligns with circular economy approaches that recover value from mine wastes while reducing long-term liabilities [10,11].

The integrated mineralogical characterisation provides a basis for evaluating the dual significance of the Roșia Poieni waste dumps as a potential secondary resource and as a material whose environmental behaviour is likely to be influenced by a heterogeneous mineral assemblage. The occurrence of Cu-, Ti-, and P-bearing phases supports further assessment of resource potential, while the coexistence of sulphides, secondary sulphate minerals, and

carbonate phases indicates that elemental release may be governed by competing oxidation, dissolution, and buffering processes. Quantifying these processes requires complementary information on bulk elemental concentrations, mineral liberation, element mobility, and recovery efficiency. In this context, validated bulk-chemical analyses, mineral liberation studies, sequential extraction and leaching experiments, acid-base accounting, and recovery tests would provide the necessary link between the mineralogical evidence presented here and the actual mobility and recoverability of the elements of interest. Such an integrated approach is particularly relevant where sulphide oxidation may promote acid mine drainage (AMD), because its environmental impact depends on site-specific mineralogy and geochemistry as well as on the balance between acid-generating and acid-neutralising reactions. Accordingly, AMD management strategies generally combine treatment and waste management measures adapted to local conditions rather than relying on a single universally applicable solution [18]. These considerations support the working hypothesis that mineralogical heterogeneity is central to both the secondary-resource potential and the environmental behaviour of the Roșia Poieni waste dumps, while defining the additional experimental evidence required to quantify these two dimensions.

The mineralogical heterogeneity identified in the Roșia Poieni waste dumps also provides a relevant framework for evaluating future resource recovery strategies based on assisted phyto-mining. The occurrence of Cu-bearing phases, together with secondary alteration products, indicates that Cu availability to plants likely depends on mineral dissolution, weathering, and associated geochemical conditions rather than solely on bulk metal concentrations. This is particularly relevant to plant-assisted recovery strategies, where metal bioavailability, plant tolerance and accumulation, biomass production, and interactions between plants and the contaminated substrate determine process efficiency [26–28]. Assisted approaches may further enhance phyto-extraction by increasing contaminant availability or improving plant performance, although their effectiveness depends on site-specific soil properties, plant species, and environmental conditions [27]. Consequently, the mineralogical baseline established in this study can support selecting suitable plant species and designing subsequent experiments addressing metal availability, plant tolerance, biomass production, uptake, and translocation [29]. In this context, assisted phyto-mining represents a potential downstream application of the present mineralogical characterisation, while its recovery efficiency at Roșia Poieni will depend on the interaction between mineral-specific metal availability and plant performance. More broadly, nature-based and biomimetic approaches are increasingly explored across diverse environmental remediation contexts, from assisted metal phytoextraction in contaminated soils to pathogen control [30], underscoring the wider relevance of plant-derived solutions to environmental management.

The environmental behaviour of these mineral assemblages may also be sensitive to changing climatic conditions. In mine wastes, variations in precipitation, temperature, wetting–drying cycles, and hydrological conditions can influence mineral weathering, sulphide oxidation, leaching, and the subsequent transport of potentially toxic elements. The coexistence of primary sulphides, secondary alteration phases, and carbonate minerals identified in the Roșia Poieni waste dumps therefore provides a mineralogical basis for investigating how changes in water availability and oxidation conditions could modify elemental mobilisation and retention. These interactions are particularly relevant where sulphide oxidation promotes acid generating reactions, while carbonate-bearing phases contribute to acid neutralisation processes. Field monitoring combined with controlled weathering and leaching experiments under defined environmental conditions would allow these mineralogical controls to be evaluated under climate-relevant scenarios. Thus, the present results establish a baseline for future assessment of climate-sensitive mobilisation processes without attributing the observed mineralogical patterns directly to climate-driven effects.

