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TITLE OF THE Ph.D. THESIS

First update of the regional database of storage facilities (mining and mining-metallurgical waste deposits) in Sardinia

GEO/09

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Table of Contents

Abstract

This doctoral thesis presents the first regional-scale inventory and geospatial database of mining and metallurgical waste deposits in Sardinia (Italy), developed within the framework of the ISPRA–UniCa GeoSciences IR project, funded by the Italian National Recovery and Resilience Plan (PNRR). The study addresses the growing interest in mining waste as a potential secondary source of Critical Raw Materials (CRMs), aligning with the objectives of the European Critical Raw Materials Act and the principles of the circular economy.

Sardinia, one of the most important historical mining regions in the Mediterranean, hosts a remarkable diversity of metallogenic systems and a long history of exploitation of Pb–Zn, Ag, Cu, Sb, W, and other mineral resources. As a result, the island is characterized by a large number of mining waste deposits derived from past extraction and processing activities. However, information on these deposits has historically been fragmented and dispersed across technical reports, archival documents, and non-standardised surveys.

To address this gap, a regional geodatabase of 1887 mining waste deposits was created through the integration of bibliographic research, archival data, historical mining cartography, and GIS-based spatial analysis. Each site was georeferenced and classified according to typology, geological setting, mining district, surface extent, and the potential presence of CRM-bearing mineral phases. The database provides, for the first time, a unified spatial and descriptive framework for the systematic evaluation of Sardinia's mining waste legacy.

Statistical analysis of the database reveals a strongly skewed distribution of dump surfaces, indicating that a limited number of large deposits dominate the cumulative mining-waste footprint at the regional scale. The spatial distribution of the dumps closely reflects the main metallogenic districts of the island and the historical organization of mining activities. Furthermore, the results highlight a clear relationship between waste typology, processing history, and the qualitative occurrence of critical raw materials within the deposits.

The thesis is structured as a compendium of three scientific contributions that investigate Sardinian mining waste deposits from complementary perspectives. The first is a critical review that synthesizes the current state of knowledge on the origin, typology, environmental impacts, and resource potential of mining wastes across the island, providing the conceptual foundation for the regional database. The second presents an original mineralogical and geochemical study of the Montevecchio mining district, focusing on the enrichment of zinc and rare earth elements (REEs) in both tailings and secondary biomineralizations along the Rio Roia Cani. The third contribution reports new data from a multi-analytical characterization of waste deposits in the Fluminése–Arburése district, documenting the occurrence of REE-bearing minerals (synchysite-(Ce)), fluorite, baryte, and elevated concentrations of Bi and Sb, and discussing the mineralogical controls on element distribution and the implications for potential recovery strategies.

Together, these contributions demonstrate that mining waste deposits in Sardinia are not only a significant environmental liability but also a potentially valuable secondary resource. The presence of critical elements such as REEs, Bi, Sb, Ba, and F, together with residual base metals, supports their consideration as targets for integrated valorization and remediation strategies, in line with the European Green Deal and the principles of the circular economy.

The research provides the first integrated and systematic framework for the identification, classification, and spatial analysis of mining waste deposits in Sardinia. The resulting geodatabase represents a fundamental tool for environmental monitoring, territorial planning, and the assessment of secondary mineral resources. Moreover, the methodological approach developed in this study is replicable and can be applied to other Italian and European regions with similar mining legacies, contributing to the broader goal of securing a sustainable and resilient supply of critical raw materials in the EU.

1. Introduction

This doctoral thesis was developed within the GeoSciences project, carried out by the Italian Institute for Environmental Protection and Research (ISPRA) and funded by the National Recovery and Resilience Plan (PNRR), Mission 4, Component 2, Investment 3.1 – Fund for the creation of an integrated system of research and innovation infrastructures.
The objective of the project was to reorganize, update and refine the existing mining data, to produce a new relational database on mineral resources and a new metallogenic map of Sardinia developed in digital format. The part developed in this doctoral thesis was focused particularly on identifying, mapping and recording the large number of waste dump bodies inherited from historical mining activities on the island, creating a dedicated database in which all available information is collected and organized, filling the current gap for such a regional-scale tool.
The current importance of identifying, characterizing and recording these deposits lies in the growing relevance of mining waste materials, which today are increasingly regarded as possible sources of critical raw materials essential to the development of modern societies.

- What Are Critical Raw Materials (CRMs)?

Mineral raw materials play a central role in the production of a wide range of everyday goods and applications, and they are involved in all stages of the supply chain in related industrial cycles. **Critical raw materials (CRMs)** are an important group defined as primary or processed natural resources considered essential for the economy and technological development in many countries of the Western world, including those in the EU, yet they also present a high supply risk (Figure 1). This risk stems from geopolitical, economic or environmental factors that may compromise the stable availability of such resources. According to the European Commission (*Grohol et al., 2023*), for a material to be classified as a CRM for the EU, it must exhibit:

1. <u>High economic importance</u>

CRMs are fundamental to numerous industrial, high-tech key sectors of EU industry, including:

- Electronics, ICT and Telecommunications;
- Renewable energy (e.g., wind turbines and solar panels);
- Defense and aerospace (speciality alloys, high-tech ceramics, etc.);
- Electric mobility (such as electric vehicle batteries).

2. Supply risk

Supply risk is associated with factors which affect the sustainability and continuity of supplies in the raw materials sector, penalizing productions and the value chains, such as:

- Strong concentration of production in a few countries (e.g., China, Russia, Congo D.R., etc.);
- Political instability;
- Extraction/processing issues and environmental constraints
- Trade issues (export taxes, export quotas, etc.).

3. Limited recycling and substitution

- Low- to very low or even null End-of-Life Recycling Input Rate (EoL RIR);
- Lacking economically and/or technically viable substitutes.

4. Growing demand forecasts

- An increase in demand for CRMs that is several times higher than the current levels is expected for the EU in the next 25 years, particularly driven by the battery market and by technological applications on renewable energy and aerospace/defense sectors (*Grohol et al., 2023*).

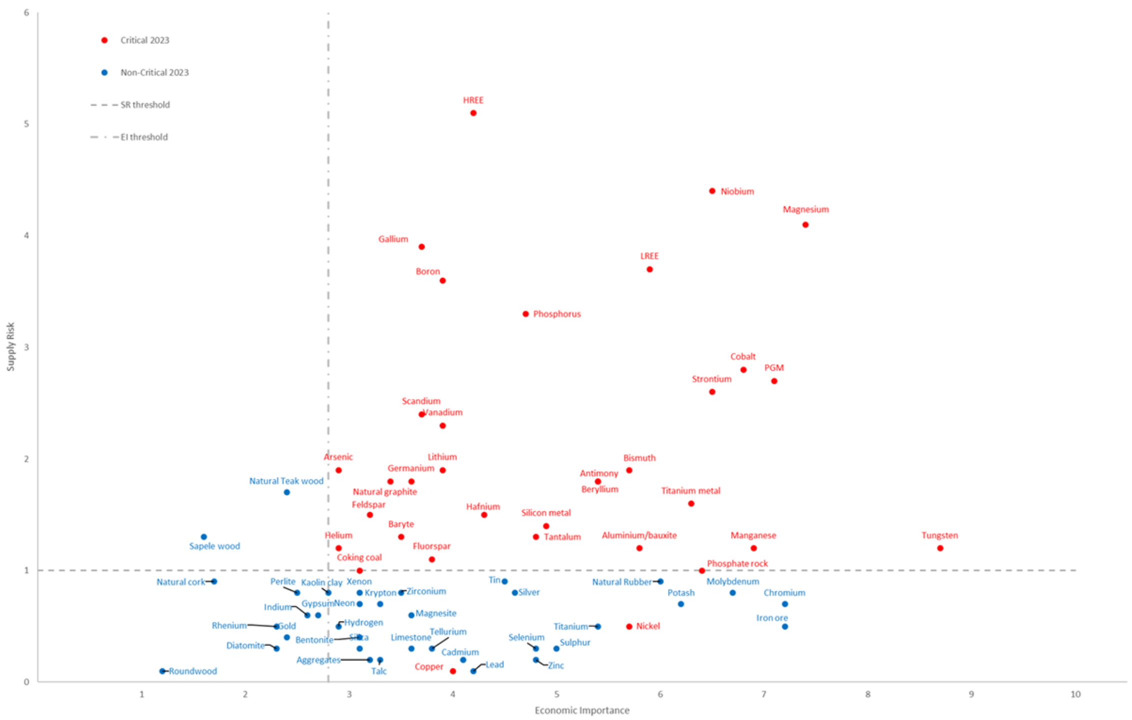


Figure 1. Critical Raw Materials as defined in 2023, based on Supply Risk and Economic Importance (Grohol et al., 2023).

CRMs are essential for the development of high-technology products and emerging innovations. Technological progress and improvements in quality of life increasingly depend on access to a growing number of such resources. Therefore, an appropriate and secure supply of CRMs is considered crucial for strengthening the EU's industrial base, a pillar of its economic growth and competitiveness.

To address growing concerns regarding the security of the supply of raw materials, the European Commission launched in 2008 the European Raw Materials Initiative. This is an integrated strategy that aims to ensure and strengthen the EU's access to essential resources through a series of specific measures. Central to these measures is the creation of the EU list of Critical Raw Materials. The most recent list (the fifth from 2011) was adopted in 2024 (https://rmis.jrc.ec.europa.eu/critical-and-strategic-materials), in parallel with the renewed EU industrial strategy, confirming the strategic importance attached to this instrument. The 2024 list now includes 34 CRMs (Fig.2).

aluminium/bauxite	antimony	**arsenic**
baryte	beryllium	bor/borate
flourspat	phosphate rock	phosphorus
feldspar	gallium	germanium
natural graphite	hafnium	**helium**
rare earth elements: HREE and LREE	silicon metal	cobalt
coking coal	copper*	lithium
magnesium	**manganese**	nickel*
niobium	platinum group metals: PGM	scandium
strontium	tantalum	titanium
vanadium	bismuth	tungsten

Figure 2. 2024 CRM List: new entries from the previous list are highlighted; strategic raw materials are in orange boxes. (source: Geological Survey of Sweden - https://www.sgu.se/en/mineral-resources/critical-raw-materials/).

Within the CRM, a specific subgroup of raw materials of strategic importance has been identified, which constitutes strategic raw materials (SRM). Copper and nickel,

although not meeting the requirements of the CRM (Fig. 1), have been included in the list of SRM due to their absolute importance in technological applications.
Other Western countries currently adopt similar concepts, so there are specific CRMs lists for the **UK** (https://www.bgs.ac.uk/mineralsuk/statistics/security-of-supply/critical-raw-materials/), **the US** (https://www.federalregister.gov/documents/2025/11/07/2025-19813/final-2025-list-of-critical-minerals), **Canada** https://www.canada.ca/en/campaign/critical-minerals-in-canada/critical-minerals-an-opportunity-for-canada.html), **Australia** https://www.industry.gov.au/publications/australias-critical-minerals-list-and-strategic-materials-list, **Japan, S. Korea**, etc.

It is important to note that the concept of critical raw materials is not exclusive to Western countries. Major economies such as Russia and China have also developed their own lists of critical minerals, although the criteria and the specific elements included may differ significantly from the EU list. For instance, China's list – closely linked to its manufacturing and high-tech sectors – includes certain rare earth elements, tungsten, and antimony, for which China holds a dominant position in global supply. Russia's list similarly reflects its domestic industrial priorities and geological endowment. Addressing this diversity of criticality lists is relevant for a global perspective on raw material supply chains, as it highlights how different nations define strategic autonomy based on their specific economic and geopolitical contexts. (*Petrov et al., 2023; Andersson, 2020*)

- Methodological assessment of criticality: the 2017 EC framework

The methodology used to determine whether a raw material is classified as "critical" for the European Union was described in detail in a European Commission document published in 2017 (*Blengini et al., 2017 – Methodology for establishing the EU list of Critical Raw Materials*). This methodology is based on the quantitative evaluation of two main parameters: the Economic Importance (EI) and the Supply Risk (SR).

Economic Importance (EI)

The Economic Importance parameter aims to provide insight into the importance of a material for the EU economy in terms of end-use applications and the value added (VA) of corresponding EU manufacturing sectors at the NACE Rev. 2 (2-digit level). The economic importance is corrected by a substitution index (SI_{EI}) related to the technical and cost performance of substitutes for individual applications.

The EI formula is as follows:

$$EI = \sum_s (A_s \times Q_s) \times SI_{EI}$$

where:

- EI = Economic Importance;
- A_s = the share of end-use of a raw material in a NACE Rev. 2 (2-digit level) sector;
- Q_s = the sector's value added (VA) at the NACE Rev. 2 (2-digit level);
- SI_{EI} = the substitution index of a raw material related to economic importance;
- s denotes sector.

The EI-specific substitution index for a given candidate material is calculated using the substitute cost-performance (SCP) parameters assigned to each substitute material, multiplied by the sub-share of each substitute in a given application, and in turn by the share of the end-use application:

$$SI_{EI} = \sum_a \sum_i (SCP_{i,a} \times Sub\text{-}share_{i,a} \times Share_a)$$

where:

- i denotes an individual substitute material;
- a denotes an individual application of the candidate material;
- SCP = substitute cost-performance parameter;
- $Share_a$ = the share of the raw material in an end-use application;
- $Sub-share_{i,a}$ = the sub-share of each substitute within each application.

Supply Risk (SR)

The Supply Risk parameter reflects the risk of a disruption in the EU supply of the material. It is based on the concentration of primary supply from raw material-producing countries, considering their governance performance and trade aspects. Depending on the EU import reliance (IR), two sets of producing countries are taken into account proportionally: global suppliers and the countries from which the EU is sourcing the raw materials. SR is measured at the "bottleneck" stage of the material (extraction or processing) which presents the highest supply risk for the EU. Substitution and recycling are considered risk-reducing measures.

The SR formula is:

$$SR=[(HHI_{WGI,t})_{GS}\times IR/2+(HHI_{WGI,t})_{EUsourcing}\times(1-IR/2)]\times(1-EoL_{RIR})\times SI_{SR}$$

where:

- SR = Supply Risk;
- GS = global supply, i.e. global suppliers country mix;
- $EUsourcing$ = actual sourcing of the supply to the EU, i.e. EU domestic production plus other countries importing to the EU;
- HHI = Herfindahl-Hirschman Index (used as a proxy for country concentration);
- WGI = scaled World Governance Index (used as a proxy for country governance);
- t = trade parameter adjusting WGI;
- IR = Import Reliance;
- $EoLRIR$ = End-of-Life Recycling Input Rate;
- SI_{SR} = substitution index related to supply risk.

The Import Reliance (IR) for a candidate material is calculated as follows:

$$IR = \frac{Import - Export}{Domestic\ production + Import - Export}$$

The ($HHI_{WGI,t}$) for global supplier country concentration and for EU actual sourcing country concentration is adjusted by a trade parameter and calculated as:

$$(HHI_{WGI,t})_{GS\ or\ EUsourcing} = \sum_c (Sc)^2 WGI_c * t_c$$

where:

- S_c = the share of country c in the global supply (or EU sourcing) of the raw material;
- WGI_c = scaled World Governance Index of country c;
- t_c = trade parameter for country c, constructed as:

$$t_c = (ET\text{-}TA_c \text{ or } EQ_c \text{ or } EP_c \text{ or } EU_c)$$

where:

- $ET\text{-}TA_c$ = parameter reflecting an export tax imposed by country c, possibly mitigated by trade agreements in force;

- EQ_c = parameter reflecting an export physical quota imposed by country c;
- EP_c = parameter reflecting an export prohibition introduced by country c;
- EU_c = parameter for EU countries, equal to 0.8.

The End-of-Life Recycling Input Rate (EoL RIR) is understood as the ratio of recycling from old scrap to European demand of a candidate raw material (equal to primary and secondary material inputs):

$$\boldsymbol{EoLRIR} = \frac{\boldsymbol{Input\ of\ secondary\ material\ to\ EU\ [from\ old\ scrap]}}{\boldsymbol{Input\ of\ primary\ material\ to\ EU + Input\ of\ secondary\ material\ to\ EU}}$$

The specific substitution index (SI_{SR}) for a candidate material is calculated as the geometric average of three parameters (SP, SCr, SCo) assigned to each substitute material, multiplied by the sub-share of each substitute in a given application, and by the share of the end-use:

$$\boldsymbol{SI_{SR}} = \sum_{\boldsymbol{i}} \left[(\boldsymbol{SP_i} \times \boldsymbol{SCr_i} \times \boldsymbol{SCo_i})^{\frac{1}{3}} \times \sum_{\boldsymbol{a}} (\boldsymbol{Sub - share_{i,a}} \times \boldsymbol{Share_a}) \right]$$

where:

- i denotes an individual substitute material;
- a denotes an individual application of the candidate material;
- SP = substitute production: reflects global production of the substitute; and the material as an indicator of whether sufficient amounts of substitute material are available;
- SCr = substitute criticality: takes into account whether the substitute was critical in the previous EU list;
- SCo = substitute co-production: takes into account whether the substitute is a primary product or mined as a co-/by-product;
- $Share_a$ = the share of the candidate material in an end-use application;
- $Subshare_{i,a}$ = the sub-share of each substitute within each application.

- **European Production, Dependencies and Value Chain Imbalances**

European industry has a strong manufacturing and refining sector, while extraction activities are less developed. This results in a marked imbalance between upstream (exploration and extraction) and downstream (production and use) stages of raw materials production, with only partial coverage of the CRM value chain.
Most CRMs come from non-European countries (Figs. 3, 4).

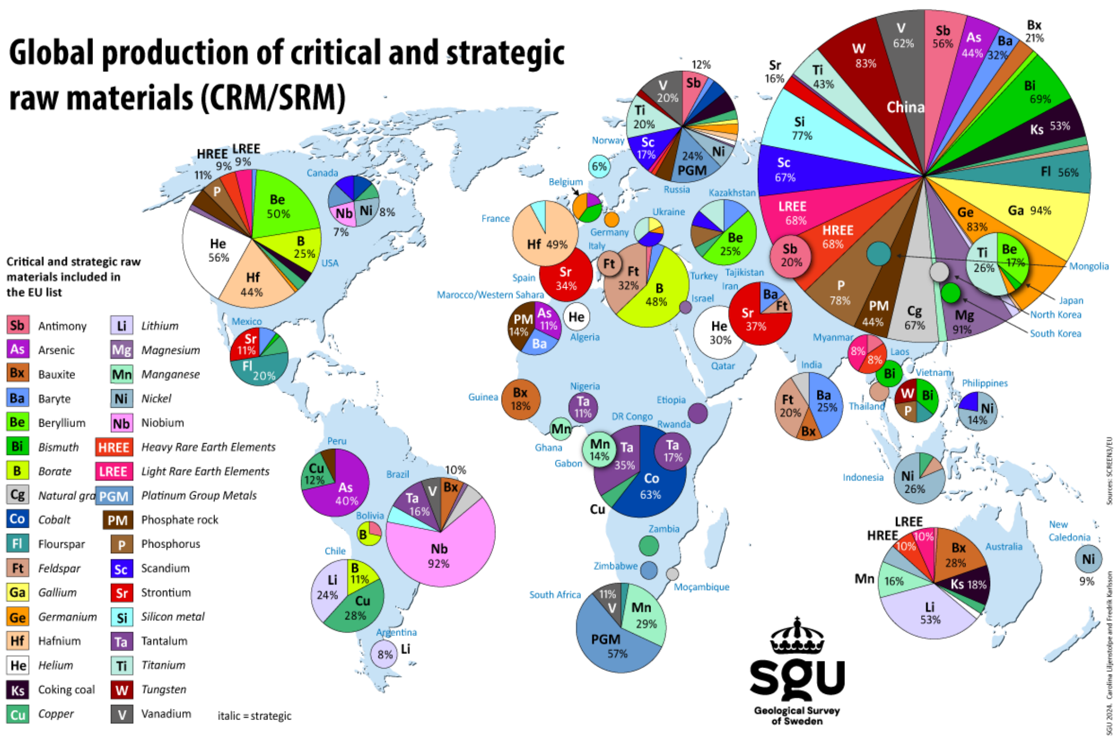


Figure 3. Global distribution of Critical and Strategic Raw Materials production (source: Geological Survey of Sweden- https://www.sgu.se/en/mineral-resources/critical-raw-materials/).

Many critical raw materials are not produced within the EU, due to limited geological availability or economic, social and environmental constraints. China is the EU's main supplier for several CRMs (LREE, HREE, gallium, germanium, magnesium, graphite, scandium, vanadium, bismuth, baryte), but other countries also play significant roles (Fig.4):

- Brazil (niobium);
- Chile (copper, lithium);
- Congo DR (cobalt, tantalum);
- Kazakhstan (phosphorus, titanium);
- Mexico (fluorspar);
- Morocco (phosphate rocks);
- Russia (PGMs);
- South Africa (PGMs, Manganese);

- Turkey (antimony, boron, feldspar);
- United States (beryllium).

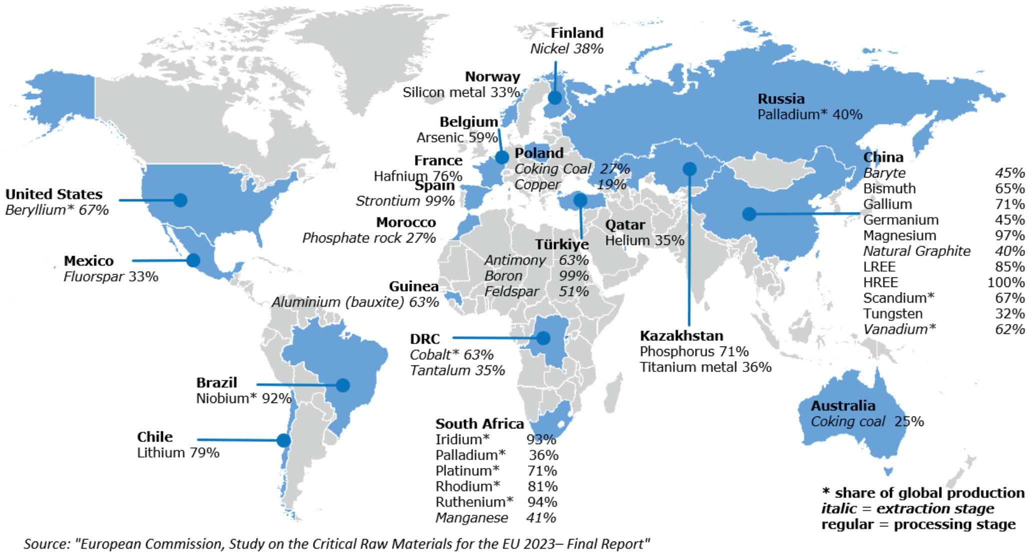


Figure 4. The EU main supplier of CRMs. (Grohol et al., 2023).

EU's internal production of CRMs is very scarce overall, limited to a few points per cent of the current consumption. Hafnium is an exception, as France is the world's primary producer (Fig.5).

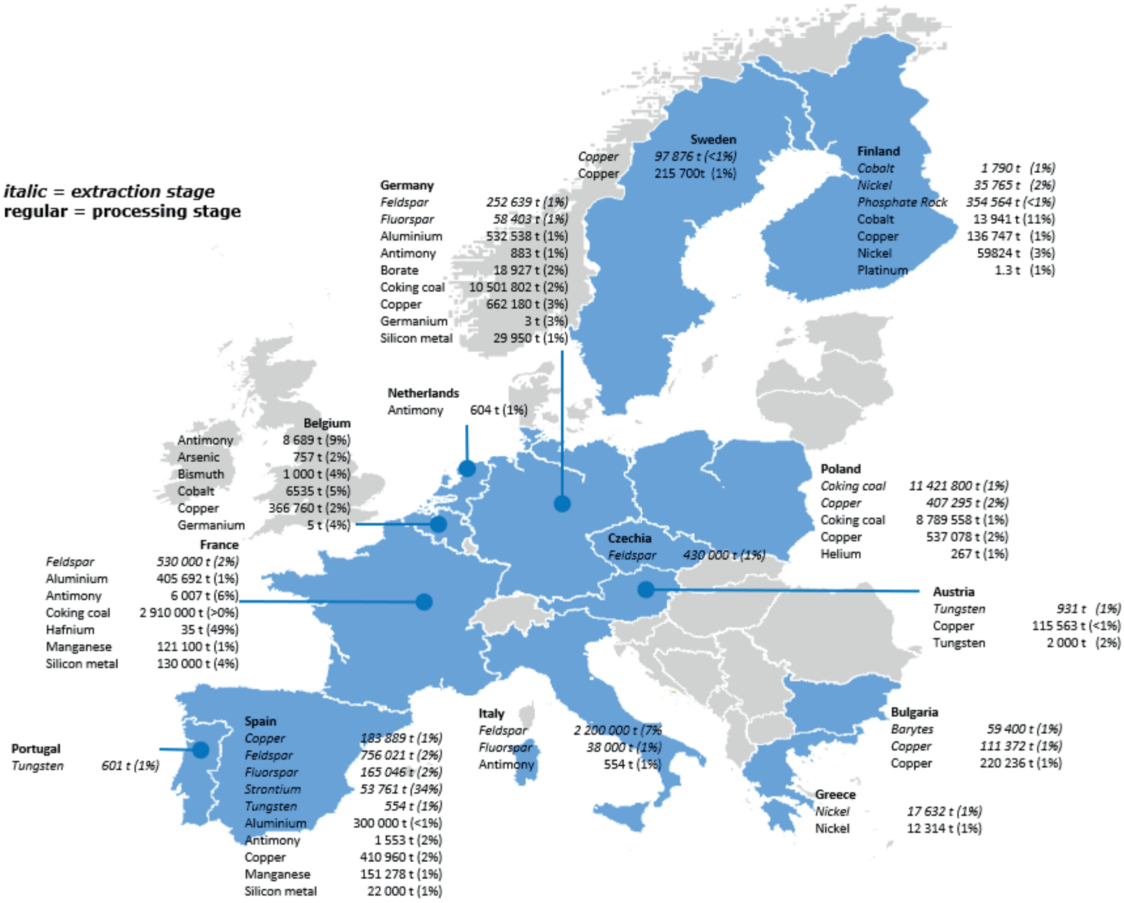


Figure 5. Distribution of Critical Raw Materials in Europe (Grohol et al., 2023).

- Circular Economy and CRMs Recycling

The transition toward a more circular economy—in which the value of products and resources is maintained for as long as possible—is essential for building a sustainable, competitive and resource-efficient economy.
From 2015, the European Commission proposed a series of actions to improve circular economy stages in the value chain: production, consumption, repair and remanufacturing of products, waste management and the reintroduction of secondary raw materials into the economic cycle.
Despite technical and economic potential, in EU, the **End-of-Life Recycled Input Rate (EoL RIR)**, defined as the percentual share of recycled material that contributes to the value chain of a definite CRM, remains low for many CRMs due to:

- Recovery technologies that are not yet economically competitive;
- Long residence times of materials within products;
- Rising demand that exceeds recycling capacity.

Some CRMs show good recycling rates (e.g., vanadium, tungsten, cobalt, antimony), while others—such as platinum-group metals (PGMs)—achieve high recovery rates (up to 95% in industrial catalysts) but still fail to meet demand. For many other materials (e.g., rare earth elements, beryllium, niobium, tantalum, graphite, germanium, etc.), the EoL RIR is very low or may be considered virtually insignificant (Fig.6).

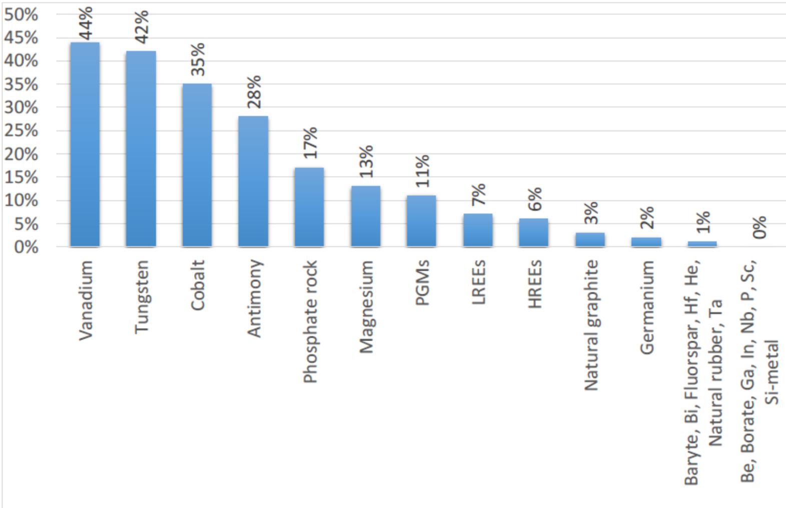


Figure 6. Contribution of recycling to meet EU demand of CRMs: End-Of-Life recycling Input Rate (EOL-RIR) (JRC elaboration, European Commission, 2018).

Circularity depends on sectors of use, product lifespan and the efficiency of end-of-life collection systems (Fig. 7). The ongoing SCRREEN3 study (2025: https://scrreen3.flexx.camp/factsheets) is confirming the need for a sector-specific approach to CRM flow analysis. Secondary CRMs from recycling offer additional benefits, such as lower energy and water consumption compared to primary materials and reduced impacts on ecosystems. (*Grohol et al., 2023*)

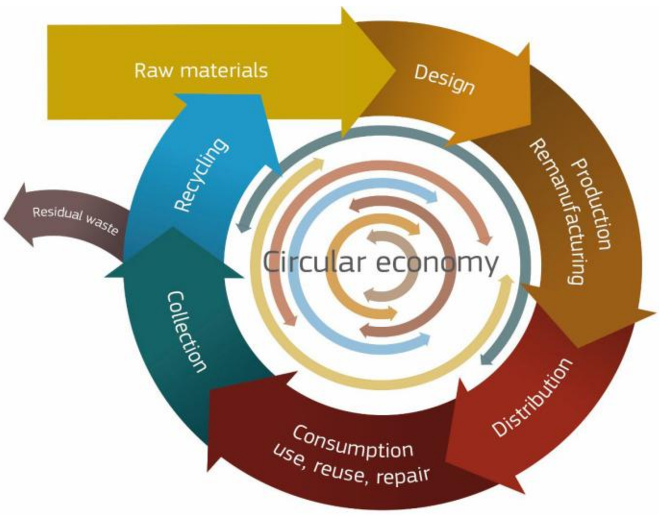


Figure 7. Conceptual diagram of circular economy (source: European Commission, 2018).

- **The Critical Raw Materials Act**

The Critical Raw Materials Act (CRMA: https://eur-lex.europa.eu/eli/reg/2024/1252/oj/eng) is the European Union regulation designed to secure a stable, sustainable, and resilient supply of critical raw materials for the EU economy. It entered into force on 23 May 2024. The CRMA's main goals are finalized to boost EU domestic capacity for a) **extraction of raw materials**, b) **processing and refining**, c) **recycling and circular use**, d) **reduce dependency** on single foreign suppliers, e) **strengthen supply chain resilience**, including preparedness for disruptions, f) **promote sustainability, innovation**, and skills development across the materials value chain. **Two annexes to the CRMA contain the lists of CRMs and SRMs, respectively.** Among the **key requirements and measures of CRMA**, there are:

- **Benchmarks for 2030 -** quantitative targets are set for the EU's contribution to its own raw materials needs by 2030 - **≥10%** of annual consumption must come from **EU extraction**, **≥40%** from **processing/refining inside EU**, **≥25%** from **recycling processes inside EU**; no more than 65% of consumption of a given strategic material at any processing stage should come from a single non-EU country;
- **Streamlining permits** - the Act simplifies and speeds up permitting for critical raw materials projects - Extraction projects: up to ~27 months, Processing & recycling: up to ~15 months; Member states must designate single points of contact to coordinate these procedures;
- **Strategic projects** and risk management – a yearly selection procedure is established for acknowledged projects of strategic relevance for EU - eligible projects may get easier access to financing and recognition as "strategic," while companies must assess supply risks and cooperate on monitoring;
- **Circularity and sustainability** - the Act encourages recycling, reuse, and environmental and social standards in supply chains, including recovery of materials from waste and by-products; an inventory of resources in European wastes, particularly in mine wastes, is promoted, to be implemented by national programs;
- **International engagement** - the EU aims to diversify external supplies and build mutually beneficial partnerships with reliable third countries under initiatives like the Global Gateway strategy.

In Italy, the CRMA has been transposed and implemented by the **L. 115, 8 August 2024** (https://www.normattiva.it/uri-res/N2Ls?urn:nir:stato:legge:2024-08-08;115) that establishes urgent provisions on critical raw materials of strategic interest. Among the key measures, national exploration plans are envisaged for mineral resources and secondary raw materials that can be extracted from mining and urban waste. The CRMA's transposition has been further supported by two key initiatives. The PNE (*Programma Nazionale di Esplorazione – National Exploration Programme: https://www.isprambiente.gov.it/it/attivita/suolo-e-*

territorio/programma-nazionale-di-esplorazione-mineraria), published by ISPRA in 2025, defines the national strategy for the exploration of mineral resources, including secondary raw materials from mining and urban waste. The PNE identifies priority areas for investigation and establishes guidelines for the assessment of CRM potential in historical mining districts. Additionally, the URBES (*URBan mining and Extractive waste information System: https://urbes.it/*) project, funded under the PNRR, focuses on the circular economy and the recovery of critical raw materials from urban, mining and extractive wastes. The URBES project shares methodological approaches with mining waste valorisation, particularly in the areas of automated mineral characterization and material flow analysis. Together, the PNE and URBES initiatives represent a coordinated effort by the Italian government to align national raw materials policy with the strategic objectives of the CRMA.

- **CRMs in Italy**

Italy currently has 76 active mines, 22 of which are extracting resources included in the EU list of 34 critical raw materials. Among these:

- 20 produce feldspar, essential for the ceramic industry;
- 2 extract fluorspar, strategic for the chemical, steel, aluminium, glass, electronics and refrigeration sectors.

Of particular importance is the Genna Tres Montis underground mine (Southern Sardinia), now on re-start, which — once preparation works are completed — will certainly become one of the main fluorspar mines in Europe. In the past, Italy had 91 fluorspar mines. Some historical sites, located in Lombardy, Trentino, Sardinia and Latium, may be reconsidered in light of current fluorspar market demand and high prices.
At present, feldspar and fluorspar are the only CRMs actively extracted in Italy. However, new assessments on historical data, new exploration activities, and recent studies indicate the possible presence of other strategic resources, including lithium, identified in significant quantities within geothermal fluids of Tuscany, Lazio and Campania (*Dini et al., 2022*).

Figure 8. CRMs resources of Italy (source: ISPRA - GEMMA geoportal - https://sinacloud.isprambiente.it/portal/apps/webappviewer/index.html?id=a3fa10ccab3840449847d27fad764152).

Overall, Italy still hosts significant resources of numerous metals crucial for the energy and digital transition (Fig.8):

- **Copper:** in VMS-type and skarn deposits - Ligurian-Emilian Apennines, Colline Metallifere, Western Alps, Trentino, Carnia, Sardinia;
- **Manganese:** in volcano-exhalative deposits - Liguria and Tuscany;
- **Tungsten:** in granite-related skarn and greisen deposits - Calabria, Sardinia, South Tyrol and central-eastern Alps;
- **Cobalt:** five-element-type (Ni-Co-As-Bi-Sb) hydrothermal veins - Sardinia and Piedmont;
- **Magnesite and magnesium salts:** in serpentinites - Tuscany or as dolostone - Venetian Prealps;
- **Titanium:** in ophiolitic/eclogitic rocks – Liguria;
- **Bauxite:** residual and/or karst bauxites - Sardinia, Central Apennines, Apulia;
- **Rare earth elements:** in monazite-rich paleoplacers and associated with bauxite and fluorite deposits - Sardinia;
- **Celestine:** associate to sulphur deposits – Sicily;
- **Graphite:** metamorphic deposits– Western Alps, Calabria.

- Secondary Mining and Mining Waste in Italy

Globally, there is growing interest in recovering secondary raw materials (SeRMs) through the valorisation of mining waste generated by past extraction activities, a process known as secondary mining (*Lottermoser, 2011*).

In Italy, past mining activities have produced approximately 150 million m^3 of extraction and processing waste (*ISPRA, 2022*), often stored in obsolete or degraded deposits and potential and actual sources of soil and water contamination due to the presence of elements such as zinc, lead, arsenic, cadmium and mercury. Paradoxically, these sources of pollution often display relevant CRMs contents, thus coinciding with resources critical to technological industries and the ecological transition. Their re-treatment (re-mining) offers an opportunity to transform an environmental threat into an economic and strategic asset (*Edraki et al., 2014; Lottermoser, 2011*). Therefore, a paradigm shift is required: considering such materials not only as waste requiring remediation, but as potential sources of critical raw materials, in line with circular-economy principles and the European Green Deal. At the same time, the re-treatment of waste materials, in accordance with the Italian Law L. 115 2024, potentially removes a source of contamination by acting on the Source–Pathway–Receptors paradigm defined by Legislative Decree 152/2006 – the Italian Environmental Code – thereby resulting in environmental remediation.
The ISPRA's national inventory of Italian mine dumps of potential environmental impact (*ISPRA, 2022*) includes 572 waste deposits deriving from various mining processes. Of them, 209 are in the district of Sardinia, the most important mining region in Italy.

The Sardinian mine waste deposits

In Sardinia, approximately 70 million m^3 of waste materials are present (*RAS, 2003*). These materials were identified, mapped, classified, and partially characterized during this doctoral project to evaluate their potential as sources of critical raw materials (CRMs). Sardinia represents an exceptionally relevant case study. For more than a century, the island was one of the leading mining districts in Italy and the Mediterranean region, hosting numerous mining areas—such as Sulcis-Iglesiente, Montevecchio-Ingurtosu, Sarrabus-Gerrei and Nurra—characterized by a wide variety of ore deposits and mineralized occurrences, combined with the presence of numerous geosites and extraordinary mining landscapes. The legacy of this long mining history is visible today in the hundreds of dumps, tailings, processing residues and mine deposits distributed across a territory still heavily influenced by past extraction activities (Fig. 9).

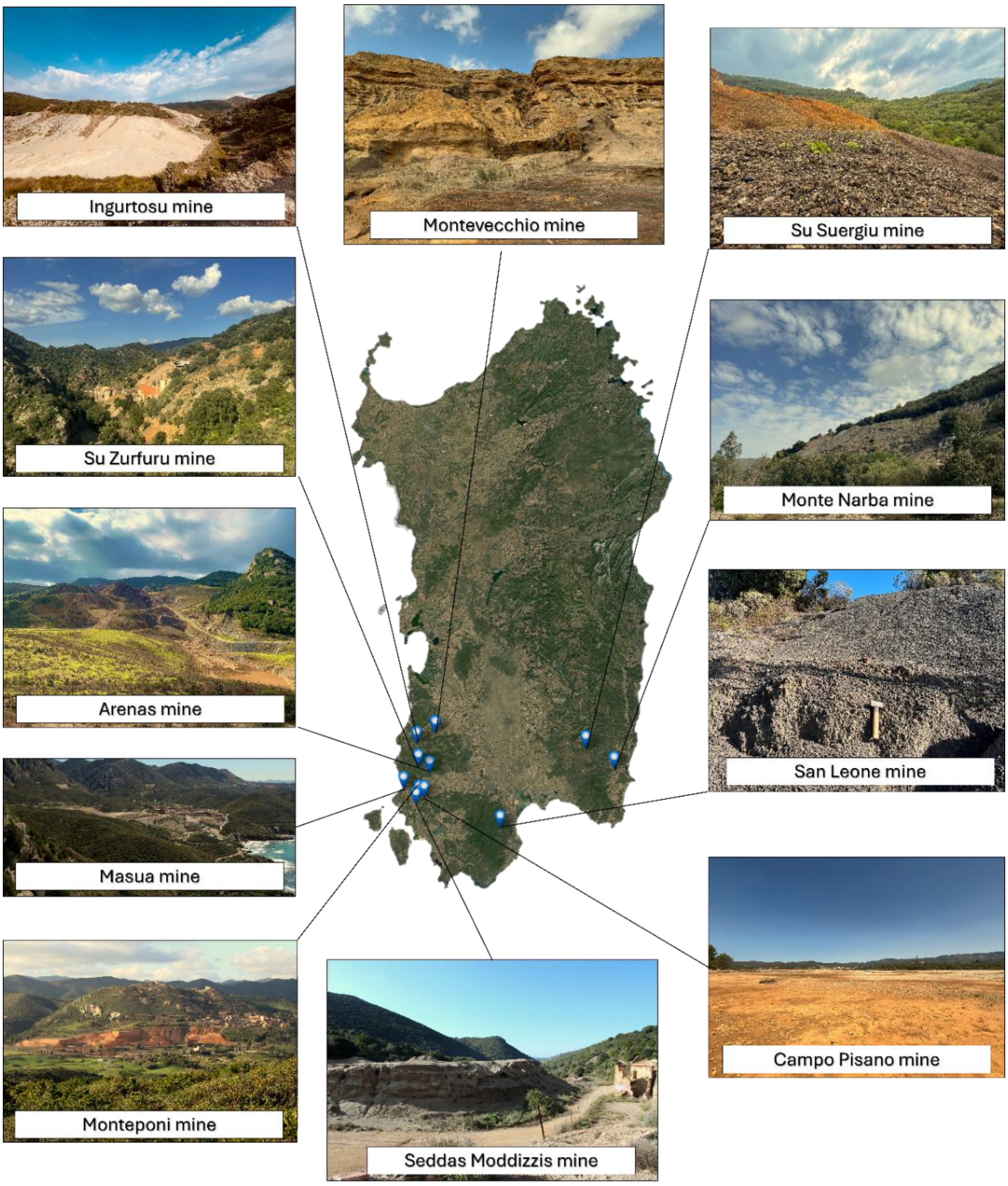


Figure 9. Some of the mining sites sampled during the doctoral research fieldwork.

Sardinian ore deposits cover a wide span of classes and types, displaying an amazing variety of geochemical and mineralogical associations, including many CRM-bearing phases. This complexity makes Sardinia not only a geological and environmental laboratory but also a potential reserve of critical mineral resources. Despite the richness and complexity of the Sardinian mining system, no unified, digital and systematic database of the island's mining dumps currently exists. Available information is fragmented, dispersed among historical archives, technical documentation, academic studies and non-standardised surveys. This lack of coherent cataloging represents a significant knowledge gap that limits environmental monitoring planning, hinders the valorisation of residual mineral potential, and complicates the integrated assessment of territorial risks related to the acid mine drainage, the heavy-metal dispersion, and the dump material alteration (Fig. 10).

Figure 10. Environmental pollution and Acid Mine Drainage in the Montevecchio mine (SW Sardinia).

This doctoral project arises precisely within this gap, aiming to build the first digital database dedicated to Sardinian mining waste dumps, forming the basis for the new digital metallogenic map of the island. The work adopts a multidisciplinary approach that integrates geology, geochemistry, mineralogy, environmental analysis, resource economics and land-management techniques.

The thesis is structured as a compendium of three scientific articles that address Sardinian mining dumps from complementary perspectives, united by the objective of providing an organic, updated and operational framework for future territorial management and resource-valorisation tools.

The first article presents a critical review of Sardinian mining dumps and their current state of knowledge, providing the conceptual foundation for the regional database. The analysis covers historical, environmental, economic and resource-potential aspects and provides the conceptual and methodological foundation for developing the regional database.

The second article focuses on a case study of Montevecchio Ponente, one of the most representative mining sites in Sardinia. It analyses the environmental impacts generated by the dumps, with particular attention to mineral-alteration dynamics, chemical-element mobility and the processes influencing contaminant dispersion.

The third article examines another case study in southwestern Sardinia, focusing on geochemical and mineralogical investigations aimed at assessing the economic potential of these deposits in terms of CRMs. The analysis highlights minerals containing strategic elements and correlates analytical results with prospects for sustainable resource recovery.

Taken together, these three articles provide an integrated picture of Sardinian mining waste dumps, emphasising both environmental criticalities and mineral-economic opportunities. The creation of the regional database and the methodological criteria underpinning the new digital metallogenic map represent one of the most innovative results of this project.

Ultimately, this thesis makes a significant contribution to the knowledge, cataloging, and valorisation of Sardinia's mining heritage, proposing an approach that can be replicated in other European regions with similar mining legacies. It aims to establish a robust and up-to-date information platform to support decision-making, research activities, and territorial management initiatives aligned with sustainability, innovation, and resource valorisation.

2. Geological framework of Sardinia

Sardinia represents one of the geologically most complex and best-preserved sectors of the western Mediterranean, characterized by remarkable lithological diversity and an evolutionary history spanning more than half a billion years. The present geological setting of the island reflects the superposition of tectonic, magmatic, and sedimentary events related first to the Variscan orogeny, subsequently to Meso-Cenozoic extensional phases, and finally to the opening of the Balearic Basin and the Tyrrhenian Sea.

The oldest rocks exposed in Sardinia belong to the Paleozoic and form the island's basement. They display a variable degree of metamorphism, ranging from anchizona (External Zone) to high-grade (Inner Zone), and record pre-Variscan and Variscan deformation. About one third of the island's surface is made up of intrusive magmatic rocks, largely attributable to the large Late Variscan Sardinian-Corsican Batholith, predominantly calc-alkaline in composition and dated to the Late Carboniferous–Permian (*Carmignani et al., 2001, 2016*).

The pre-Palaeozoic geological history is not documented unambiguously. Localized outcrops in the southern sector (Capo Spartivento) and in the northern sector (Gallura, Baronie, Anglona, Asinara), once attributed to the Precambrian, are now mostly referred to Palaeozoic successions based on more recent geochronological data (*Pavanetto et al., 2012; Rossi et al., 2009*).

During the Palaeozoic, the island was subdivided into different paleogeographic domains. In the Sulcis-Iglesiente sector, a coastal environment initially developed with the deposition of siliciclastic sediments of the Nebida Group, later evolving into a carbonate platform represented by the Gonnesa Group (*Pillola et al., 1995*). In the Sarrabus-Gerrei domain, by contrast, sandstone and schist successions prevailed, deposited in more unstable marine environments characterized by heterogeneous sedimentation (*Carmignani et al., 2001*). This differentiation testifies to the existence of distinct structural and paleogeographic domains, fundamental for the subsequent tectonic evolution of the island (*Cocco et al., 2023*).

During the Ordovician, the so-called "Sardic Phase" developed in the south-western sector with upright folds with E–W-oriented axes (e.g., the Iglesias syncline) and by a thick sedimentary succession. In the south-eastern sector, after a phase of isoclinal folding, an important calc-alkaline magmatic cycle developed (*Cocco et al., 2023*). In the Silurian and Devonian, a common passive-margin phase followed in both domains, with the deposition of black shales and carbonate successions (*Corradini & Ferretti, 2009*).

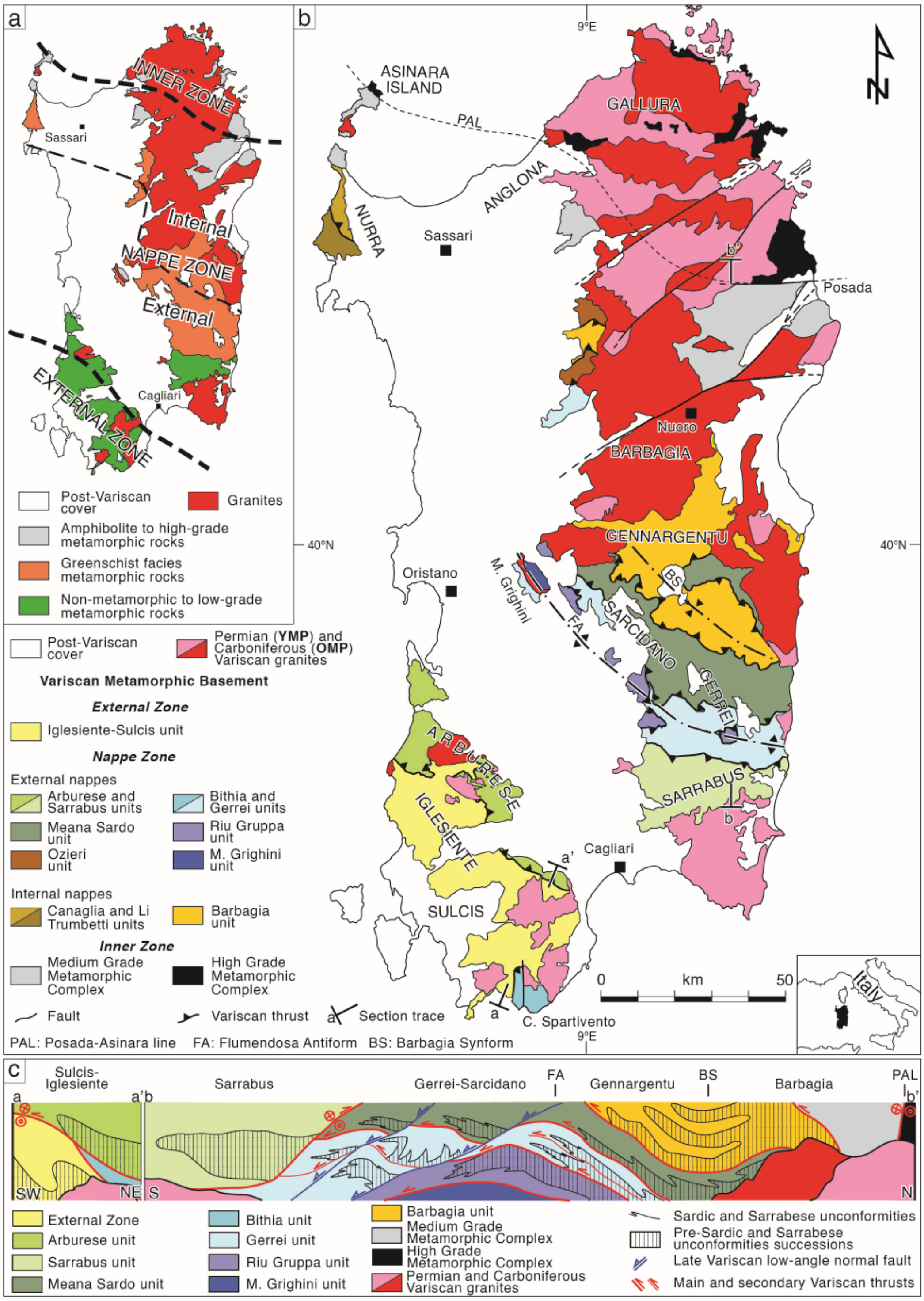


Figure 11. Schematic map of the Variscan basement of Sardinia (Naitza et al., 2024). a) Metamorphic zonation; b) tectonic sketch map; c) a section along the basement (a-a' and b-b' traces in Fig. 11b).

During the Variscan orogeny (Carboniferous–Early Permian), the Palaeozoic successions underwent intense deformation and metamorphism, resulting in the development of isoclinal folds and thrusts, associated with regional metamorphism and followed by granitoid intrusions.
The structural arrangement of the Sardinian basement is organized into three major domains (Fig.11):
(i) a medium- to high-grade metamorphic complex in northern Sardinia (Inner Zone);
(ii) a nappe zone in eastern Sardinia;
(iii) an external zone in south-western Sardinia.
During the Mesozoic, Sardinia entered a relatively stable passive-margin tectonic regime, characterized by the establishment of a vast carbonate platform. In this interval, thick successions of limestones and dolostones were deposited in warm, shallow seas, today exposed in the main carbonate massifs of the island (Supramonte, Monte Albo, eastern Iglesiente) and responsible for the widespread karst phenomena (*Cherchi et al., 2000; Ronchi & Sarti, 1999*).

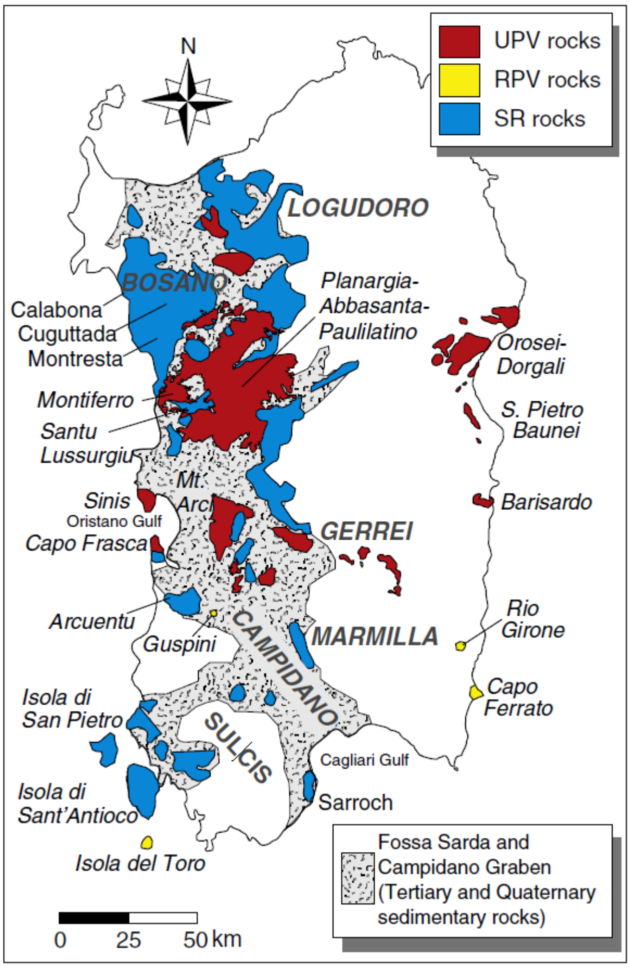


Figure 12. Cenozoic volcanic outcrops of Sardinia. Blue - calc-alkaline suites; yellow and red – alkaline suites (Lustrino, 2013).

In the Cenozoic, the detachment of the Sardinian-Corsican block from the European plate began. Between the Oligocene and Early Miocene, intense calc-alkaline volcanic activity developed and, above all, the rotation of the Sardinian-Corsican Block occurred, leading to the opening of the Balearic Basin and subsequently of the Tyrrhenian Sea (*Carmignani et al., 2001; Cherchi et al., 2000*). This rotation, which occurred primarily during the Miocene, significantly influenced the arrangement of lithological units and the regional deformation pattern.

During the subsequent Plio-Pleistocene tectonic phase, in conjunction with the opening of the Tyrrhenian Sea, a new and widespread alkaline magmatism developed, responsible for the formation of the Montiferru and Monte Arci volcanic complexes, as well as the extensive basaltic plateaus (*Doglioni et al., 1999*). In this phase, important extensional structures of the horst-and-graben type were also established, including the Campidano tectonic depression.

The present-day morphological setting of the island is the result of Late Cenozoic tectonic uplift, fluvial and marine erosion, and sea-level variations related to Quaternary glaciations (*Casini et al., 2020; Mariani et al., 2009*). Sardinia thus preserves an almost complete succession of geodynamic events, from the Variscan orogeny to the formation of the Neogene horst-graben system, making it one of the most significant geological settings in the western Mediterranean.

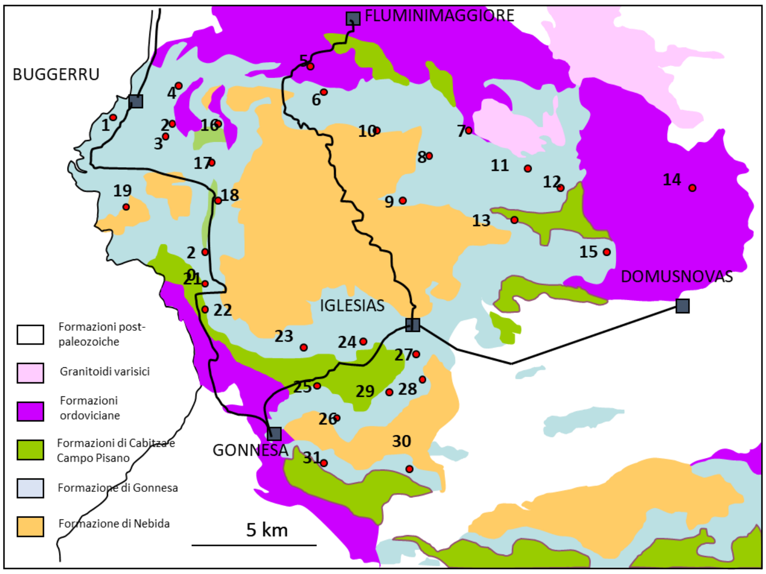
3. Metallogenic Framework of Sardinia

Sardinia represents, from a geological perspective, a part of a microcontinent characterized by a complex tectonic and stratigraphic evolution, recording orogenic events from the Palaeozoic to the Cenozoic. The Paleozoic pre-Variscan successions, the Variscan tectonics and the late Variscan granitoid Batolith exerted fundamental lithological, structural, and thermal controls on the distribution and evolution of the main ore deposits of Sardinia. This geodynamic history, therefore, represents a key element for understanding the mineralization processes affecting the region.

Several major metallogenic “peaks” can be recognized in the geological history of Sardinia, corresponding to periods of intense ore-forming activity (*Naitza et al., 2024*):

1. **Pre-Variscan (Cambrian):** ca. 515–510 Ma;
2. **Variscan (Late Carboniferous–Permian):** ca. 305–280 Ma;
3. **Post-Variscan (Permian–Cretaceous):** ca. 270 (?)–90 Ma;
4. **Cenozoic (Oligo–Miocene):** 32–15 Ma.

Within the Sulcis–Iglesiente districts, major stratabound Pb–Zn ± Ag sulfide ores occur within Cambrian carbonate sequences, representing the most important metalliferous deposits of Sardinia. These deposits (Fig.13), also associated to stratiform baryte occurrences, have been variably interpreted as Mississippi Valley-Type (MVT)/Irish-type and/or SEDEX systems (*Santoro et al., 2023*), genetically related to the circulation of basin-derived marine fluids and to subsequent episodes of metal remobilization and concentration during Paleozoic tectono-metamorphic stages.



1- Pranu Sartu
2- Malfidano
3- Caitas
4- Nanni Frau-Su Sollu
5- Su Zurfuru
6- Gutturu Pala
7- Arenas – Tinì
8 – Malacalzetta-Baueddu
9- San Benedetto
10- Antas
11- Sa Duchessa
12- Barraxiutta
13- Reigraxius
14- Maciurru
15- San Michele Corovau
16- Pira Roma
17- Scalittas
18- Aquaresi
19- Canal Grande
20- Montecani
21- Masua
22- Nebida
23- Monte Agruxiau
24- Monteponi
25- San Giovanni
26- Seddas Moddizzis
27- Campo Pisano
28- Genna Luas-Funtana Perda
29- Cabitza
30- Barega
31- Monte Onixeddu

Figure 13. Main mining areas of the Iglesiente MVT district. The largest mineral deposits are highlighted in bold.

Lead and zinc sulfide ores are associated with large supergene oxide deposits ("calamine") associated with karstic baryte deposits, developed during repeated phases of basement exposure in continental conditions, starting from the middle Ordovician (Sardic Phase) and, particularly, during the post-Variscan times.

In Eastern Sardinia, the pre-Variscan middle to late Ordovician successions are characterized by crustal fertilization stages related to a convergence setting, subduction and development of a calc-alkaline magmatic arc. Heavy minerals-rich, Ti-Zr-REE-bearing paleoplacers were deposited in sediments resulting from the erosion of magmatic products belonging to the volcanic arc; these deposits are considered as protores for the following stages of mineralization (*Naitza et al., 2024*).

Variscan metallogeny is characterized by two main classes of deposits (*Naitza et al., 2024*, Fig. 14):

a) orogenic-type As–Au ± Sb-W mesothermal deposits, mainly occurring in southeastern Sardinia; they consist of large-scale structurally-controlled vein systems (*Funedda et al., 2018*) originated from fluids with a strong metamorphic signature (*Dini et al., 2005*), exploited in the past for antimony and arsenic;

b) granite-related deposits, originated during the emplacement of the Sardinian Batolith; they include different kinds of ores (Cu-Zn-Pb ± REE skarns; Fe-Sn-F and +Fe-W-F skarns with or without base metals; Mo ± W-Sn-Bi-F greisens; Sn-As, W-Bi-Te-Au and F-Pb veins, etc.) mostly related to early Permian fertile granite suites of ferroan, ilmenite series-type (*Naitza et al., 2017*).

Important feldspar deposits are also associated with the emplacement of the Batholith, particularly the albititic belt of central Sardinia, which represents an European-scale district of raw materials for the ceramic industry.

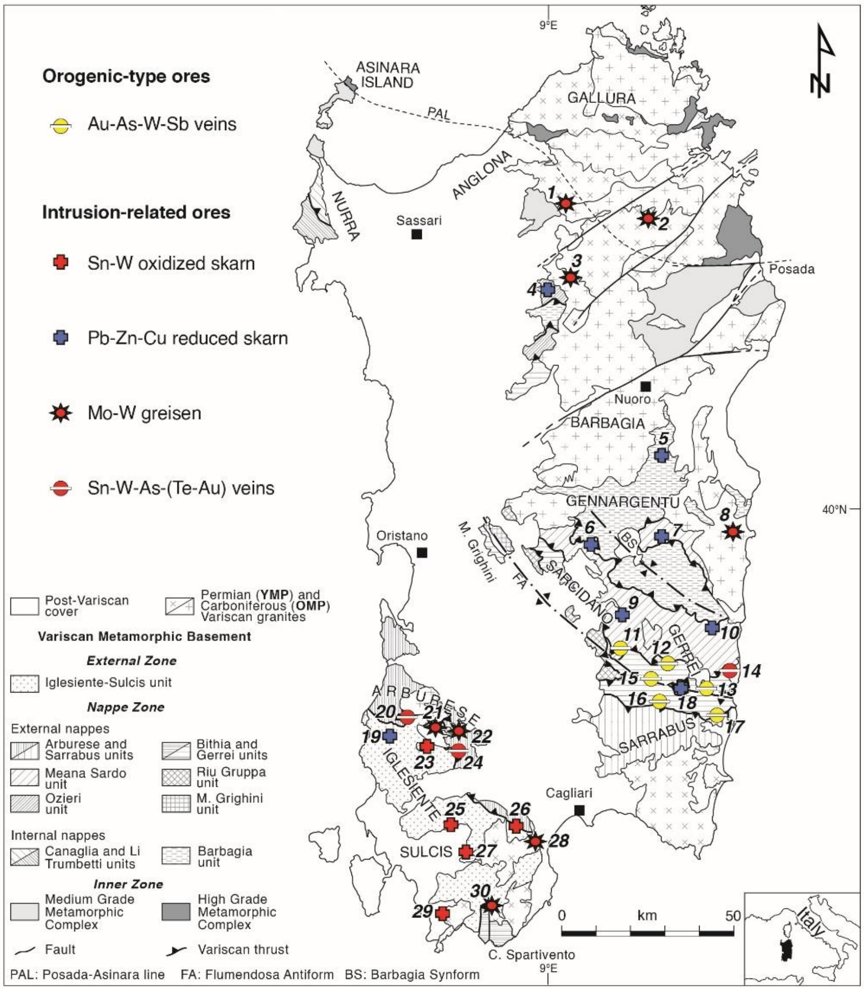


Figure 14. Variscan mineral deposits of Sardinia. 1. Su Laccheddu, 2. S'Abbagana, 3. Monte Unne, 4. Bena de Padru, 5. Correboi-Funtana Bona, 6. Funtana Raminosa-Giacurru, 7. Lago Alto Flumendosa, 8. Goene, 9. Monte Nieddu, 10. Talentinu, 11. Genna Ureu, 12. Monte Ollasteddu, 13. Baccu Locci, 14. Perda Majori-Quirra, 15. Corti Rosas, 16. Su Suergiu, 17. Brecca, 18. Sa Lilla, 19. Perda S'Oliu-Medau Ganoppi, 20. Santa Vittoria-Perdu Cara-Togoro, 21. Perd'e Pibera, 22. Perda Lada, 23. Perda Niedda-Oridda, 24. Canale Serci, 25. Rosas-Sa Marchesa, 26. San Leone, 27. Monte Tamara, 28. Su Seinargiu-Flumini Binu, 29. Teulada, 30. Malfatano (Naitza et al., 2024).

A new relevant metallogenic peak occurred during the post-Variscan (late Permian to Mesozoic) period, originating some of the most important mineral deposits of Sardinia. The main mineralizing events of this period are related to large-scale, shallow crustal fluid circulation in a (presumed) extensional setting, originating three main types of low-temperature hydrothermal veins (Fig. 15):

1) polymetallic Pb-Zn (Cu-Ag-Sb-Bi-Ni-Co-Ga-Ge-In-REE) "Montevecchio-type" quartz-carbonate-sulfide veins (*Moroni et al., 2019a*), clustered to form large to small districts in SW and N Sardinia (Montevecchio-Ingurtosu-Gennamari; Lula-Sos Enattos; Argentiera, etc.);

2) polymetallic "five element-type" Ni-Co-As-Bi-Sb (Pb-Zn-Cu-Ag-REE) quartz-carbonate-arsenide-sulfide veins (*Moroni et al., 2019b*), mainly occurring in SW Sardinia;

3) Ba-F-Pb (± REE, ± Ag-Sb-Ni-Co) "Silius-type" veins (*Scano et al., 2023*), widespread in all the region but particularly abundant in SE Sardinia (Silius mine; "Sarrabus silver lode", etc.).

Regional tectonic setting, paleogeographic factors and local structural features are identified as the main controlling factors of mineralization. The age of the event(s) is still undetermined, but several lines of evidence and geological constraints point to late Permian-Triassic times, during the breakup of Pangea and in good agreement with recent reconstructions for south European metallogeny (*Burisch et al., 2022*).

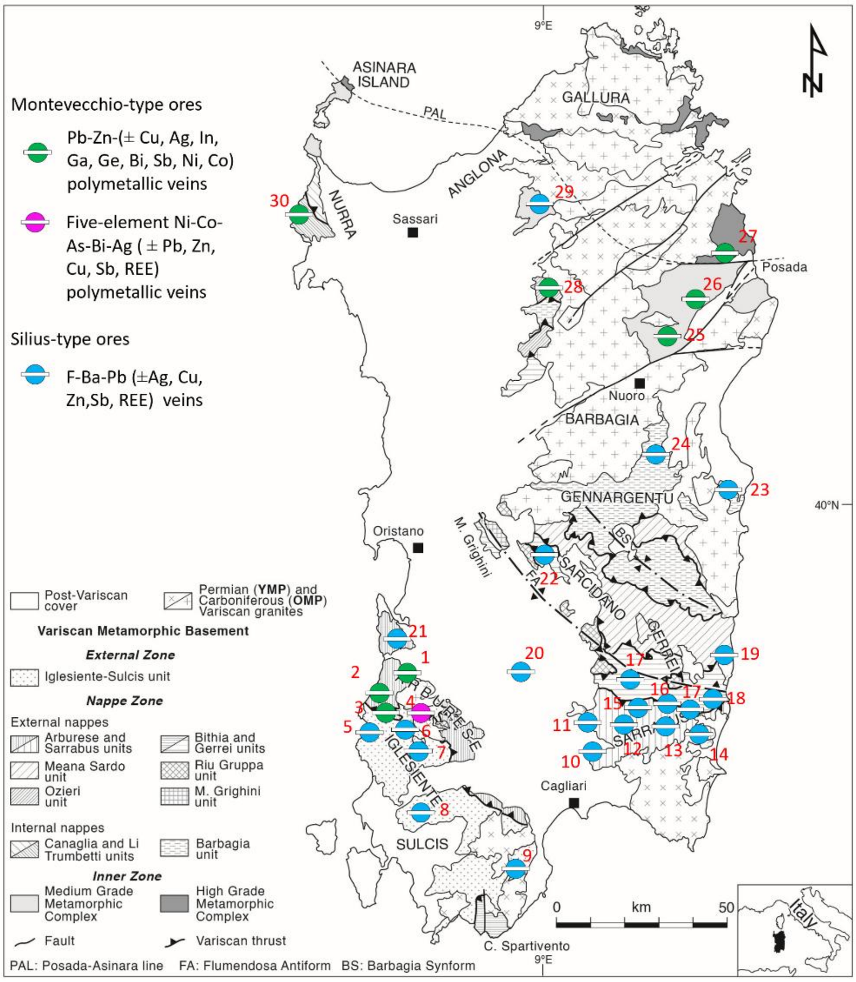


Figure 15. Post-Variscan mineral deposits of Sardinia (Naitza et. al., 2026, in print).

In northern Sardinia, Upper Cretaceous bauxite deposits represent important residual accumulations formed under tropical palaeoclimatic conditions, showing significant potential in terms of gallium, REEs, scandium and other critical materials (*Mongelli et al., 2021*).

The Cenozoic metallogenic peak is closely related to the onset of Oligocene-Miocene calc-alkaline volcanism in W Sardinia within a post-orogenic extensional geodynamic setting related to the evolution of the western Mediterranean (*Lattanzi, 1999*). The main mineralized deposits (Fig.16) are:

1) porphyry copper-type Cu ± Au, Mo, Pb-Zn ores related to andesitic, tonalitic and monzodioritic sub-volcanic intrusive bodies, occurring both in NW (e.g., Calabona) and SW Sardinia (e.g., Siliqua, Sarroch);

2) epithermal mineralization, both of High Sulfidation type with Au-As-Te (e.g., Furtei gold mine) and of Low Sulfidation type with Au-Ag-Sb (e.g., Osilo);

3) volcano-exhalative manganese deposits, always of small size. Several industrial minerals, large deposits (bentonite, kaolin, quartz-feldspar sands) are also related to this setting.

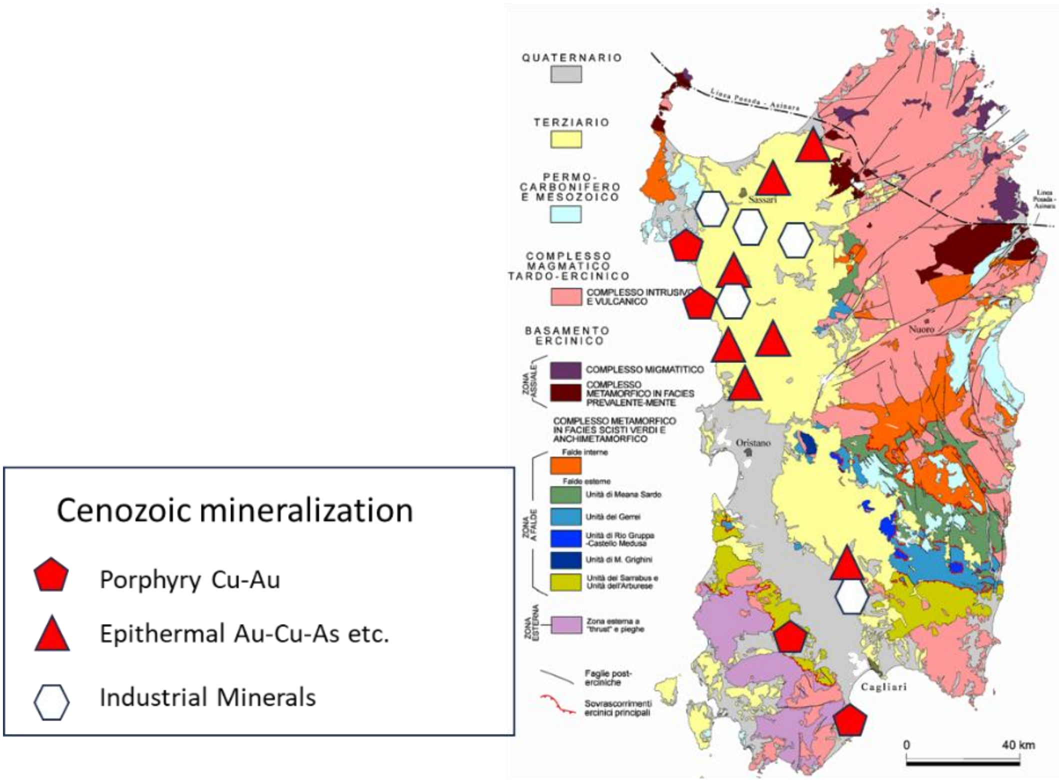


Figure 16. Cenozoic mineral deposits of Sardinia.

This complex metallogenic legacy is the direct reason for the extreme mineralogical and geochemical variability that characterizes the mining waste deposits discussed in the following chapters.

The main Sardinian mining districts and the chronology of metallogenic events are reported in Fig. 17 and Table 1, respectively.

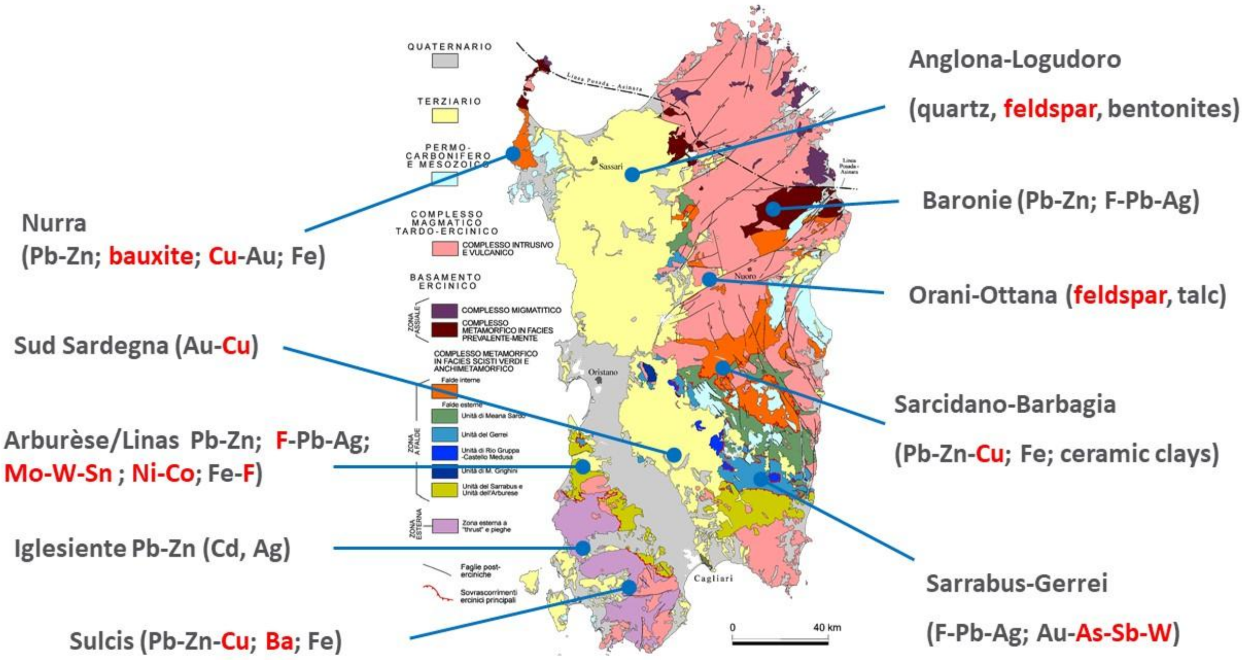


Figure 17. Main mining districts of Sardinia. CRMs are highlighted in red.

Table 1. Main metallogenic events in Sardinia.

Mining districts	Ore deposits and mineralisations	Type of deposit
Pre–Sardic Phase metallogenic peak (Cambrian–Early Ordovician)		
Iglesiente-Sulcis	Ba, Pb	Evaporite
Iglesiente-Sulcis	Fe-Zn-Pb	SEDEX
Iglesiente-Sulcis	Pb-Zn	MVT
Sardic Phase period (middle-upper Ordovician)		
Iglesiente-Sulcis	Ba, Zn-Pb	Karst, supergene
Eastern Sardinia	Pre-enrichment of base metals	Sedimentary, volcanic-exhalative
Eo-Variscan Period (Upper Ordovician–Devonian)		
Eastern Sardinia	Ti, Zr, LREE	Placers
Nurra	Fe	Oolitic iron
Iglesiente/ Eastern Sardinia	Pre-enrichment of base metals, U, V	Sedimentary
Variscan peak (Upper Carboniferous–Lower Permian)		
Eastern Sardinia	As-Sb-W-Au (Pb-Zn-Cu-Ag)	Orogenic hydrothermal gold veins
Central Sardinia	Pb-Zn-Cu (Ag, Au)	Skarns associated with granitoids
Southern Sardinia	Mo-W-Sn-F, F-Ba-Pb-Ag	Hydrothermal veins, greisen and skarn associated with rare-metal granites
Post-Variscan I period (Permian-Triassic)		
Arburèse/Baronie/Nurra	Pb-Zn (Ag, Ga-Ge, In), Ni-Co	"Montevecchio-type" polymetallic Pb-Zn hydrothermal veins; 'Five-element-type' veins
Southern Sardinia	F-Ba-Pb-Ag- REE	"Silius-type" low-temperature hydrothermal veins
Iglesiente-Sulcis	Ba, Zn-Pb	Karst, supergene
Post-Variscan II period (Cretaceous)		
Nurra	Bauxite	Paleosols
Cenozoic peak (Oligocene-Miocene)		
Western Sardinia	Au-Ag-Te-Cu	Epithermal HS and LS, porphyry
Sulcis/Logudoro	Mn	Volcano-sedimentary/exhalative
Logudoro	Cu, Pb	Sedimentary

4. Materials and methods

4.1 Creation of the Sardinian mining dumps geodatabase

A regional-scale geodatabase was created to systematically identify, map, and classify mining waste deposits across Sardinia (Italy), as part of an ISPRA–UniCa project aimed at producing a new regional-scale mapping of mineral resources (*Update of the regional mining and mineral resources database with priority on CRMs and SRMs for Decarbonization and Ecological Transition – Geoscience IR Project, WP 5.1*). The main goal of this project was to develop a structured, georeferenced dataset that supports both environmental assessments and resource evaluation, particularly for Critical Raw Materials (CRMs) potentially present in historical mining residues.

The construction of the geodatabase involved an integrated workflow that combined bibliographic research, archival documentation, analysis of existing metallogenic (1978 and 2008 – Fig. 18) and mining-related cartography, and extensive GIS-based spatial interpretation. Focus was given to identifying historical mining waste deposits that are not explicitly documented in previous regional syntheses and metallogenic maps, which mainly concentrated on ore bodies and exploited mineral deposits.

Using this systematic approach, 1887 mining dumps were mapped and georeferenced throughout the Sardinian territory. Each site was digitized as a spatial entity and stored within the QGIS software, resulting in the first comprehensive regional inventory dedicated specifically to mining waste deposits. The dataset produced is a key methodological output of this PhD research, providing a coherent spatial framework for future field investigations and laboratory characterization activities.

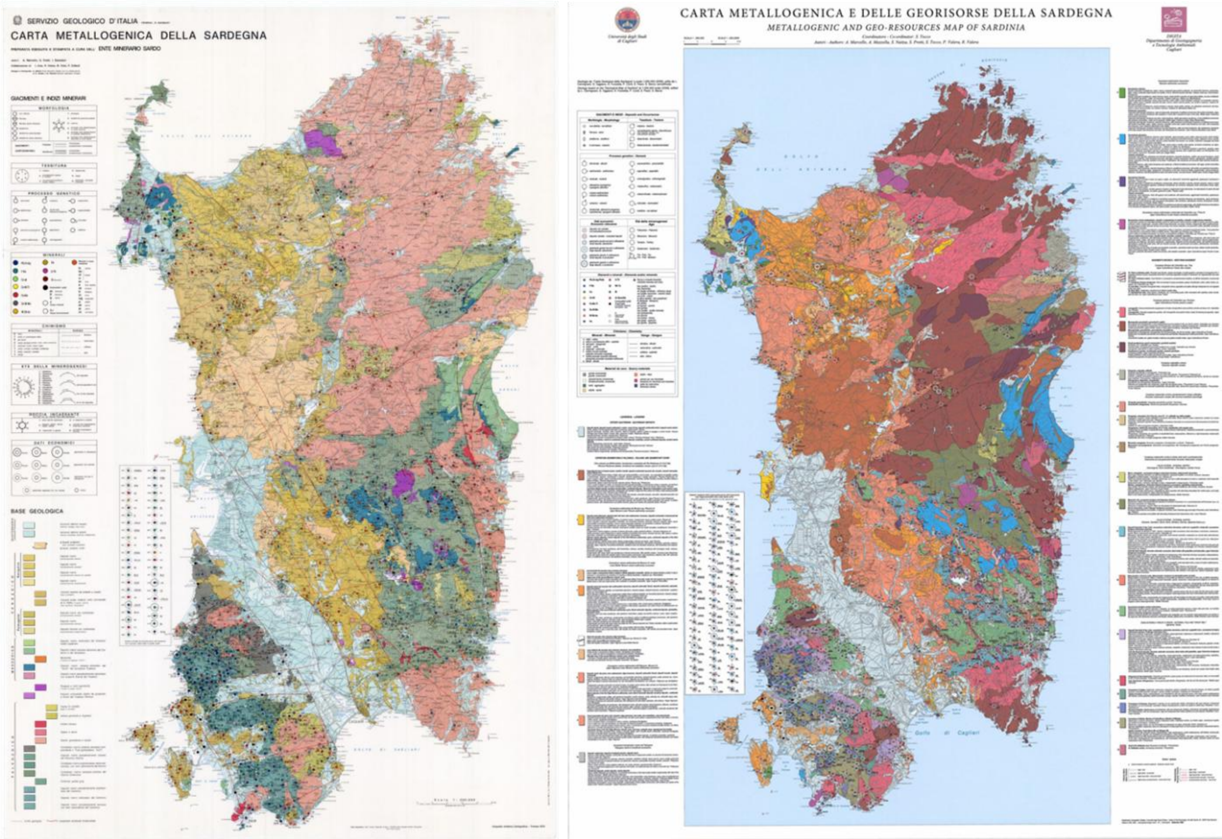


Figure 18. The previous metallogenic maps of Sardinia. On the left, the 1978 version, on the right, the 2008 version.

4.2 Data sources and preliminary screening

The initial identification of mining waste dumps was based on a critical revision of published scientific literature, technical reports, and historical mining documentation. These sources were integrated with information derived from regional metallogenic maps and mining district descriptions, which provided a preliminary reference framework for the location of former extraction and processing areas.

Subsequently, GIS analysis was performed to refine the spatial distribution of mining waste dumps and to identify additional waste deposits not previously documented. The screening phase aimed at distinguishing between different types of mining residues (e.g., flotation tailings, waste rock dumps, mixed waste) and at defining their spatial relationship with mines, processing plants, and historical mining infrastructures. In addition, Google Earth was used to obtain a 3D view of the mining waste dumps in order to avoid mapping landslide deposits such as scree slopes. *This approach allowed to discriminate between anthropogenic waste accumulations and natural gravitational deposits, reducing the risk of false positives in the inventory.*

4.3 GIS mapping and spatial database development

All identified mining waste dumps were digitized and organized into a georeferenced spatial database developed within a Geographic Information System (GIS). The mapping procedure consisted of manual interpretation and vectorization of dump bodies based on geomorphological evidence, spatial clustering around known mining sites, and comparison with available historical and modern cartographic datasets.

For each mapped mining waste dump, a dedicated attribute table was created that included, where available: (i) identification number, (ii) coordinates, (iii) type of mining waste, (iv) surface area in m^2, (v) mining location, (vi) reference CARG geological sheet, (vii) type of substrate on which the mining waste dump rests, (ix) predominant grain size classes, (x) minerals present, (xi) chemical elements present, (xii) CRMs and SRMs present, (xiii) mining period, (xiv) company that operated most, and (xv) any environmental interaction of the mining waste dump.

The dataset was progressively refined through iterative checks, ensuring internal consistency and minimizing spatial duplication. The final output consists of a regional geodatabase that provides standardized information for each site and enables spatial queries, statistical analyses, and prioritization of targets for sampling campaigns (Fig. 19).

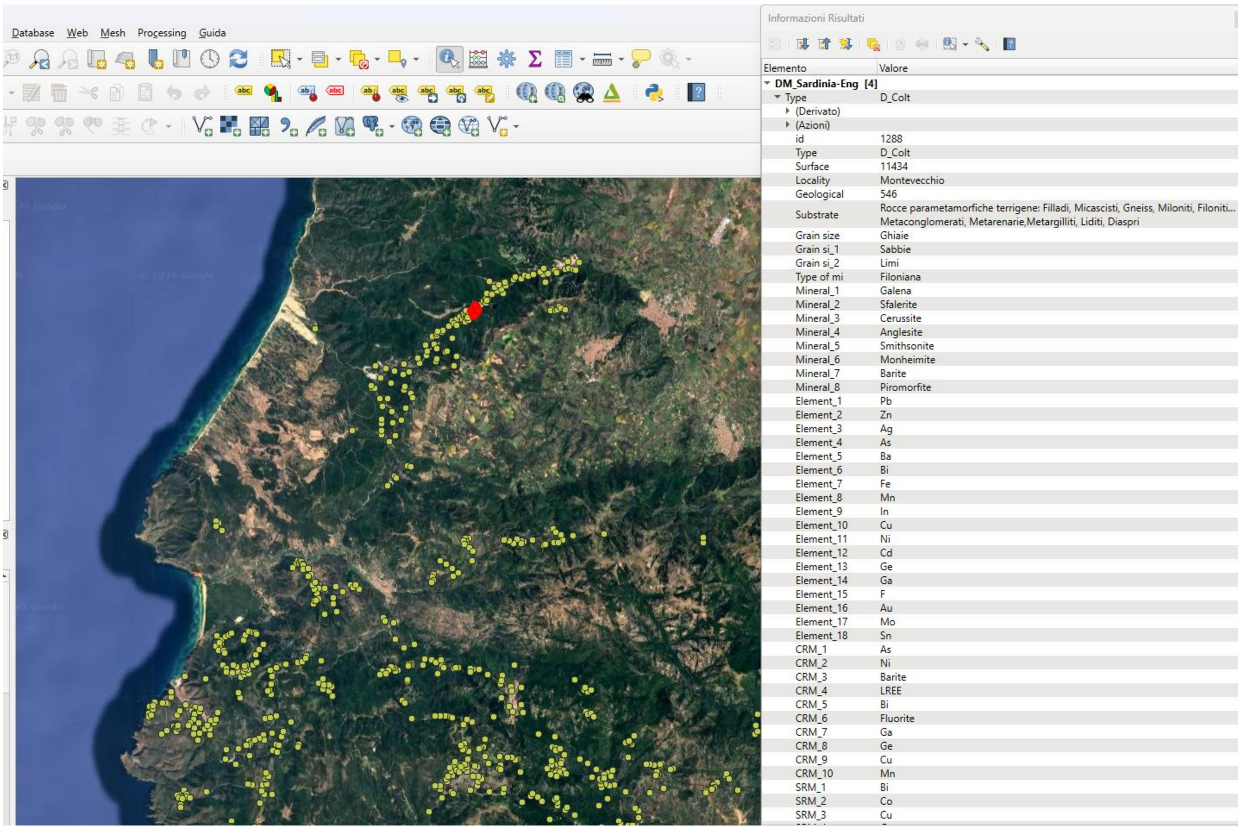


Figure 19. Example of the GIS-based database developed in this study. The red point indicates a mapped waste rock dump located in the Montevecchio mining district.

4.4 Field validation and selection of representative sites

A selection of mining waste dumps was further investigated through field surveys to validate the GIS interpretation, confirm the nature of the mapped deposits, and identify representative sites for detailed mineralogical and geochemical characterization.

Field observations were conducted to verify waste dump typology, mineralogical composition, evidence of metallurgical residues, and potential indicators of environmental instability (e.g., erosion features, mine drainage, secondary mineral precipitation – Fig. 20). The selected sites were subsequently targeted for sampling and laboratory analyses to evaluate the presence and potential enrichment of economically relevant elements, including critical CRMs.

Figure 20. Field observations and sampling in the flotation tailings pond of Santa Lucia mine (SW Sardinia).

4.5 Analytical methods (overview)

Selected samples collected during field campaigns were prepared and analyzed using a multi-analytical approach, including mineralogical and geochemical techniques. Mineralogical characterization was performed by X-Ray Diffraction (XRD), while elemental composition was investigated in the field through Portable X-Ray Fluorescence (P-XRF – Fig. 21). Microtextural and compositional analyses were carried out using Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). For selected samples, bulk chemical composition and trace element concentrations were determined through Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) and X-Ray Fluorescence (XRF), with specific attention to the CRMs content.

Figure 21. Field use of portable X-ray fluorescence (p-XRF) for the geochemical screening of secondary mineral patinas in flotation tailings at the Campo Pisano mine.

4.6 Database relevance and methodological novelty

The development of this geodatabase constitutes a key innovative aspect of the research, as it represents the first attempt to systematically integrate Sardinian mining waste deposits into a coherent regional-scale spatial dataset. Unlike previous metallogenic syntheses, which mainly focused on mineral occurrences and exploited deposits, this work explicitly includes mining waste dumps as targets of investigation, considering them not only as potential sources of environmental impact but also as potential secondary resources in the framework of circular economy strategies and sustainable raw material supply.

The database provides a reproducible methodological framework (Fig. 22) for the update of Sardinian mining knowledge and represents a fundamental tool for future regional planning, remediation strategies, and possible reprocessing projects aimed at recovering valuable metals from historical mining residues.

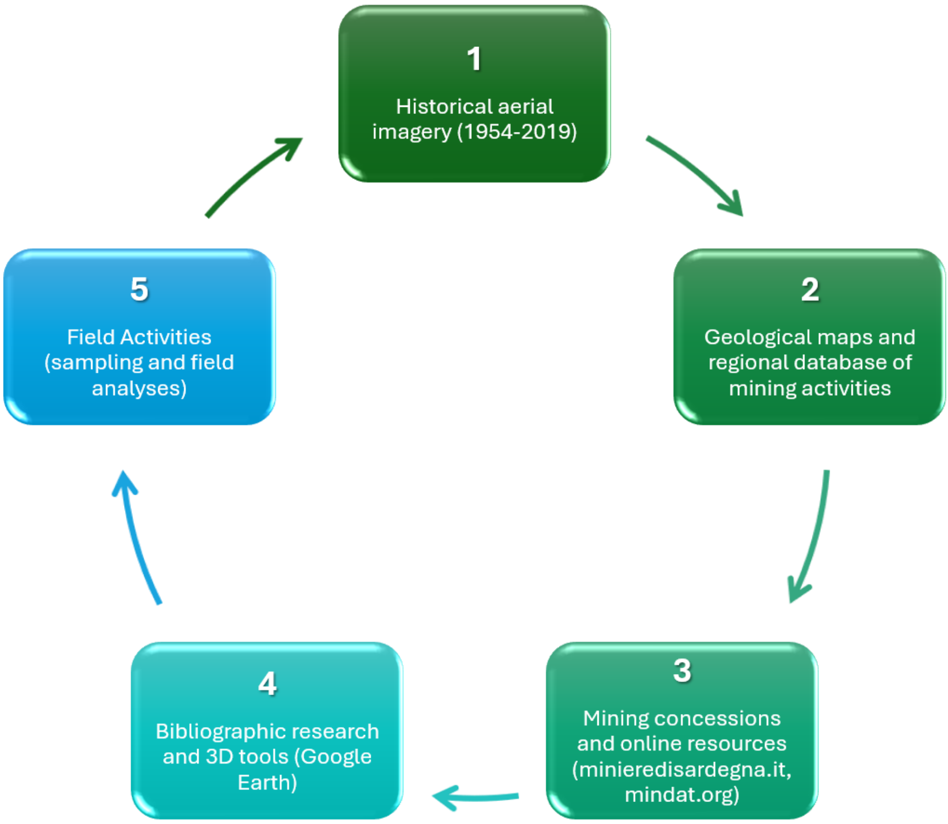


Figure 22. A flowchart that shows the various stages of work development.

4.7 Data availability, Open Data policy and terms of use

The geodatabase developed in this study, containing 1,887 georeferenced mining waste deposits across Sardinia, was created within the framework of the GeoSciences IR project, funded by the Italian PNRR and coordinated by ISPRA in partnership with the University of Cagliari. The database is intended to serve as a reference tool for environmental monitoring, territorial planning, and secondary resource assessment, and it will be made publicly available through the project's data dissemination infrastructure.