4.4. Limitations

The present study focuses on mineralogical and grain-scale characterisation and should therefore be interpreted within this analytical scope. Although the investigated samples capture relevant mineralogical heterogeneity, broader spatial assessment, and complementary bulk geochemical, mobility and recovery studies would further strengthen the evaluation of resource potential and environmental behaviour. Nevertheless, the convergence of XRD, SEM-EDS, and Raman results provides consistent mineralogical support for the central hypothesis, linking heterogeneous Cu-bearing phases to potential secondary-resource targets and identifying sulphides, secondary alteration phases, and carbonates as relevant controls on environmental behaviour. The detailed quantitative dataset presented here focuses on five representative samples selected from a larger field set of ten, chosen to represent contrasting mineralogical assemblages (Section 3.1); the remaining five samples (RP3–RP6 and RP10) are not included in the reported PXRD percentages. This selection strategy means that the reported ranges (e.g., 12.88–13.48% chalcopyrite, up to 15.78% cuprite) should be regarded as indicative of the heterogeneity observed within the most contrasting samples rather than as a statistically representative average of the entire waste dump, and the true proportion of Cu-rich versus low-grade material across the site remains to be established. In addition, no laboratory bulk elemental data (e.g., ICP-MS) are yet available for these samples; the field pXRF measurements served only for screening, so Cu, Ti, and P grades of the waste material cannot be estimated from the present dataset. Extending quantitative phase analysis, together with analytical replicates, to the full sample set, and broadening the sampling grid, would be required to convert the present qualitative heterogeneity assessment into a statistically defensible estimate of resource potential across the Roșia Poieni waste dumps.

5. Conclusions

Integrated XRD, SEM-EDS, and Raman characterisation revealed pronounced mineralogical heterogeneity in the Roșia Poieni copper waste dumps. Among the five bulk samples analysed by PXRD, chalcopyrite contents ranged from 12.88% to 13.48%, while bornite and rutile reached values of up to 7.84% and 7.60%, respectively, and cuprite reached up to 15.78%. SEM-EDS further confirmed Cu-rich bornite at grain scale (55.25 wt.% Cu in the analysed spot), while Raman spectroscopy identified secondary alteration products, including melanterite, together with carbonate phases associated with geochemical buffering.

The complementary analytical evidence is consistent with the central hypothesis that mineralogical heterogeneity influences both the secondary-resource potential and the environmental behaviour of these waste dumps. The heterogeneous distribution of Cu-bearing sulphides and oxides identifies mineralogical targets of interest for resource recovery, whereas the coexistence of sulphides, secondary sulphates, carbonates, and clay minerals reflects contrasting processes associated with sulphide oxidation, acid buffering, and elemental retention. In the context of Regulation (EU) 2024/1252, the identified Cu-, Ti-, and P-bearing minerals also host raw materials of critical and/or strategic relevance [8].

The contrasting sulphide-rich and oxide-rich Cu assemblages identified in RP8/RP9 and RP7, respectively, provide a rationale for testing different recovery routes in subsequent beneficiation and hydrometallurgical studies. Establishing recoverable resources will, however, require representative bulk geochemical data, mineral liberation analysis, and metallurgical testing.

Overall, the Roșia Poieni waste dumps represent a heterogeneous secondary material in which resource potential and environmental behaviour are linked through mineralogical composition. The integrated mineralogical framework established in this study provides a scientific basis for targeting Cu-bearing materials, such as those represented by RP7, RP8,

and RP9, for subsequent recovery assessment while simultaneously identifying mineral assemblages relevant to environmental monitoring and sustainable mine waste management.

From an environmental perspective, the occurrence of pyrite, melanterite, and carbonate minerals highlights the potential for both acid-generating and acid-neutralising reactions within the investigated mining waste. Nevertheless, these mineralogical observations do not provide direct evidence of acid mine drainage, contaminant release, or effective neutralisation under field conditions. Additional assessments, including leaching experiments, acid-base accounting, and geochemical monitoring, are necessary to determine the actual environmental behaviour of these materials. Further geochemical, mobility, and recovery investigations can build on this framework to advance the transition from mineralogical characterisation towards integrated resource recovery and environmental stewardship.

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Geissdoerfer, M.; Savaget, P.; Bocken, N.M.P.; Hultink, E.J. The Circular Economy—A new sustainability paradigm? *J. Clean. Prod.* **2017**, *143*, 757–768. [CrossRef]
2. Kirchherr, J.; Reike, D.; Hekkert, M. Conceptualizing the circular economy: An analysis of 114 definitions. *Resour. Conserv. Recycl.* **2017**, *127*, 221–232. [CrossRef]
3. Makhathini, T.P.; Bwapwa, J.K.; Mtsweni, S. Various Options for Mining and Metallurgical Waste in the Circular Economy: A Review. *Sustainability* **2023**, *15*, 2518. [CrossRef]
4. International Energy Agency (IEA). *Global Critical Minerals Outlook 2024*; IEA: Paris, France, 2024. Available online: https://www.iea.org/reports/global-critical-minerals-outlook-2024 (accessed on 20 October 2026).
5. Helbig, C.; Bradshaw, A.M.; Kolotzek, C.; Thorenz, A.; Tuma, A. Supply risks associated with CdTe and CIGS thin-film photovoltaics. *Appl. Energy* **2016**, *178*, 422–433. [CrossRef]
6. Milu, V.; Milesi, J.-P.; Leroy, J.L. Roșia Poieni copper deposit, Apuseni Mountains, Romania: Advanced argillic overprint of a porphyry system. *Miner. Depos.* **2004**, *39*, 173–188. [CrossRef]
7. Berbeleac, I.; Săbău, G.; Pintea, I.; Nuțu-Dragomir, M.-L.; Udubașa, S.S.; Refec, I. Neogene porphyry systems in South Apuseni Mountains (Romania): An overview. *Rev. Roum. Géophys.* **2018**, *61–62*, 3–30.
8. European Parliament and Council of the European Union. Regulation (EU) 2024/1252 of 11 April 2024 establishing a framework for ensuring a secure and sustainable supply of critical raw materials (Critical Raw Materials Act). *Off. J. Eur. Union* **2024**. Available online: https://eur-lex.europa.eu/eli/reg/2024/1252/oj/eng (accessed on 20 October 2026).