- **Open Data and FAIR principles**

In accordance with the GeoSciences IR project's data management strategy, the published products follow the FAIR principles (Findable, Accessible, Interoperable, Reusable), in line with best practices for research data management and sharing. Specifically, the geodatabase will be published as interoperable web services (e.g., WMS – Web Map Service and WFS – Web Feature Service) compliant with OGC (Open Geospatial Consortium) standards. These services will be hosted on institutional web portals, either by ISPRA (Italian Institute for Environmental Protection and Research) as part of the national GeoSciences IR project outputs, or by the University of Cagliari through its institutional open data repository. It is noted, however, that the level of FAIRness may vary depending on the specific characteristics of the data, the production methodologies, and the scientific and technical requirements of the different project outputs.

- **Terms of use**

The products available on GeoSciences IR are the results of scientific research conducted by universities and research institutions, which guarantee their rigorous scientific validity according to relevant academic and methodological standards. However, unless otherwise specified, these products should not be considered as certified or officially validated data for administrative, regulatory, or legal purposes. The use of GeoSciences IR products is under the sole responsibility of the user, who is required to evaluate their suitability for their own research or application purposes.

- **Future dissemination**

A final decision on the specific hosting platform and on the exact level of accessibility (e.g., open access vs. restricted access for specific data layers) will be made upon completion of the project, in agreement with the funding bodies and data owners. The publication of the database in compliance with FAIR principles will ensure transparency, reproducibility, and reusability of the research results, while respecting the limitations outlined in the terms of use. *(as defined by the GeoSciences IR project*)

5. Results

This chapter presents the main outcomes of the regional-scale mapping of mining waste deposits carried out during this research. A total of 1887 individual waste dump bodies were identified, delineated and catalogued across Sardinia, providing the first systematic spatial inventory of mining waste deposits at the regional scale. First, the three scientific articles are introduced, followed by the mapping of mining waste deposits in different mining districts. These deposits are distributed across the main historical mining districts of the island and display highly variable morphologies and spatial organization.

Sustainable Perspectives on Historical Mining Dumps: Challenges and Opportunities

(READY TO BE SUBMITTED)

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Abstract:

Historical mining activities in Sardinia (Italy), which extended from ancient times to the late 20th century, generated more than 70 million m^3 of waste materials, including waste rocks, processing tailings, metallurgical slags, and industrial by-products. These deposits represent both a major environmental challenge—due to mine drainages, metal and metalloid mobilization, and dust dispersion—and a potential secondary resource of Critical and Strategic Raw Materials (CRMs and SRMs), in line with the objectives of the European Critical Raw Materials Act. This review provides an updated synthesis of Sardinia's mining waste legacy, integrating historical data, metallogenic information, and recent research outcomes. Particular attention is paid to the assortment of waste types, their environmental impacts, and their resource potential, with a focus on the ongoing Geosciences IR Project, which aims to systematically map and characterize Sardinian mining waste. Mineralogical investigations and SEM-EDS analyses have revealed the presence of CRMs such as LREE, Ni, Co, and W, highlighting promising perspectives for future resource recovery. These encouraging results underscore the need for complementary chemical analyses to quantify grades and assess the economic and environmental implications of potential reprocessing. From this review, Sardinia emerges as a unique natural laboratory for the development of

integrated strategies that combine raw material supply security, circular economy approaches, and environmental remediation.

Keywords: Mining waste; Critical Raw Materials; Circular Economy; Environmental Sustainability; Sardinia.

1. Introduction

Critical and Strategic Raw Materials (CRMs and SRMs) are essential for the development of advanced technologies that increasingly permeate modern society and form the foundation of a low-carbon future (*Arrobas La Porta et al., 2017*). The "critical" designation reflects not only the economic importance of these materials but also the risks associated with their availability and supply, which are influenced by geological, economic, and geopolitical factors. Since 2010, the European Commission has defined, expanded, and regularly updated the list of CRMs for the European Union. The most recent update (2023) identified 34 Critical Raw Materials such as Sb, W, Al, REE, As, baryte, Bi, Co, Fluorspar, etc. (*European Commission, 2023).* Most of these elements/minerals occur in nature as mineral resources and are found in several ore deposit types, including orogenic Au deposits (Sb-W-As), Volcanogenic Massive Sulfide (Sb, Bi), skarn (W-Cu-As-REE-Bi-Mo), bauxite (Al, REE, Ti, V, Sc), Iron Oxide Copper-Gold (REE-Ti-V), Layered Mafic Intrusions (Ni-Co, PGE), Mississippi Valley-Type and Sedimentary Exhalative (baryte), and hydrothermal vein systems (fluorspar, baryte, LREE, Ni-Co). Over the past decade, numerous reconnaissance and mapping programs of CRM resources in Europe have been undertaken by various institutions and research centres (e.g., *Bertrand et al., 2016*; *Flindt Jørgensen et al., 2023*; *European Union, 2024a*). With the adoption of the Critical Raw Materials Act (*European Union, 2024b*), a comprehensive European plan was launched to map and evaluate the CRM potential of historical mining districts. This initiative encompasses not only primary mineralized deposits but also waste material dumps derived from past mining activities. In fact, waste materials may represent potential sources of CRMs and SRMs, as their residual contents of minerals and economically relevant elements are worth investigating (*Ubaldini et al., 2026*). Moreover, recent estimations point out that over 14 billion tons of waste yearly originate from mineral processing worldwide (*Adiansyah et al., 2015*). Projections indicate that this volume could nearly double by 2030 (*International Energy Agency, 2024*).

Waste materials can be classified based on the type of processing they are derived from, which influences features such as grain size and degree of mineralization, with approximately 95% falling into two categories: waste rock and mine tailings (*Falagán et al., 2017*; *Agboola et al., 2020*). Waste rock refers to poorly mineralized material extracted during mining, typically consisting of host rock and gangue minerals. Tailings are the fine-grained residues generated by ore beneficiation in processing plants and commonly deposited in basins or dams (*Lottermoser, 2011*). Waste rock and tailings are first distinguished by their grain size: waste rock typically consists of coarser fragments ranging from gravel to large blocks, whereas tailings are generally fine-grained due to comminution processes (*Gorakhki and Bareither, 2024*). Although considered waste, these materials often retain appreciable concentrations of valuable elements, in some cases exceeding the grades found in primary ores (*Sarker et al., 2022*). The way in which waste is generated strongly influences its environmental impact. Particularly severe issues arise from artisanal mining, where the use of inappropriate techniques often results in excessive waste production and considerable environmental damage (*World Bank, 2023*). Grain size is especially significant from an environmental perspective, as it influences the specific surface area of the materials and thereby the potential release of contaminants. This is most commonly associated with the oxidation of sulfide minerals, especially pyrite [FeS_2], which leads to Acid Mine Drainage (AMD) and Acid Rock Drainage (ARD). These processes contribute to the contamination of water, soil, and entire ecosystems through the mobilization and transport of toxic elements (*Nordstrom, 2011; Grita et al., 2026*). Furthermore, the type of treatment applied to the ore (e.g., hydrogravimetric separation, flotation, etc.) critically shapes the mineralogical and chemical characteristics of the resulting materials, yielding products that are variably depleted or enriched in specific elements and thus exerting markedly different impacts on the environment.

In metalliferous mining, the volume of waste generated during processing is nearly equivalent to the volume of raw ore treated, making the management and disposal of such materials a critical aspect of mining operations. Two principal strategies for tailings disposal are recognized: direct disposal and indirect disposal (*Adiansyah et al., 2015*). Direct disposal consists of discharging tailings into rivers, lakes, or marine environments. Historically widespread across numerous mining districts, this practice is now prohibited by international conventions and is banned in most countries due to its severe ecological consequences, which include large-scale contamination of terrestrial and aquatic systems (*International Maritime Organization, 2013*; *Morello et al., 2016*). Indirect disposal involves the transport of tailings, typically in the form of thickened slurries, to engineered impoundments or dams. While this method reduces the extent of widespread pollution, it poses inherent risks related to the structural instability of containment facilities. Between 1917 and 2009, 237 tailings dam failures were documented globally (*Rico et al., 2008*; *Lottermoser, 2011; Luino and De Graaf, 2012*; *Adiansyah et al., 2015*), including the catastrophic events at Val di Stava, Italy (1985), and Baia Mare, Romania (2000). More recently, the 2019 collapse of a tailings dam in Brumadinho, Minas Gerais (Brazil), after only three years of disposal activity, caused hundreds of fatalities and extensive environmental contamination across a large area (*Silva Rotta et al., 2020*; *Zhu et al., 2024*). Consequently, current research increasingly addresses the socio-environmental and health risks associated with tailings, as well as the development of safer, more responsible, and sustainable extraction and waste management practices (*Cacciuttolo et al., 2023*). The social and environmental impacts of mining and associated wastes have been widely documented in Europe (*Lèbre et al., 2020*; *Mononen et al., 2022*; *Hoxha et al., 2025*). More recently, however, attention has shifted toward evaluating the raw material potential of mining waste and developing appropriate recovery technologies, not only as a strategy for resource supply but also as a means of reducing environmental burdens (*Rankin, 2017*; *Blengini et al., 2019*; *Sarker et al., 2022*; *Villa Gomez et al., 2022; Zeng et al., 2022; Lemos et al., 2023*). Within Europe, mining wastes have been identified as potential sources of CRMs, with significant prospects reported in Sweden, Finland, Portugal, Spain, and the Balkan regions (*Dino et al., 2016*; *López et al., 2018*; *Parviainen et al., 2020*; *Žibret et al., 2020*; *Mulenshi et al., 2021*; *Šajn et al., 2022*; *Rosario-Beltré et al., 2023*; *De Oliveira et al., 2024*). In the Iberian Pyrite Belt, the occurrence of rare earth elements (REEs) in acid mine drainage derived from sulfide oxidation has also been investigated, providing insight into alternative recovery pathways (*León et al., 2023*).

Mine waste deposits in Italy have been inventoried by ISPRA, the Italian Environmental Agency (*ISPRA, 2022*). Numerous studies have investigated their environmental impacts across several mining districts, including Tuscany (*Benvenuti et al., 1997, 1999, 2000*; *Mascaro et al., 2001*; *Rimondi et al., 2012*; *Meloni et al., 2021*), Liguria (*Marescotti et al., 2008, 2010*), and Sardinia (*Buosi et al., 2001*; *Cidu and Fanfani, 2002*; *Frau and Ardau, 2004*; *Contini et al., 2009*; *Da Pelo et al., 2009*; *De Giudici et al., 2019*; *Fancello et al., 2023*). However, comparatively limited information is available on the potential of mining waste as secondary sources of raw materials (*Lucarini et al., 2020*). This knowledge gap extends to both non-metalliferous (*Careddu et al., 2018*; *Dino et al., 2021*; *Tazzini et al., 2024*; *Zhao et al., 2024*; *Gioiello et al., 2025*) and metalliferous (*Rossetti et al., 2017*; *Dino et al., 2018*; *Baldassarre et al., 2023*) mining sectors. Even in Sardinia, Italy's most significant mining region, relatively few studies have addressed the economic characterization of mining waste with a view to their potential reprocessing (*Medas et al., 2013; Manca et al., 2019*; *Balassone et al., 2021*; *Sedda et al., 2024*; *Vaccaro et al., 2024*; *Aquilano et al., 2025*). Sardinia has a long and complex mining history, beginning in the Nuragic period (ca. 1500 B.C.) and extending into the present, although nearly all metalliferous mines were closed by the late 1990s. This prolonged mining activity has profoundly shaped the island's landscape, leaving massive open-pit excavations, extensive underground networks, and an estimated 70 million cubic meters of mining and metallurgical waste (*Regione Autonoma Sardegna, 2003*). These deposits, more than 60% of which are concentrated in the Sulcis-

Iglesiente–Arburèse district (Figure 1), represent a significant resource that could be reconsidered for their Critical and Strategic Raw Materials (CRMs and SRMs) content.

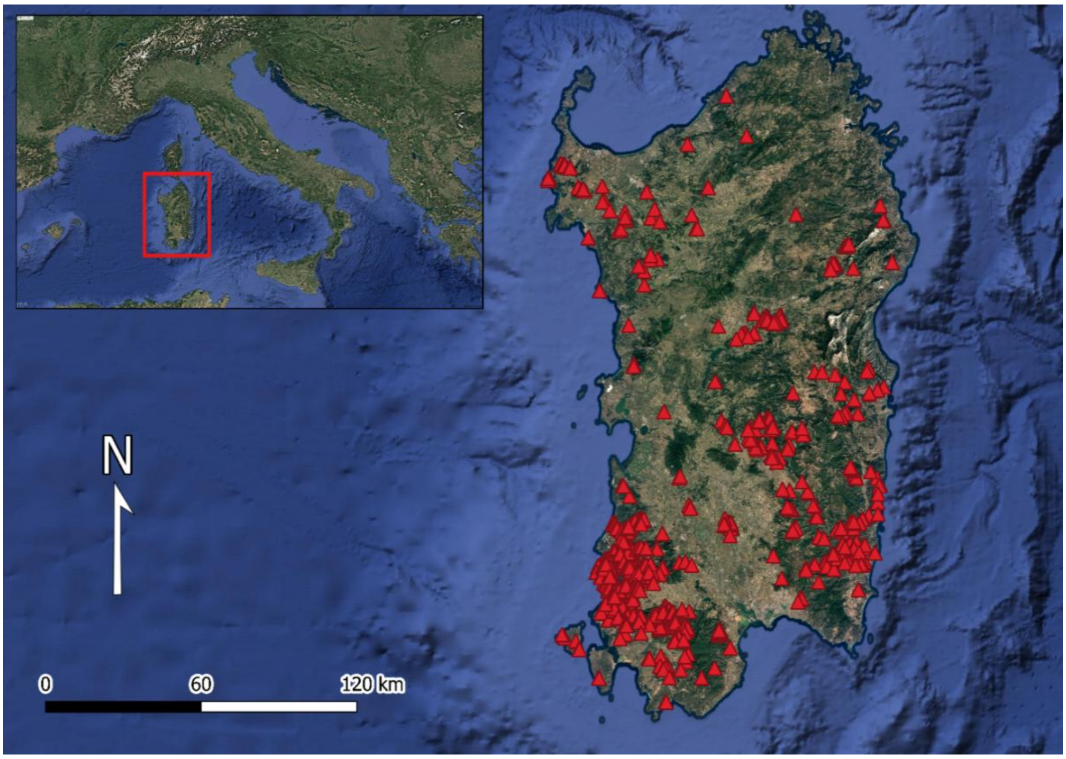

Figure 1. Distribution of mining waste deposits in Sardinia. Each red dot shows a deposit. Over 60% of sites are located in the Sulcis-Iglesiente and Arburèse areas of western Sardinia.

In the framework of the ISPRA's GEOSCIENCES-IR project, a new campaign of field investigations and archival research is conducted by the University of Cagliari (UniCa) to obtain a regional-scale resource mapping. Preliminary results increasingly highlight the Critical Raw Material (CRM) potential of mining waste deposits across Sardinia. The primary objective of the project is to develop a comprehensive database documenting the CRM content of these deposits, together with a new metallogenic map of Sardinia that explicitly incorporates waste deposits of potential economic significance—features not included in the previous editions (*Marcello et al., 1978*; *Tocco et al., 2008*). This digital resource is intended to serve as a model for the broader mapping of secondary raw material resources on the national scale. The present review aims to provide an updated overview of Sardinian mining waste deposits, focusing on their potential as sources of CRMs, their environmental implications, and the research initiatives currently addressing them. The study is based on an extensive re-examination and reinterpretation of the abundant scientific and technical literature on Sardinian ore deposits, spanning from the late 19th century to the present. This work also includes a critical revision of existing metallogenic databases (*Marcello et al., 1978*; *Tocco et al., 2008*; *ISPRA, 2024*), particularly concerning mineral deposits that historically served as primary sources of mining waste. Archival data from public institutions (e.g., AMMI, Ente Minerario Sardo, Progemisa S.p.A.) and private mining companies (e.g., Montevecchio, Monteponi, Pertusola, Mineraria Silius) active in Sardinia during the 20th century were further integrated to support this reassessment.

2. Origin and type of mining waste deposits in Sardinia

The Sardinian mining districts host a diverse array of ore deposit types, including Mississippi Valley-Type (MVT) Pb-Zn stratabound deposits, mesothermal orogenic-type As-Au±Sb±W veins, granite-related Fe, Cu-Pb-Zn, Sn, and W skarns, Mo-bearing greisens and veins, several varieties of low-temperature hydrothermal veins (e.g., polymetallic Pb-Zn-Ag veins, “five-element-type” Ni-Co-As-Bi-Ag veins, and F-Ba-Pb veins), as well as volcanic-related Au-Cu, Au-Ag and Mo epithermal and porphyry systems (*Naitza et al., 2024*, and references therein). This metallogenic diversity encompasses a broad spectrum of geochemical, mineralogical, and textural characteristics. Therefore, the historical exploitation of Sardinian districts required different mineral processing techniques for ore concentration and distinct metallurgical treatments of concentrates, depending on the mineralogical composition (e.g., sulfides, arsenides, sulfates, oxides, carbonates, halides) and on the textural/microstructural associations of the ores (intergrowth, dissemination, concentration in veins, etc). A significant proportion of the mining waste deposits in southwestern Sardinia derives from the processing of Pb and Zn MVT sulfide ores, which were dominated by galena [PbS] and sphalerite [ZnS]. The largest ore-dressing plants were established in proximity to major mining operations in western Sardinia, including Campo Pisano, Monteponi, San Giovanni (Iglesias valley), Masua, and Buggerru along the western coast, as well as Arenas in the hinterland of the Iglesiente district. Additional large-scale Pb and Zn processing facilities were located at the Montevecchio and Ingurtosu mines (Arburèse–Guspinese district), which exploited polymetallic hydrothermal vein systems. Additional ore-dressing plants were in the Sulcis area (Rosas and San Leone), dedicated to the processing of Cu- and Fe-bearing skarns, respectively. In the Sarrabus–Gerrei district (southeastern Sardinia), facilities treated Sb–As and Ag–Pb–Zn ore bodies at Ballao–Corti Rosas, Baccu Locci, and Monte Narba. In central Sardinia, the Funtana Raminosa plant was established for the processing of Cu-bearing skarn ores. In northern Sardinia, the Lula–Sos Enattos and Argentiera plants were devoted to Pb–Zn mineralizations. (Fig. 2).

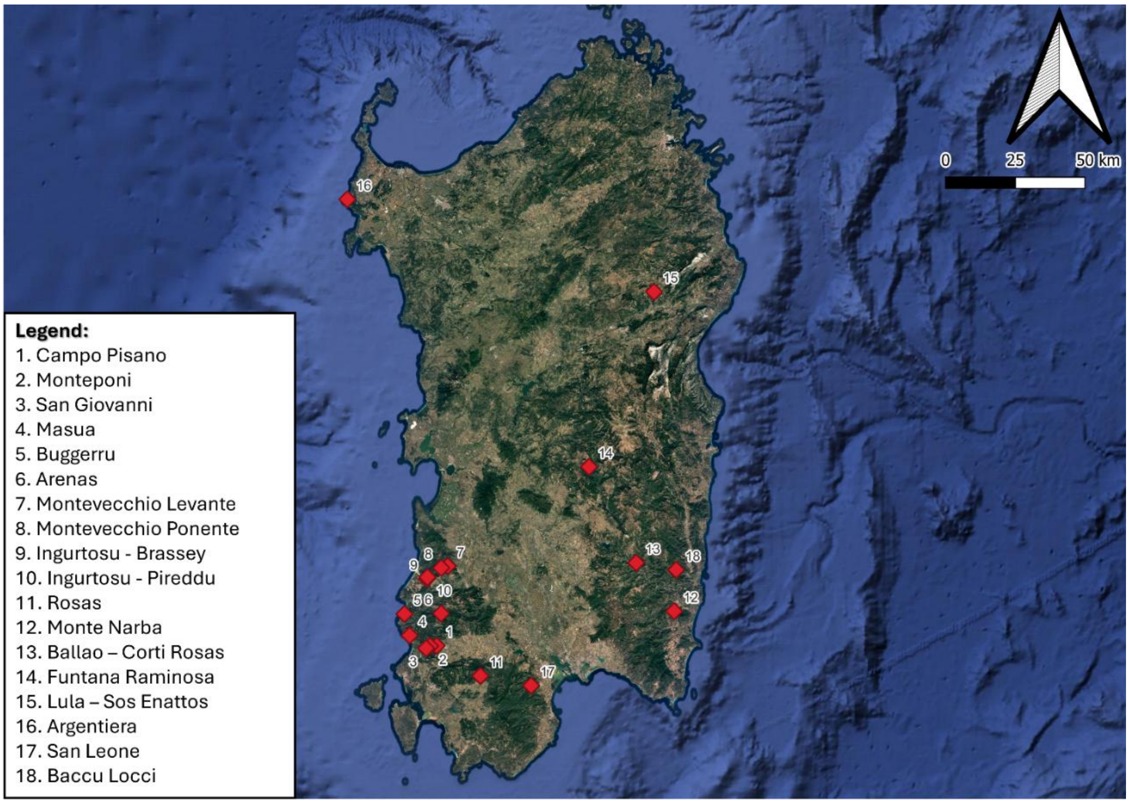

Figure 2. Distribution of the main mineral processing plants in Sardinia. The largest group is located in south-west Sardinia.

In the mineral processing plants, the essential operations comprised: (1) ore crushing and grinding, (2) separation of ore from gangue, and (3) mineral enrichment to produce concentrates (Fig. 3). During the 19th and early 20th centuries, separation processes were primarily based on hydro-gravimetric techniques, which utilized the combined action of water and gravity to discriminate mineral phases according to density (e.g., shaking tables, sieves, and jigs). These methods were subsequently complemented by sink-and-float techniques, which further exploited density contrasts among mineral phases using fluids of varying specific gravities. From the early 20th century onward, a technological shift occurred with the introduction and progressive adoption of froth flotation, a method that selectively separates finely ground sulfide minerals based on differences in surface chemistry. Flotation rapidly became the dominant processing technology for Pb-Zn ores in Sardinia, allowing for the recovery of more finely disseminated mineralizations. This innovation significantly increased metal recovery rates but also generated very large volumes of fine-grained tailings, which now constitute a major component of Sardinia's mining waste deposits.

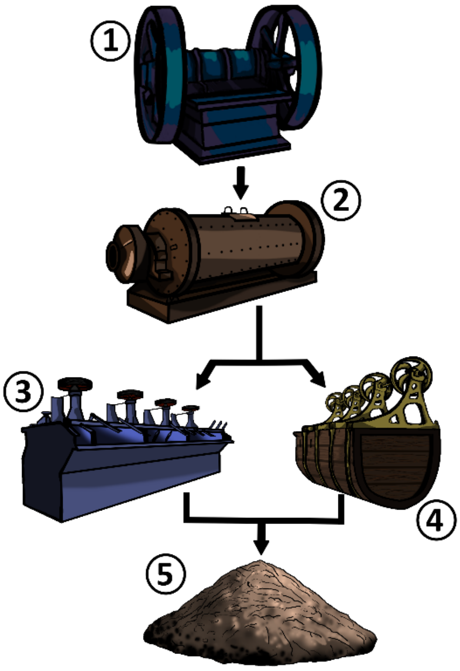

Figure 3. Simplified schematic diagram of the operation of a mineral processing plant. 1) Crushing by jaw crusher; 2) Grinding by ball mill or rod mill;3) Mineral separation by flotation (physico-chemical process); 4) Mineral separation by gravity concentration with screens (physico-mechanical separation); 5) Economic concentrate.

Mineral enrichment by froth flotation was first introduced in Sardinia in 1917 at the Funtana Raminosa mine (*Sanna, 1920*) and became widespread across the island's mining districts during the 1920s (*Ghiani, 1986*). Initially developed to complement hydro-gravimetric methods, flotation greatly enhanced the exploitation of low-grade ores. This technique significantly improved plant performance, enabling higher recovery rates of economic minerals from a wider range of deposits. The process required the systematic use of chemical reagents—including frothers, promoters, depressants, activators, sulfidizers, and regulators—that selectively promoted or inhibited the flotation of mineral phases within flotation cells. The adoption of flotation in several smaller Sardinian districts (e.g., Rosas, Ballao–Villasalto, Baccu Locci, Lula–Sos Enattos, and Argentiera) (Fig. 2) allowed for the beneficiation of complex ores characterized by finely intergrown mineral phases, such as the so-called "mixed sulfide" Zn-Pb-Cu-Fe assemblages. This innovation also facilitated the economic recovery of accessory minerals, including stibnite, arsenopyrite, Ag-bearing sulfosalts, and native silver. The same general sequence of operations was subsequently adapted for other ore types, including baryte–fluorspar deposits and "calamine" ores. The latter, consisting of secondary Pb and Zn minerals (carbonates, sulfates, silicates, oxides, hydroxides, etc.), required specialized separation and enrichment techniques. However, their recovery efficiencies were often lower than those achieved for primary sulfide ores (*Ciccu et al., 1979*). A distinct processing scheme was applied to iron ores. A prime example is the San Leone mine plant (Fig. 4), one of the largest iron ore processing facilities in Italy. There, magnetite-bearing skarn mineralization was treated through successive cycles of crushing and milling, followed by staged dry and wet magnetic separation to achieve ore concentration.

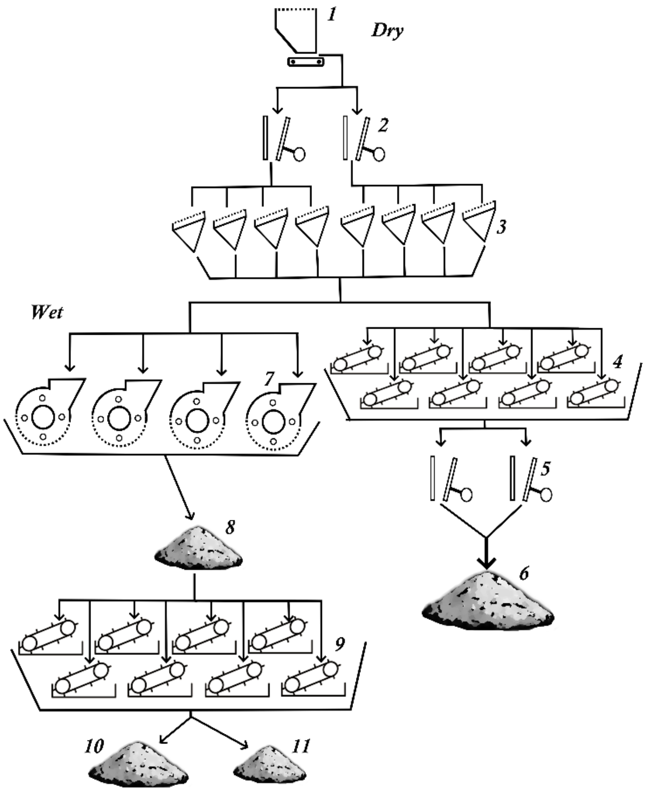

Figure 4. Flow sheet of the San Leone mine processing plant. 1) Hopper; 2) Jaw crushers; 3) Vibrating screens; 4) Electromagnetic separators; 5) Jaw crushers; 6) Waste residue rich in mixed granules and gangue; 7) Ball mills; 8) Ground residue; 9) Electromagnetic separators; 10) Concentrate (65% Fe); 11) Tailings.

In all the abovementioned localities, tailings and other waste materials generated by mineral processing contributed to mining waste volumes in addition to waste rock derived from excavation. These deposits occur in various forms, including dumps piled near processing plants, accumulations along hillslopes, and tailings retained in sedimentation basins or dams. The physical characteristics of these materials largely depend on the employed processing techniques, which were in turn dictated by ore composition. In terms of grain size, tailings from hydro-gravimetric methods typically range from millimeters to centimeters, whereas flotation processes produced finer, sub-millimeter tailings. Residual metal contents vary considerably depending on ore type, processing technology, and recovery efficiency.

Smelting for the recovery of lead and silver from sulfide ores has a long history in Sardinia, beginning in Roman and medieval times, particularly in the Iglesiente and Fluminèse areas of the southwestern districts. The largest early smelter in this region was established in Villacidro in the 18th century (*Rolandi, 1974*). With the onset of the industrial era in the first half of the 19th century, many mines across the island were equipped with metallurgical furnaces dedicated to roasting "calamine" ores, the only viable method at the time for producing metallurgical-grade zinc oxide. Consequently, most mines in the southwestern district possessed their own furnaces. A major technological advancement came with the construction of the Monteponi plant in 1926, which marked the introduction of electrolysis as the most efficient method for extracting zinc from calamine ores. From that point onward, zinc production from Sardinian calamine was largely centralized at Monteponi, which remained in operation until 1983. Lead smelting during the 19th century was carried out using pyrometallurgical methods at coastal plants such as those in Funtanamare and Masua. Substantial quantities of Roman and medieval metallurgical slags were also reprocessed to recover residual lead and silver. By the late 19th and early 20th centuries, modern lead smelters were established at Monteponi (1898) and San Gavino (1934), supplying the major mines of the southwestern district (*Rolandi, 1974*). In 1907, an antimony smelting facility was constructed at the Su Suergiu mine in Villasalto. From the late 1960s onward, zinc sulfide metallurgy—previously conducted outside Sardinia—was centralized in the newly established Portovesme plants, which also hosted aluminum metallurgical facilities beginning in the 1970s. These various metallurgical processes generated distinct waste types, including slags, sands, and dusts. A further category, known as electrolytic muds, was produced during refining processes and stored in tailing dams together with sludges from aluminum metallurgy. At present, all these waste types remain stored in proximity to the main metallurgical facilities (Fig. 5). Strictly speaking, metallurgical slags are industrial wastes generated by pyrometallurgical smelting and refining processes, rather than by mining or mineral processing activities. According to the European Waste Catalogue, slags fall under different waste codes compared to mining wastes (waste rocks and tailings). However, in the specific context of historical mining districts, smelting operations were often spatially and economically integrated with mining activities, and slags were frequently disposed of in close proximity to mine waste dumps or tailings ponds. For this reason, and because slags may contain significant concentrations of residual base metals and CRMs (e.g., Zn, Pb, Cu, REEs), they were considered like metallurgical wastes.

The principal characteristics of selected mining and metallurgical waste deposits in Sardinia are summarized in Table 1.

Table 1. Main mining waste deposits in Sardinian districts.

District	Mine	Ore deposit type [a]	Exploited RM	Type of mining waste	Potential residual resources	Grainsize	Volumes [m^3]
Iglesiente	*Malfidano*	MVT, "Calamine" ore	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn – Ag - Ba	Clays, Sands, Gravels	1-1,6 x 10^6 m^3
	Barraxiutta	MVT	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn - Cu	Clays, Sands, Gravels	0.3-0.5 x 10^6 m^3
	Sa Duchessa	Skarn	Pb-Zn-Cu	Waste rocks, HG and FT tailings	Cu – Pb - Zn	Clays, Sands, Gravels	0.2-0.3 x 10^6 m^3
	Campo Pisano	SEDEX	Zn-Pb	Waste rocks, HG and FT tailings	Zn – Pb - Ba	Clays, Sands, Gravels	0.7-8 x 10^6 m^3
	Masua/Nebida/Acquaresi	MVT, "Calamine" ore	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn – Cd	Clays, Sands, Gravels	0.3-6 x 10^6 m^3
	Monteponi	MVT, "Calamine" ore	Pb-Zn	Waste rocks, HG tailings, hydrometallurgy, pyrometallurgy	Zn – Pb – Cd	Clays, Sands, Gravels	2-5 x 10^6 m^3
	San Giovanni	MVT, "Calamine" ore	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn – Ag - Ba – As – Sb - Cu	Clays, Sands, Gravels	1-7 x 10^6 m^3
	Seddas Moddizzis	SEDEX, MVT, "Calamine" ore	Zn-Pb	Waste rocks, HG and FT tailings	Zn - Pb	Clays, Sands, Gravels	0.25-0.5 x 10^6 m^3
Sulcis	*Tasua*	Karst	Ba	Waste rocks, HG and FT tailings	Ba	Clays, Sands, Gravels	0.1-0.6 x 10^6 m^3
	Mont'Ega	Hydrothermal vein (LTFB)	Pb-F-Ba	Waste rocks, HG and FT tailings	Ba – F – Pb – Ag - Zn	Clays, Sands, Gravels	0.5-1 x 10^6 m^3
	Rosas/Truba Niedda	Skarn	Pb-Zn-Cu	Waste rocks, HG and FT tailings	Pb – Zn – Ag – Cu – As- Sn	Clays, Sands, Gravels	0.25-1.5 x 10^6 m^3
	Sa Marchesa	Skarn	Pb-Zn-Ba-Cu	Waste rocks, and Ft tailings	Pb-Zn-Ba-Cu-As-W	Sands, Gravels	0.15-0.2 x 10^6 m^3
	Orbai	Hydrothermal vein (LTFB)	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn - Ba	Clays, Sands, Gravels	0.1-0.25 x 10^6 m^3
	Barega	Hydrothermal vein	Ba	Waste rocks, HG tailings	Ba - Pb	Sands, Gravels	0.1-1 x 10^6 m^3
	San Leone	Skarn	Fe	Waste rocks, MS tailings	W – Sn - F	Sands, Gravels	0.5-2.5 x 10^6 m^3

Fluminèse	*Su Zurfuru*	Skarn	Pb-Zn-F	Waste rocks, HG and FT tailings	F – Pb - Zn	Gravel, Clays	0.25-0.5 x 10^6 m^3
	Santa Lucia/S'Oreri	Hydro-thermal vein (LTFB)	F-Ba-Pb	Waste rocks, HG and FT tailings	F – Ba – Pb – Zn – LREE – Ni - Co	Sands, Gravels	0.5-2 x 10^6 m^3
	S. Vittoria	Hydro-thermal vein (HT)	As	Waste rocks, HG	As - Sn	Gravels, Sands	0.1-0.2 x 10^6 m^3
	Arenas - Tiny	MVT (remobilized)	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn - Ba	Clays, Sands, Gravels	0.5-2 x 10^6 m^3
	Sa Menga/Acqua Is Prunas/ Pira Inferida/Fenugu Sibiri	Hydrothermal vein (LTP)	Ni-Co-Pb-Zn	Waste rocks, HG	Ni-Co-Bi-As-Pb-Zn-Sb- Ag-LREE	Gravels, Sands	0.1-0.25 x 10^6 m^3
Guspinese - Arbùrese	*Gennamari/Bau/S'Acqua Bona*	Hydrothermal vein (LTP)	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn – Ag – LREE – Ga – In – Ge – Ni – Co – As – Sb – Bi - Cu	Gravels, Sands	0.5-1 x 10^6 m^3
	Ingurtosu/Naracauli	Hydrothermal vein (LTP)	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn – Ag – LREE – Ga – In – Ge – Ni – Co – As – Sb – Bi - Cu	Clays, Sands, Gravels	0.5-2 x 10^6 m^3
	Montevecchio	Hydrothermal vein (LTP)	Pb-Zn	Waste rocks, HG and FT tailings	Pb – Zn – Ag – LREE – Ga – In – Ge – Ni – Co – As – Sb – Bi - Cu	Clays, Sands, Gravels	2-9 x 10^6 m^3
	Perd'e Pibera	Greisen	Mo	Waste rocks, HG tailings	Mo, W, Bi, Sn	Gravels	0.1-0.25 x 10^6 m^3
Campidano	*Perda Lai*	Hydro-thermal vein (LTFB)	F-Ba-Pb	Waste rocks, HG and FT tailings	F-Ba-Pb	Clays, Sands, Gravels	0.1-0.25 x 10^6 m^3
	Furtei	Epithermal HS	Au-As-Cu	Waste rocks, FT and CN tailings	Au-Cu-As-Te	Clays, Sands, Gravels	0.25-0.5 x 10^6 m^3
Sarrabus - Gerrei	*Corti Rosas*	Hydrothermal vein (MT)	Sb	Waste rocks, FT tailings, pyrometallurgy	W – Sb – As – Cu- Au	Clays, Gravels	0.1-0.25 x 10^6 m^3
	Monte Narba	Hydrothermal vein (LTP)	Ag-Pb	Waste rocks, HG and FT tailings	Pb – Ba – F – Ag - Cu	Gravels, Sands	0.15-0.25 x 10^6 m^3

	Silius	Hydrothermal vein (LTFB)	F-Pb	Waste rocks, SF tailings	Pb – Ba – F – LREE	Gravels, Sands	0.1-0.25 x 10^6 m^3
	Assemini	Hydro-thermal vein (LTFB)	F-Pb	HG and FT tailings	Pb – Ba – F – LREE	Clays, Sands	1-3 x 10^6 m^3
	Baccu Locci	Hydrothermal vein (MT)	Pb-As	Waste rocks, HG and FT tailings	As – Pb – Zn- Cu-Sb-Ag-Au	Gravels, Sands	0.1-0.25 x 10^6 m^3
	Su Suergiu	Hydrothermal vein (MT)	Sb-W	Waste rocks, pyrometallurgy	Sb – W-Au-Pb-Zn-Cu	Gravels	0.1-0.25 x 10^6 m^3
Central-Northern Sardinia	*Funtana Raminosa*	Skarn	Cu (Pb, Zn, Ag)	Waste rocks, HG and FT tailings	Cu – Pb – Zn- Ag-W – Sb - LREE	Clays, Sands, Gravels	0.25-0.3 x 10^6 m^3
	Argentiera	Hydrothermal vein (LTP)	Pb-Zn (Cu, Sb)	Waste rocks, HG and FT tailings	Pb – Zn - Cu-Sb	Clays, Sands, Gravels	0.1-0.25 x 10^6 m^3
	Sos Enattos	Hydrothermal vein (LTP)	Pb-Zn (Cu, Sb)	Waste rocks, HG and FT tailings	Pb – Zn – Cu-Sb-Ni-Co	Clays, Sands, Gravels	0.15-0.5 x 10^6 m^3
	Guzzurra-Arghentaria	Hydrothermal vein (LTFB)	Pb-Zn	Waste rocks, HG	Pb – Zn - Ba – F	Gravels, Sands	0.1-0.25 x 10^6 m^3

Acronyms: HG - hydro-gravimetric; FT-flotation; SF – Sink and Float; MS- Magnetic Separation; CN-Cyanidation; RM – Raw Materials; LTP- Low-Temperature Polymetallic; LTFB- Low Temperature fluorite-baryte; MT – Mesothermal; HT – High Temperature; HS: High Sulfidation; a): ore deposit type according to Boni et al., 1996; Lattanzi, 1999; Naitza et al., 2024.

3. Environmental impacts and remediation strategies

Sardinian former mining areas act as emission centers of pollutants in multiple forms, leading to the contamination of soils, surface waters, and groundwaters (*De Vivo et al., 1998*; *Boni et al., 1999*; *Buosi et al., 2001*; *Cidu and Fanfani, 2002*; *Cidu et al., 2009*; *Cidu, 2011*; *Vacca et al., 2012*). According to the Italian environmental agency ISPRA (2022), waste dumps in approximately 60 of these areas are considered to pose a high ecological and health risk. The release of contaminants from mining waste depends primarily on the mineralogical composition and pollutant content of the materials (*Brough et al., 2013; Jamieson et al., 2015*), as well as their physical properties (e.g., grain size, texture). The environmental impact of mining-cycle waste—encompassing extraction, processing, and metallurgy—therefore reflects both the original composition of the exploited deposits and the efficiency of beneficiation processes (*Jamieson, 2011*). Over time, improvements in mining techniques and mineral processing methods led to the exploitation of deposits with lower ore grades, resulting in greater volumes of waste materials (*Lottermoser, 2010*). This evolution is reflected in temporal variations in mining waste. Flotation tailings - mainly produced in the second half of the 20th century - generally contain lower metal and metalloid concentrations due to the higher recovery efficiency of the process, although they may also retain chemical reagents such as xanthates, arsenates, or cyanides. In contrast, tailings from earlier hydro-gravimetric techniques are typically richer in metals, but their volumes are smaller overall. Even earlier metallurgical wastes commonly show the highest pollutant contents—often an order of magnitude greater than mining or processing waste. Technological progress gradually improved metal recovery, such that the most contaminated metallurgical residues are those produced in earlier periods.

Pollutants commonly associated with Sardinian mining waste include base metals (Pb, Zn, Cu and Fe) and other metals associated with base metal sulfides (Cd, Hg), metalloids (As, Sb), as well as S, Ba, and F. The dispersion of contaminants is controlled by local physical–chemical conditions, particularly the interaction of waste materials with meteoric waters and atmospheric oxygen. In Sardinia, Acid Mine Drainage (AMD) has been documented in sulfide-bearing wastes, especially pyrite- and arsenopyrite-rich tailings and mine heaps, producing strongly acidic waters that mobilize metals (*Cidu et al., 1997*; *Frau, 2000*; *Frau and Ardau, 2003, 2004*; *Concas et al., 2006*; *Da Pelo et al., 2009*; *Cidu et al., 2011*). However, significant metal transport has also been reported under near-neutral conditions in the Iglesiente, Montevecchio, and Funtana Raminosa districts (*Cidu, 2001, 2007*; *Cidu and Frau, 2009*; *Frau et al., 2015, 2017*; *De Giudici et al., 2019*), as well as under alkaline conditions in some metallurgical wastes, where strong releases of metalloids such as antimony have been observed (*Contini et al., 2009*; *Cidu et al., 2013, 2021*; *Fancello et al., 2023*). The Su Suergiu mine in Eastern Sardinia provides a notable example, where Sb-rich wastes contaminated the Flumendosa River system. Downstream waters received up to 14 kg of Sb and 0.6 kg of As per day under high flow conditions (*Cidu et al., 2017*).

Contamination has also been recorded in beach sands and marine sediments downstream of mining areas, with elevated concentrations of metalloids and trace metals (including As, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn). The elevated concentrations of these elements are clear evidence that mining-derived particulates and tailings can be transported into littoral and seabed sediments (*Caredda et al., 1999*; *Romano et al., 2017*). Research has also critically extended its focus beyond water and soil pollution to include airborne dust emissions from dumps and tailings dams, particularly the study of fine particulate matter (PM), such as the red mud tailings where 90% of particles are generally below 20 µm, posing a significant suspension risk (*Cigagna et al., 2014*; *Dentoni et al., 2019*), and impacts on vegetation and associated biologically mediated mineralization processes, like the formation of Zn-carbonate biominerals along the riverbed (*Medas et al., 2012, 2015, 2019, 2023*; *Podda et al., 2014*; *De Giudici et al., 2014, 2015*; *Concas et al., 2015*; *Kharazian et al., 2022*; *Onnis et al., 2024*). Finally, the potential consequences for human health, connected to metals and metalloid dispersion in the environment, have been investigated (*Varrica et al., 2014*). On the other hand, natural attenuation of AMD and biologically driven resilience processes have been documented in several districts, including Iglesiente and Montevecchio (*De Giudici et al., 2017*; *Dore et al., 2020*). Remediation strategies for polluted mining areas encompass chemical, physical, and biological approaches, as well as phytoremediation, soil amendments, and the use of bio- and nanotechnologies (*Hussain et al., 2022*, and references therein). These approaches may be applied in situ or ex situ, and include techniques such as soil washing and flushing, mechanical separation, microbial degradation, phytostabilization, phytoextraction, and the use of additives or soil conditioners. In Sardinia, however, remediation has so far focused primarily on securing waste deposits and mitigating contaminant dispersion rather than on fully implementing restorative treatments. Major interventions have included geomorphological restoration and slope stabilization (e.g., through reshaping dumps and backfilling voids), safety measures such as sealing adits, shafts, and processing facilities, hydrological controls to limit water–waste interactions, and revegetation to encourage ecological recovery. Notable examples include interventions at the Arenas–Tiny Pb-Zn mine, the Baccu Locci As-Pb mine, the Furtei Au mine, the Malfidano Pb-Zn mine, and the Rio San Giorgio–Iglesias valley area (Figure 5).

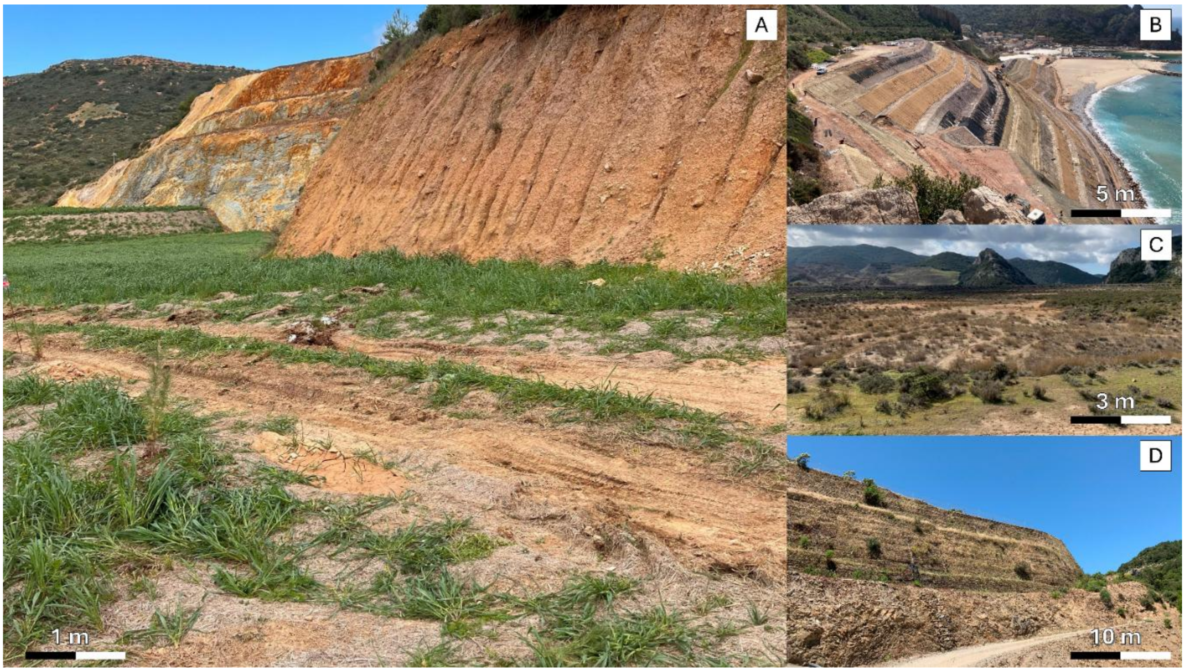

Figure 5. Some environmental actions carried out in Sardinia. A) Furtei mine: revegetation and geomorphological reshaping of the excavation fronts of the Au-Ag-Cu epithermal deposit; B) Malfidano mine: stacking and geomorphological recontouring of the Pb–Zn flotation tailings; C) Pb-Zn Arenas-Tiny mine: revegetation of the flotation pond; D) Baccu Locci mine: storage of As-flotation tailings in a single disposal facility, stabilized with mesh and geomembrane liners, and revegetated.