9. Lewicka, E.; Guzik, K.; Galos, K. On the Possibilities of Critical Raw Materials Production from the EU's Primary Sources. *Resources* **2021**, *10*, 50. [CrossRef]
10. Tayebi-Khorami, M.; Edraki, M.; Corder, G.; Golev, A. Re-Thinking Mining Waste through an Integrative Approach Led by Circular Economy Aspirations. *Minerals* **2019**, *9*, 286. [CrossRef]
11. Kinnunen, P.; Karhu, M.; Yli-Rantala, E.; Kivikytö-Reponen, P.; Mäkinen, J. A review of circular economy strategies for mine tailings. *Clean. Eng. Technol.* **2022**, *8*, 100499. [CrossRef]
12. Van Zyl, D.; Shields, D.; Agioutantis, Z.; Joyce, S. Waste not, want not—Rethinking the tailings and mine waste issue. *AusIMM Bull.* **2016**, *6*, 38–40.
13. Borcoș, M.; Vlad, Ș.; Udubașa, G.H.; Găbudeanu, B. Qualitative and Quantitative Metallogenetic Analysis of the Ore Genetic Units in Romania. *Rom. J. Miner. Depos.* **1998**, *78*, 7–107.
14. Wavrer, P.; Morvan, B.; Louis-Rose, S. A European standard for sampling of waste material: EN 14899. *TOS Forum* **2015**, *5*, 221.
15. Report CEN/TR 16376:2012, Characterization of Waste—Overall Guidance Document for Characterization of Waste from the Extractive Industries. Available online: https://standards.iteh.ai/catalog/standards/cen/796ac165-c65d-4448-b06b-4b796651ecad/cen-tr-16376-2012?srsltid=AU7gw4VHC5ie8Lt_b5xeOIIUPHfu52czXN_5oUquZfgCZ6SQ53tMh-0N (accessed on 20 October 2026).
16. Gray, C.A.; Van Rythoven, A.D. A Comparative Study of Porphyry-Type Copper Deposit Mineralogies by Portable X-ray Fluorescence and Optical Petrography. *Minerals* **2020**, *10*, 431. [CrossRef]
17. Dold, B. Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals* **2014**, *4*, 621–641. [CrossRef]
18. Thisani, S.K.; Kallon, D.V.V.; Byrne, P. Review of Remediation Solutions for Acid Mine Drainage Using the Modified Hill Framework. *Sustainability* **2021**, *13*, 8118. [CrossRef]
19. Li, Z.; Sun, F.; Jiang, W.; Li, X.; Jiang, J.; Jin, F.; Lu, J.; Yang, F. Bibliometric Analysis of Trends and Research Progress in Acid Mine Drainage Remediation from 1990 to 2023. *Water* **2024**, *16*, 1826. [CrossRef]
20. Mancini, S.; Casale, M.; Tazzini, A.; Dino, G.A. Use and Recovery of Extractive Waste and Tailings for Sustainable Raw Materials Supply. *Mining* **2024**, *4*, 149–167. [CrossRef]
21. Sedda, L.; De Giudici, G.; Fancello, D.; Podda, F.; Naitza, S. Unlocking Strategic and Critical Raw Materials: Assessment of Zinc and REEs Enrichment in Tailings and Zn-Carbonate in a Historical Mining Area (Montevecchio, SW Sardinia). *Minerals* **2024**, *14*, 3. [CrossRef]
22. Delgado, J.; Lozano, O.; Ayala, D.; Martín, D.; Barba-Brioso, C. Geochemistry and Mineralogy of Precipitates from Passive Treatment of Acid Mine Drainage: Implications for Future Management Strategies. *Minerals* **2025**, *15*, 15. [CrossRef]
23. Popescu, I.; Stănescu, R.; Biasioli, M.; Ajmone Marsan, F.; Constantinescu, I. Assessing human risks through CSOIL exposure model for a soil contamination associated to heavy metals. *Univ. Politeh. Buchar. Sci. Bull. Ser. B* **2013**, *75*, 81–94.
24. Binner, H.; Sullivan, T.; Jansen, M.A.K.; McNamara, M.E. Metals in urban soils of Europe: A systematic review. *Sci. Total Environ.* **2023**, *854*, 158734. [CrossRef]
25. Wan, Y.; Liu, J.; Zhuang, Z.; Wang, Q.; Li, H. Heavy Metals in Agricultural Soils: Sources, Influencing Factors, and Remediation Strategies. *Toxics* **2024**, *12*, 63. [CrossRef]
26. Sheoran, V.; Sheoran, A.S.; Poonia, P. Phytomining: A review. *Miner. Eng.* **2009**, *22*, 1007–1019. [CrossRef]
27. Balint, R.; Popescu Boajă, I. Assisted phytoextraction as a nature-based solution for the sustainable remediation of metal(loid)-contaminated soils. *Integr. Environ. Assess. Manag.* **2024**, *20*, 2003–2022. [CrossRef]
28. Akinpelu, E.A.; Nchu, F. Advancements in Phytoremediation Research in South Africa (1997–2022). *Appl. Sci.* **2024**, *14*, 7660. [CrossRef]
29. Mlalazi, N.; Mbohwa, C.; Ramuhaheli, S.; Chimwani, N. Towards Circularity and Sustainability: Phytoremediation Approaches, Legislative Challenges, and Bioenergy Potential in South African Mine Tailings Remediation. *Processes* **2025**, *13*, 3400. [CrossRef]
30. Grinzeanu, M.; Orbuleț, O.D.; Dăncilă, A.M.; Bobirică, C.; Modrogan, C.; Bobirică, L.; Pandele, M.A. Biomimetic Studies on the Antimicrobial Activity of Some Biocides Based on Garlic and Lavender in Surface Waters. *Biomimetics* **2024**, *9*, 591. [CrossRef]

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