Remediation in the Baccu Locci As-Pb mine area represents the most advanced effort in Sardinia (*Angeloni et al., 2011*; Fig. 6). In this area, intense AMD and metalloid leaching, especially for As, has been documented. The remediation strategy involved the removal of exposed mining dumps and tailings, which were consolidated into a single, large upstream heap. This consolidated deposit was encapsulated with a waterproof geotextile membrane and underlain by a bentonite base layer. The capping system was further complemented by permeable reactive barriers (PRBs) specifically designed to mitigate the release of arsenate anions in residual runoff. However, subsequent investigations revealed only a limited effect on the overall contamination levels of stream waters in the area, highlighting the need for a more detailed understanding of the mineralogical and geochemical processes affecting the heterogeneous materials deposited and mixed at the collection site (*Ardau et al., 2013*).

Figure 6. Remediation actions conducted at the Baccu Locci mine. A) An overview of the tailings disposal facility, highlighting stabilization structures with mesh systems and implemented revegetation interventions; B) A detail of the interventions; C) Panoramic view of the mining area.

Alternative strategies for addressing AMD-affected areas have been explored in the Iglesiente and Montevecchio districts (*De Giudici et al., 2014, 2017, 2018*). Using a quantitative approach that calculated metal load in stream waters via hydrologic tracer techniques, the studies revealed differences of several orders of magnitude in metal contamination between rivers where biogeochemical barriers—formed by vegetation and associated microbial activity—are present and those where such natural barriers lack. These findings suggest that low-cost passive bioremediation methods, which enhance the natural resilience of affected areas through the establishment of artificial biogeochemical barriers along streams, may be an effective approach. In these reducing systems, analogous to constructed wetlands, metals can precipitate as sulfides under low-oxidation conditions. Additionally, several recent studies focused on phytoremediation strategies metal uptake by plants in soils contaminated by Sardinian mining waste, using plant species such as *Pistacia lentiscus L.*, *Pinus halepensis*, *Atriplex halimus*, and *Helichrysum tyrrhenicum* (*Boi et al., 2021*; *Kharazian et al., 2022, 2023*; *Tamburini et al., 2023*; *Canu et al., 2025*). Active treatments have also been tested on tailings from the Masua Pb-Zn mine (Iglesiente district), stabilized using Portland cement (*Desogus et al., 2013*). An emerging approach in active strategies of remediation involves combining different waste materials with complementary properties to mitigate and buffer the release of pollutants and AMD. *Grieco et al. (2024)* investigated the mixing of sulfide-bearing wastes from several Sardinian AMD-affected sites (Campo Pisano, Furtei, Telle, Seddas Moddizzis) with slightly alkaline sludges produced during quartz–feldspar processing at Florinas (Northern Sardinia). The calcite and feldspar components of these sludges provided both short-term and long-term buffering capacity, resulting in effective reduction of contaminant mobilization in runoff waters.

4. Remining potential and reuse of mining waste

The recycling and reuse of mining waste (*Lottermoser, 2011; Maest, 2023*) are being increasingly recognized as rising aspects during strategic planning of remediation activities of historical mining sites. This is due to the double advantage of generating economic value through the recovery of secondary raw materials while simultaneously mitigating contaminant loads in situ. Nevertheless, the recovery of raw materials raises several important challenges, including: (1) the availability of suitable technologies for reprocessing and extracting metals from materials previously subjected to mining and beneficiation processes, and (2) the availability of appropriate sites for the disposal of newly generated, albeit less contaminating, waste, or alternatives for its reuse. (3) Handling large volumes of contaminated material while minimizing dust dispersion. (4) Logistical problems relating to the reopening of closed plants or the creation of new treatment facilities. (5) Logistical problems related to access sites that have been abandoned for years and often lack functioning infrastructure. Throughout Sardinia's mining history from the mid-19th century until the 1970s, reprocessing and recycling (remining) of mining and metallurgical waste were common practices among mining companies (*Rolandi, 1974*; *Ghiani, 1981*; *Marzocchi, 1995*). Simultaneously, the reuse of waste rocks, tailings, and metallurgical slags as backfill for exploitation voids or as aggregate in embankments, road foundations, and construction materials was widespread. Most studies of Sardinian historical mining waste deposits have focused primarily on environmental impacts. Notable exceptions include investigations of metallurgical wastes and their potential for raw material recovery in the Iglesias district (e.g., "red muds" from the Monteponi electrolytic Zn plant: *Buosi et al., 2001*) and in Villasalto (residues from historical Sb smelting: *Contini et al., 2009*). *Naitza et al. (2019)* identified mine waste as a priority target for mineral exploration in Sardinian districts. In recent years, new studies have explored waste deposits from historical metalliferous mines in Sardinia as potential sources of raw materials. Relevant studies include assessments of F, Ba, Pb, and REE contents in tailings from the Silius mine processing plant in Assemini (*Balassone et al., 2021*) and Zn, Pb, and REE contents in tailings from the "Ponente" plant in Montevecchio (*Sedda et al., 2024*), which also highlighted how REE concentrated in carbonate biominerals. The CRM potential of "red muds" from alumina hydrometallurgy (Bayer process) in the Portovesme industrial area has also been recently investigated (*Mameli et al., 2025; Schingaro et al., 2025*).

Technical and economic challenges associated with reprocessing mine dumps have been discussed by Dentoni et al. (2017) and Manca et al. (2021), while experimental studies have focused on improving processing technologies, particularly flotation, to facilitate the recovery of raw materials from tailings in the Montevecchio district (*Manca et al., 2019*).

The reuse of waste materials from Sardinian metalliferous mines (Fig. 7) remains a largely underexplored theme. One potential application, proposed by *Manca et al. (2014)*, involved the removal of tailings from dams in the Masua mine to refill and stabilize large voids in the nearby Acquaresi mine, an area affected by severe subsidence, following mixing with Portland cement.

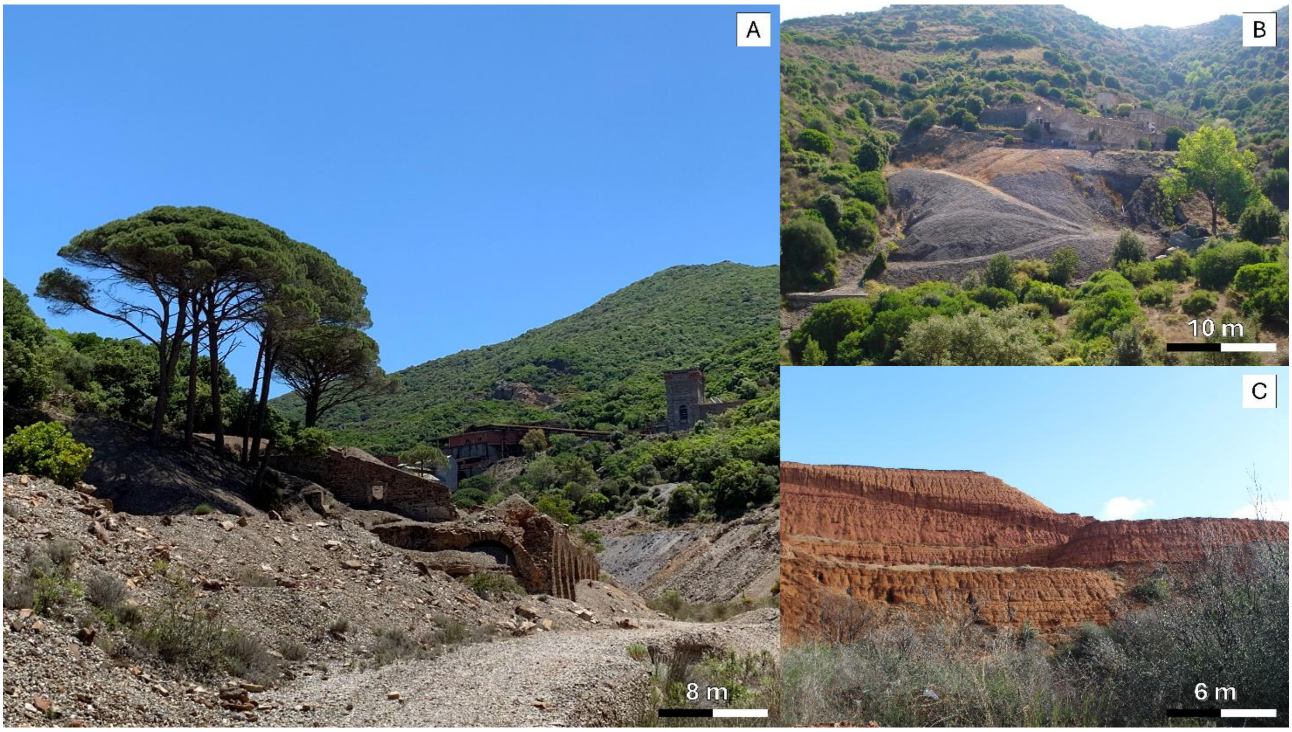

Figure 7. Sardinian mining waste whose metal potential has been assessed to date. A) Hydrogravimetric and flotation tailings from Sanna works of the Montevecchio mine; B) Metallurgical waste from Su Suergiu mine; C) Metallurgical waste from Monteponi mine.

5. Identification of CRM potential of Sardinian mining waste: the contribution of the IR Geosciences project

The first large-scale recognition and mapping of mining waste dumps in Sardinia was conducted by the Sardinian Regional Administration (RAS) in the late 1990s to early 2000s (*RAS, 2003*). The potential recovery of raw materials from selected waste deposits was subsequently considered within the framework of regional mining activity planning, notably in the "Progetto Valore" initiative (*RAS, 2007*). However, to date, no dedicated recovery projects have been implemented, and a systematic, regional-scale evaluation of the recovery potential of historical mining waste is still lacking. The Geosciences IR Project, coordinated by ISPRA, includes a dedicated work package aimed at assessing the potential for critical raw materials (CRMs) in Sardinian mining districts. A pivotal objective of the project is the production of a new metallogenic map of Sardinia at a 1:250,000 scale, which digitally updates and substantially enhances the previous version (*Tocco et al., 2008*), formerly available only in paper format. This updated map is complemented by an expanded database of Sardinian mineral resources, encompassing both deposits and occurrences, as well as a comprehensive remapping of all mining waste dumps across the region. The database consists of 1887 entries classified according to waste type (e.g., waste rocks, process tailings), physical characteristics (e.g., grain size), surface area, volume, and additional relevant attributes (see also Table 1 for a summary of selected historical mining areas). An initial step toward establishing a ranking of waste deposits based on their CRM potential involves a comparative analysis of the mineral resource and waste dump databases. The mineral resource database provides detailed information on the mineralogy and geochemistry of the ores from which the waste originated, together with geological data and conceptual models of Sardinian mineral deposits. These datasets form the foundation for a preliminary hierarchical classification of waste dumps in terms of CRM prospectivity, thereby enabling the identification of priority targets for detailed waste characterization and CRM exploration. This approach was first experimented in SW Sardinia, where new samplings were conducted on selected targets including waste deposits (flotation tailings and magnetic tailings) from Montevecchio, Santa Lucia and San Leone mines. SEM-EDS investigations on collected samples (Fig.8) confirmed the presence of LREE, Ni, Co, and W phases in the waste materials, stimulating further studies aimed at determining the CRM potential of mining waste deposits in these areas.

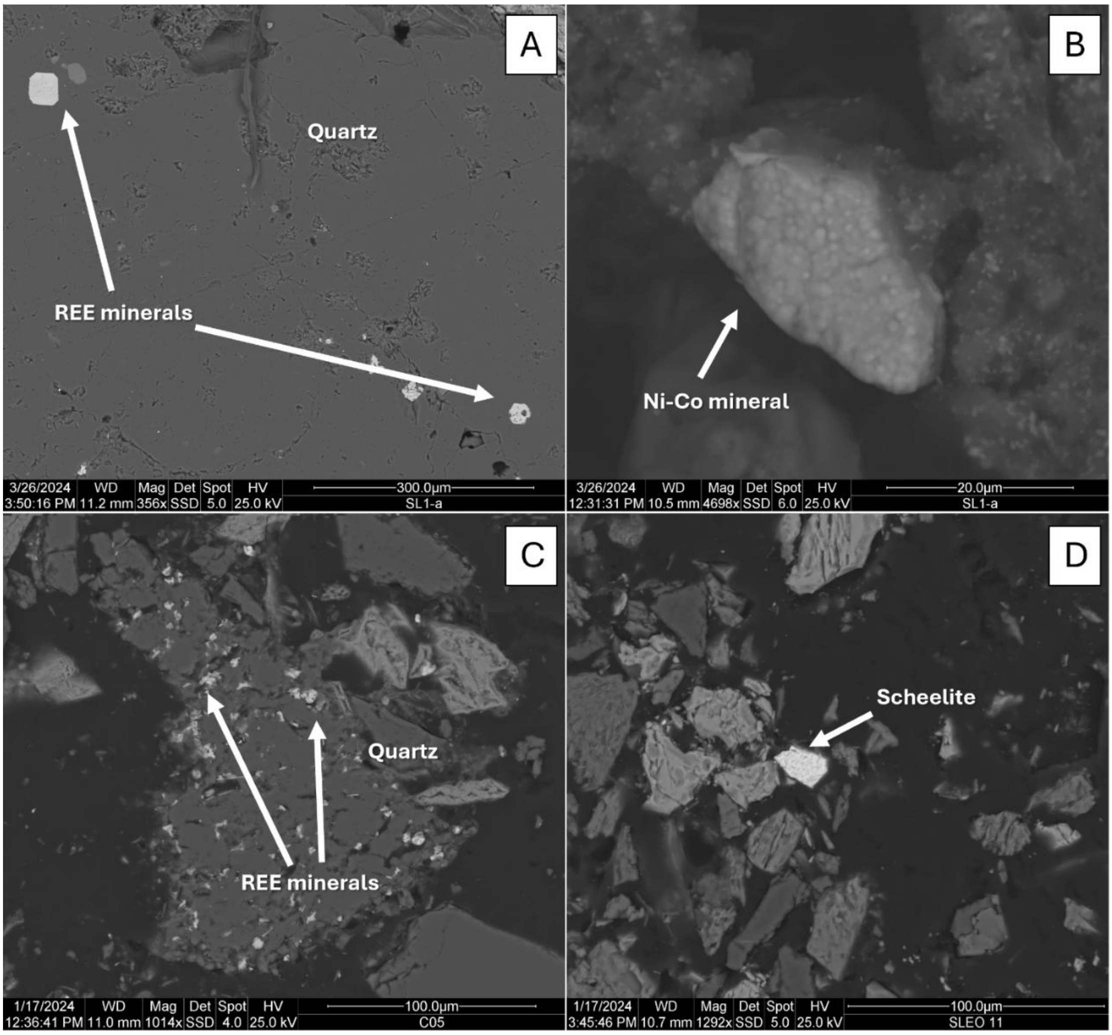

Figure 8. Scanning Electron Microscope (SEM-EDS) images revealing the presence of Critical Raw Materials in some mining dumps in Sardinia. A) A sample from Santa Lucia mine (Fluminimaggiore, SW Sardinia) displaying euhedral crystals of Light Rare Earth Elements within the quartz. B) A sample from Santa Lucia showing the presence of a Ni-Co mineral phase. C) A sample from Montevecchio mine (Arbus, SW Sardinia) exhibiting Light Rare Earth Elements minerals within the quartz. D) A sample from San Leone mine (Assemini, SW Sardinia) where scheelite [CaWO4] is visible.

6. A sustainable path to resource enhancement

The regional mapping of mining waste dumps and the systematic characterization of the materials they contain represent the first essential steps toward identifying and implementing potential recovery options, while simultaneously defining the technical, economic, and environmental criteria that underpin the prioritization of interventions across different mining districts. These preliminary activities provide the quantitative and qualitative framework necessary to discriminate between deposits that may represent viable secondary resources and those that primarily require containment or remediation measures. At the scale of individual mining areas, detailed geological mapping, together with chemical and mineralogical characterization, must be embedded within a hierarchical methodological approach to historical mining waste management (*Lèbre et al., 2017*). This approach relies on a multi-stage decision-making process that progressively narrows the range of feasible management options and ultimately leads to three main outcomes: (1) reprocessing, (2) downcycling, and (3) waste disposal combined with site remediation (Fig. 9).

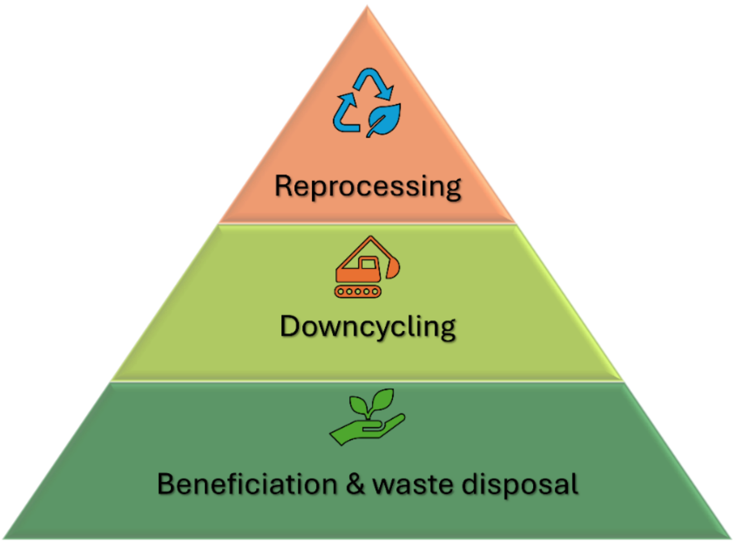

Figure 9. Hierarchical framework of mining waste management options. The diagram prioritizes reprocessing as the preferred strategy; when reprocessing is not technically or economically feasible, downcycling is considered, followed by beneficiation and final waste disposal.

Reprocessing involves a re-evaluation of mining waste using mining and mineral processing parameters. This includes the integration of ore grade and resource volume assessments with the selection of best available techniques for mineral processing and resource recovery, explicitly accounting for environmental performance and sustainability criteria (*Khajuria et al., 2022*). A typical workflow (Fig. 10) begins with preliminary estimates of grade, tonnage, and cut-off values, which are closely linked to market conditions, metal or mineral prices, processing costs, and regulatory constraints. These parameters define an initial decision point. If the outcome is favorable, laboratory-scale tests are undertaken to identify suitable processing routes and assess recovery efficiencies. A second decision point follows, after which pilot-scale testing is carried out to validate technical feasibility and economic robustness under semi-industrial conditions. Successful pilot testing may ultimately lead to full-scale industrial operations, following a final decision stage that integrates technical, economic, environmental, and social considerations.

Downcycling, defined as the reuse of waste materials in applications with a lower unit economic value, represents an alternative pathway for materials that do not meet cut-off grades for reprocessing or for residues generated during reprocessing operations. Potential downcycling options strongly depend on the mineralogical and chemical composition of the wastes—particularly with respect to residual contaminant release—as well as on their physical properties, such as grain size, particle shape, and mechanical behavior. Possible applications range from industrial uses (e.g., raw materials for bricks and ceramics, additives for cement production, or aggregates for concrete and bituminous mixtures) to geotechnical applications such as backfilling, embankments, or land reshaping. Although downcycling options are generally preferable from a sustainability perspective, their implementation is constrained by economic viability, regulatory acceptance, and logistical factors, including transport distances and the availability of local markets. As a result, waste disposal combined with site remediation remains a realistic and, in some cases, unavoidable outcome of the decision-making process.

As highlighted in the previous chapters, the systematic application of these concepts to Sardinian mining waste dumps is still at an early stage. Nevertheless, the characterizations carried out to date clearly demonstrate the presence of economically relevant concentrations not only of base metals but also of several Critical Raw Materials (CRMs) in a variety of waste types, warranting further investigation for potential recovery. Addressing this challenge effectively requires a regional-scale strategy, based on the establishment of centralized treatment facilities for compositionally homogeneous materials and on the identification of reliable, technically feasible, and economically consistent downcycling applications. Such an integrated approach is essential to move from isolated case studies toward a coherent framework for the sustainable management and valorization of Sardinia's mining waste legacy.

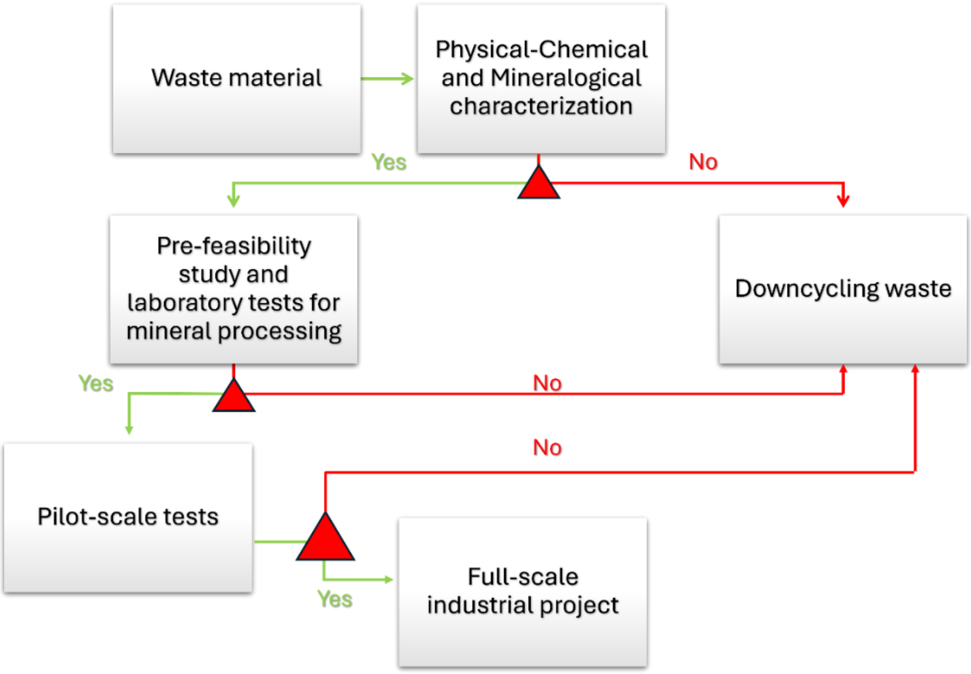

Figure 10 Flow path and possible outcomes of decisional processes on mining waste materials.

7. Conclusions

The historical mining and metallurgical wastes of Sardinia represent not only a significant environmental challenge but also a strategic resource for the recovery of CRMs and SRMs, in alignment with European policies on circular economy and the secure supply of raw materials. The review of historical sources, metallogenic databases, and field surveys has enabled a comprehensive delineation of this legacy, estimated at approximately 70 million cubic meters distributed across 1887 waste bodies, including waste rocks, tailings, metallurgical slags, and industrial sludges derived from heterogeneous mineralizations and processing methods.

Certain mining districts, such as Iglesias, Montevecchio, and Silius, exhibit residual concentrations of strategic elements—including Zn, Pb, REEs, F, and Ba—comparable to, or even exceeding, those of primary deposits, while numerous sites continue to present considerable environmental concerns, such as acid mine drainage, the mobilization of metals and metalloids into aquatic systems, and the dispersal of contaminated dust. In this context, the Geosciences IR Project is particularly notable for integrating geological, mineralogical, and historical datasets into a unified digital platform, thereby updating and expanding the regional metallogenic mapping to incorporate, for the first time, mining waste deposits as potential resources. The new mapping and accompanying databases constitute essential tools for defining priorities and guiding operational strategies in the coming years. The recovery of raw materials, and particularly CRMs and SRMs, from these deposits represents a critical strategy for the sustainable development of contemporary societies. Such approaches reduce energy consumption and CO_2 emissions relative to primary extraction, while generating both economic and environmental benefits. Moreover, they offer the potential to remediate degraded landscapes, transforming them into productive or natural areas and fostering the socio-economic development of local communities. Sardinia, with its rich historical mining heritage, thus emerges as an open-air laboratory for the development of European models for the recovery and reuse of mining waste, demonstrating how a legacy of environmental degradation can be transformed into a driver of innovation, sustainability, and industrial competitiveness.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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CRediT

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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)

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Abstract: Mining wastes are often both a potential source of Strategic and Critical Raw Materials (SRMs and CRMs) and a threat to the environment. This study investigated the potential of mining wastes from the Montevecchio district of Sardinia, Italy, as a source of SRMs and CRMs. The tailings from Sanna mine processing plant were characterized by X-ray diffraction, Scanning Electron Microscopy, and Plasma Mass Spectrometry, showing contents of 1.2 wt% of lead, 2.6 wt% of zinc, and about 600 mg/kg of Rare Earth Elements (REEs). White patinas formed in the riverbed, composed by Zn-bearing minerals (hydrozincite and zincite), also contain about 2900 mg/kg of REEs. Characterization of white patinas along the Rio Roia Cani evidenced that their precipitation from water also involves an uptake of Rare Earth Elements, enhancing their contents by an order of magnitude compared with tailings. The process of REEs concentration in Zn-bearing minerals of white patinas is a candidate as a tool for the economic recovery of these elements. These findings suggest that mining wastes from the Montevecchio district could be considered a potential resource for extracting SRMs and CRMs.

Keywords: metal recovery; critical raw materials; green economy

1. Introduction

The search for Critical Raw Materials (CRMs) for the energy transition and an ever- greener economy is increasingly important for the European Union in order to secure supplies and reduce dependence on unsafe sources. Since 2011, the EU updates its list of CMRs every three years, now including 35 raw materials of critical and strategic relevance [1]. This prompted the European Commission to support new exploration activities in the old mine districts of the EU members. A specific target of this new research is represented by mining wastes and tailings, whose exploitation may allow the recovery of neglected resources, enhancing at the same time the environmental quality of the involved areas by removing large volumes of contaminated materials [2].

Tailings are different types of waste materials produced by the processing of ore bodies, containing economic metals and minerals, which pose a threat to the environment and various ecosystems. That implies that tailings represent an important source of contamination for the environment for various ecosystems and for the people. A solution could be the re-treatment of these tailings for the extraction of these metals and metalloids if these are contained in economic contents, implicating the removal of a source of contaminations. This solution has several advantages: it allows the recovery of valuable resources that would otherwise have been lost; it reduces the amount of tailings that need to be stored, thus reducing the risk of environmental contamination; and it improves the overall sustainability of the mining sector. Tailings reprocessing must adhere to responsible and sustainable practices, minimizing environmental impact, ensuring worker and community safety, and maintaining cost-effectiveness through market price recovery of metals and metalloids. An essential phase for the definition of these projects consists in the mapping and characterization of the various mining landfills, to define their volumes, surfaces, and concentrations of raw materials [3–5].

Sardinia was a relevant mining region at the European scale, particularly for the extraction of lead and zinc ores. The Montevecchio district, located in SW Sardinia, was one of Italy's most important mining areas for over a century. Mining activities in the district ended in 1991 [6]. Today, it is one of Sardinia's most historically significant mining sites, featuring architecturally valuable abandoned mining buildings and shafts. Beyond this legacy of industrial archaeology, in Montevecchio there are numerous and very large mining dumps that represent a serious environmental problem on a national scale [7]. At the same time, it is increasingly evident from recent studies and geochemical/environmental characterizations [8,9] that these materials may contain significant amounts of base metals and strategic elements, thus becoming a potentially relevant target for CRM research.

The mining area is located between the municipalities of Arbus and Guspini, in South-western Sardinia (Figure 1). The intense underground mining activity deeply exploited a huge, NE-SW-directed mineralized vein system, producing about 2 million cubic meters of excavations voids and over 2 million cubic meters of mining dumps. Moreover, the processing plants produced over 6 million cubic meters of tailings [10]. The mining activity was focused on the extraction of minerals containing lead, zinc, and silver, but a large set of associated metals (Cu, Ni, Co, Bi, Sb, In, Ga, Ge, etc.) was recovered in the metallurgical cycles. The mine exploited two types of mineralization, sulfide, and oxidated ores, that required two different treatments to be recovered. Accordingly, two different plants were built in the mine area: the eastern plant (named the Principe Tommaso plant) processed the sulfide minerals, and the western plant (named the Sanna plant) processed the oxidate minerals. Thus, very different tailing materials are currently accumulated in the two old plant areas.

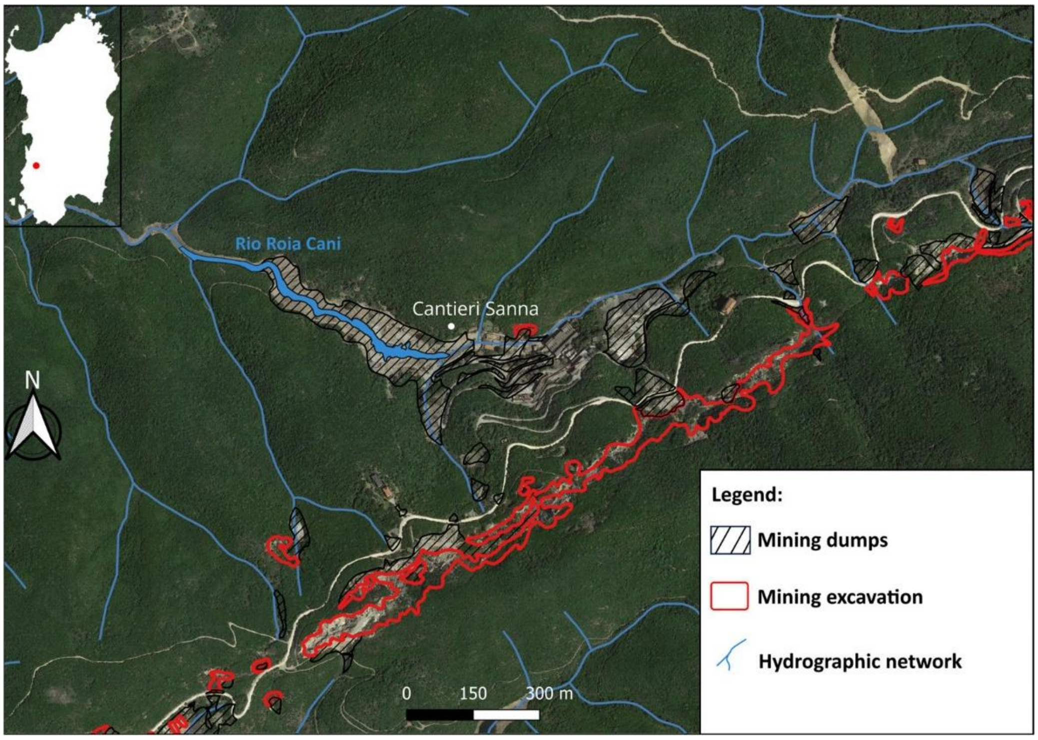

Figure 1. The study area. The main elements related to mining operations (mining dumps and excavation) are evidenced.

This work is focused on the tailings of the Sanna plant, whose composition and current arrangement are a product of the technological evolution of the processing systems for over a century. In detail, oxidate minerals from the whole Montevecchio district were initially processed in the earlier Sanna-Eleonora plant (1869–1936). The process involved a first hammer-sorting, a second hand-sorting, and finally, a separation using jigs and shaking tables. Starting from 1937 and up to 1980, the ores were treated in the new Sanna plant where minerals were first comminuted by jaw and gyratory crushers, then finely grounded by ball mills, and finally enriched by flotation [11]. Both the old and the new plants were set along the valley of the Rio Roia Cani stream, which flows from the mine area toward the west. The resulting tailings, of variable grain size, are now accumulated along the valley and are affected by important erosional phenomena that imply instability of the dumps and produce solid and chemical transport of potentially polluting materials, generating contamination over a large area downstream. Several past studies in the Montevecchio district pointed out that rivers of the area may carry high amounts of metals in solution after having interacted with the mining environments [12–17]. Evidence of the extent of these phenomena are the mineral precipitates (white patinas) that frequently encrust outcropping rocks, pebbles, and sediments at the bottom of the Roia Cani riverbed. They appear analogous to the hydrozincite bio-precipitates induced by bacterial activity, extensively documented in another mining area of the same district (Ingurtosu Mine) along the Rio Naracauli [18,19]. With the dual objective of verifying the possible presence of metals and CRMs in the tailings and the environmental conditions of the area, the study starts from a mineralogical and chemical characterization of the wastes of the Sanna plant but also encompasses some representative minerals of the ore that fed the plant, the Rio Roia Cani waters that directly interact with the wastes, and particularly, the white patinas along the Rio Roia Cani riverbed. Indeed, these latter not only may be considered as markers of the grade of diffusion of pollutants and of their biologically mediated interactions with the natural environment but also may provide interesting information about natural processes of re-concentration of metals and CRMs that may have potential economic implications.

2. Geological Setting

The Montevecchio mine area is located in the external nappe zone (allochthonous Arburese unit) of the Palaeozoic basement of Southwestern Sardinia, close to the contact with the Variscan Foreland (Autochthonous Iglesiente Unit). These low-grade metamorphic units are intruded by the granitoids of the Arbus pluton (304 +/− 1 Ma), which determined only moderate thermometamorphic effects in a relatively thin aureola [20].

The geology of the area is dominated by the Upper Cambrian-Lower Ordovician rocks of the Arenarie di San Vito Formation (Arburèse tectonic Unit), consisting of fine metasandstones, metasiltstones, and metargillites [21]. This sequence is unconformably covered by Middle-Ordovician felsic metavolcanic rocks of rhyolitic-rhyodacitic composition [22,23].

The Palaeozoic rocks are in turn unconformably covered by Tertiary clastic sediments of the Ussana Formation, consisting of conglomerates, breccias, and sandstones with a red-purple clayey-sandstone matrix [21], and by the Oligo-Miocene calc-alkaline sequences of the Monte Arcuentu volcanic complex [23].

3. The Montevecchio Ore Deposits

The large Montevecchio hydrothermal vein system [6] consists of a series of mineral- ized veins that follow with a “pinch-and-swell” attitude the northern contact of the Arbus pluton for a length of over ten kilometres in a NE-SW direction (Figure 2). The vein field has held great economic importance in the past, having been among the largest in Western Eu- rope; the thickness of the mineralized veins could reach 25–30 m at some points. From east to west, the veins are called: Sant’Antonio, Piccalinna, Sanna, Telle, and Casargiu. Although dominated by lead and zinc sulfides, the composition of the ore may vary significantly from one vein to another, and sometimes even within the same vein, characterized by banded to brecciated textures. In order of abundance or frequency, the economic minerals at Montevec- chio are sphalerite [ZnS], galena [PbS], fahlore [$(Cu_6[Cu_4(Fe,Zn)_2](As,Sb)_4S_{13}$], chalcopyrite [$CuFeS_2$], bournonite [$PbCuSbS_3$], Ni-Co sulfoarsenides, and pyrite [FeS_2]. The nature of the minerals forming the gangue is equally variable, they are quartz [SiO_2], baryte [$BaSO_4$], siderite [$FeCO_3$], Zn carbonate [$ZnCO_3$], calcite [$CaCO_3$], ankerite [$(Ca,Mg,Mn,Fe)(CO_3)_2$], and goethite [FeO(OH)] [24–26].

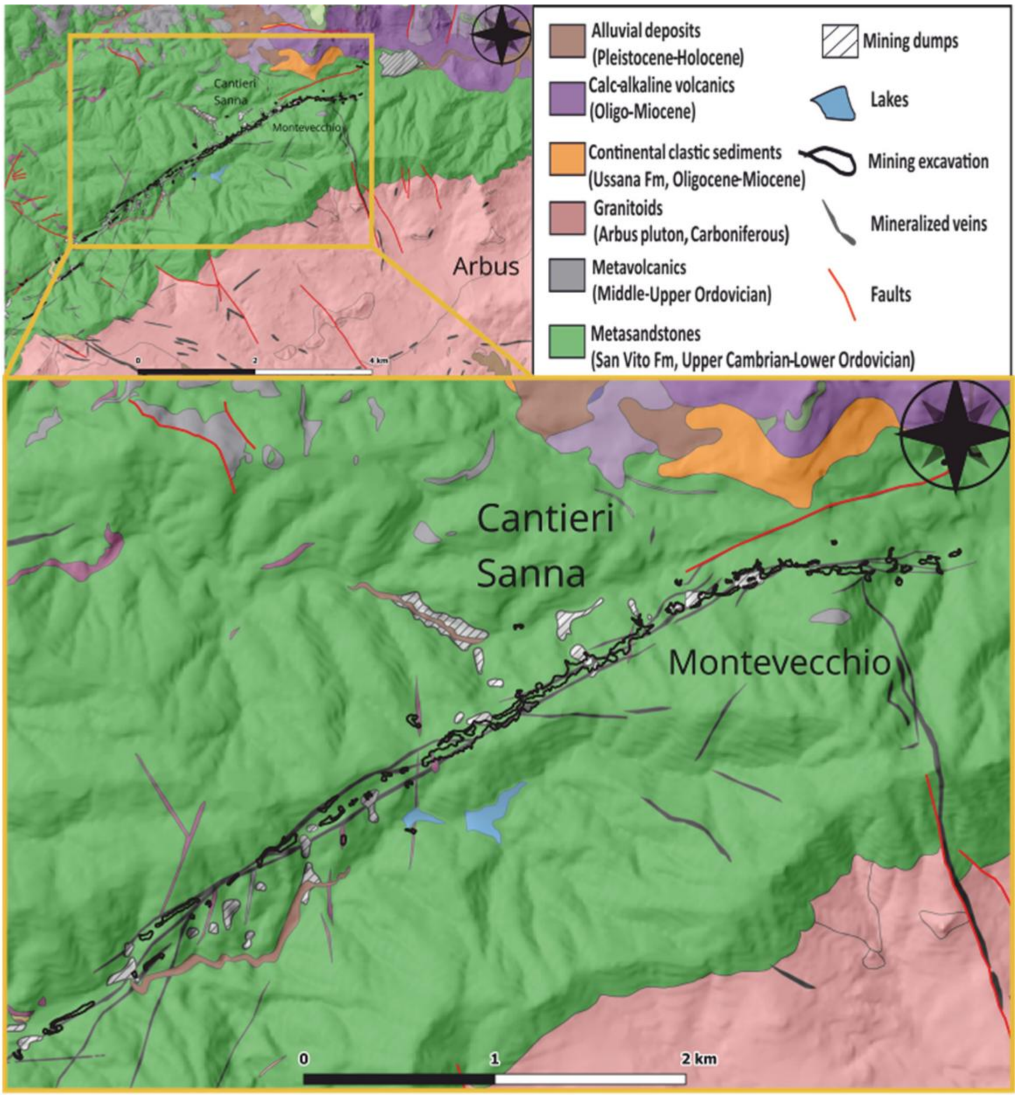

Figure 2. Geological sketch map of the study area.

- *The Sanna Vein*

The Sanna vein was the primary feeder of the Sanna processing plant in Western Montevecchio. The vein displays a smaller longitudinal extension than the other veins of the district (about 300 m), but it has a considerable thickness (15–20 m). A distinctive feature of the Sanna vein is its composition, dominated by supergene minerals. Supergene oxidation processes strongly affected the vein, with an average portion of the oxidated ore reaching about fifty meters in depth and oxidized columnar portions that go down up to 200 m below the topographic surface. The development of supergene processes has deeply transformed the primary sulfide ore (basically: galena, sphalerite, chalcopyrite, and fahlore, with Zn grades of 5–6 wt%, and Pb grades of 1–2 wt%) into secondary phases as anglesite [$PbSO_4$], cerussite [$PbCO_3$], iron hydroxides, zinc, and copper secondary minerals (Figure 3). The gangue is mainly sideritic with subordinate quartz; baryte may become relatively abundant in the upper parts of the vein; the lead tends to increase at depth while remaining subordinate to zinc [27].

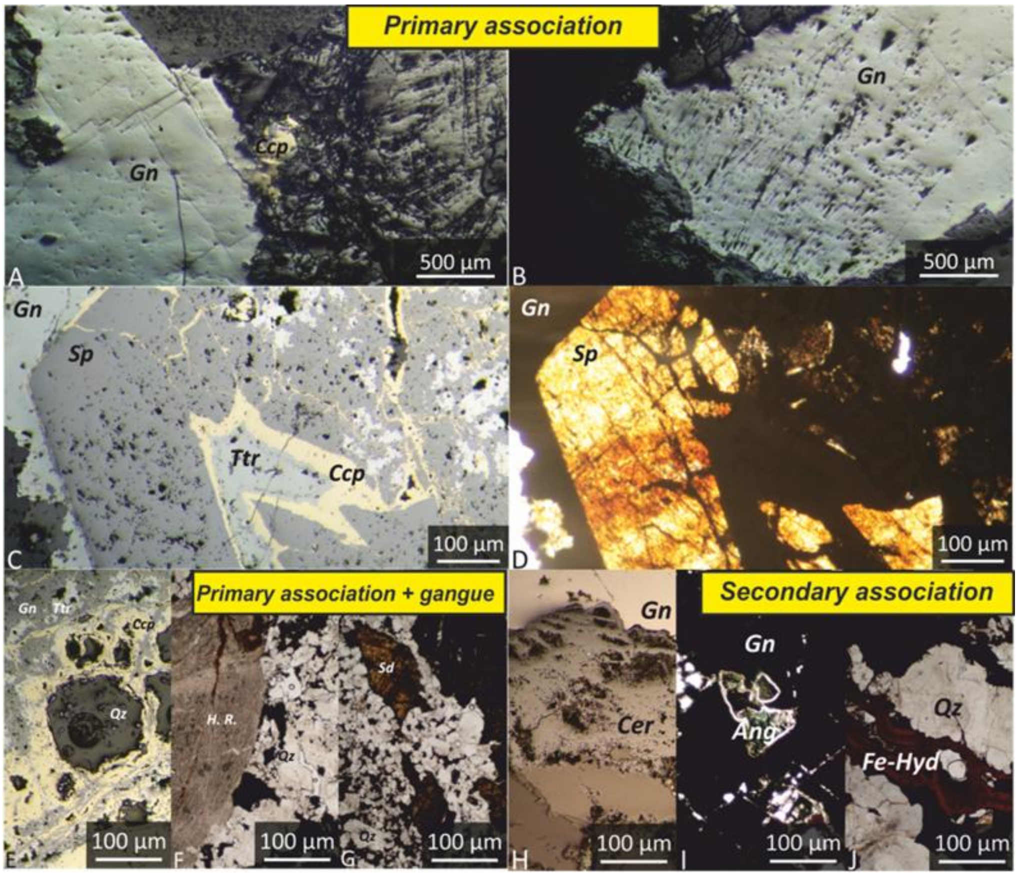

Figure 3. Mineral assemblage of the Sanna vein. (**A**) Yellow chalcopyrite (Ccp) growing at the edge of galena (Gn). (**B**) Galena (Gn) brecciated and deformed (as evidenced by the various orientations assumed by the triangular pits), probably grown during a dynamic phase. (**C**) Tetrahedrite (Ttr) and chalcopyrite (Ccp) included in sphalerite (Sp), in contact with galena (Gn). (**D**) Sphalerite (Sl) in transmitted light, transparency suggests low iron content. (**E**) Quartz crystals (Qz), inside galena (Gn), surrounded by chalcopyrite (Ccp) and tetrahedrite (Ttr). (**F**) Breccia texture with a host rock fragment (H.R.) surrounded by quartz fragments (Qz). (**G**) Siderite (Sd) crystals surrounded by quartz crystals (Qz) forming a mosaic texture. (**H**) Cerussite (Cer) aggregate growing on galena (Gn). (**I**) A crystal of anglesite (Ang) grown within galena (Gn). (**J**) Iron hydroxides (Fe-Hyd) precipitated between quartz crystals (Qz). (**A**–**C**,**E**,**H**): plane-polarized reflected light; (**D**,**F**,**G**,**I**,**J**): plane-polarized transmitted light. Mineral abbreviations according to Warr (2021) [28].

4. The Sanna Plant Area

The Sanna plant area (about 130,000 m2) is characterized by the remnants of two past mineral processing plants, consisting of tailings, jigging residues, and waste rocks accumulated along the Rio Roia Cani. During mining operations, tailings were discharged as sludge from the treatment plant to the stream, through a drainage tunnel. Initially, sludge was blocked by a series of dams to form tailing ponds. In past mining operations, dams were opened periodically to make space in the ponds. After the mine closure, the main dam collapsed, and the tailings were partially eroded and washed away. Evidence of a consistent solid transport of these materials may be easily traced several kilometres downstream. Currently, the drainage tunnel is damaged, and tailings are affected by rills and gullies that induce instability and small landslides. Tailings preserve the original flat attitude of the pond surface, whilst the jigging wastes form large heaps along the flanks of the valley (Figure 4), quite unstable and incised by surface waters. In the field, tailings and jigging residues are also easily distinguishable by their granulometry; tailings vary from fine sands to clays, while jigging residues vary from gravel to coarse sand. The tailings cover a surface of about 46.800 m^2, attaining a thickness of more than 10 m. They display a positive gradation that is interpreted as resulting from sedimentation processes into the tailing pond where the waste materials from the plant were discharged. In addition to the solid transport of the waste materials, evidence of solution transport of elements in the water of the Rio Roia Cani is provided by the frequent occurrence of reddish mineral precipitates and white patinas along the riverbed, particularly where the drainage gallery is broken (Figure 4). The area downstream the Rio Roia Cani is low-populated: main potential targets of contamination are surface- and groundwaters and, in general, the flora and fauna present along the river valley, whose habitat and whose development could be conditioned by the presence of pollutants.

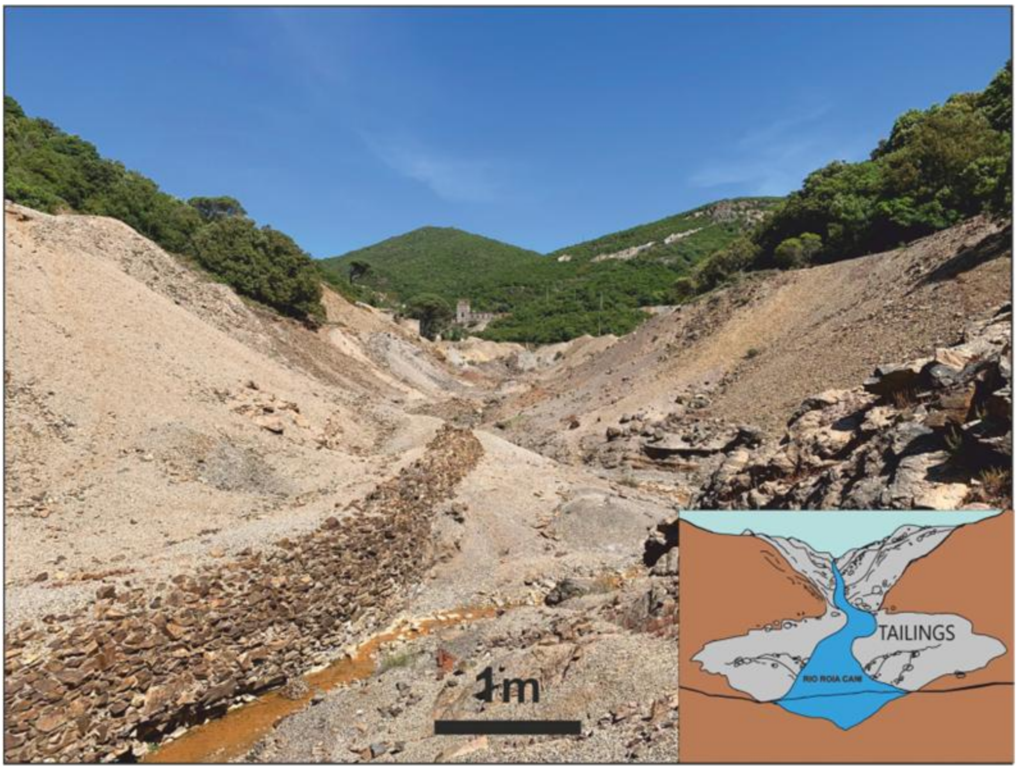

Figure 4. The interaction between the flow of the Rio Roia Cani and the mining wastes.

To complete the environmental frame of this old industrial area, also the mine exca- vations, located upstream close to the plant area must be considered. They constitute an environment of interaction between surface water and mineralized, potentially polluting rocks. Only part of these waters is now conveyed to the Rio Roia Cani, the great part feeds the groundwater system through the underground mining works.

5. Materials and Methods

5.1. Sampling

Eight samples were collected from the tailings of the Sanna processing plant (Figure 5). Sampling was carried out following the stratigraphic overlap of different materials,

distinguished by chromatic differences and different granulometry (Figure 6).

Nine samples of the white patinas present along the bed of the Rio Roia Cani (Figure 7) were also collected. Sampling was realized paying particular attention to avoid the removal of detrital material present under the patinas.

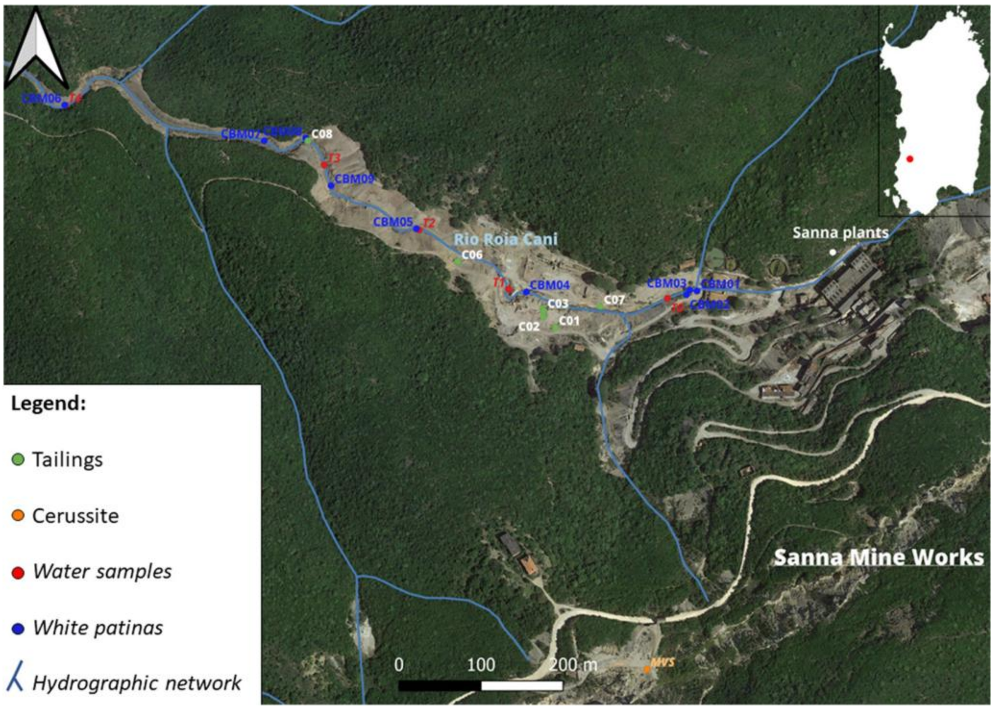

Figure 5. Map with the collected samples. In green, the samples of tailings; in orange, the samples of cerussite; in red, the samples of water; in blue, the samples of white patinas.

Figure 6. The eight sampled layers of tailings along the Rio Roia Cani.

Some cerussite specimens were collected from the oxidate ore in the mine excavations close to the Sanna plant. Moreover, some water samples were taken on the same day of the white patinas sampling, at different points of the Rio Roia Cani, downstream from the processing plant, to have the same environmental conditions for the two sampling sets (Figure 5).

5.2. X-ray Diffraction Analyses

The eight samples of tailings underwent granulometric analyses at first, then they were analysed by an X-Ray Diffractometer (XRD) to detect the main mineralogical phases. An X'Pert Pro PANalytical diffractometer (Malvern Panalytical, Malvern, UK) with an X-ray tube with Cu anticathode (Cu-Kα1 λ = 1.54060 Å), nickel monochromator filter, and X'Celerator detector, was used; data were acquired at 40 kV and 40 mA in an angular range of 5–70 ◦2θ.

Figure 7. Sampling of the white patinas of the Rio Roia Cani riverbed.

5.3. Scanning Electron Microscope Analyses

The nine samples of white patinas were analysed by XRD, then by Scanning Electron Microscope (SEM) Quanta Fei 200 unit equipped with a ThermoFisher Ultradry EDS detector (ThermoFisher Scientific, Waltham, MA, USA) operating under low-vacuum conditions, 25–30 KeV voltage, and variable spot size) to study their structure and assess their composition. Samples were not carbon-coated.

5.4. Inductively Coupled Plasma Spectrometry

Chemical analyses of tailings were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Perkin-Elmer Elan DRC-e, Shelton, CT, USA), after solubilization through acid digestion by aqua regia and hydrofluoric acid, to detect the possible presence of critical materials, metals, and Rare Earth Elements. Eight tailing samples were analysed, together with a certified reference sample (SRM2711), and a blank. Some samples (C04, C07 and C08) were analysed two times, to verify the correctness of the analytical procedures and analyses performed After acid digestion using aqua regia, cerussite samples were analysed for trace elements by ICP-MS.

White patinas samples were analysed by Inductively Coupled Plasma-Optical Emis- sion Spectroscopy (ICP-OES, Thermo Scientific ARL-3520B Waltham, MA, USA) and ICP- MS, after solubilization by acid digestion by aqua regia and hydrogen peroxide to break down the organic matter component. The water samples were analysed by ICP-MS and by ICP-OES.

6. Analytical Results

Results of the analyses performed on the various types of samples collected on-site are presented below. Samples of tailings were taken in different layers of the old tailing pond, based on chromatic and granulometric variations evidenced in erosional surfaces and gullies along the valley of Rio Roia Cani (Figures 5 and 6). The white patinas were sampled at various points of the riverbed, based on the type of precipitate (Figure 7). The cerussite samples were sampled in the upper part of the Sanna vein, where the primary mineralization was strongly affected by supergene phenomena. The water samples were collected near some inflows and emergencies, trying to maintain a regular interval between the various sampling points.

6.1. Tailings

Mineralogical analyses (X-ray diffraction) on tailing samples (Figure 8 and Table 1), revealed a composition mainly consisting of host rock and gangue minerals, such as quartz and muscovite (present in all the samples), siderite and baryte (found in some samples: C04 and C08 siderite, C03, C04 and C05 baryte), and montmorillonite. Primary ore phases are represented by galena and sphalerite. Only one sample (C05) shows the presence of zincite, a secondary phase.

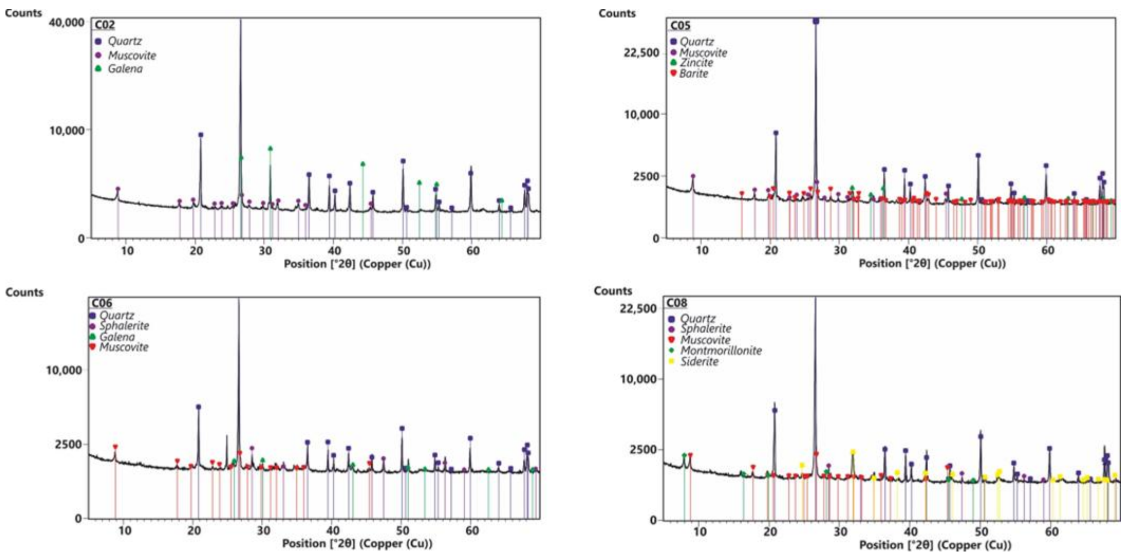

Figure 8. XRD patterns of the mineral phases detected in the different tailing samples. Counts in the *y*-axis are reported in square root to highlight minor peaks.

Table 1. Summary table of the main characters of sampled tailing layers. Qz = quartz, Ms = muscovite, Dol = Dolomite, Gn = galena, Brt = baryte, Sd = siderite, Znc = zincite, Sp = sphalerite, Mnt = montmorillonite. Abbreviation as in [28].

Layer	Approximately. Thickness	Sample	Granulometry	Mineralogy
1	50 cm	C01	Moderately graded sand with clays	Qz, Ms, Dol
2	70 cm	C02	Poorly graded sand with clays	Qz, Ms, Gn
3	40 cm	C03	Poorly graded sandy silt with clays	Qz, Ms, Brt
4	50 cm	C04	Poorly graded sand with clays	Qz, Ms, Sd, Brt
5	20 cm	C05	Poorly graded sandy silt with clays	Qz, Ms, Znc, Brt
6	40 cm	C06	Poorly graded gravelly sand with clays	Qz, Ms, Sp, Gn
7	10 cm	C07	Moderately well-graded sand with clays	Qz, Ms
8	50 cm	C08	Poorly graded sandy gravel, with clays	Qz, Ms, Sp, Mnt, Sd

Chemical analyses on the tailing samples show significant amounts of base metals and Rare Earth Elements. A selection of data from the analytical set is reported in Tables 2 and 3. Overall, the dataset displays high Lead and Zinc values, ranging between 760 and 12,300 ppm, and 6600 and 26,500 ppm, respectively. Critical elements once exploited as byproducts in the mine concentrates (Cobalt, Gallium, Indium, Germanium, Antimony, etc.) show low contents (from 15 to 36 ppm of Co, from 8 to 24 ppm of Ga, from 1 to 13 ppm of In, from 4 to 15 ppm of Ge, from 14 to 170 ppm of Sb). On the other hand, the Rare Earth Elements contents show ranges between 69 and 576 ppm. The highest values are shown by Cerium (26–190 ppm), Lanthanum (10–97 ppm), and Neodymium (11–92 ppm).

Table 2. Analytical data for trace elements in tailings. Values are in mg/kg (ppm).

Sample	Al	As	Ba	Bi	Cd	Co	Cu	Fe	Ga	Ge	In	Mn	Ni	Pb	Sb	Sn	V	W	Zn
C01	19,000	78	1400	ND	47	15	140	61,000	ND	ND	ND	3100	25	2400	28	ND	ND	ND	6800
C02	20,100	55	1200	ND	100	15	110	75,400	10	5	2	4300	35	3000	20	2	27	2	7500
C03	19,000	57	1700	ND	110	22	90	80,200	12	4	2	4500	39	2300	19	3	34	3	8700
C04	17,200	58	2000	ND	70	26	65	93,000	8	4	1	5900	34	760	14	2	21	2	6600
C05	22,700	60	3800	ND	140	25	83	88,200	13	4	2	5800	42	1100	19	3	37	3	11,300
C06	18,700	430	270	5	180	24	2070	135,000	24	15	13	6700	23	12,300	170	10	25	2	26,500
C07	16,700	83	5200	ND	150	36	280	154,000	8	5	2	8000	48	5200	40	2	17	2	15,500
C08	17,200	79	2300	ND	57	15	180	64,600	ND	ND	ND	3300	28	3800	34	ND	31	ND	8700

Table 3. Analytical data for Rare Earth Elements in tailings. Values are in mg/kg (ppm).

Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REEs + Y
C01	9	12	30	3	12	3	1	3	ND	2	ND	1	ND	1	ND	77
C02	27	45	81	10	38	9	4	10	1	6	1	2	ND	2	ND	236
C03	65	83	180	20	83	22	10	26	4	17	3	6	1	3	ND	523
C04	64	97	180	22	86	23	10	25	3	15	2	5	1	3	ND	536
C05	76	91	190	23	92	26	11	29	4	19	3	6	1	4	1	576
C06	35	73	130	16	65	16	6	17	2	9	1	3	ND	2	ND	375
C07	48	88	140	19	74	19	8	20	3	11	2	4	ND	3	ND	439
C08	8	10	26	3	11	3	1	3	ND	2	ND	1	ND	1	ND	69

In detail (Tables 2 and 3), some elements such as Cu (65–2070 ppm) and Pb (760–12,300 ppm) vary greatly between the various samples, while others, such as As (55–430 ppm), Ba (270–5200 ppm), Cd (47–180 ppm), Fe (64,600–154,000 ppm), Ga (8–24 ppm),

Ge (4–15 ppm), In (1–13 ppm), Sb (14–170 ppm), Sn (2–10 ppm), and Zn (6600–26,500 ppm) vary by only one order of magnitude or zero orders of magnitude, such as Al (16,700–22,700 ppm), Co (15–36 ppm), Mn (3100–8000 ppm), Ni (23–48 ppm), V (17–37 ppm), and W (2–3 ppm). Rare Earths Elements show little variability between samples. The C06 sample is particularly enriched in As, Bi, Cd, Cu, Ga, Ge, In, Pb, Sb, Sn, and Zn, the C02 sample shows the highest contents in Al, the C05 in Ba, W, and REEs, and the C07 in Co, Fe, Mn, and Ni. The samples C01 and C08 display the lowest REEs contents.

6.2. The White Patinas

From XRD mineralogical analyses on white patinas, only slight compositional differ- ences between all the samples are found (Figure 9). They are essentially represented by hydrozincite [$Zn_5(CO_3)_2(OH)_6$], except for the CBM03 and CBM05 samples, consisting of zincite [ZnO].

Based on XRD results, SEM-EDS analyses were performed on the selected CBM01 (hydrozincite) and CBM05 (zincite) representative samples. The morphological study evidenced in the CBM01 sample abundant organic filaments (Figure 10). The EDS spectrum and the EDS compositional maps (Figure 11), show filaments that are made of carbon

(C) and oxygen (O). Mineral grains recognizable in the sample are made of zinc (Zn) and oxygen (O), thus confirming the abundance of hydrozincite. Organic filaments are considered to be indicative of biologically mediated formation, as reported for similar occurrences in the same district [18].

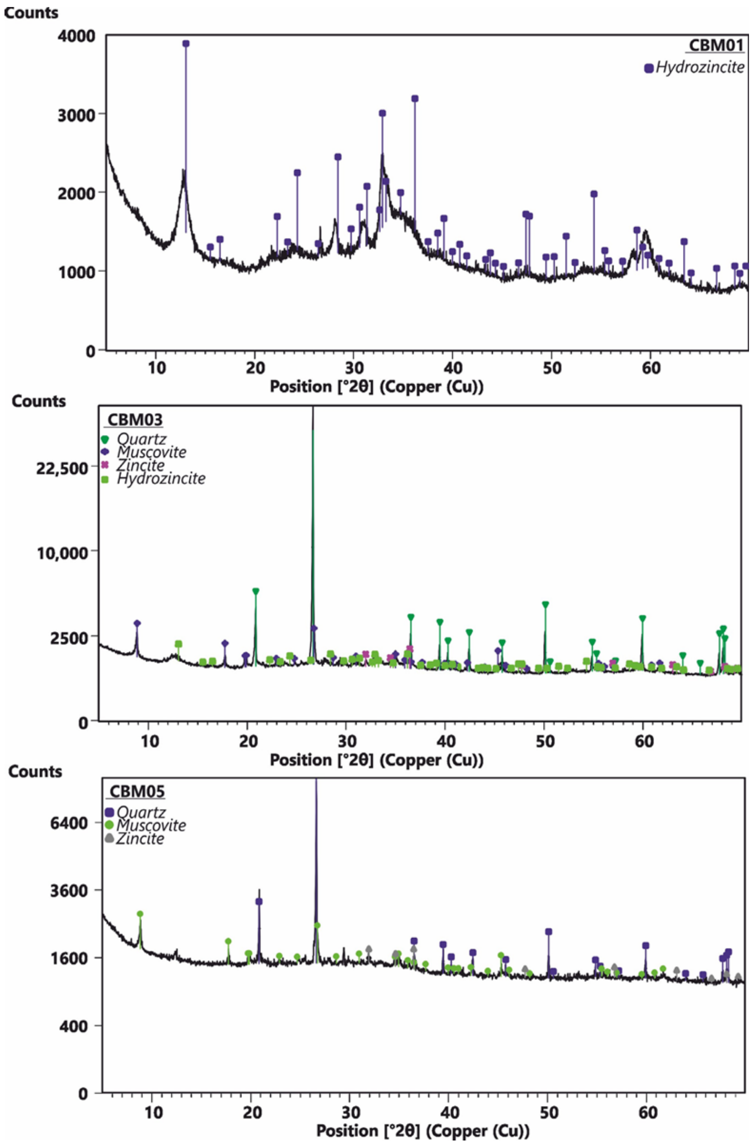

Figure 9. XRD patterns with the mineral phases detected in white patinas. *Y*-axes report counts in square root to highlight the minor peaks, except the first XRD pattern.

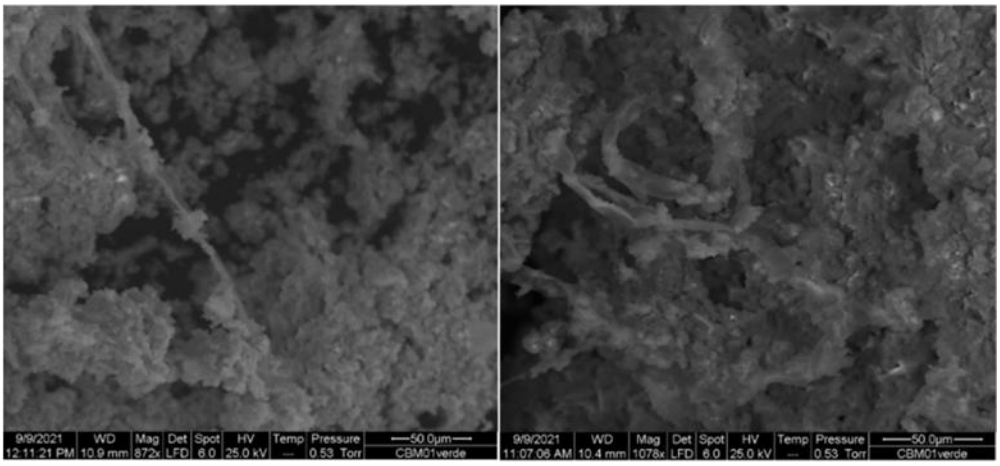

Figure 10. SEM images of CBM01 sample.

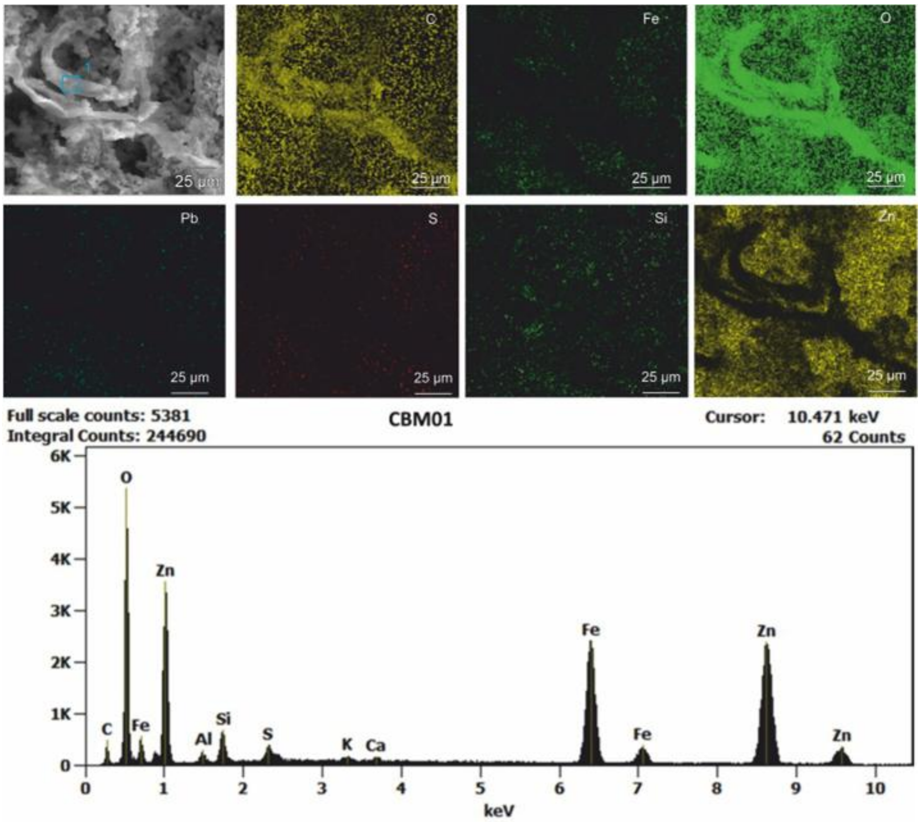

Figure 11. Compositional EDS maps and spectrum for the sample CBM01. The blue square indicates the analysed point.

The CBM05 sample displays a texture dominated by <20 µm elements of globular shape (Figure 12). EDS spectra and compositional maps (Figure 12), confirm the composi- tion reported by the XRD analyses. Moreover, SEM-EDS maps identified grains with traces of arsenic, lead, iron, and oxygen contents, and presence of aluminum-silicates grains.

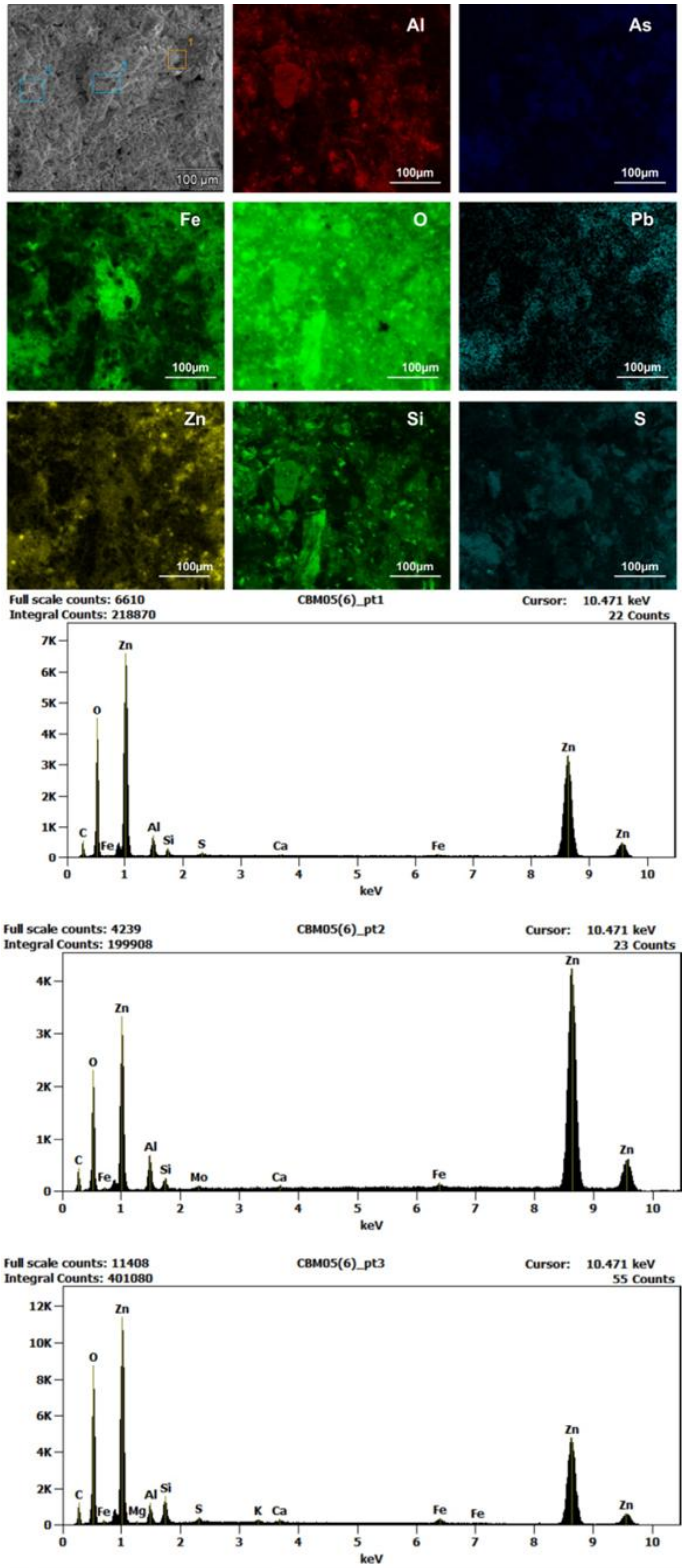

Figure 12. Compositional EDS maps and spectrums for the sample CBM05. The blue and yellow squares indicate the analysed points.

Chemical analyses were performed on each white patinas sample, except for the CBM09, completely utilized for the previous analyses. Trace elements, such as Rare Earth Elements, were analysed by ICP-MS, while major elements were analysed by ICP-OES (Tables 4 and 5).

Table 4. Analytical data for trace elements in white patinas. Values are in mg/kg (ppm).

Sample	Al	As	Ba	Cd	Co	Cu	Fe	Mn	Ni	Pb	Sb	Sr	Zn
CBM01	1770	23	31	610	11	850	27,700	360	150	14,800	8	8	433,200
CBM02	1800	41	310	580	18	730	26,700	650	130	14,600	8	14	415,000
CBM03	10,400	920	16,500	550	84	1430	355,200	14,400	190	33,000	42	200	82,400
CBM04	550	14	120	640	14	300	4870	290	170	6400	5	7	509,000
CBM05	9010	270	1530	400	46	1690	199,800	7450	90	74,500	67	55	90,300
CBM06	10,020	230	11,300	680	29	1490	91,400	4100	92	55,600	110	76	274,300
CBM07	880	23	250	450	10	570	9350	340	130	20,650	13	9	512,200
CBM08	1350	29	860	460	9	660	15,100	400	120	23,370	1	10	489,000

Table 5. Analytical data for Rare Earth Elements in white patinas. Values are in mg/kg (ppm).

Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REEs + Y
CBM01	250	250	140	61	270	63	24	89	11	45	7	15	1	8	1	1235
CBM02	200	200	110	45	200	44	17	65	8	34	6	12	1	6	1	949
CBM03	250	550	970	120	520	130	52	140	18	72	10	20	2	11	2	2867
CBM04	100	86	38	15	61	13	5	22	3	12	2	5	ND	2	ND	364
CBM05	140	180	280	47	220	56	22	68	8	36	5	11	1	6	1	1081
CBM06	91	140	220	33	140	35	14	40	5	2	3	6	1	3	ND	733
CBM07	84	86	41	13	51	11	4	17	2	9	2	4	ND	2	ND	326
CBM08	100	100	54	17	69	15	6	23	3	13	2	5	ND	2	ND	409

Some elements such as Al (550–10,400 ppm), Ba (31–16,500 ppm), Fe (4870–355,200 ppm), Mn (290–14,400 ppm), Sb (1–110 ppm), and Sr (7–200 ppm), vary by two or three orders of magnitude between the various samples, while others, such as As (14–920 ppm), Cd (400–680 ppm), Co (9–84 ppm), Cu (300–1690 ppm), Ni (90–190 ppm),

Pb (6400–74,500 ppm), and Zn (82,400–512,200 ppm) vary by only one order of magnitude. The CBM03 sample is particularly enriched in Al, As, Ba, Co, Fe, Mn, Ni, and Sr, the CBM05 sample is the richest in Cu and Pb, the CBM06 in Cd and Sb, and the CBM07 in Zn.

REEs analyses (Table 5) show little variability among the samples, except for the sample CBM03 which appears to be consistently enriched in REEs (2867 ppm).

6.3. Cerussite

To investigate the origin of the REEs contents found in the tailings of the Sanna plant, a study of supergene mineralization of Sanna vein, which was among the main suppliers of the plant, was performed. An interesting aspect of this mineralization is its predominantly carbonate composition, given that from the most recent literature on Sardinian low-temperature hydrothermal ores [29], high concentrations of REEs are found in carbonate phases. Three samples of cerussite ore, prevalently composed of cerussite and goethite, were collected in the upper part of the Sanna vein (Figure 5). Cerussite crystals were therefore selected from the ore by hand picking, and then analysed by ICP-MS, after acid digestion, to investigate their REEs contents (Table 6).

Table 6. Analytical data for Rare Earth Elements in cerussite. Values are in mg/kg (ppm).

Sample	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REEs + Y
MVS_1	ND	110	4	ND	120	20	4	6	1	1	ND	ND	ND	ND	ND	266
MVS_2	ND	96	3	ND	100	17	4	5	ND	1	ND	1	ND	ND	ND	227
MVS_3	ND	61	2	ND	64	10	2	3	ND	ND	ND	ND	ND	ND	ND	142

In Table 6 the results of analyses are reported. Lanthanum and Neodymium show the higher values among the REEs.

6.4. Water Analyses

Water samples collected together with the white patinas were analysed by ICP-MS. Overall, water shows a calcium-magnesian sulphate composition [30], characteristic of sulphide mining areas, and amounts of total REEs plus Y of thousands of ng/L (Table 7), several orders of magnitude below the values reported in the literature for mine drainage waters in Montevecchio area [14].

Table 7. Analytical data for Rare Earth Elements in water. Values are in ng/L.

Sample	T [°C]	pH	Eh [mV]	EC [μs/cm]	TDS [mg/L]	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	∑REEs + Y
T0	16.4	6.3	490	1318	989	1130	730	300	90	340	82	30	130	15	89	17	40	4	19	3	3019
T1	17.5	6.1	491	1301	1071	190	620	750	36	150	34	17	43	4	21	3	5	1	3	ND	1877
T2	16.6	5.7	320	1390	1060	1990	1490	830	240	1040	240	97	400	43	220	35	72	7	45	6	6755
T3	18.6	5.4	471	1365	1030	880	800	290	78	270	64	25	91	10	55	11	22	2	11	1	2610
T4	20.0	4.7	414	1399	1036	450	580	180	57	220	47	25	64	7	34	6	15	1	8	2	1696

From Table 7, the most concentrated REEs in waters are: Y (190–1990 ng/L), La (580–1490 ng/L), Ce (180–830 ng/L), Pr (36–240 ng/L), Nd (150–1040 ng/L), Sm (34–240 ng/L), Gd (43–400 ng/L) and Dy (21–220 ng/L). The sample T0, collected in the stream flow on the tailings immediately downstream to the Sanna processing plant, is among the richest samples in REEs. The sample T1, sampled near a large encrustation of white patina precipitate, is among the poorest samples in REEs. The sample T2 is the richest in REEs, it was sampled where the water leaked off from a collapsed zone of the drainage tunnel of the old tailing pond. The sample T3, among the richest in REEs, was sampled downstream of sample T2. Sample T4, the poorest in REEs, was sampled downstream of other samples and near two tributaries of the Rio Roia Cani (Figure 5).

7. Discussion

Understanding the chemical and mineralogical properties of mining wastes is crucial for the assessment of their economic potential, improving environmental risk assessment, and optimizing the design and execution phases of remediation operations [31]. Raw materials recovery from mining wastes is a specific target for EU policies to improve the supply of CRMs to the Union for the next years [1]. At the same time, these activities provide fundamental contributions to solving environmental issues in abandoned mine areas, as they result in effective remediations of the polluted sites. Effectual recovery of raw materials requires significant technological insight but also requires a strong effort in mineral characterization of waste materials. For the reprocessing of these tailings, it is important to know in detail the initial composition of the ore, the methods used in ore processing, the chemical additives used for mineral beneficiation, how and where tailings were discharged, their current mineralogical composition, and the elements of economic interest contained in them [32]. In environmental studies, tailings characterization generally starts from studies of their granulometry and mineralogy. These characteristics provide essential information on the behavior of the tailings when they encounter the water [33]. The mineralogy of tailings may change through a single deposit, which may constitute a very heterogeneous system. Minerals in tailings may be very reactive and often soluble in waters under a wide range of environmental conditions; mineralogical characterization of reactive phases (e.g., sulphide and carbonate minerals) allows for predicting the extension and intensity of phenomena such as acid drainage and leaching [31].

7.1. Environmental Issues and Resilience Factors

Several environmental issues emerge from the study in the Sanna plant area. The occurrence in mine wastes, tailings, and secondary precipitates (i.e., the white patinas) of anomalous geochemical contents of metals (i.e., Fe, Al, Zn, Pb, Mn, Cu, Cd, and Hg) and metalloids (As and Sb), represents a supply of several contaminants having various grades of toxicity that imply different threats for the environment. Depending on the physicochemical conditions of the different interactions of these materials with the Rio

Roia Cani waters and with atmospheric agents, it may be produced a prevailing dispersion in solution of metalloids (high-pH interaction), or metals and metalloids (low-pH interaction), followed by diffusion in the environment [34–40]. This chemical transport combines with the solid transport of waste constituents due to high erosion rates in poorly consolidated materials.

X-ray diffraction analyses on the tailings of the Sanna plant identified several metallic minerals which must be regarded as fundamental sources of pollution. Indeed, secondary oxidated phases as zincite are more soluble than sulphides, easily releasing zinc in solution, which is confirmed by the frequent occurrence of hydrozincite/zincite mineral precipitates (white patinas) along the riverbed. The equilibrium between the release of contaminants and their precipitation is influenced by the hydrological regime of the Rio Roia Cani, the temperature, the concentration of metals in the solution, and the Eh-pH conditions.

The co-precipitation of Iron and Lead oxy-hydroxides with zincite, suggested by the red colour of the waters and of the riverbed at the sampling point, is confirmed by SEM-EDS in some white patinas samples (i.e., CBM05 sample), which detected Lead, Iron, and Oxygen. Moreover, precipitation of iron-bearing phases is predicted by saturation calculations (Phreeqc Interactive 3.6.2-15100 software) of the water samples collected along the Rio Roia Cani (Figure 5). Where the T2 water sample was collected, the water was oversaturated in ferrite-Zn and goethite, with saturation indexes of 11.54 and 5.94, respectively.

According to Dore et al., 2020 [41], the microscopic processes that control the dis- solution and precipitation of minerals in a polluted mining area may act both positively and negatively toward the environment, favouring the natural abatement or, conversely, the dispersion of pollutants. These microscopic processes may be fundamental for the increase or decrease in metal loads in a river; when positive processes dominate, the load decreases or is limited, but, when negative processes dominate, the load increases, and the dispersion of pollutants can become significant. Overall, metal-enriched precipitates such as white patinas may act as resilience factors in a positive process for the natural environment of the area, removing and fixing relevant amounts of pollutants from the Rio Roia Cani waters. This shows the importance of biologically mediated processes as natural remediation agents, as already observed in the waters of Rio Naracauli [42].

7.2. Raw Materials Potential

Chemical analyses of the Sanna plant tailings (Tables 2 and 3) show that they contain high grades of lead and zinc (up to 1.23 wt% and 2.65 wt%, respectively). The highest Pb grades are attained for sample C06, which is also arsenic and antimony-rich (430 and 170 ppm, respectively), representative of a tailing layer which may have been derived from a fahlore-rich primary ore. Although the materials show generally relatively high contents in total REEs, there is no apparent correlation between the metals present in the highest grades (Pb and Zn) and the REEs. On the other hand, the primary source of REEs in the ore has not yet been discovered; this may lead to the conclusion that the REEs are contained in the gangue and/or in the host rock minerals included in the exploited ore, as reported by Moroni et al., 2019 [20] for the five element-type veins of the southern part of the Montevecchio vein system. The analysed cerussite samples (Table 6) show a slight anomaly in lanthanum and neodymium, indicating a possible role of supergene processes in concentrating these elements in secondary phases. Although the role of weathering processes in REEs mobilization and reconcentration is extensively recognized in lateritic and regolith-hosted, ion-adsorbed-type deposits as well as in weathered carbonatite envi- ronments [43,44], REEs behaviour in supergene ore zones of hydrothermal vein deposits is less documented [45].

The white patinas in the Rio Roia Cani are made of Zn-carbonate minerals, thus displaying high Zn contents up to 51.22 wt% (Table 4). Remarkably, they show high contents of REEs (up to 2867 ppm ∑REEs + Y) (Table 5), which display little correlation with Zn and good correlations with As, Fe, and Mn (Figure 13). The zincite samples (CBM03 and CBM05) show the highest values of REEs. A possible role of biological processes in concentrating REEs from waters in the Rio Roia Cani environment can be inferred. Studies on REEs mineralizing processes in exogenic environments evidenced the role of microorganisms in REEs mobilization from primary minerals (phosphates, carbonates, silicates, etc.) to waters, their capabilities in uptaking REEs from waters and fractionating LREEs from HREEs, and to favour and accelerate REEs concentrations in secondary (bio-) minerals [46,47].

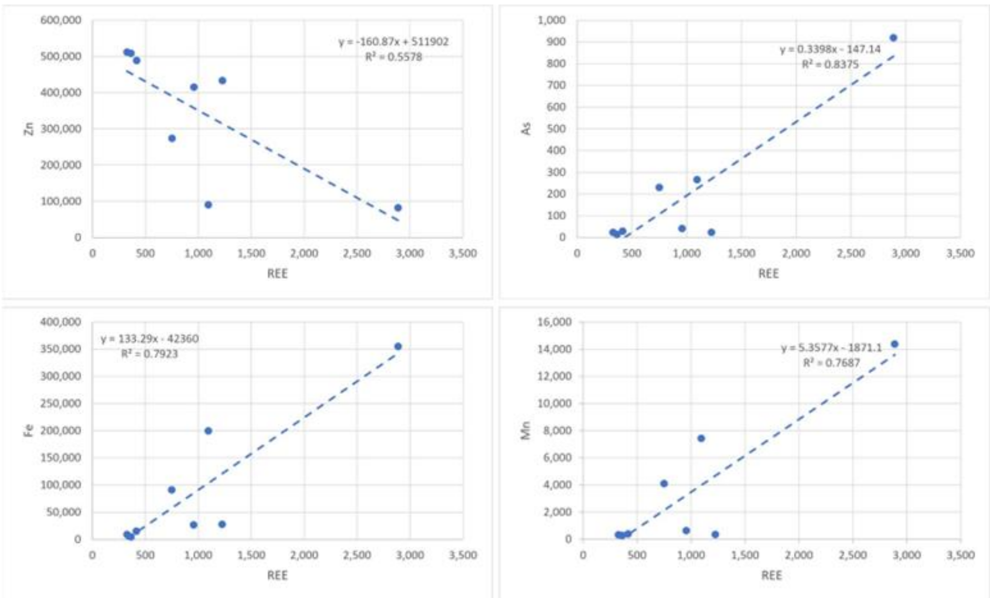

Figure 13. Correlation graphics between some metals and REEs contained in white patinas. Values are in ppm.

The relatively low REEs contents resulting from water analyses of Rio Roia Cani are in good agreement with an effective process of removal of these elements by precipitation of white patinas.

Further insights into the behaviour of REEs in the studied systems are provided by REEs patterns from tailings, white patinas, cerussites and waters, normalized to Post- Archean Australian Shales (PAAS) [48] (Figure 14). Tailings, white patinas, and waters display similar trends: patterns show a flat trend, with a slight enrichment in MREEs and a positive Eu anomaly. They show a good agreement with the patterns reported for the Montevecchio primary ore [6]. Conversely, the cerussite samples show an evident w-type tetrad effect, with strong depletions in Ce, Pr, and HREEs, confirming different paths of REEs fractionation during supergene processes and formation of the secondary ore.

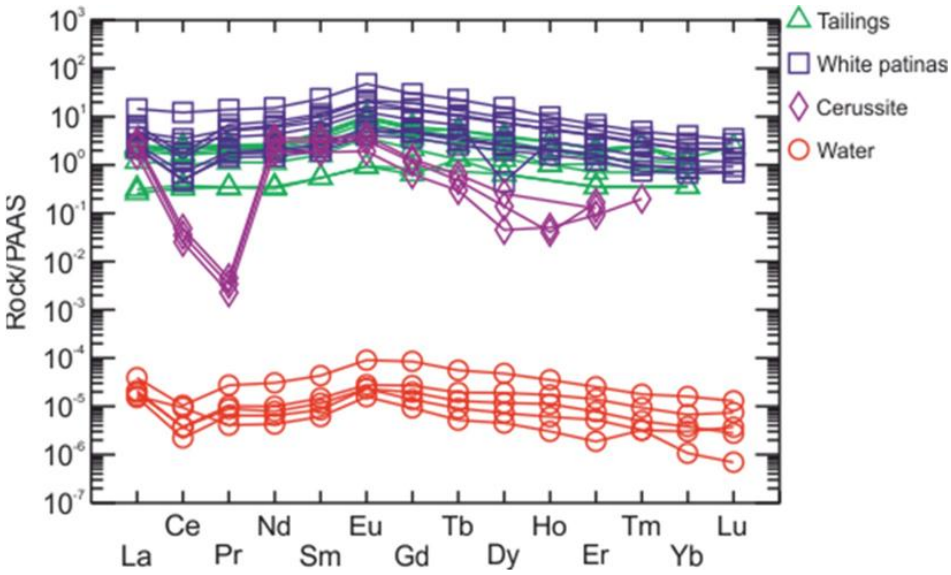

Figure 14. PAAS-normalized REEs patterns for tailings, white patinas, cerussite and waters of the Sanna area.

7.3. Insights for Metals Recovery

Mineral and chemical characterization may also provide some insights into different raw materials recovery from wastes. The measured contents of Zn and Pb in the tailings may support a project for the recovery of these base metals [49]. In this view, the application of processing techniques essentially depends on different physical (i.e., granulometry) and mineralogical characteristics of waste materials. Due to their fine-grained nature, sulphide-bearing tailings can be effectively treated by flotation, although a large amount of fines increases the consumption of reagents, causing the so-called slime coating phenomenon, hampering the effectiveness of the treatment and, often, making it unfeasible [50]. Successful application of advanced flotation techniques in the processing of the lead and zinc sulphide-bearing tailings of the Principe Tommaso plant in Montevecchio has been recently described in Mercante et al., 2021 [51] and in Sogos et al., 2022 [52]. Different approaches may be required for waste materials in which lead and zinc are contained as oxidate minerals (cerussite, anglesite, smithsonite, hemimorphite, hydrozincite, zincite, etc.), for which metal recovery can be also obtained by leaching techniques (e.g., with sulfuric acid, caustic soda, etc. [53,54]).

The limited presence of economic deposits of REEs and the serious environmental issues related to REE minerals beneficiation [55–59] promoted the studies on alternative and more sustainable treatment techniques, such as biohydrometallurgy, to extract REEs both from primary ores and from secondary resources, as industrial and mining wastes. Recovery of base metals from low-grade ores by bioleaching is a common technique used in the mining industry since the 1970s; it was used with success to leach REEs from mining wastes [60]. As in classical processing techniques, the efficiency of bioleaching is closely linked to the physical and mineralogical composition of the waste materials; actually, the se- lection of a suitable microorganism depends on the type of REEs minerals (e.g., phosphates, carbonates, etc.) present in the waste, which present different degrees of solubilization in presence of the chemical agents (i.e., organic acids) secreted from microorganisms as chemo- heterotrophic bacteria. Biosorption and bioaccumulation processes have been documented for various microorganisms, capable of REEs uptake from leachates [61,62]; conversely, REEs-bearing biomineralization is documented only in a few studies [57,58].

The REEs contents measured in the tailings from the Sanna plant are currently sub-economic, even if with a view to an integral recovery of raw materials from these mine wastes they must certainly be taken into consideration. The current limited knowledge of Rare-Earth-bearing minerals in the Montevecchio system, however, makes treatment hypotheses for the recovery of these metals premature. Nevertheless, the identification of secondary processes of REEs enrichment in the white patinas constitutes a significant incentive to improve biologically mediated techniques for the recovery of REEs elements from suitable mineral phases. To achieve these goals, the characterization of the REEs min-eralogical carriers from primary ore to tailings and the identification of the microorganisms associated with hydrozincite forming the white patinas is of primary importance. Until now, a large part of recent investigations on waste materials in Sardinian mine sites was almost exclusively oriented to the environmental aspects [12–19,41,63]; only a few studies faced the wastes as potential sources of raw materials and CRMs [64–66]. The data acquired in this study allow a series of considerations regarding both the raw material potential and the environmental issues of the Sanna-Rio Roia Cani area.

8. Conclusions

The mineralogical and chemical studies on the tailings of the Sanna processing plant area in Montevecchio confirm that these materials constitute sources of environmental risk. At the same time, they must be regarded as potential economic sources of raw materials, primarily Zinc and Lead. The chemical analyses on the various materials present in the site also highlighted specific layers of REEs-enriched fine-grained products along the stratigraphic sequence of the old tailings pond. The mineralogical carrier of REEs is not yet identified, but an origin from gangue and/or host rock minerals may be reasonably inferred. Some indication of supergene REEs-enrichment of the ore mineralization comes from analyses on cerussite from Sanna mine works. Further evidence of remobilisation processes of REEs in the studied area is provided by the analyses on the white patinas precipitated into the riverbed of the Rio Roia Cani, which display 7.45 wt% of Pb, 51.2 wt% of Zn and about 2900 mg/kg of REEs + Y.

Among the various waste materials present on the site, tailings are confirmed as a primary source of contamination, due to their high contents of pollutants (Pb, Zn, Fe, etc.). Contaminants are transported in solution by rainwater and by the flow of the Rio Roia Cani that erodes the mining dumps. Contamination is partially buffered by white patinas that allow the precipitation of Zn in solution as hydrozincite and zincite, a situation similar to the one currently underway in the Rio Naracauli (Ingurtosu mine, west of Montevecchio), where the riverbed is covered by hydrozincite bio-precipitates [18,63]. Furthermore, the analyses indicate that these white patinas retain other metals, preventing them from remaining in solution and from being dispersed into the environment, generating a sort of remediation process.

This study highlights the presence of CRMs in the tailings, suggesting the possibility of considering these materials as sources of secondary raw materials, as also proposed by recent studies in the Eastern Montevecchio area [66]. REEs found in tailings and white patinas are present in sub-economic to economic values, deserving further studies and insights, for defining their origin, and their processes of mobilisation and concentration in the Rio Roia Cani environment.

Overall, the amount of Zinc, Lead, and CRMs found in the solid matrix led to a hypothesis of evaluation of re-treatment of these solids by various techniques of mineralur- gical processing. This re-treatment would entail two benefits: one environmental, through the removal of a primary source of contamination, and the other of an economic nature, through the implementation of a circular economy chain linked to the sale and re-use of these raw materials.

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Geochemical and mineralogical characterization of historical mining waste deposits in SW Sardinia: implications for potential critical raw materials (CRM) recovery

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Abstract

Within the framework of the European Critical Raw Materials (CRM) strategy, waste deposits in historical mining districts represent potential secondary sources of strategic and critical raw materials. Southwestern Sardinia (Italy) hosts the largest concentrations of mining waste in Italy, generated by long-term exploitation of several classes of ore deposits, from carbonate-hosted Mississippi-Valley-Type (MVT) to granite-related (skarn, greisen) to sediment-hosted low-temperature Pb-Zn and Ba-F-Pb hydrothermal polymetallic veins. This study investigates selected waste materials resulting from the exploitation and processing of different ores in the Fluminése–Arburése district (SW Sardinia), one of the most important in Italy during the 20th century. Forty-two samples were collected from flotation tailings and hydrogravimetric tailings at Montevecchio, S'Acqua Bona, Santa Lucia, and Su Zurfuru past mining areas. With a multi-analytical approach, samples underwent mineral characterization using X-ray diffraction (XRD) and scanning electron microscopy with energy-dispersive spectroscopy (SEM–EDS), while bulk geochemistry was determined by ICP–MS, complemented by XRF (Pb, Zn, Ba) and ion chromatography (F). From mineral characterization, waste materials result dominantly composed by gangue minerals (e.g., quartz, carbonates, iron hydroxides/oxides) and minerals from the host rocks (e.g., micas, kaolinite, feldspars), with small and variable amounts of primary (e.g., sphalerite, galena and other sulfides; baryte, fluorite) and secondary ore minerals (e.g., supergene minerals as cerussite, smithsonite, hydrozincite, etc.). Bulk geochemistry allowed to identify site-specific enrichments, including up to 30.4 wt.% Pb and up to 14.5 wt.% Zn in waste deposits from Montevecchio mine processing plant ("Sanna plant”); up to 10.25 wt.% Ba and > 2 wt.% F in tailings from Santa Lucia mine plant, and up to 2761 ppm ΣREE+Y at Montevecchio–Telle. Tailings from Su Zurfuru mine show Bi (up to 660 ppm) and Sb (up to 115 ppm) enrichment. SEM–EDS analyses confirmed the presence, as significant accessory, of metal- and CRM- bearing phases, and particularly the distinct occurrence of REE minerals, as fluorocarbonates (synchysite-(Ce), bastnäsite-(Ce)) and phosphates (xenotime). Overall, these results confirm the CRM potential of historical mining wastes in the studied district; distinct geochemical and mineralogical associations, with the presence of significant CRM concentrations, support their consideration as potential targets for resource recovery integrated with remediation strategies.

Keywords: *Waste Valorization, Economic Geology, Secondary Raw Materials, Geochemical Exploration*

1. Introduction

Modern society increasingly depends on a wide range of raw materials, many of which are classified as Strategic and Critical Raw Materials (S-CRMs). The European Commission defines these materials as resources of high economic importance and a significant risk of supply disruption due to their limited geological availability and strong dependence on imports from geopolitically unstable regions. (*Blengini et al., 2017; Carrara et al., 2023; Grohol et al., 2023*)

S-CRMs are indispensable in several high-technology sectors, including renewable energy, aerospace, electronics, and advanced manufacturing. Their role is central in enabling the transition toward a low-carbon and circular economy, as promoted by the European Green Deal implemented by the Critical Raw Materials Act (*European Parliament and Council of the European Union, 2024*). Minerals such as lithium, cobalt, rare earth elements (REEs), and platinum-group metals are essential components of batteries, electric vehicles, wind turbines, and photovoltaic technologies (*Helbig et al., 2018; Kim et al., 2023*).

The European Union—currently heavily reliant on imports—anticipates a dramatic increase in the demand for these materials. By 2030, lithium demand is projected to rise by 18%, while cobalt demand is expected to increase by 5%. Looking to 2050, demand may surge up to 60 times for lithium and 15 times for cobalt compared with today’s levels. Similar trends are predicted for REEs, such as neodymium, used in permanent magnets for wind turbines and electric motors (*Grohol et al., 2023*).

However, developing new mining operations within Europe is not always feasible due to environmental constraints, limited social acceptance, and stringent regulatory requirements. As a result, increasing attention is being devoted to Secondary Raw Materials (SeRMs), including those recoverable from historical mining waste. Mining waste, traditionally perceived as an environmental liability, may act as a significant reservoir of S-CRMs. Recovering these materials can offer dual benefits: reducing environmental impacts and enhancing resource efficiency in line with circular economy principles. (*Lottermoser, 2010 ; Bian et al., 2012; Edraki et al., 2014; Pires and Martinho, 2019; Lèbre et al., 2020*)

Sardinia represents a particularly relevant case study, hosting nearly half of Italy's former mining sites and associated historical waste deposits, linked to a millennia-long mining history that spans from the Nuragic civilization to Roman, Medieval, and modern industrial operations. The extraction of metalliferous ores (Pb, Zn, Ag, Fe) and industrial minerals (baryte, fluorite) has left behind about 70 million cubic meters of mining residues (*RAS, 2003*). These materials may contain valuable concentrations of S-CRMs, firstly depending on the mineralogy of the ore and on technological grade and efficiency of processes applied in the past to mineral beneficiation and refining. Among Sardinia's mining districts, the southwestern region is particularly significant, hosting approximately 70% of the island's historical mining waste (Figure 1). This area hosts several distinct mineralization styles, including:

- The Iglesiente district, characterized by Pb–Zn MVT and SEDEX deposits (*Boni et al., 1996; Santoro et al., 2023*);

- The Sulcis district, known for Fe and base metals skarn deposits and for residual (karst) baryte deposits (*Padalino et al., 1973; Boni et al., 1990; Cocco et al., 2022*);

- The Fluminése-Arburése district, containing low-temperature hydrothermal veins rich in fluorite, baryte, Pb, Zn, Ag, and locally Ni and Co (*Moroni et al., 2019a, b*)

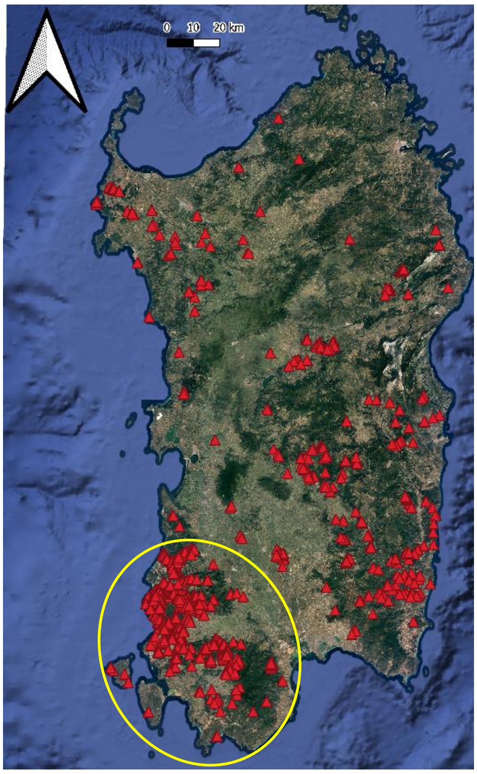

Figure 1 Distribution of historical mining dumps in Sardinia. The yellow square highlights the Sulcis-Iglesiente-Fluminése–Arburése areas, which contain approximately 70% of the deposits.

However, the mineralogical hosts and geochemical controls of critical elements in historical mine tailings from SW Sardinia remain poorly constrained. To date, a comprehensive and systematic characterization of CRM-bearing mining residues in Sardinia is still lacking. This knowledge gap is particularly critical in the Fluminése–Arburése district, once one of the most important mining districts in Italy, where large volumes of material have already been excavated, crushed, and exposed at the surface, while their CRM concentrations remain largely unknown. These residues may represent a potentially significant secondary resource of CRMs, but at the same time they constitute a major and persistent source of environmental contamination.

This study addresses these issues by focusing on the Fluminése–Arburése district as an ideal natural laboratory for assessing mining waste valorization strategies. The district is characterized by a varied geology, numerous ore deposits of different classes and sizes, a long history of industrial mining and large volumes of tailings and waste materials, with widespread environmental degradation affecting soils and water bodies. To address this issue, extensive sampling of waste dumps in the main mining areas of the district was carried out, followed by mineralogical (XRD, SEM-EDS) and geochemical (ICP-MS, XRF) analyses. The aim of this study is to provide mineralogical and geochemical data to evaluate the potential for re-mining and metal recovery from historical mining wastes, integrating resource valorization into future environmental remediation strategies. This approach moves beyond

traditional contamination-focused assessments of Italian environmental laws (e.g., Legislative Decree 152/2006), favored by a new regulatory framework (Law 115/2024) that introduces specific rules for the retreatment and valorization of mining dumps, aligning national strategies with the CRM Act and European policies on raw materials. In this context, this study aims to:
(1) characterize the mineralogical and geochemical variability of different types of mining wastes in a key mining district of SW Sardinia;
(2) identify the mineralogical hosts of critical raw materials (CRM) and evaluate the geochemical controls on their distribution;
(3) assess the potential of these wastes as secondary resources in the framework of recent European and Italian policies on critical raw materials.

2. Geological and Mining Context

2.1 Geological and ore deposit setting

The study area lies within the External Zone and the External Nappe Zone (Arburése Unit) of the Sardinian Variscan transect (Fig. 2). The two tectonic units are separated by the Arburése Thrust (AT), a regional SW-verging structure formed during peak Variscan compression (*Carmignani et al., 1994; Funedda, 2009*). These stages were marked by the emplacement of magmatic intrusions and by NW–SE and E–W high-angle faults associated with orogenic collapse. The main local intrusions are the 304 ± 1 Ma Arbus Pluton to the north and the 289 ± 1 Ma Monte Linas pluton to the east and south (*Cuccuru et al., 2016; Naitza et al., 2017*). The External Zone (Sulcis-Iglesiente) basement comprises two main sedimentary successions: 1) a early Cambrian-early Ordovician succession made of terrigenous sandstones (“Nebida Fm”), carbonate platform deposits (“Gonnesa” and “Campo Pisano” Formations) and deep-marine siltstones and claystones of the “Cabitza” Formation – this succession was deformed and folded in middle Ordovician, during the “Sardic Phase” tectonic event (*Cocco and Funedda, 2019, and references therein*); 2) a late Ordovician-Devonian succession, including late Ordovician dominantly siliciclastic sediments, Silurian black shales and early Devonian limestones (*Loi et al., 2023*). These successions underwent very low grade metamorphism, deformation and folding during the Variscan tectonic phases. The Arburèse tectonic unit is part of the SW-to W-verging fold-and-thrust belt of the External Nappe Zone. It comprises a thick Cambrian-early Ordovician siliciclastic sequence with interspersed volcanics (“Arenarie di San Vito” Fm), deformed and folded during the early Ordovician “Sarrabese phase” tectonic event and followed by Ordovician calc-alkaline felsic to intermediate volcanics. The whole succession underwent low-grade metamorphism, was deformed and isoclinally folded during Variscan Orogeny.
Variscan tectonics exerted a strong control on the mineralizing processes at a regional scale. Multiple deformation and folding of pre-Sardic Phase Cambrian succession caused deformation and remobilization of Pb-Zn MVT/SEDEX sulfide

ores (*Santoro et al., 2023*); in the AT footwall, recurrent shear zones acted as preferential pathways for magmatic and hydrothermal fluids during late to post-Variscan stages (*Cocco et al., 2022*). Variscan tectonic structures, further evolved during post-Variscan extensional tectonics, not only controlled fluid circulation but also created favorable conditions for lithologically-controlled geochemical traps, particularly within Cambrian carbonates and Silurian black shales. Metal sources for ores are debated (*Moroni et al., 2019a, b*) but may reasonably include the remobilized early Cambrian lead and zinc ores in carbonate rocks, sulphur and other metals in organic matter-rich black shales, and fertile intrusions like the Monte Linas pluton, which supplied a wide range of elements including fluorine, barium, nickel, cobalt, bismuth, tungsten, and molybdenum (*Naitza et al., 2024*).
The main metallogenic events of the area can be summarized as follows (*Naitza et al., 2024* - Table 1):

- During the "Pre-Sardic Phase" times (early Cambrian to early Ordovician), the Pb-Zn SEDEX and MVT deposits formed in the Cambrian carbonate host rocks, in turn marked by a strong lead, zinc and barium geochemical anomaly (*Garbarino et al., 1989; Boni et al., 1996*).
- The "Sardic" Phase (Middle to Late Ordovician) was characterized by the first formation of Zn-Pb "calamines" and karstic baryte deposits (*Garbarino et al., 1989*).
- The Variscan Orogeny created a hydraulically-conductive tectonic framework for mineralization through faults, backthrusts (*Cocco et al., 2022*) and shear zones. The associated magmatic intrusions drove the large-scale circulation of mineralizing fluids, which generated various types of granite-related ore deposits, including Mo-W-Sn-As-Bi-F greisen and base metal (Zn-Pb-Cu-F±Sn±W) skarn deposits (e.g., Su Zurfuru mine - Fig.1) in which a contribution from lead and zinc remobilized from Cambrian ores has been evidenced (*Aponte et al., 1988*).
- The post Variscan (late Permian? Triassic?) extensional tectonics developed a new pattern of structures (in many cases inherited from Variscan ones) for low-temperature hydrothermal fluids that originated major polymetallic Pb-Zn (Cu-Ag-Sb-Bi-Ni-Co-Ga-Ge-In-REE) quartz-carbonate vein systems (e.g., Montevecchio Sanna and Telle veins; S'Acqua Bona mine - Fig.1) also including the "five-element-type" Ni-Co-As-Bi-Sb veins of Flunese sector - and F-Ba-Pb (Zn, Cu, Ni, Co, Bi) veins (e.g. Santa Lucia mine – Fig.1) (*Boni et al., 1992; Moroni et al., 2019a,b; Naitza et al., 2024*). During the Mesozoic, prolonged exposure of the bedrock to continental conditions favored the formation of large supergene deposits (non-sulfide zinc deposits – "calamine," karstic baryte).

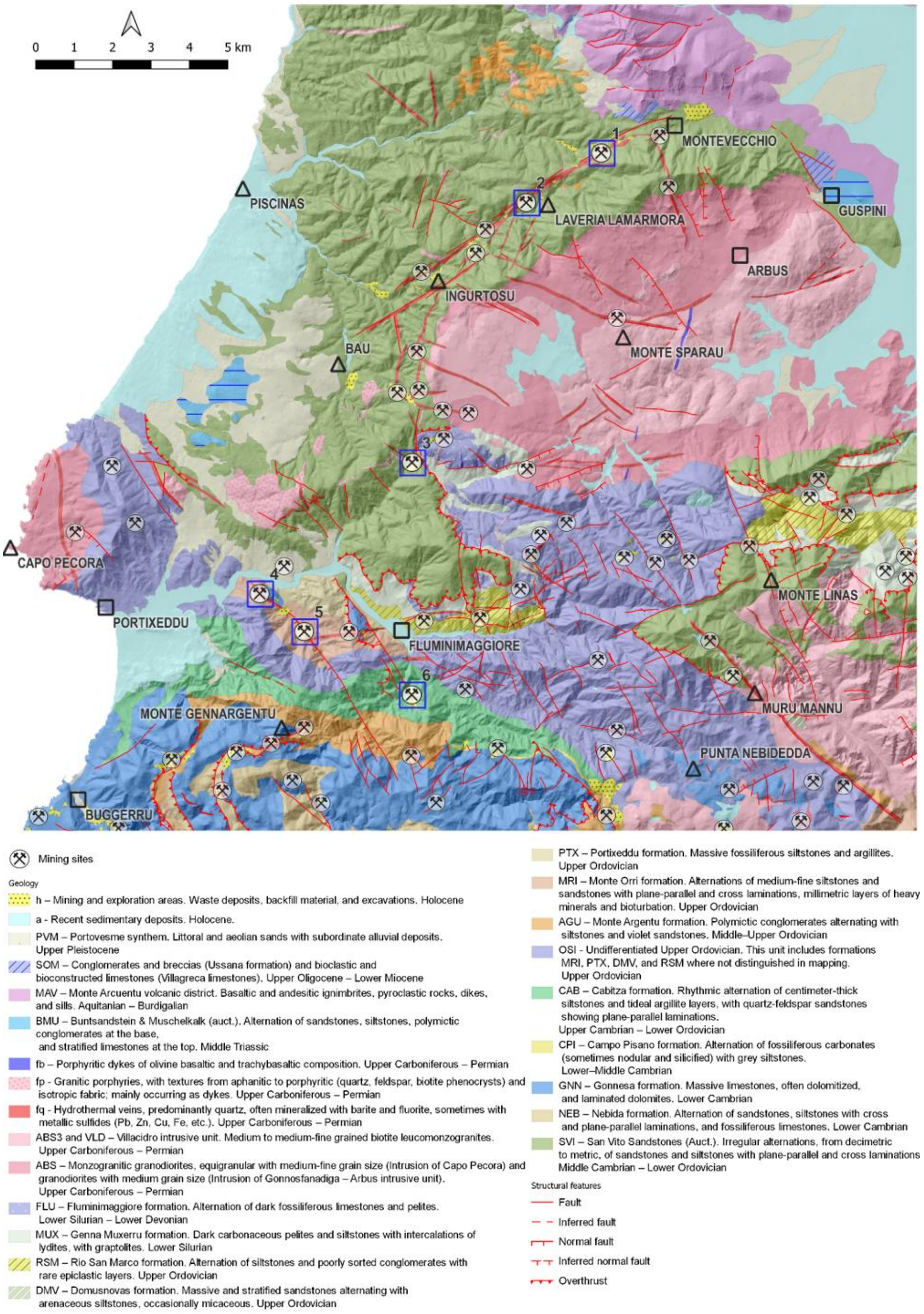

Figure 2 Geological sketch map of the study area. Mining sites and the study sites are highlighted by a blue square and numbered: 1. Montevecchio – Sanna, 2. Montevecchio – Telle, 3. S'Acqua Bona, 4 and 5 Santa Lucia, respectively, S'Oreri and Filone Palazzo, 6. Su Zurfuru.

Table 1 The main depositional stratigraphic sequences, tectonic evolution and associated metallogenic events.

Time / Stage	Stratigraphy and ore deposit setting	Tectonic Evolution	Metallogenic Events
Early Cambrian – Early Ordovician (Pre-Sardic Phase)	Shallow-water carbonate sequences (Gonnesa, Campo Pisano Fm.),	Stable platform, minor tectonic activity	Pb–Zn MVT and Fe-Zn (Pb) SEDEX
Middle–Late Ordovician (Sardic Phase)	Siliciclastic sequences	E–W open folds, Sardic Unconformity	Karstic baryte, Zn-Pb non-sulphide ores ("calamine")
Late Ordovician – Late Devonian (Post-Sardic)	Mixed terrigenous, carbonate, and tidal sequences; Silurian carbonaceous black shales (Genna Muxerru, Fluminimaggiore, Mason Porcus Fm.)	Relative tectonic quiescence, continued subsidence	Non-relevant in SW Sardinia
Carboniferous (Variscan Orogeny)	Deformation of Palaeozoic successions	Nappe stacking (SSW–W transport), low-grade metamorphism and shearing	Tectonic emplacement of reactive lithologies and generation of fluid pathways
Late Carboniferous – Permian (Late–Post Variscan)	Intrusive suites: Arbus & Villacidro Plutons; dike swarms	Collapse of the orogen, exhumation, and high-angle faulting	Pb–Zn–Cu–Fe (Sn, W) skarn and Mo-W-Sn-As-Bi-F greisen;
Permian – Triassic (Post-Variscan)	Post-orogenic cover sequences	Hydrothermal fluid circulation, basin reorganization	Polymetallic Pb-Zn (Cu-Ag-Sb-Bi-Ni-Co-Ga-Ge-In-REE) "Montevecchio-type" veins; F-Ba-Pb-Ag (Zn, Cu, Ni, Co, Bi) "Silius-type" veins; remobilization of older ores; secondary Pb–Zn supergene deposits;

2.2 Mining context

Sardinia hosts the most extensive historical mining district in Italy, with approximately 500 documented mining sites, the majority of which are

concentrated in the southwestern region. Among the most significant operations are the mines in Montevecchio (Pb–Zn), Monteponi (Pb–Zn–Ag), San Giovanni (Pb–Zn–Ag), Serbariu (coal), Funtana Raminosa (Cu–Pb–Zn–Fe), Lula–Sos Enattos (Pb–Zn), San Leone (Fe) and Rosas (Cu–Pb–Zn–Ag). Mining wastes in these districts represent the legacy of more than a century of intensive exploitation of polymetallic veins, skarns and hydrothermal deposits.
Underground extraction in these districts is commonly carried out using overhand stoping with footwall backfilling, a mining method well-suited to moderately to steeply dipping ore bodies hosted in competent rock. Extraction proceeded upward from a basal drift, removing the ore in successive benches while the voids were filled with waste rock to maintain stability and ensure safe access for workers. (*Hamrin et al., 2001; Hartman and Mutmansky, 2002)*

After extraction, ores were processed in mineral processing plants where ore minerals were separated from gangue material (*Wills and Finch, 2015*). The typical workflow comprised (Fig. 3):

1) Crushing: The jaw or cone crushers reduce large ore blocks to smaller pieces.
2) Grinding: The crushed material is processed into fine particles in mills to separate the mineral grains from the surrounding waste.
3) Classification: The ground slurry is separated according to particle size using screens or hydrocyclones.
4) Concentration: Valuable minerals are separated from the gangue using methods such as flotation (for sulfide ores), magnetic separation (for magnetite), or hydrogravimetric separation.
5) Filtration and Dewatering: The concentrate is thickened and filtered to eliminate excess water.
6) Tailings Disposal: Residual waste materials, known as tailings, are stored in tailing ponds or dams.

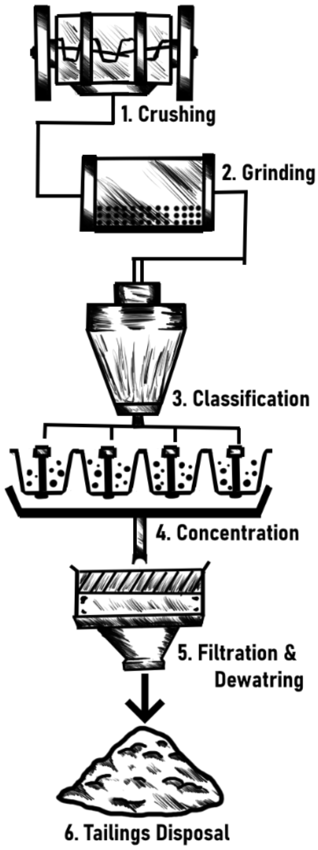

Figure 3. A typical schematic workflow of a mineral processing plant.

Although essential for economic extraction, these processing stages generated large quantities of fine-grained tailings that often contain sulfides, heavy metals and potentially acid-generating materials (*Nordstrom, 2011*). Historical disposal practices—commonly involving unlined settling ponds or direct discharge into streams—resulted in widespread contamination of soils, sediments and water bodies (*Lottermoser, 2011; Adiansyah et al., 2015)*.
Tailings and other mine wastes from these districts represent both an environmental liability and a potential source of SeRMs. Depending on the mineralization style, these residues may still contain significant concentrations of critical and strategic elements, including Ba, F, REE, Pb, Zn, Ag, and locally Ni and Co. For example, mine tailings derived from sulfide ore processing often contain significant concentrations of residual metals hosted in specific mineral phases, making them potential secondary resources for critical elements. Understanding their mineralogical and geochemical composition is therefore essential not only for environmental assessment but also for evaluating recovery potential in line with the current EU Critical Raw Materials strategy. (*Grohol et al., 2023*)

3. Materials and Methods

Various samples representative of different types of mining waste, related to historical ore extraction and processing activities, have been collected from four abandoned mine districts in the Fluminése–Arburése area: Montevecchio (Sanna and Telle mineworks), S'Acqua Bona, Santa Lucia, and Su Zurfuru mines (Fig. 4). In these mines, several types of ore dressing processes (gravity concentrations, flotation) generated tailings of differing granulometric sizes. Flotation was primarily utilized in the Sanna plant of Montevecchio, Santa Lucia, and Su Zurfuru mines, resulting in fine-grained flotation tailings. In contrast, the ore dressing plants in Telle mineworks of Montevecchio and in S'Acqua Bona mine employed gravity concentration by jigs (hydrogravimetry), leading to coarser hydrogravimetry tailings. Sampling sites were selected based on the presence of CRM-bearing minerals (fluorite, baryte, LREE carbonates, Ni-Co arsenides, Pb-Zn-Ag sulfides) and on the representativeness of different processing technologies.

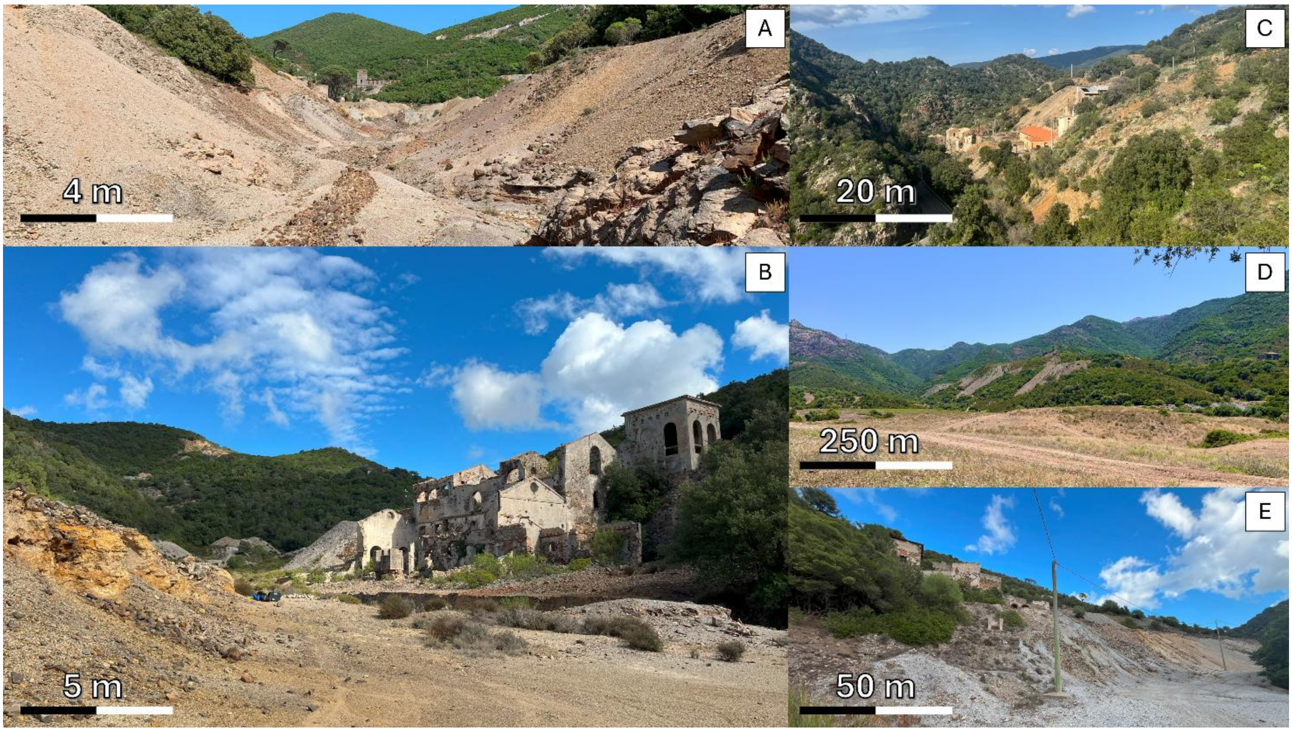

Figure 4. Waste dumps in the studied mining sites A) Sanna works of Montevecchio mine; B) Telle works of Montevecchio mine; C) Su Zurfuru mine; D) Santa Lucia mine; E) S'Acqua Bona mine.

3.1 Mapping and sampling

A preliminary spatial analysis and mapping of the mining waste deposits were conducted using QGIS software, to identify and delineate the different mining waste deposits present in the study area, and to plan the sampling activities. This approach made it possible to identify that most of the waste deposits in the area are related to excavation/exploitation and consist of waste rock, commonly referred to as barren or gangue materials (Fig. 5). Sampling was focused on mixed waste deposits derived from flotation and hydrogravimetric processing, except for the Santa Lucia mine, where only two flotation-related tailings ponds were sampled.

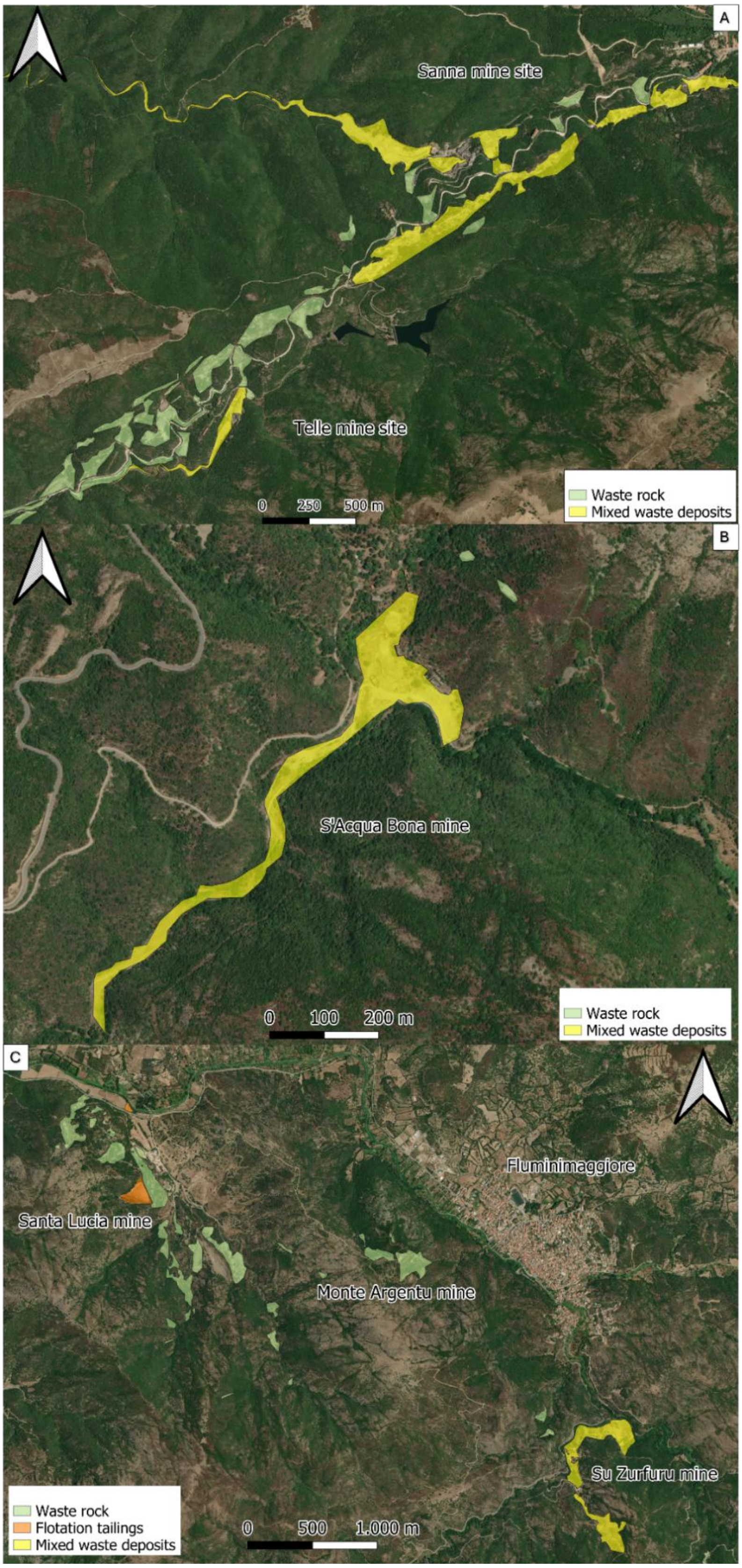

Figure 5 Mapping mining waste deposits in the study areas. Different colors indicate waste rock (light green), mixed waste deposits (yellow), and flotation tailings (orange). A) Montevecchio mine - Sanna and Telle mineworks; B) S'Acqua Bona mine; C) Mining waste dumps in the mines of the Fluminimaggiore area.

Sampling followed the stratigraphic stacking of different materials, identified based on color and grain-size variations. The different ore-treatment processes were also considered. During sampling, a portable X-ray fluorescence (Olympus Vanta C-series pXRF analyser) was used to investigate the chemical composition of the samples (Fig. 6). A total of 42 samples were collected. Lateral continuity and compositional homogeneity were assessed using multiple-point measurements with p-XRF within the same layer, complemented by visual inspection evaluating color consistency and grain-size uniformity. For each recognized compositional ("stratigraphic") level in the waste deposits, an aliquot of approximately 2 kg was collected. The collected samples are considered representative of the main lithological and mineralogical variability of the tailings deposit. In the laboratory, samples were repeatedly quartered to obtain representative subsamples.

Figure 6 Field activities. A) The portable X-Ray Fluorescence used during the sampling activity. B) The sampling activity.

Two mineworks were sampled in the Montevecchio mine: Sanna and Telle, with seven and eight collected samples, respectively. Two of these samples (TL-3 and TL-8) were further differentiated based on results of pXRF field analyses and on macroscopic observations (grain size, color, Fig.8), and were subdivided into sub-samples (e.g., TL-3A, TL-3B, TL-3C, TL-3D and TL-8A, TL-8B), resulting in a total of twelve samples. In total, nineteen samples were collected from the Montevecchio area (Fig. 7A).
In the S'Acqua Bona mine, five samples were collected (Fig. 7B). As in the previous case, three samples were further subdivided in two (SB-1, SB-3 and SB-5 samples), leading to a total of eight samples.
In the Santa Lucia mine, ten samples were collected (Fig. 7C). Six of them were collected inside the tailing pond (SLu-1, SLu-2, SLu-7, SLu-8, SLu-9 and SLu-10 samples). The other four were sampled on a floodplain terrace composed of tailings that were washed out by a flood that occurred in the 1970s at the mine, affecting the tailings basin.
In the Su Zurfuru mine, five samples were collected in the flotation tailing pond (Fig. 7D).

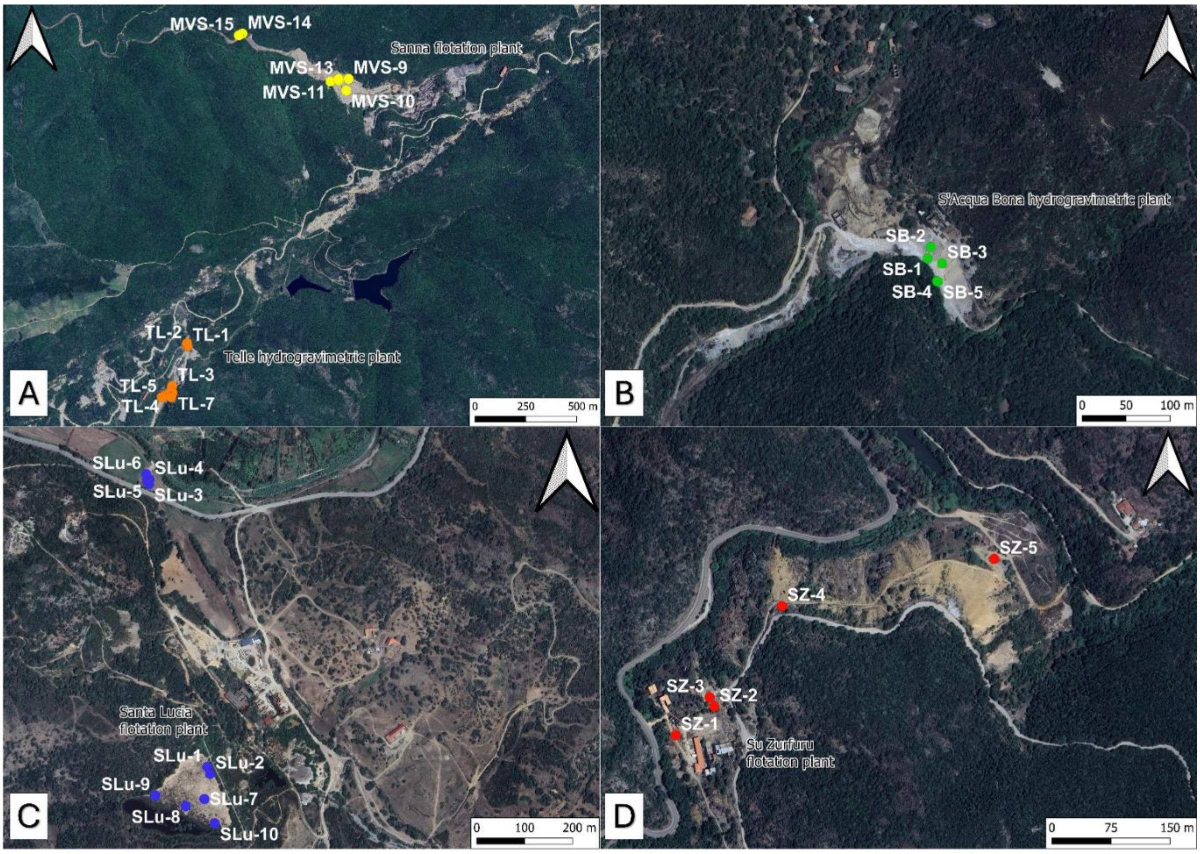

Figure 7 The four sampled areas and the corresponding samples. (A) Montevecchio Mine, including the Sanna and Telle mineworks; (B) S'Acqua Bona Mine; (C) Santa Lucia Mine; (D) Su Zurfuru Mine.

Figure 8 Field-collected samples from the investigated mine sites: (A) Telle mineworks, sample TL-3 and its sub-samples (3A–B–C–D), selected based on chromatic differences and grain size; (B) S'Acqua Bona mine, sample SB-1 and its sub-samples (1A–B), selected according to grain size variations; (C) Santa Lucia mine, sample SLu-5; (D) Su Zurfuru mine, sample SZ-2. Hydrogravimetric wastes characterize the Telle and S'Acqua Bona sites, whereas flotation tailings occur at the Santa Lucia and Su Zurfuru mines.

3.2 Analytical methods

Before sampling, selected mining dump layers were analysed using pXRF to obtain a preliminary assessment of elemental concentrations. All collected samples were analysed by X-ray diffraction (XRD) to identify the main mineralogical phases. Analyses were performed using an X'Pert Pro PANalytical diffractometer (Malvern Panalytical, Malvern, UK) equipped with a Cu anode (Cu–Kα_1 radiation, λ = 1.54060 Å), a nickel filter, and an X'Celerator detector. Data were acquired at 40 kV and 40 mA over an angular range of 5–70° 2θ.
Microtextural and mineralogical analyses aimed at identifying CRM-bearing phases were carried out using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS). Samples were mounted in resin, polished, and carbon-coated prior to analysis. SEM–EDS investigations were conducted using a JEOL Neoscope JCM-7000 (at Cagliari University) and a ZEISS EVO MA15 microscope (at Andalusian Earth Sciences Institute), both operated under high-vacuum conditions at accelerating voltages

ranging from 15 to 17 kV. Backscattered electron (BSE) imaging was performed using a ZEISS HDBSE detector.

Sample preparation and bulk geochemical analyses were carried out at ALS Global laboratories (Romania). Samples were prepared following the PUL-31 procedure, which involves pulverization to a grain size of <75 µm. Geochemical analyses were performed using the ME-MS61r™ and F-IC881™ analytical packages. The ME-MS61r™ package includes multi-element determination by inductively coupled plasma mass spectrometry (ICP-MS) after multi-acid digestion (HNO_3–HCl–HF–$HClO_4$), whereas the F-IC881 package involves KOH fusion followed by ion chromatography (IC) for fluorine determination.

Due to detection limit constraints for elements such as Pb, Zn, and Ba occurring at high concentrations in several samples, ICP-MS data were integrated with X-ray fluorescence (XRF) analyses performed at the laboratories of the Regional Agency for Environmental Protection of Sardinia (ARPAS).

The integration of mineralogical and geochemical techniques provides a comprehensive characterization of the mining waste materials: XRD identifies the dominant crystalline phases, SEM–EDS allows the recognition of CRM-bearing mineral phases and their textural relationships, while ICP-MS and XRF ensure quantitative determination of bulk elemental compositions.

4. Results

The analytical results are presented below. Due to the large number of samples, the data are reported in a summarized form. The complete dataset is available in the Supplementary Material.

4.1 Mineralogical analyses

Mineralogical analyses (X-Ray diffraction) on various samples (Fig. 9 and table 2), revealed a composition mainly consisting of gangue minerals (quartz [SiO_2], muscovite [$KAl_2(AlSi_3O_{10})(OH)_2$], kaolinite [$Al_2(Si_2O_5)(OH)_4$], calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$], siderite [$FeCO_3$], K-feldspar [$KAlSi_3O_8$], plagioclase [$(Na,Ca)[(Si,Al)AlSi_2]O_8$]). In several samples also primary ore minerals have been recognized: sphalerite [ZnS], baryte [$BaSO_4$], galena [PbS], wurtzite [(Zn,Fe)S], galenobismutite [$PbBi_2S_4$], fluorite [CaF_2], bornite [Cu_5FeS_4], stibarsen [AsSb]. Moreover, secondary -supergene - minerals like anglesite [$PbSO_4$], cerussite [$PbCO_3$], mimetite [$Pb_5(AsO_4)_3Cl$], goethite [$Fe^{3+}O(OH)$], ferrihydrite [$Fe^{3+}_{10}O_{14}(OH)_2$], smithsonite [$ZnCO_3$], hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$], jarosite [$KFe^{3+}_3(SO_4)_2(OH)_6$], leadhillite [$Pb_4(CO_3)_2(SO_4)(OH)_2$], zinkenite [$Pb_9Sb_{22}S_{42}$], bassanite [$Ca(SO_4) \cdot 0.5H_2O$], corkite [$PbFe^{3+}_3(PO_4)(SO_4)(OH)_6$], gypsum [$CaSO_4 \cdot 2H_2O$], coronadite [$Pb(Mn^{4+}_6Mn^{3+}_2)O_{16}$], arsenolite [$As_2O_3$] have been identified.

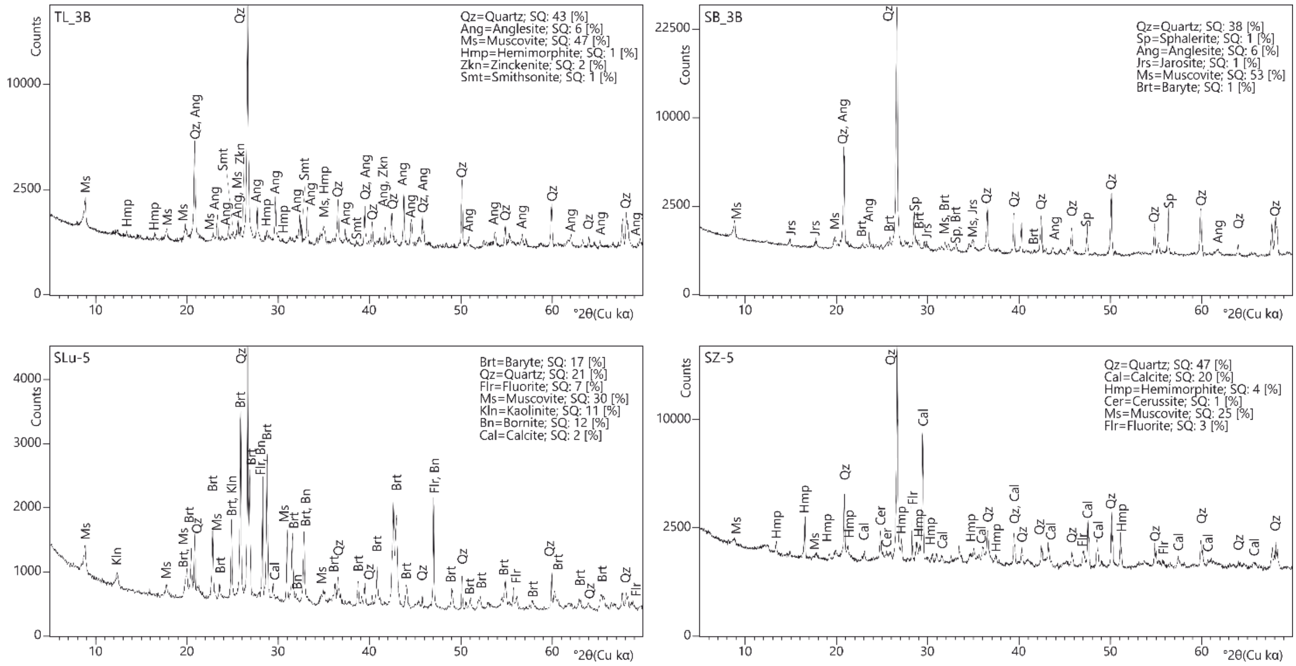

Figure 9 XRD patterns of the mineral phases detected in some samples. Counts in the y-axis are reported in the square root to highlight minor peaks.

Table 2 Summarized results of the mineralogical analyses on samples collected from the various mining sites.

Locality	Mine site	Grain size	Mineralogy		
			Primary minerals	**Secondary minerals**	**Gangue minerals**
Montevecchio	*Sanna*	*20 - <0.002 mm*	*Sp, Brt, Gn*	*Ang, Cer, Mim, Gth, Fhy*	*Qz, Ms, Kln, Cal*
	Telle	*20 – 0.2 mm*	*Brt, Gn, Sp, Wur, Gbit*	*Ang, Smt, Hmp, Jrs, Cer, Lhi, Zkn*	*Qz, Ms, Dol, Kln, Sd, Kfs*
S'Acqua Bona	*S'Acqua Bona*	*63 - <0.063 mm*	*Sp, Brt, Gn*	*Ang, Jrs (Pb?)*	*Qz, Ms, Sd, Kln, Dol*
Fluminimaggiore	*Santa Lucia*	*2 - <0.063 mm*	*Brt, Flr, Bn, Gn, Sbr*	*Gth, Cer*	*Qz, Cal, Dol, Ms, Kln, Pl, Kfs*
	Su Zurfuru	*2 - <0.063 mm*	*Brt, Flr*	*Bss, Cer, Cok, Hmp, Jrs, Gp, Cor, Aso*	*Qz, Ms, Cal, Dol*

Sp= sphalerite, Brt= baryte, Gn= galena, Wur= wurtzite, Gbit= galenobismutite, Flr= fluorite, Bn= bornite, Sbr= stibarsen, Ang= anglesite, Cer= cerussite, Mim= mimetite, Gth= goethite, Fhy= ferrihydrite, Smt= smithsonite, Hmp= hemimorphite, Jrs=jarosite, Lhi= leadhillite, Zkn= zinkenite, Bss= bassanite, Cok= corkite, Gp= gypsum, Cor= coronadite, Aso= arsenolite, Qz= quartz, Ms= muscovite, Kln= kaolinite, Cal= calcite, Dol= dolomite, Sd= siderite, Kfs= K-feldpsar, Pl= plagioclase. Abbreviation as in Warr, 2021.

4.2 Geochemical analyses

Bulk geochemical data revealed marked compositional differences among the investigated mining sites, reflecting site-specific mineralogical signatures and processing histories.
Samples from Sanna mineworks in Montevecchio exhibit the highest base-metal concentrations, with Pb reaching 30.4 wt.% and Zn up to 14.5 wt.%. Pb values are

consistently expressed in wt.% (30.4 – 0.7 wt%) and generally cluster around the mean, except for a single low outlier at 0.7 wt.%. Zn values fluctuate around the average (14.5 - 1 wt%), with two samples exceeding 10 wt.%.

Elevated Mn (up to 8460 ppm) and Cu (up to 5310 ppm) further characterize this site, confirming that the Montevecchio residues still contain significant base-metal concentrations (*Sedda et al., 2024*).

Samples from Telle mineworks show lower maximum Pb values (up to 4.43 wt.%) than Sanna, but with higher internal variability. Pb concentrations are generally in the wt.% range, except for three samples displaying lower values. Zn is even more variable, ranging from wt.% levels to ppm concentrations. The site is distinguished by the highest ΣREE_tot+Y contents (up to 2761 ppm), which are themselves highly variable: six samples exceed 1000 ppm, whereas six remain below this threshold. Mn reaches up to 5420 ppm. This pattern suggests heterogeneous distribution of REE-bearing accessory phases in different waste materials stacked in the dumps, possibly related to compositional variations of the ore minerals that fed the plant.

Samples from S'Acqua Bona waste dumps display an intermediate geochemical signature. Pb values are generally below 1 wt.%, except for three samples, while Zn concentrations cluster around 3 wt.% with a single low outlier at 0.4 wt.%. Trace elements include Sb up to 349 ppm and As up to 350 ppm, indicating persistent sulfide-related metal enrichment.

Samples from Santa Lucia tailing dam are clearly distinguished by Ba concentrations systematically exceeding 2 wt.% and typically approaching 10 wt.%. Fluorine is >2 wt.% in four samples and never falls below 3000 ppm. These data confirm the dominance of baryte and fluorite in the waste material and identify this site as the most significant for Ba–F enrichment among those investigated.

Su Zurfuru samples are characterized by consistently high Pb values (>3.8 wt.%), whereas Zn generally clusters around 1 wt.%, with two marked outliers at 8.5 wt.% and 0.7 wt.%. The site is further enriched in Bi (up to 660 ppm) and Sb (up to 115 ppm), consistent with complex sulfide and sulfosalt mineralization. Cu reaches up to 4090 ppm.

Overall, the pronounced intra- and inter-site variability highlights distinct geochemical fingerprints closely linked to the original ore mineralization and subsequent processing history.

Table 3 Summary statistics (minimum, median, maximum) for major elements (wt.%) and trace elements (ppm) in samples from the surveyed mining sites. XRF analyses examined Pb, Zn, and Ba. F-KOH fusion and IC analyses measured F. All other elements were analysed using ICP-MS. F value reported as > 20000 ppm exceeds the upper analytical limit.

Mine site	Value	Pb	Zn	Ba	Ti	Sb	As	Bi	Co	F	Ga	Li	Mn	Cu	P	Sr	W	V	Ni	$\Sigma REE_{TOT}+Y$
		%				ppm														
Sanna	Max	30.4	14.5	2.4	0.29	1045	727	16	47	990	54	49	8460	5310	860	648	4	74	63	2268
	Med	10.7	6.3	0.6	0.14	400	282	7	25	461	29	35	3212	2221	401	300	2	45	39	808
	Min	0.7	1	0.06	0.07	60	86	0.78	5	140	12	25	641	337	190	67	0.5	19	11	284
Telle	Max	9.9	7.5	1.6	0.32	246	554	2	24	1340	24	63	4520	713	710	281	6	77	59	2761
	Med	4.4	2.4	0.5	0.15	110	240	1.12	11	577	16	46	1906	373	347	136	3	37	23	947
	Min	0.03	0.3	0.02	0.09	9	73	0.18	1	310	9	39	171	24	140	14	2	22	5	153
S'Acqua Bona	Max	1.2	4.6	0.9	0.26	349	350	6	34	1640	56	59	2480	1330	970	240	10	89	54	345
	Med	0.7	2.9	0.4	0.16	226	213	4	15	803	38	52	1170	798	413	104	6	49	35	210
	Min	0.3	0.4	0.1	0.09	110	99	2	3	300	20	47	120	308	160	47	3	22	10	73
Santa Lucia	Max	1.2	0.78	10.25	0.22	52	105	7	21	>20000	16	43	4620	272	570	1985	8	113	45	230
	Med	0.8	0.34	6.27	0.13	35	74	2	11	6210	9	31	1942	131	332	903	4	45	24	110
	Min	0.34	0.07	2.27	0.09	20	56	0.23	6	3570	5	21	734	49	220	264	2	28	15	65
Su Zurfuru	Max	9.75	8.51	1.57	0.23	115	1465	660	26	9510	11	36	3040	4090	430	247	60	48	65	96
	Med	6.56	2.55	1.17	0.15	51	716	252	8	3110	8	22	1243	2206	296	125	26	37	16	62
	Min	3.78	0.67	0.96	0.03	12	197	13	2	540	3	13	264	561	130	31	2	12	2	35

4.3 SEM analyses

SEM–EDS elemental mapping was performed on selected samples to evaluate the spatial distribution of major elements (Figure 10). The composite maps highlight differences in grain size, particle morphology, and elemental distribution among the samples.

Sample MVS-13 is characterized by coarse, angular particles and pronounced compositional heterogeneity, with localized Zn- and Pb-rich domains within a predominantly silicate-rich matrix. SB-5B is dominated by large silicate grains, whereas Zn- and Pb-bearing phases are limited and spatially restricted. SLu-3 exhibits a fine-grained texture with a more homogeneous and widely dispersed elemental distribution. In contrast, SZ-5 contains abundant medium- to fine-grained particles and clear phase differentiation, including Ca- and Zn-enriched areas associated with silicate-rich grains.

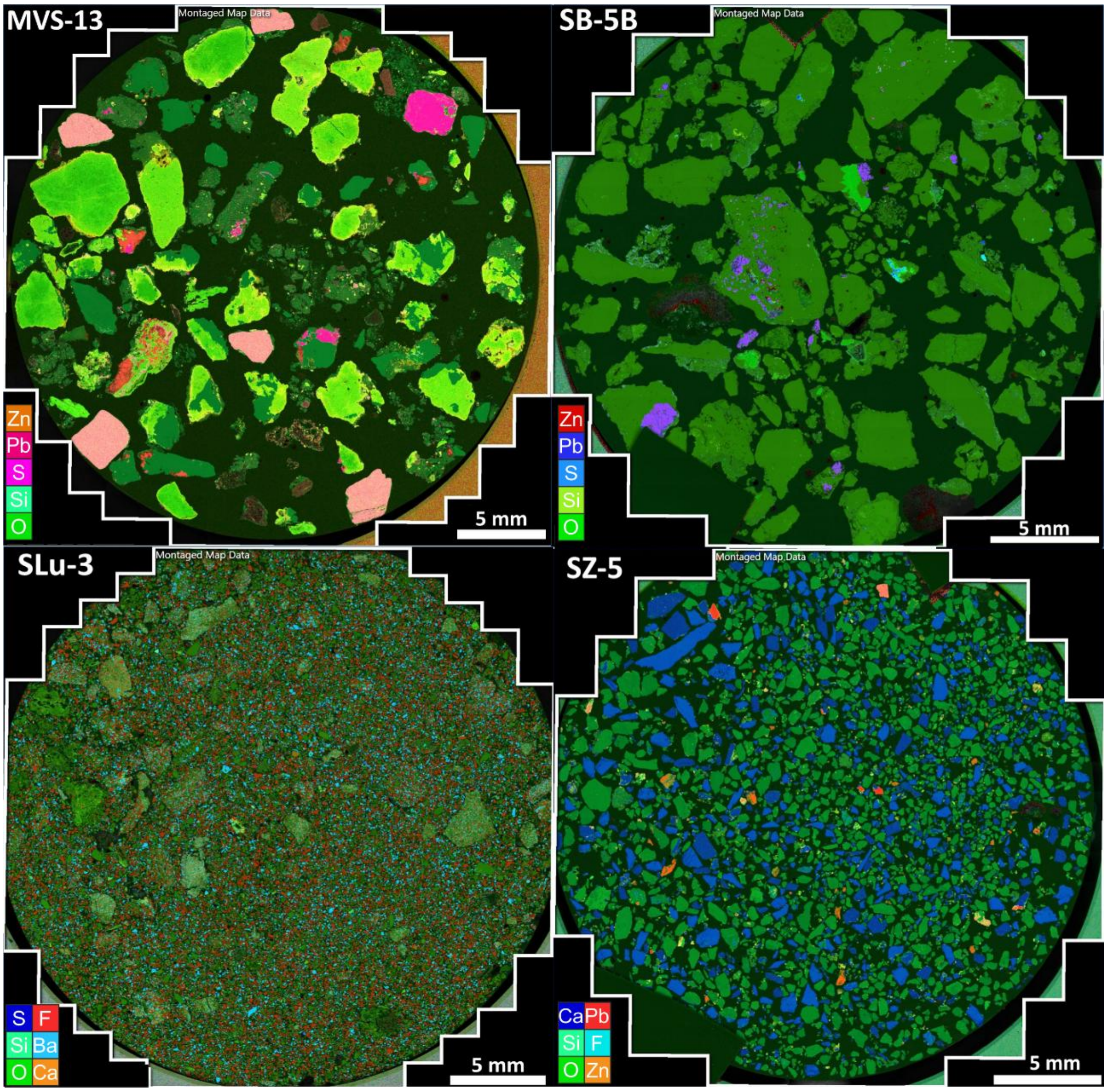

Figure 10 Representative SEM–EDS elemental distribution maps of some investigated samples. The composite maps show the spatial distribution of the main detected elements, highlighting compositional heterogeneity and differences in particle morphology among samples. Scale bar: 5 mm.

Several samples were further examined in backscattered electron (BSE) mode to identify mineral phases of potential economic interest occurring in modal amounts below the XRD detection limit. Representative examples are shown in Figure 11.

At low magnification (Fig. 11A), the strong atomic number contrast clearly distinguishes gangue minerals—mainly coarse, angular quartz grains—from higher-density phases. In the Santa Lucia waste material, free baryte grains are readily identifiable even at low magnification, confirming the abundance of liberated baryte within the tailings. At higher magnification, textural and microstructural relationships become evident. In the Telle samples (Fig. 11B), sphalerite (Sp) occurs in association with quartz (Qz) and baryte (Brt), mainly within the intergranular matrix. Quartz grains locally host disseminations of synchysite-(Ce) (Syn-Ce), while small grains of secondary minerals such as anglesite (Ang) are also observed within the matrix.

In the Sanna samples (Fig. 11C), bismutite (Bit) is recognised as a phase with a higher average atomic number (Z) than the surrounding phases, forming discontinuous rims along quartz grain boundaries, indicating secondary alteration processes affecting primary mineral phases.
In the S'Acqua Bona material (Fig. 11D), rutile (Rt) microcrystals and synchysite-(Ce) occur preferentially in association with pores and microfractures within quartz grains, suggesting their precipitation or concentration along secondary porosity pathways. Overall, the SEM–BSE observations document a quartz-dominated assemblage with accessory baryte, sphalerite, anglesite, rutile, bismutite, and synchysite-(Ce), preferentially concentrated within the intergranular matrix, along grain boundaries, and within secondary porosity features.

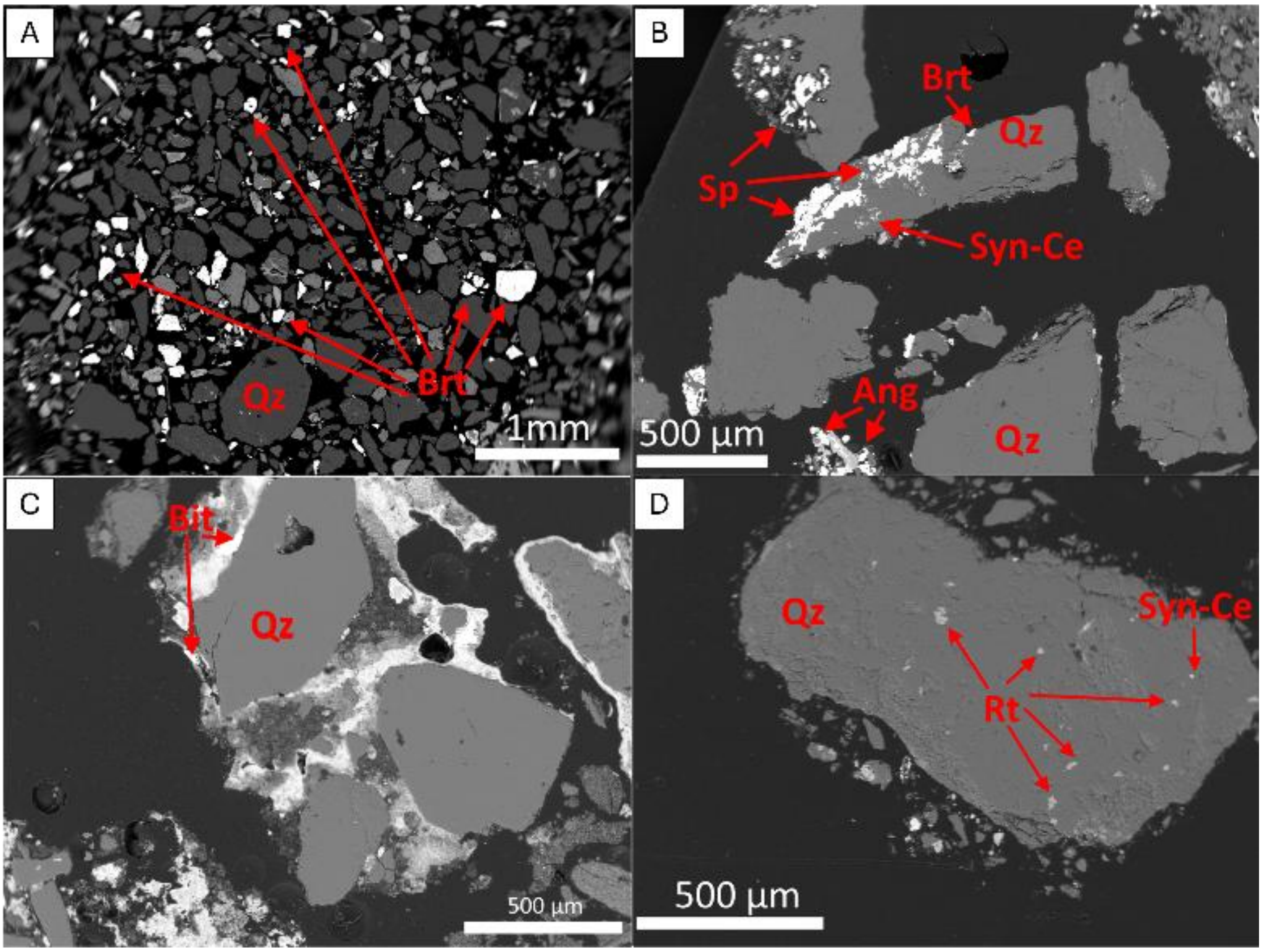

Figure 11 Backscattered electron (BSE) SEM images showing the mineralogical assemblage and textural relationships of the investigated sample. (A) Overview of the clastic texture dominated by quartz (Qz) with dispersed baryte (Brt) grains – Santa Lucia mine. (B) Detail of baryte (Brt) associated with sphalerite (Sp), anglesite (Ang), and synchysite-(Ce) (Syn-Ce) within the intergranular matrix – Telle mineworks, Montevecchio mine. (C) Quartz grains (Qz) locally coated and surrounded by bismutite (Bit) – Sanna mineworks, Montevecchio mine. (D) Quartz grain (Qz) containing rutile (Rt) micro-inclusions and associated synchysite-(Ce) (Syn-Ce)- S'Acqua Bona mine. Scale bars: 1 mm (A); 500 µm (B–D).

5. Discussion

5.1. Controls on mineralogical variability among mining waste deposits

The mineralogical variability observed between sites is consistent with the geological variety of SW Sardinia, where multiple metallogenic events and distinct ore deposit types occur in close proximity. In this context, mining residues derived from flotation and hydrogravimetric processing retain a mineralogical signature strongly dependent on sources (e.g., the mineral associations of the exploited ore bodies) and on the historical beneficiation technology applied.

The Montevecchio deposits (Sanna and Telle) are characteried by the presence of sphalerite and galena, locally associated with baryte and wurtzite, coherent with a polymetallic Pb–Zn assemblage (*Moroni et al., 2019a*). The occurrence of galenobismutite and bismutite in Telle further suggests the presence of accessory Bi-bearing sulfosalts in the processed ores, confirming historical mine reports on ore concentrate compositions from Montevecchio plants (*Bianchini et al., 1960*). The abundance of sulfide minerals observed in the Sanna mineworks is likely related to ore-processing practices. In particular, the Sanna processing plant employed flotation primarily targeting oxidised minerals, which may have resulted in the partial preservation and accumulation of sulfide phases within the tailings. (*Sedda et al., 2024*)

Analyses of S'Acqua Bona samples revealed the presence of sphalerite, baryte and galena, associated with secondary phases such as anglesite and jarosite, which are consistent with partial sulfide oxidation and sulfate formation within the hydrogravimetric tailings (*Lindsay et al., 2015*). The occurrence of sulfide minerals within the waste material can be attributed to the incomplete efficiency of the hydrogravimetric separation process (*Burt, 1984; Concha and Bascur, 2024*). The persistence of these phases in the tailings suggests that density-based concentration was not entirely effective in recovering the finer or compositionally heterogeneous sulfide grains. (*King and Cross, 2003*)

Santa Lucia tailings exhibit a distinct mineralogical association, with baryte and fluorite occurring together with minor sulfides and secondary minerals. This assemblage is coherent with the known F–Ba hydrothermal mineralization style typical of the Fluminimaggiore area *(Bakos and Valera, 1973; Padalino et al., 1973*). The persistence of baryte and fluorite in the tailings may reflect limited processing efficiency, particularly in the recovery of these minerals. (*Wills and Finch, 2015*)

Su Zurfuru tailings are marked by baryte as the dominant primary phase and by the presence of a complex set of secondary minerals including corkite, coronadite and arsenolite. This mineral association indicates both the presence of Pb-bearing precursors and significant post-depositional geochemical reworking under oxidising conditions (*Jambor et al., 2000*). The limited occurrence of fluorite and Pb–Zn minerals in the Su Zurfuru tailings suggests that the processing plant achieved a comparatively effective recovery of the main economic phases.

Overall, the mineralogical dataset indicates that the investigated mining wastes cannot be treated as a uniform material type, but rather as a heterogeneous set of deposits whose mineralogy reflects both primary ore composition and secondary weathering processes (*Lottermoser, 2010; Hudson-Edwards and Dold, 2015*). Such heterogeneity poses significant challenges for potential reprocessing strategies, as each deposit represents a distinct material requiring site-specific treatment approaches. At the same time, the diversity of mineral phases and residual resources enhances the potential economic interest of these waste deposits, making them attractive for different recovery, reprocessing, or secondary raw material applications. (*Binnemans et al., 2013; Grohol et al., 2023; Kursunoglu, 2025*)

5.2. Implications for critical and strategic raw materials (S-CRMs) potential

The European strategy for critical raw materials promotes the evaluation of mining residues as potential secondary resources (*Blengini et al., 2017; Grohol et al., 2023*). In this study, several elements relevant for CRM frameworks are present in significant concentrations, including Ba, F, Sb, Bi, Co, Ni and REE+Y.
Among the investigated sites, Santa Lucia represents the most significant deposit in terms of Ba and F enrichment. The coexistence of high Ba (up to 10.25 wt.%) and fluorine values exceeding the analytical upper limit (>20000 ppm) suggests a strong dominance of baryte and fluorite in the tailings, making this material potentially relevant for industrial mineral recovery pathways.
The enrichment of ΣREEtot+Y in Telle (up to 2761 ppm) is also significant. Although the bulk concentrations remain below typical high-grade REE ores, these values are relatively elevated for mining residues and indicate that the deposit may represent a relevant secondary target, particularly if REE-bearing phases occur as discrete mineral grains that can be physically concentrated (*Lottermoser, 2010; Binnemans et al., 2013; Peelman et al., 2016*). The chondrite-normalized REE patterns (Fig. 12 - *Taylor and McLennan, 1985*) show a general enrichment in light rare earth elements (LREE) relative to heavy rare earth elements (HREE), with broadly parallel trends among the investigated sites. Such parallel patterns suggest that the overall REE distribution is largely controlled by similar mineralogical sources, most likely inherited from the host lithologies rather than directly associated with sulfide mineralization (*Henderson, 2013*). A slight enrichment in middle REE (MREE) is also observed in several sites. This feature may reflect preferential adsorption of REE onto secondary Fe-oxyhydroxides formed during the oxidation and weathering of sulfide minerals within the tailings. Similar processes have been documented in weathering environments, where REE released during mineral alteration are subsequently scavenged by newly formed Fe-oxyhydroxides (*Nesbitt, 1979; Bau and Dulski, 1999; Ohta and Kawabe, 2001; Sedda et al., 2024*). A comparable behavior was also documented by Sedda et al. 2024, where REE were identified in secondary minerals and gangue minerals such as cerussite and goethite, and subsequently remobilized into the drainage system. In that study, the mobilized REE were further trapped by white biomineral patinas mainly composed of hydrozincite, forming along the riverbed. These observations suggest that both lithological inheritance and secondary alteration processes may play an important role in controlling the REE distribution in the studied mine tailings.

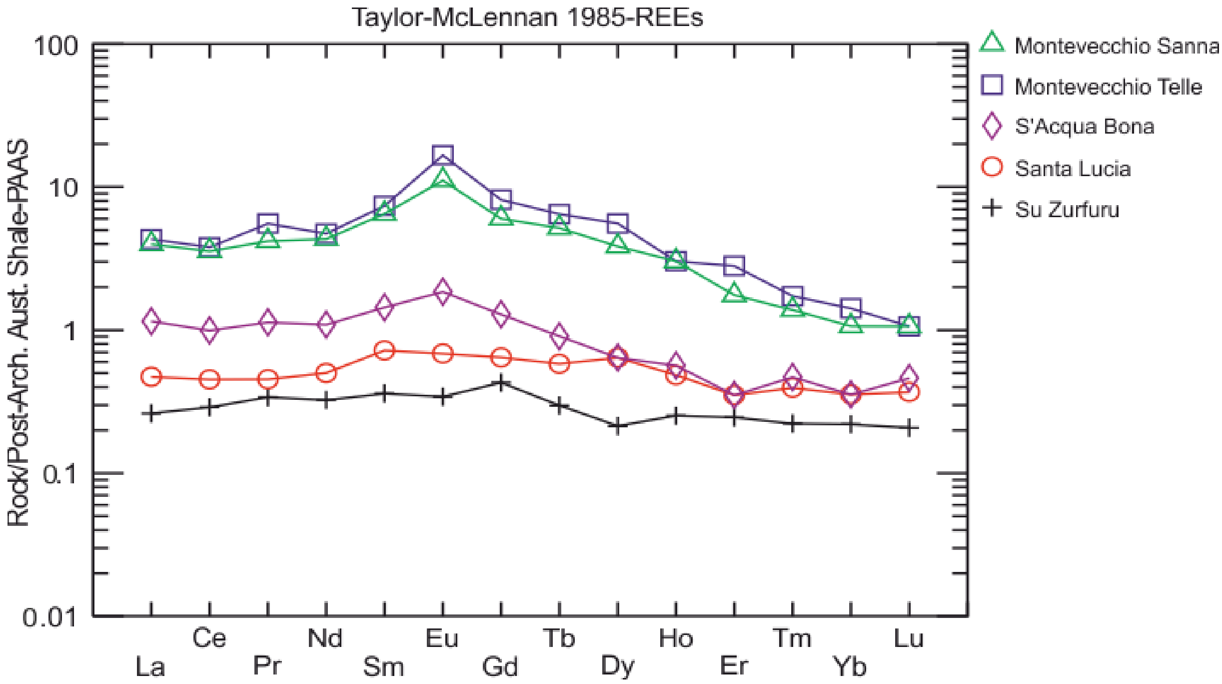

Figure 12 Chondrite-normalized rare earth element (REE) patterns of tailings samples from the investigated mining areas. Normalization values are from Taylor and McLennan (1985). The samples display LREE-enriched patterns relative to HREE with broadly parallel trends, indicating similar controls on REE distribution among the investigated deposits.

The calculated REE parameters (Table 4) indicate a moderate enrichment of light REE relative to heavy REE ($(La/Yb)_N = 1–3$. The low $(La/Sm)_N$ ratios (0.6–0.8) suggest that the lightest REE are not strongly enriched relative to middle REE. Together with the relatively high $(Gd/Yb)_N$ values (2–5), this indicates a slight enrichment in MREE and supports the interpretation of a non-monotonic REE pattern, possibly influenced by secondary mineral phases and adsorption processes (*Bau and Dulski, 1999; Ohta and Kawabe, 2001*; *Henderson, 2013*). Europium anomalies range from slightly negative to moderately positive ($Eu/Eu^* = 0.9–2.2$), whereas cerium anomalies are generally weak ($Ce/Ce^* \approx 0.8–1.0$). Overall, these features suggest that REE distribution is mainly controlled by lithological inheritance (*Rollinson, 1994*), with a secondary contribution from adsorption processes.

Table 4 Calculated rare earth element (REE) geochemical parameters for the investigated mining sites. Chondrite-normalized ratios $(La/Yb)_N$, $(La/Sm)_N$ and $(Gd/Yb)_N$ were calculated using the normalization values of Taylor and McLennan (1985). Europium and cerium anomalies were calculated as $Eu/Eu^* = Eu_N/(Sm_N \cdot Gd_N)^{1/2}$ and $Ce/Ce^* = Ce_N/(La_N \cdot Pr_N)^{1/2}$.

Mining site	La_N/Yb_N	Gd_N/Yb_N	La_N/Sm_N	Eu/Eu*	Ce/Ce*
MVS	3	5	0.6	2	0.9
TL	3	5	0.6	2	0.8
SB	2	3	0.8	1	0.9
SLu	1	2	0.7	1	0.9
SZ	1	2	0.6	0.9	1

The presence of Co and Ni is moderate across the investigated sites (Co up to 47 ppm, Ni up to 65 ppm), suggesting that these elements are not relevant components of the investigated wastes.
Sb and Bi are particularly enriched in Su Zurfuru, with maximum values of 115 ppm and 660 ppm, respectively. These enrichments suggest that this site could represent a specific target for minor critical metals, especially if associated with identifiable mineral phases amenable to beneficiation.
Overall, the results indicate that the CRM potential of the studied mining wastes is highly site dependent. The most promising targets are represented by Santa Lucia for Ba–F, Telle for REE+Y, and Su Zurfuru for Bi–Sb enrichment.

5.3. Mineralogical controls on element retention and mobility

The mineralogical assemblage identified by XRD and SEM–EDS provides important information on the phases controlling metal retention and potential element mobility.
Primary sulfides such as sphalerite and galena are still present in several deposits, particularly in Montevecchio residues. Their persistence suggests incomplete recovery during historical treatment and indicates that part of the Pb–Zn mineralization is still hosted in stable sulfide phases. (*Lotter, 2011; Wills and Finch, 2016*)
However, the occurrence of secondary phases such as anglesite, cerussite, smithsonite, hemimorphite and jarosite indicates that sulfide oxidation has occurred to variable extents (*Dold, 2010; Jamieson, 2011*). These minerals typically form during weathering of sulfides in near-surface environments and may control the redistribution of Pb and Zn within tailings. This secondary redistribution has important implications for potential reprocessing strategies (*Önal et al., 2005; Wills and Finch, 2016*). The coexistence of primary sulfides and secondary oxidised Pb–Zn phases generates a complex mineralogical assemblage requiring different processing approaches, as sulfide and oxide minerals respond differently to conventional separation techniques (e.g., flotation versus gravity or leaching methods). Consequently, the mixed nature of these phases may complicate mineralurgical and metallurgical recovery and reduce overall treatment efficiency unless specifically tailored flowsheets are adopted. (*Hajati and Soltani, 2023*)
Iron oxyhydroxides (goethite and ferrihydrite) are widespread in several sites. These phases are known to act as effective reservoirs of trace elements, including As, Sb and potentially REE, through adsorption and co-precipitation processes (*Dzombak and Morel, 1991; Paikaray and Peiffer, 2010*). Their presence, therefore, suggests that part of the trace metal may be hosted in secondary Fe-bearing phases rather than in primary minerals.
The occurrence of jarosite in several deposits, including S'Acqua Bona and Su Zurfuru, indicates the development of acidic micro-environments related to sulfide oxidation. Jarosite formation implies sulfate-rich and low pH conditions, which are relevant for understanding both the evolution of the waste material and the potential release of metals (*Nordstrom, 2011*). Its presence suggests that localized acidification has promoted metal mobilization during sulfide breakdown, followed by partial reprecipitation and secondary phase formation (*Norlund et al., 2010*). Although jarosite can temporarily incorporate Pb and other trace elements within its structure, it is metastable under changing environmental conditions (*Shi et al., 2012*). Variations in pH or redox conditions may

therefore lead to its dissolution and renewed metal release. Consequently, jarosite-bearing tailings may represent dynamic geochemical systems, with implications for both long-term environmental stability and the potential redistribution of economically relevant metals.

In Su Zurfuru, the presence of arsenolite suggests significant arsenic remobilization and reprecipitation under oxidising conditions (*Roussel et al., 2000*). The association of arsenic with secondary phases highlights the potential for chemical reworking of hazardous elements in the tailing environment (*Đorđević et al., 2019*)

Therefore, the mineralogical dataset indicates that element distribution is controlled by a combination of residual primary ore minerals and secondary weathering products, which may strongly influence both recoverability and environmental behavior of metals. (*Lindsay et al., 2015*)

Moreover, the results highlight the importance of mineralogical controls on metal distribution in sulfide-rich mine tailings, a feature that may be common in similar mining districts worldwide (*Cánovas et al., 2021; Šajn et al., 2022; Yesares et al., 2023*)

5.4. Waste heterogeneity and its implications on valorization strategies.

SEM–EDS elemental mapping confirms that the investigated materials are heterogeneous at the millimeter scale, with variable grain size distribution and spatially restricted domains enriched in Pb and Zn. The observed heterogeneity reflects the incomplete homogenization typical of historical tailings and mixed waste deposits and is consistent with the XRD and bulk geochemical data.

In the MVS-13 sample, coarse angular grains are associated with discrete Pb- and Zn-rich areas dispersed within a silicate-dominated matrix, indicating that metal-bearing phases occur as localized fragments rather than as uniformly distributed fine particles. The SB-5B sample is dominated by silicate-rich grains with limited Pb–Zn domains, whereas the SLu-3 sample shows a fine-grained texture with more dispersed elemental patterns. The SZ-5 sample exhibits distinct Ca- and Zn-enriched regions, indicating the presence of multiple phases with different compositions.

Backscattered electron imaging further documents the occurrence of baryte and sphalerite concentrated within the intergranular matrix and along grain boundaries, as well as minor anglesite and accessory phases such as synchysite-(Ce), bismutite and rutile. These observations support the presence of both base-metal and REE-bearing mineral phases occurring as accessory grains, potentially relevant for CRM evaluation.

The presence of synchysite-(Ce) is particularly relevant, as it provides direct mineralogical evidence for REE hosting phases in the investigated residues, consistent with the elevated ΣREEtot+Y values observed in some samples; however, SEM observations indicate that these REE-minerals occur at the micrometre scale and are closely associated with quartz, suggesting that their degree of liberation is likely to be limited. In this mining district, xenotime is typically enriched in heavy rare earth elements (HREE), whereas fluorocarbonates preferentially host light rare earth elements (LREE).

Overall, SEM results indicate that CRM-bearing minerals occur as discrete grains and aggregates, often concentrated in fine matrix fractions. This suggests that grain size and mineral liberation may play an important role in any potential recovery strategy (*Lotter, 2011; Wills and Finch, 2016*).

These micro- and bulk-scale characteristics also highlight that the investigated deposits cannot be approached through a single valorization model. The distinct enrichment patterns observed among sites imply that any recovery strategy must be deposit-specific. For instance, Santa Lucia represents a clear target for industrial mineral recovery due to its baryte and fluorite enrichment, whereas the Montevecchio tailings retain significant residual Pb and Zn concentrations that may justify sulfide base-metal reprocessing (galena and sphalerite).

The REE+Y enrichment at Telle, combined with the occurrence of synchysite-(Ce), indicates that further targeted mineralogical studies are necessary to assess the abundance, grain size distribution, and liberation behavior of REE-bearing phases. If these minerals occur as discrete grains, physical separation methods could allow pre-concentration prior to metallurgical treatment.

Moreover, the heterogeneity documented at the SEM scale suggests that selective sampling and detailed particle-size fraction analyses are essential to identify the fractions most enriched in target elements, particularly in fine-grained tailings where secondary phases may concentrate critical metals.

Overall, the integration of geochemical and mineralogical datasets provides a robust framework for prioritizing mining waste deposits in SW Sardinia according to both their CRM recovery potential and associated environmental constraints.

5.5. Environmental implications of residual sulfides and secondary phases

The investigated mining waste deposits represent a definite source of environmental contamination (*Cidu and Fanfani, 2002; Frau and Ardau, 2003; Da Pelo et al., 2009; Kossoff et al., 2014; Musilova et al., 2016; Masindi and Muedi, 2018*). The high Pb and Zn concentrations recorded in the Montevecchio sites, together with the widespread presence of oxidized Pb phases (anglesite, cerussite, mimetite), indicate that Pb mobility may be influenced by carbonate and sulfate precipitation processes (*Cidu et al., 2011; Courtin-Nomade et al., 2016; De Giudici et al., 2019*).

Similarly, the presence of jarosite and Fe-oxyhydroxides suggests ongoing sulfide oxidation and secondary mineral formation, which may control the retention and redistribution of trace elements such as As and Sb (*Herbert Jr, 1995; Frau and Ardau, 2003*). In the Su Zurfuru mine, the enrichment in As (up to 1465 ppm) and the occurrence of arsenolite highlight the importance of arsenic-bearing secondary minerals. High fluorine concentrations at the Santa Lucia mine indicate the presence of fluorite-rich residues. Overall, these findings highlight the dual role of the investigated mining wastes, which represent both a potential secondary resource and a source of environmentally relevant elements, emphasizing the importance of integrated mineralogical and geochemical characterization for effective remediation and resource management strategies.

5.6. Limitations and future perspectives

This study provides a first systematic multi-analytical characterization of selected mining waste deposits in SW Sardinia; however, some limitations should be considered. The dataset is based on bulk geochemical analyses and qualitative mineralogical identification and therefore does not allow a precise quantification of the abundance and mass

distribution of CRM-bearing phases within each deposit. In addition, SEM–EDS investigations were conducted on selected samples and may not fully capture the mineralogical variability at the scale of entire waste bodies.
A major limitation in assessing the resource potential of historical mining waste deposits is the uncertainty in estimating dump and tailings volumes. In many cases, the exact thickness of the waste accumulations and the depth to bedrock are unknown, making it difficult to calculate reliable tonnage estimates. For this reason, future work should include dedicated investigations (e.g., drilling campaigns and stratigraphic logging), combined with geophysical surveys (e.g., electrical resistivity tomography, seismic methods, or ground-penetrating radar), in order to constrain the geometry of the deposits and to define their total volumes more accurately.
Further mineralogical investigations are also required to better constrain the composition of CRM-bearing phases and their chemical variability. Although XRD and SEM–EDS provide robust mineral identification, complementary high-resolution techniques such as Raman spectroscopy, Electron Microprobe Analyses (EPMA), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) would be essential for quantitative mineral chemistry, particularly for complex sulfosalts, REE-bearing phases, and fine-grained secondary minerals. These methods would allow a more accurate identification of elemental hosts and would improve the interpretation of both recovery potential and environmental behavior.
Future research should therefore integrate (i) quantitative mineralogical approaches (e.g., Rietveld refinement), (ii) grain-size fractionation coupled with geochemical analyses, (iii) advanced microanalytical mineral characterization (Raman and EPMA), and (iv) metallurgical testing to evaluate the feasibility of physical concentration and chemical extraction (*Essilfie-Dughan et al., 2010; Das and Hendry, 2011; Santini, 2015; Sarker et al., 2023; McFarlane et al., 2025*). Additionally, leaching tests and hydrogeochemical monitoring would be necessary to assess the mobility of environmentally relevant elements under different environmental conditions. (*Wang et al., 2019; Zheng et al., 2024*)
Despite these limitations, the results demonstrate that mining waste deposits in SW Sardinia contain variable but locally significant concentrations of base metals and critical elements, representing promising targets for integrated valorization and remediation strategies.

6. Conclusions

This study provides a comprehensive mineralogical and geochemical characterization of historical mining wastes in the Fluminése–Arburése district (SW Sardinia), addressing a critical knowledge gap and evaluating their potential as secondary resources of Critical Raw Materials (CRMs). The multi-analytical approach, integrating XRD, SEM–EDS, and bulk geochemistry, allowed us to achieve the three main objectives of the research.
First, we demonstrated that the waste materials are highly heterogeneous and retain distinct geochemical and mineralogical signatures that directly reflect the different compositions of primary ore mineralization (skarn, various types of hydrothermal veins) and the historical processing technologies (flotation vs. hydrogravimetry). This variability is not random but is systematically linked to the specific geological and industrial context of each site.

Second, we successfully identified the mineralogical hosts of key CRMs. Beyond the expected occurrence of residual sulfides (sphalerite, galena), baryte, and fluorite, we documented for the first time in these residues the presence of REE-bearing accessory minerals such as synchysite-(Ce). The quantitative analysis of REE patterns supports dual control on REE distribution: a primary lithological inheritance and a secondary overprint related to adsorption onto Fe-oxyhydroxides formed during sulfide weathering.

Third, our assessment of the CRM potential reveals that these wastes are not a uniform resource. Instead, they represent site-specific exploration targets: Montevecchio (Sanna) for residual base metals (up to 30.4 wt.% Pb, 14.5 wt.% Zn), Santa Lucia for industrial minerals (Ba up to 10.25 wt.%, F >2 wt.%), Telle for REE+Y (up to 2761 ppm), and Su Zurfuru for Bi and Sb (up to 660 and 115 ppm, respectively). However, a critical evaluation tempers this potential: while the REE concentrations are significantly above crustal averages, they remain approximately one order of magnitude below typical cut-off grades for primary deposits, suggesting that economic recovery would likely be feasible only as a by-product of bulk processing for remediation or base-metal extraction. Furthermore, the fine-grain size and close association of REE-minerals with quartz gangue, observed via SEM, imply significant minerallurgical and metallurgical challenges for liberation and concentration, implying that simple physical separation methods (like gravity or magnetic separation) may be ineffective, and more complex (and potentially costly) hydrometallurgical or bioleaching approaches would need to be evaluated.

From an environmental perspective, the widespread presence of both residual sulfides and secondary soluble phases (anglesite, jarosite, arsenolite) confirms that these deposits are not merely static resource reservoirs but remain geochemically active, with the potential to release hazardous elements (Pb, Zn, As). This duality reinforces the concept that any future valorization strategy must be tightly integrated with environmental remediation efforts, as advocated by the new Italian regulatory framework (Law 115/2024).

In conclusion, this study moves beyond a traditional contamination-focused assessment to provide a process-oriented understanding of mining waste as a potential secondary resource. By linking the mineralogical and geochemical signatures to their geological and industrial controls, we offer a robust, site-specific framework for prioritizing future investigations. The findings underscore that while the path to economic recovery is fraught with technical challenges—particularly concerning volume estimation, mineral liberation, and mixed oxide-sulfide mineralogy—the historical mining wastes of SW Sardinia represent a strategic opportunity. They embody the principles of the circular economy, where environmental liability can be potentially transformed into a resource, aligning with the EU's goals for strategic autonomy in raw materials.

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- **Spatial distribution of mining waste deposits in Sardinia**

One of the main outcomes of this research is the systematic identification and spatial mapping of mining waste deposits across the Sardinian territory. The development of the regional geodatabase was carried out in parallel with a detailed GIS-based mapping of mining waste dumps, allowing the integration of spatial and descriptive information into a unified dataset. This approach enabled the recognition, digitization and cataloging of 1887 individual waste dump bodies, representing the first comprehensive regional-scale inventory of mining waste deposits in Sardinia (Fig. 23).

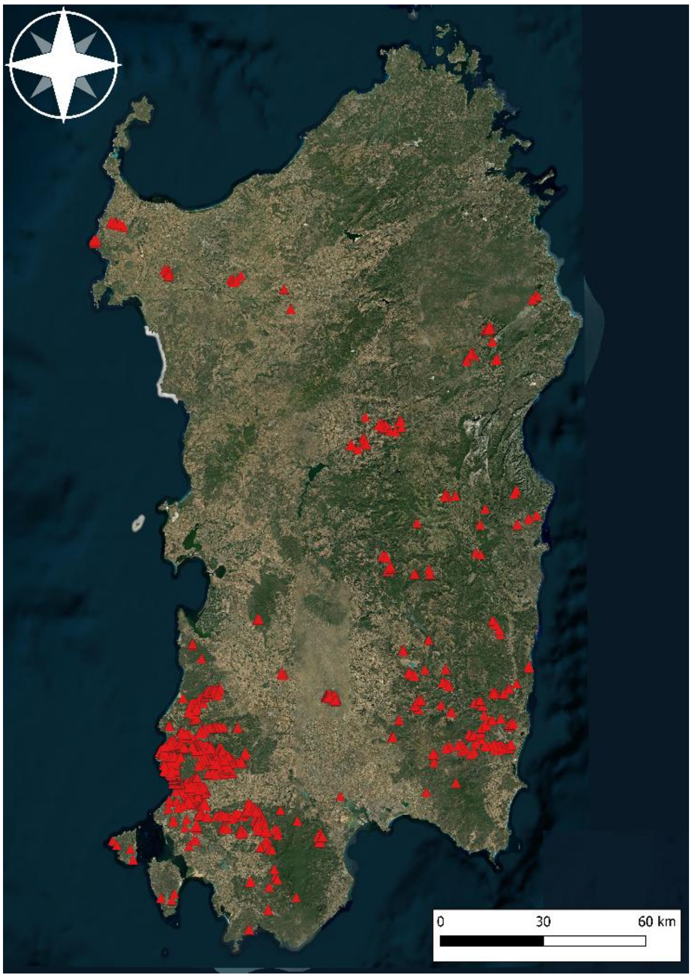

Figure 23. Regional distribution of mapped mining waste dumps in Sardinia.

The mapping procedure was based on the interpretation of high-resolution satellite imagery, comparison with historical photos, and analysis of geomorphological features typically associated with waste accumulations. Each dump body was manually delineated as a polygon in QGIS, enabling calculation of its areal extent and integration of spatial attributes into the database structure. This process ensured spatial consistency and avoided duplication of deposits previously reported in different sources.

The spatial distribution of the mapped waste dumps reflects the historical development of mining activities in Sardinia and shows a strong concentration in the main mining districts, particularly in south-western Sardinia, where mining exploitation was most intensive between the eighteenth and nineteenth centuries. Major clusters of waste deposits occur within the Sulcis-Iglesiente, Fluminèse, Guspinese-Arburèse, and Sarrabus-Gerrei districts, while smaller but significant accumulations are also present in central and northern Sardinia.

To illustrate the spatial configuration of the mapped deposits, examples of dump delimitations for the principal mining districts are shown in Figures 24-28. In these figures, each red triangle shown represents the point feature used to identify the classified mining waste facilities. At certain zoom levels, only the triangle may be visible because the polygon delimiting the facility is too small to be clearly displayed.

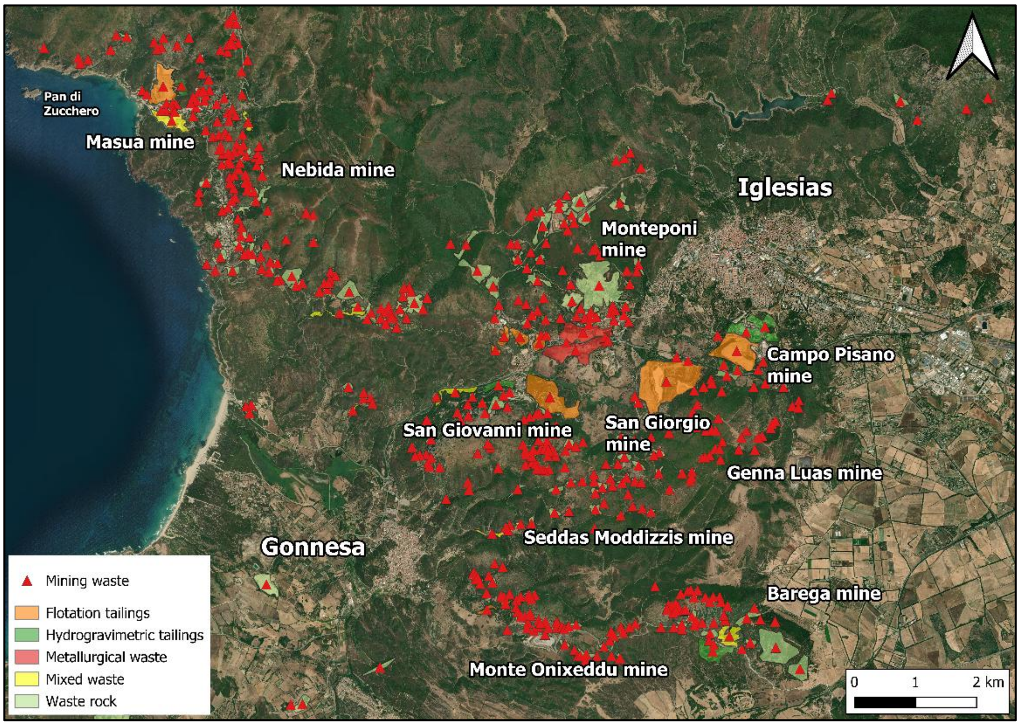

Figure 24. The extensive distribution of mining waste dumps in the Iglesiente district. This figure shows the presence of metallurgical wastes (Red Muds) from the Monteponi mine, along with tailings ponds at the Campo Pisano, San Giorgio, San Giovanni, and Masua mines.

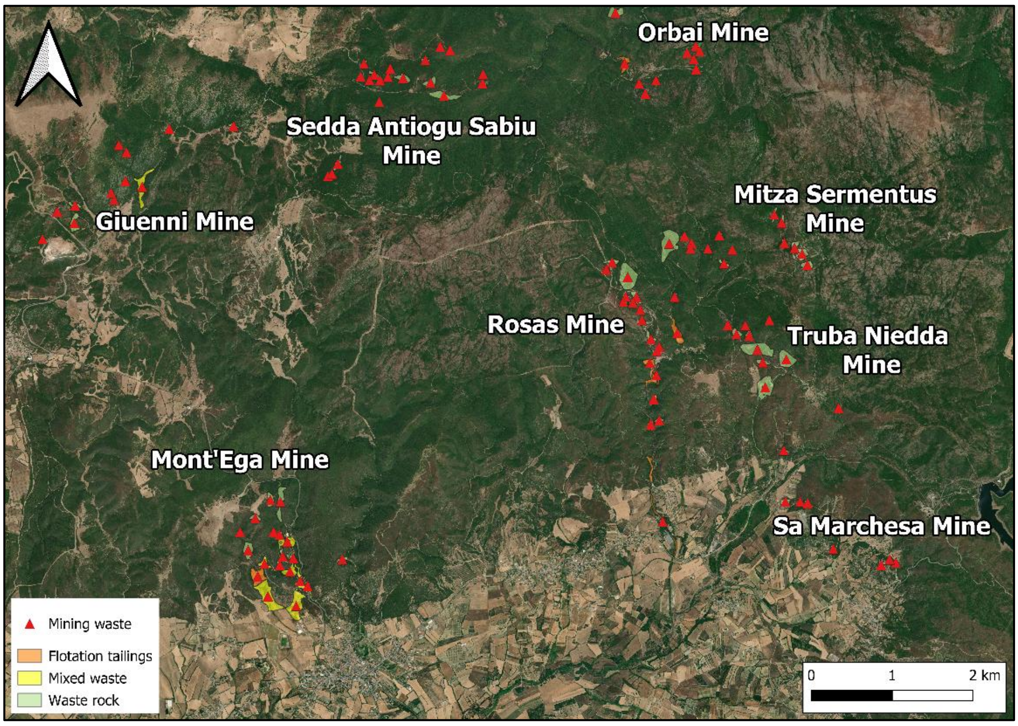

Figure 25. The spatial distribution of the mapped waste dumps in the Sulcis district.

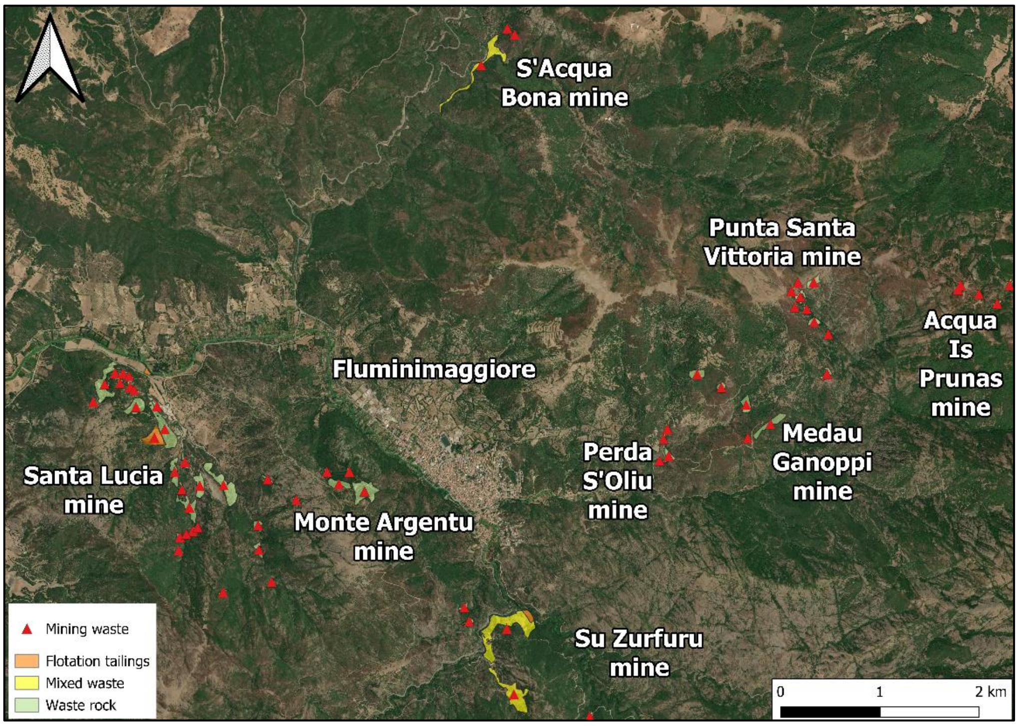

Figure 26. Presence of mining waste deposits in the Fluminimaggiore (Fluminèse) mining district. The figure shows the flotation tailings pond of the Santa Lucia mine and the large waste dumps associated with the Su Zurfuru mine.

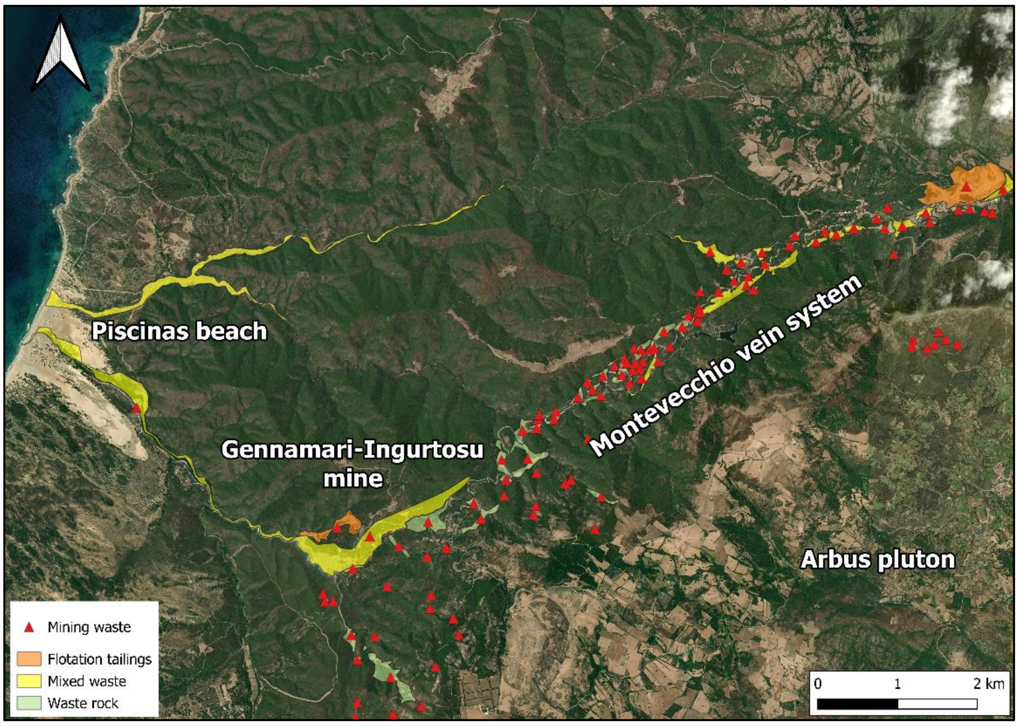

Figure 27. Spatial distribution and polygon delineation of mining waste deposits in the Montevecchio mining district (SW Sardinia). The mapped dumps correspond mainly to historical waste rock piles and flotation tailings associated with Pb–Zn hydrothermal vein exploitation.

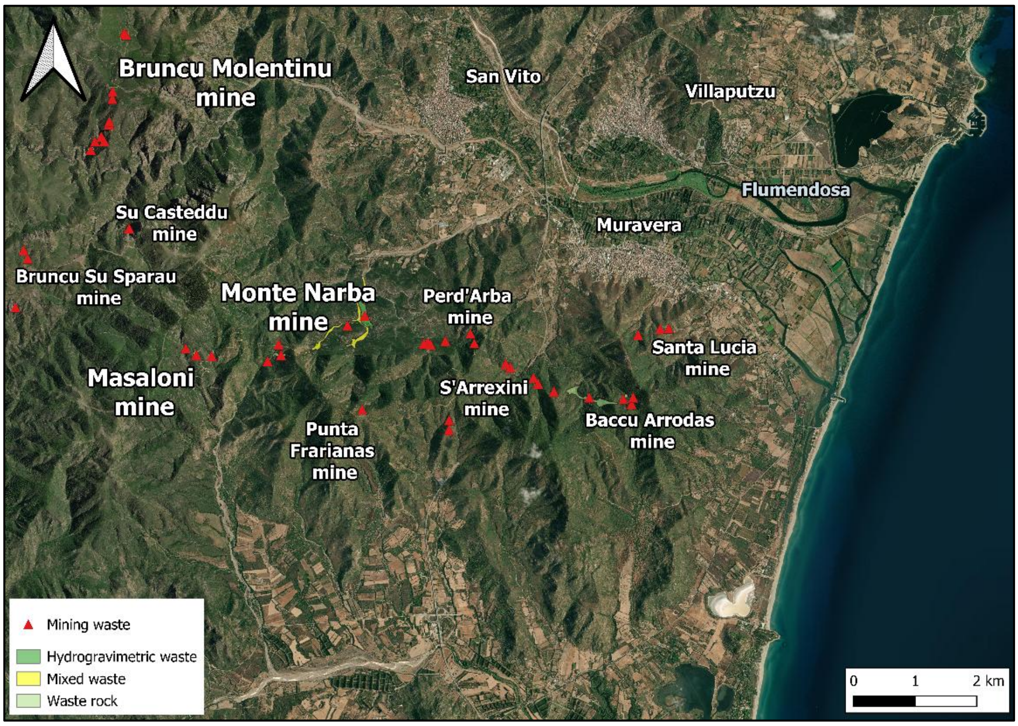

Figure 28. Example of waste dump delineation in the Sarrabus district.

These maps highlight the morphology, spatial organization and distribution of mining waste deposits within each mining area and demonstrate the high density and complexity of mining residues inherited from historical extraction and processing activities.

In addition to spatial mapping, the areal extent of each waste dump was calculated from the digitized polygons. The resulting dataset allowed the exploration of relationships between dump size and the historical duration of mining activity.

The calculation of dump surface areas also allowed a preliminary quantitative analysis of the relationship between mining activity duration and the spatial extent of waste deposits. Figure 29 shows the relationship between the total areal extent of mapped waste dumps and the duration of mining activity in the main Sardinian districts. This analysis provides a first-order quantitative perspective on the scale of waste production associated with historical mining phases and highlights how districts with longer exploitation histories tend to host larger cumulative waste surfaces.

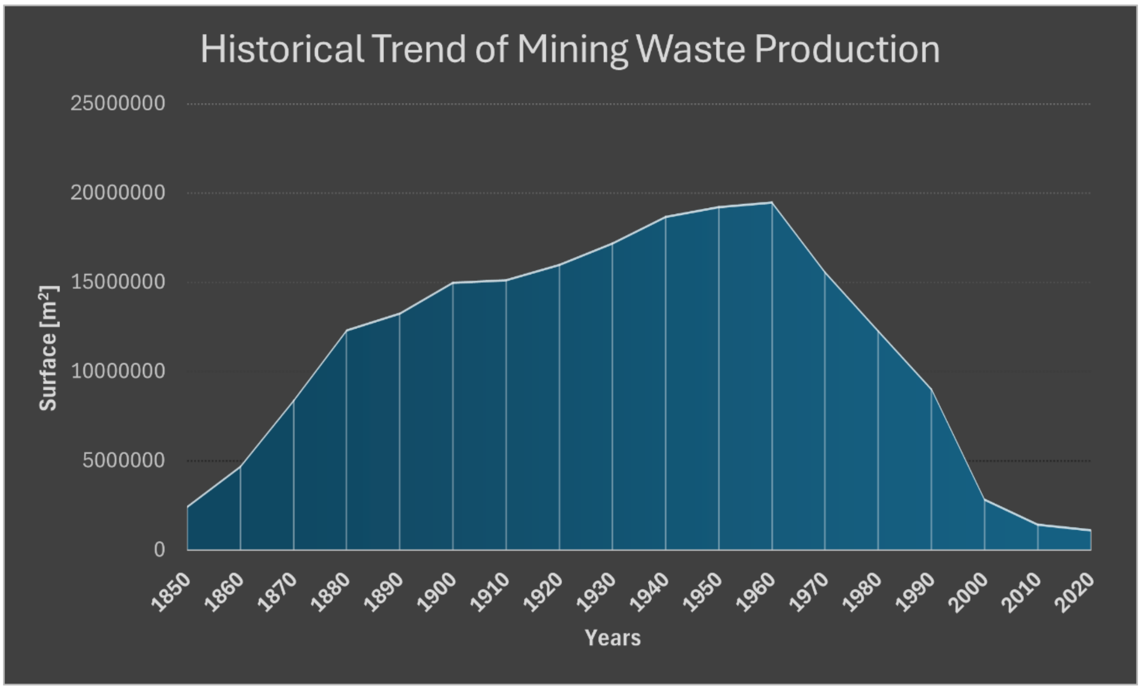

Figure 29. The relationship between the surface of mining dumps and the main year of mining production.

This inventory represents the first regional-scale spatial dataset specifically dedicated to mining waste deposits in Sardinia. Overall, the mapping results emphasize the remarkable spatial density of mining waste deposits in Sardinia and confirm the importance of a regional-scale geodatabase for supporting environmental assessment, territorial planning, and the evaluation of potential secondary raw material resources.

- Preliminary investigations in other Sardinian mining districts

Alongside the detailed characterization of the Fluminése-Arburése district presented in the previous sections, reconnaissance sampling campaigns were also conducted in other historical mining districts of Sardinia. These activities aimed to extend the regional applicability of the methodological approach developed in this thesis and to provide a preliminary assessment of the mineralogical and geochemical variability of mining waste deposits across the island.
Field surveys and sampling were carried out in the following districts (see Fig. 30 for their location):

- ***Sarrabus-Gerrei district (SE Sardinia)***: Sampling focused on waste deposits associated with the historical exploitation of Sb-As-(W) veins and Pb-Ag veins. Representative sites include the Su Suergiu mine (Sb-As metallurgical wastes) and the Corti Rosas mine (Sb-As flotation tailings), and the Monte Narba mine (Pb-Ag gravimetric tailings);
- ***Central Sardinia***: Sampling targeted waste materials from the Perda Lai mine, a historically important fluorite-baryte vein system;
- ***Sulcis-Iglesiente district (SW Sardinia)***: Reconnaissance sampling included waste deposits from the Seddas Modditzis mine (Zn-Fe-Pb SEDEX deposit), Monte Onixeddu, Barega and Monte Tasua mines (Pb-Zn MVT deposit and Ba karst deposit), Domus Nieddas mine (Pb-Zn-Cu MVT deposit), and San Leone mine (Fe-skarn).

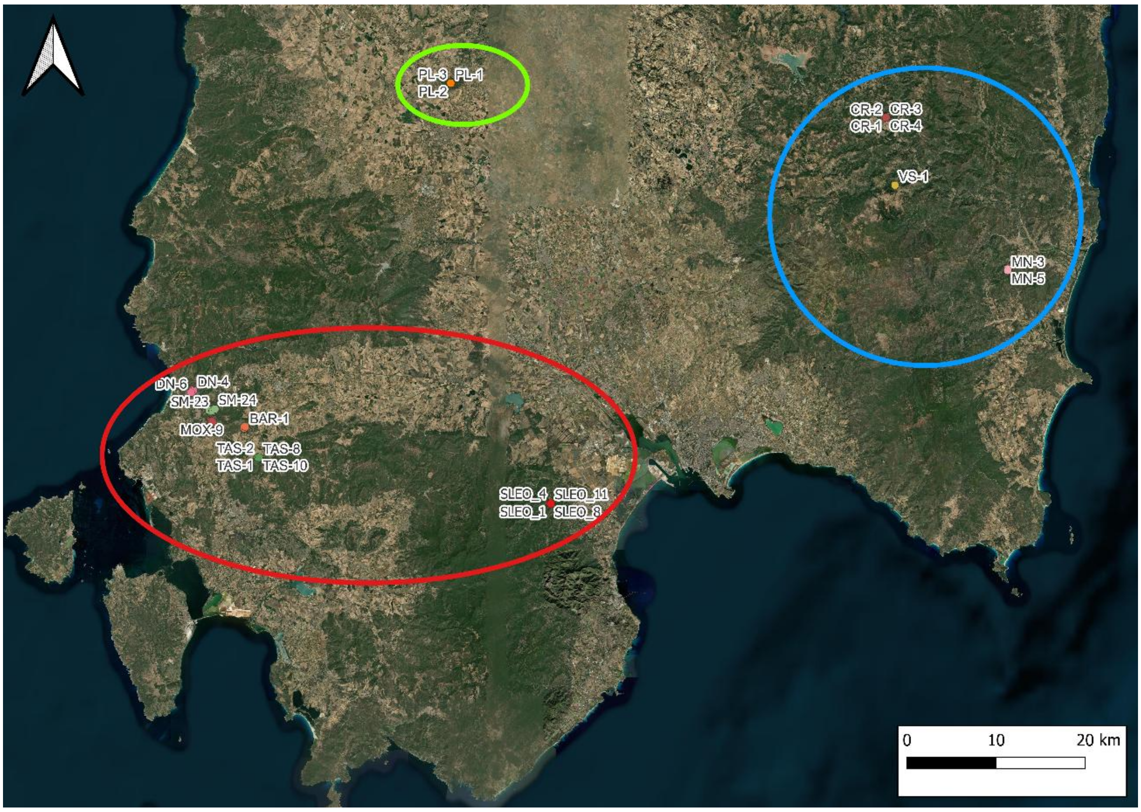

Figure 30. Location of reconnaissance sampling sites across the main historical mining districts of Sardinia. The red circle highlights the Sulcis-Iglesiente district (SW Sardinia), the blue circle the Sarrabus-Gerrei district (SE Sardinia), and the green circle Central Sardinia. Each point represents an individual sample.

A total of 89 additional samples were collected during these campaigns (Fig. 31). Although a comprehensive analytical program for these samples is beyond the scope of the present thesis and is planned for future research, preliminary field observations and portable XRF (p-XRF) screening confirmed the persistence of elevated base metal concentrations (Pb and Zn) and the potential presence of critical raw materials in several of these deposits, mainly baryte and fluorite.

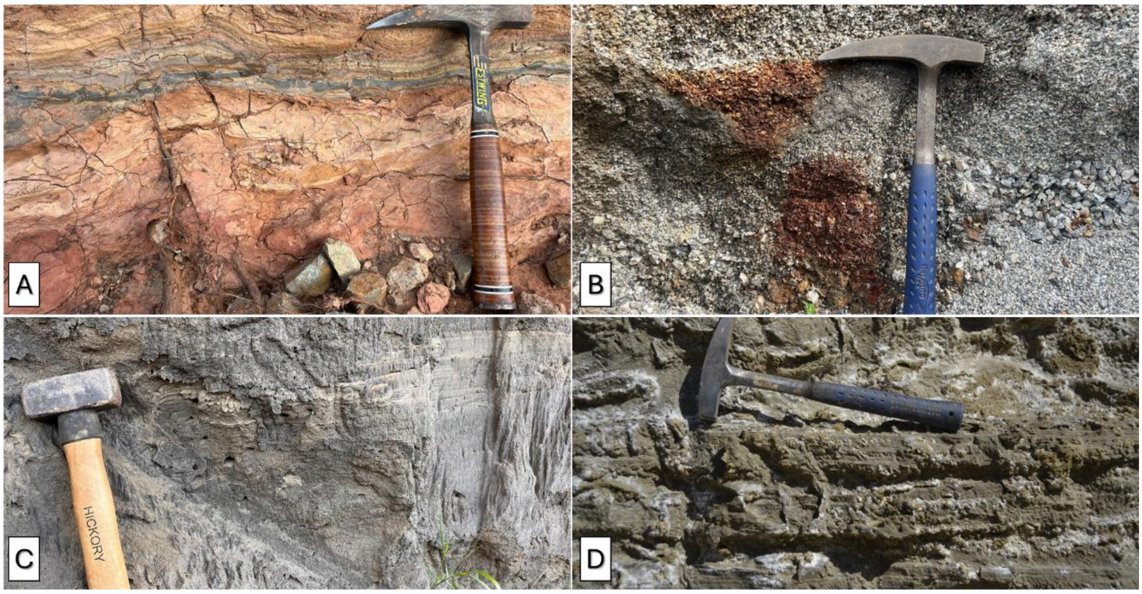

Figure 31. Representative examples of sampled mining waste materials. (A) Flotation tailings from the Perda Lai mine; (B) hydrogravimetric residues from the Monte Narba mine; (C) magnetic separation tailings from the San Leone mine; (D) flotation tailings from the Seddas Moddizzis mine.

For instance, p-XRF analyses on waste rock dumps at the Su Suergiu mine confirmed high Sb and As values, consistent with the known metallurgy of the site (*Contini et al., 2009*).

This preliminary work underscores the considerable potential of Sardinian mining waste deposits as a target for secondary raw materials across multiple districts. It also highlights the need for systematic, regional-scale characterization programs to fully assess this potential. The samples collected during this thesis constitute a valuable archive for future, more detailed mineralogical and geochemical investigations, which will further refine the understanding of CRM distribution in Sardinia's mining heritage.

6. Discussion

6.1 Contribution of the doctoral research

The research carried out during the three-year PhD project resulted in the development of a regional database of Sardinian mining waste deposits and in the production of three scientific articles including a general review and two studies developing specific aspects of mining waste materials in selected districts. In detail, the first article provides a comprehensive review of Sardinian mining waste deposits, integrating historical information, metallogenic data, and recent research results to address a first regional-scale analysis of their potential as secondary sources of Critical Raw Materials (CRMs). The second and third articles focus on selected case studies, investigating mineralogical, geochemical and environmental aspects of representative mining waste deposits through field observations and laboratory analyses.

Together, these studies provide an integrated perspective on the characteristics, environmental implications, and potential resource value of historical mining waste deposits in Sardinia. From the data, it is possible to elaborate some statistics, like the distribution of mining waste (Figs. 32 and 33), the relationship between waste frequency and the occupied surface (Figs. 34 and 35).

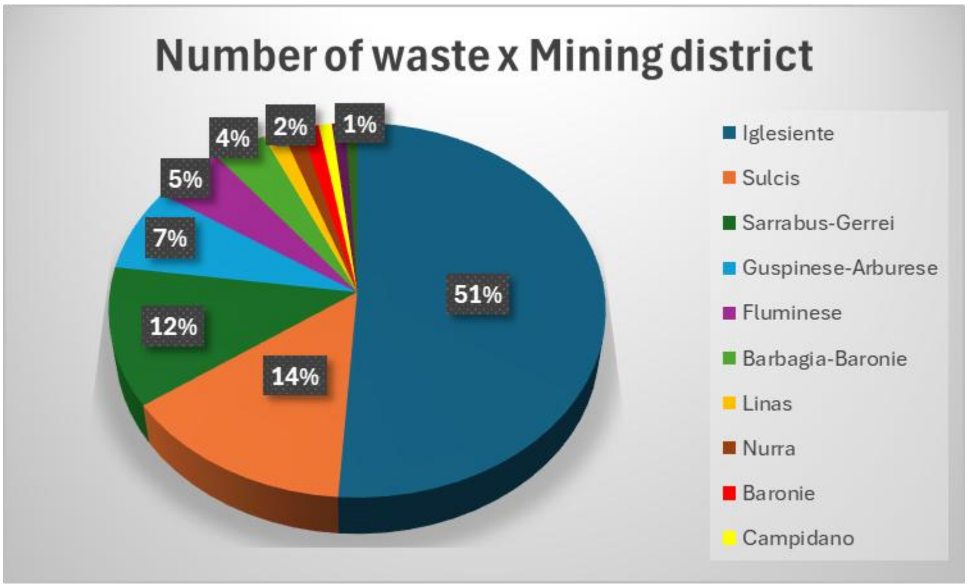

Figure 32. Distribution of mapped mining waste deposits in different Sardinian mining districts. The diagram shows the percentage of mining waste in different districts.

The distribution of mining waste in Sardinia is not homogeneous; the largest part is in the Iglesiente mining district, followed by Sulcis, Sarrabus-Gerrei, Guspinese-Arburèse, and Fluminèse mining districts.

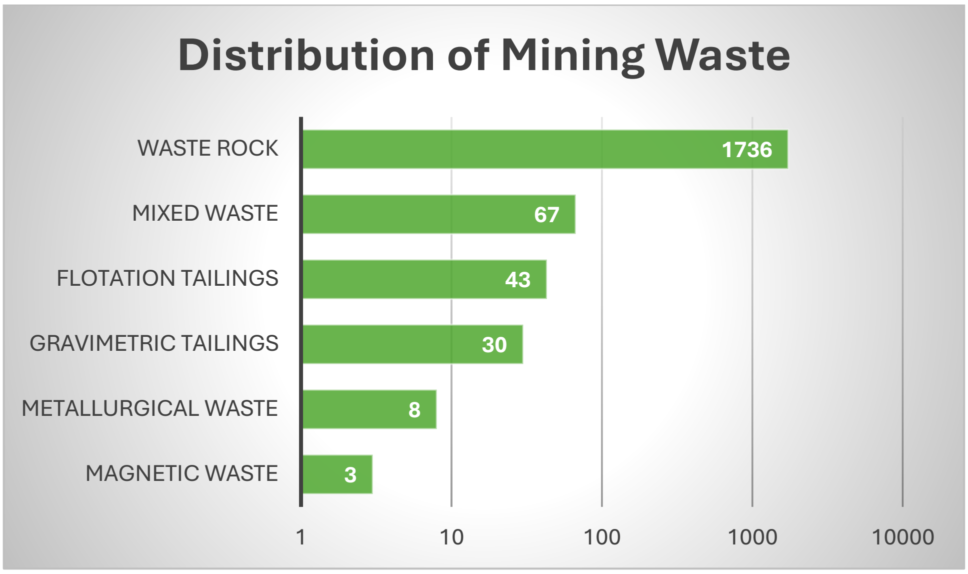

Figure 33. Distribution of mapped mining waste deposits by waste type. The diagram shows the number of deposits identified for each waste category within the regional geodatabase developed in this study.

The statistical distribution of mining waste deposits highlights a clear predominance of waste rock dumps within the Sardinian mining districts (Fig. 33). Out of the 1887 mapped deposits, the vast majority correspond to waste rock accumulations derived from excavation activities, while significantly smaller numbers correspond to mixed wastes, flotation tailings, gravimetric tailings, metallurgical residues and magnetic wastes. This distribution reflects the historical mining practices adopted in Sardinia, where large volumes of waste rock were generated during ore extraction, whereas processing residues were generally confined to areas surrounding ore dressing and metallurgical plants.

The relationship between the number of waste deposits and their total occupied surface shows a strong dominance of waste rock dumps within the Sardinian mining landscape (Fig. 34).

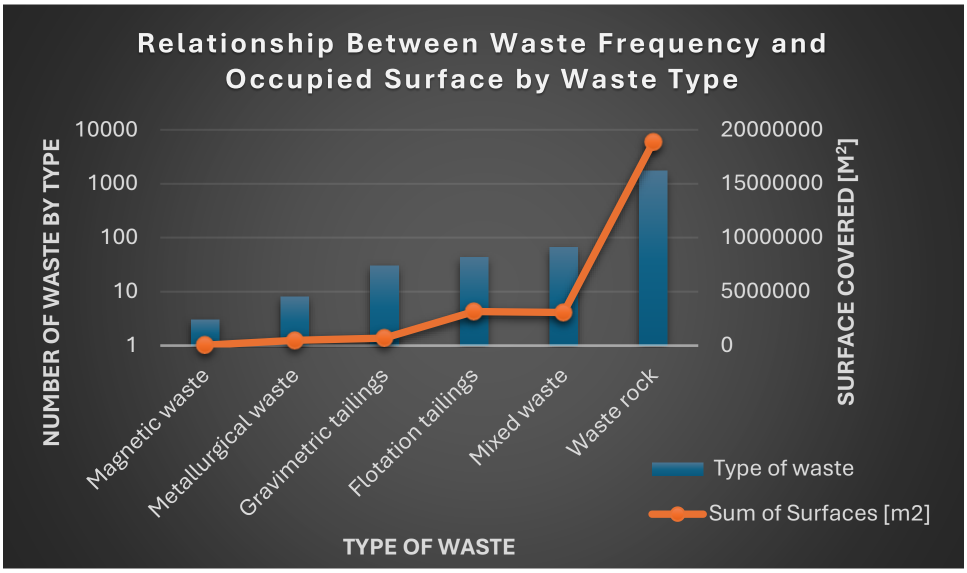

Figure 34. Relationship between the frequency of mining waste deposits and the total surface area occupied by each waste type. The bar chart represents the number of mapped waste deposits for each waste category, while the line graph indicates the cumulative surface area occupied by the corresponding waste type (m^2). The diagram highlights the predominance of waste rock deposits both in terms of frequency and total spatial extent.

Waste rock deposits represent the largest category both in terms of frequency and cumulative area, reflecting the large volumes of barren material produced during historical mining operations. In contrast, processing-related residues such as flotation tailings and gravimetric tailings occur less frequently and generally occupy smaller total surfaces, as they are typically associated with specific mineral processing plants rather than with extraction activities.

The comparison between the number of deposits and their mean surface area reveals significant differences among waste types (Fig. 35).

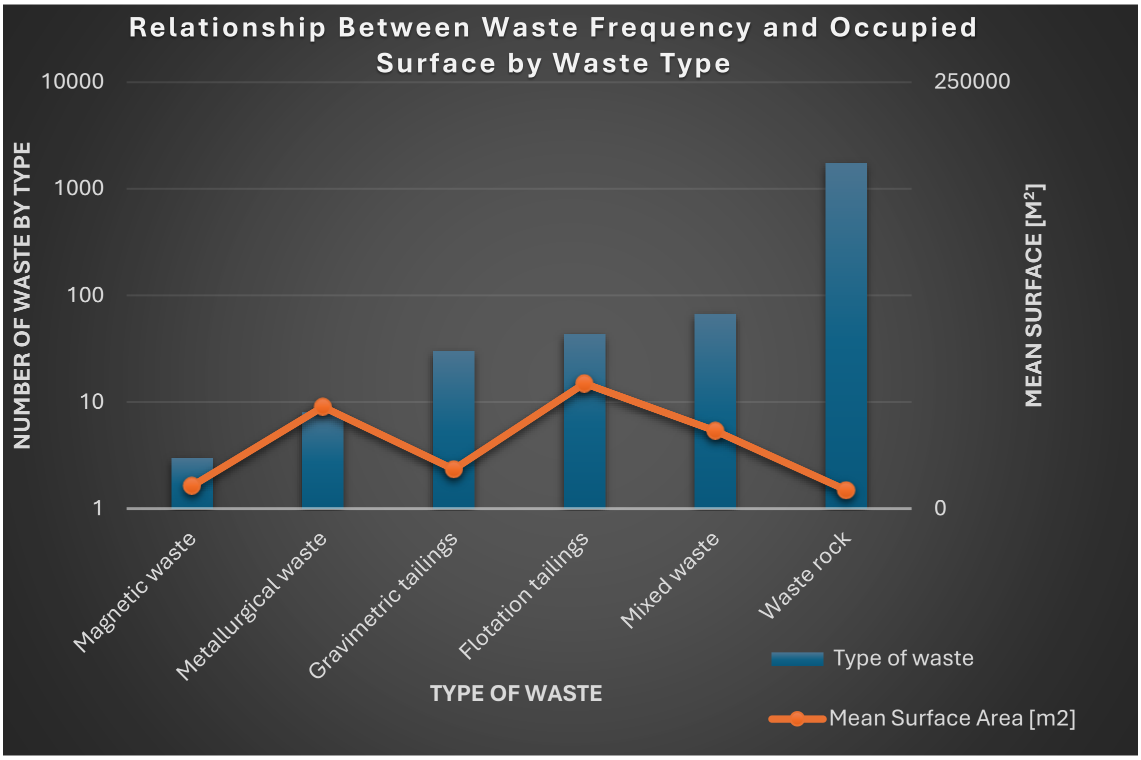

Figure 35. Relationship between the frequency of mining waste deposits and their mean surface area by waste type. The bar chart shows the number of mapped deposits for each waste category, while the line graph represents the mean surface area (m^2) of individual deposits within each category.

Although waste rock deposits are the most frequent, their average surface area is generally lower compared to some processing-related wastes. Flotation tailings and mixed wastes tend to display larger mean surface areas, reflecting the spatial requirements of mineral processing facilities and tailings storage systems.

6.2 CRM potential of Sardinian mining waste deposits

The results obtained during this research confirm that several Sardinian mining waste deposits contain significant concentrations of economically relevant elements. Mineralogical and geochemical investigations revealed the presence of a variety of elements belonging to the group of Critical and Strategic Raw Materials, including rare earth elements (REEs), fluorite, baryte, Ni, Co and W, together with major residual concentrations of Pb and Zn that often remain at weight-per-cent levels (*Sedda et al., 2024*). The distribution of critical and strategic elements across the main Sardinian mining districts shows a marked variability reflecting the metallogenic characteristics of the different mineralized provinces of the island (Fig. 36). Southwestern districts such as Iglesiente, Sulcis and Guspinese–Arburèse display a predominance of elements typically associated with Pb–Zn MVT and hydrothermal ores, still preserved in related ore-processing residues. In contrast, districts such as Anglona and Logudoro (NW Sardinia) show a stronger presence of industrial minerals and feldspar-related materials, reflecting different geological and mining histories.

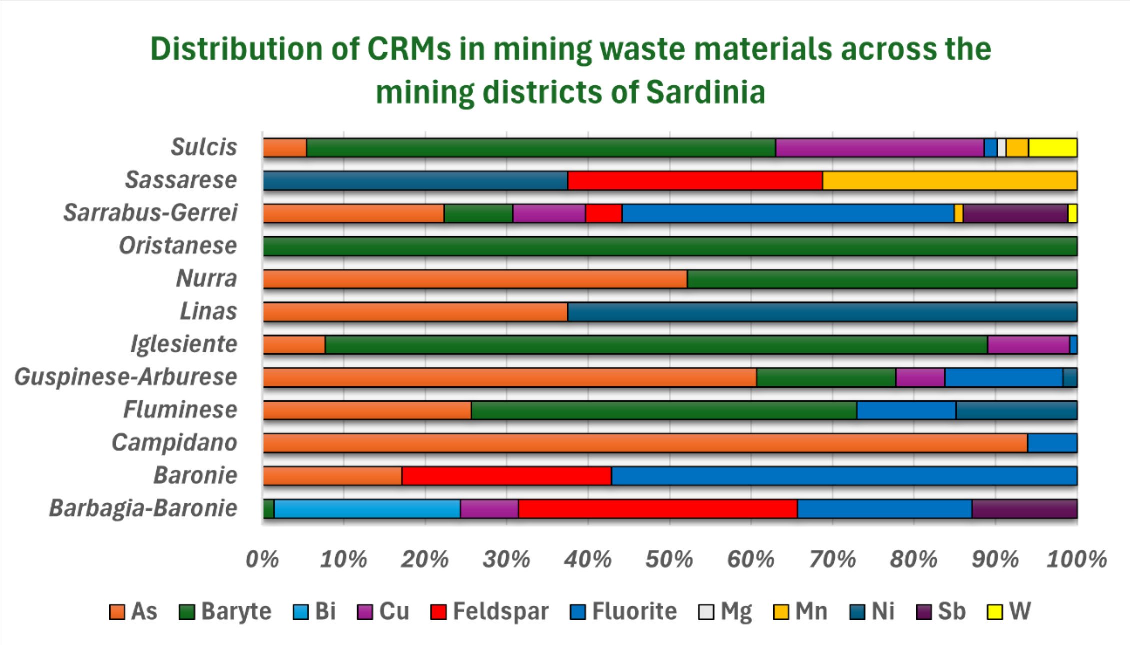

Figure 36. Distribution of Critical Raw Materials (CRMs) and strategic elements in mining waste materials across the main Sardinian mining districts. The stacked bar chart shows, for each district, the percentage of waste deposits where the presence of a given element has been confirmed.

The diagram also highlights the occurrence of several elements belonging to the group of Critical Raw Materials, including antimony, tungsten, magnesium and nickel, together with industrial minerals such as baryte and fluorite that are widely distributed in several districts. This compositional variability descends from the complex metallogenic evolution of Sardinia and suggests that mining waste deposits across the island may represent heterogeneous but potentially valuable secondary sources of raw materials.

The relationships between waste types and the associated mineralization styles provide insights into the geological origin of the mapped mining waste deposits. The dataset shows that most deposits are related to hydrothermal and carbonate-hosted mineralization systems typical of the Sardinian metallogenic framework (Tab. 2). In particular, hydrothermal vein-type deposits represent the most abundant group (660 occurrences), followed by Mississippi Valley-Type (MVT) deposits (466 occurrences) and skarn systems (197 occurrences). Other mineralization styles, such as SEDEX, stratiform, and epithermal deposits, are less frequent but still contribute to the overall diversity of mining waste types across the island.

Table 2. Relationship between waste deposit types and associated mineralization styles in Sardinian mining districts. The table summarizes the number of mapped mining waste deposits classified according to waste type and related ore deposit style (e.g., MVT, SEDEX, skarn, hydrothermal vein-type, epithermal systems). The dataset includes a total of 1887 mapped waste deposits stored in the regional geodatabase developed in this study.

Type of waste	Disseminated	Epithermal	Hydrothermal vein-type	Karst	Massive	MVT	MVT-Karst	SEDEX	Skarn	Stratiform	Total
Flotation tailings		1	11	3		11	2	2	13		43
Gravimetric tailings			4	3		14	3	6			30
Magnetic waste									3		3
Metallurgical waste		2	2			4					8
Mixed waste		1	38	6		8	3	5	6		67
Waste rock	3	89	605	174	91	429	8	82	175	80	1736
Total	***3***	***93***	***660***	***186***	***91***	***466***	***16***	***95***	***197***	***80***	***1887***

Waste rock deposits dominate all mineralization types, reflecting the large volumes of barren material generated during extraction activities. In contrast, flotation tailings, gravimetric tailings and metallurgical wastes are more closely associated with specific ore-processing technologies and therefore occur in lower numbers (Fig. 37).

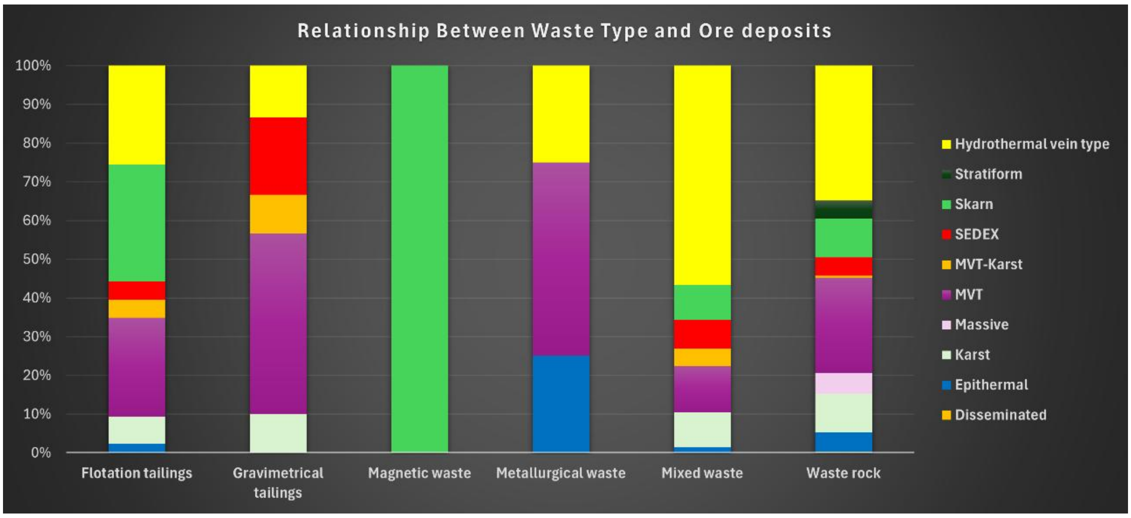

Figure 37. Relationship between mining waste types and associated mineralization styles. The stacked bar chart illustrates the proportional distribution of mineralization types associated with each waste category identified in the database.

The frequency distribution of Critical Raw Materials across different ore deposit types is summarized in Table 3. The data represent the number of occurrences (counts) of each element within deposits classified by type. Row and column totals allow for the rapid identification of the most ubiquitous elements and the ore deposit types characterized by the highest elemental diversity. Baryte is the most widespread component, with a total of 841 occurrences, followed by arsenic (318) and copper (155). Among the different ore deposit types, vein-type and skarn deposits show the highest elemental variability, with skarns hosting a wide range of elements including As, baryte, Bi, Cu, fluorite, Sb, and W. This table therefore provides a robust quantitative basis for understanding the elemental associations that characterize Sardinian metallogenesis.

Table 3. Frequency distribution of CRMs across different ore deposit types. The data represent the count of occurrences for each CRM within deposits classified by type. Row and column totals highlight the most common elements (e.g., Baryte) and the most elementally diverse ore deposit types (e.g., skarns), providing a quantitative overview of Sardinia's metallogenic associations.

Ore deposit type	As	Baryte	Bi	Cu	Feldspar	Fluorite	Mg	Mn	Ni	Sb	W	Total
Disseminated	3											3
Epithermal	93											93
Hydrothermal						5						5
Karst		150		12								162
Massive		11			50							61
MVT	57	361										418
MVT-Karst		16										16
SEDEX		57										57
Skarn	23	18	16	101		9				13	13	193
Stratiform		6					2	17				25
Vein-Type	142	222		42	1	136			23	19		585
Total	**318**	**841**	**16**	**155**	**51**	**150**	**2**	**17**	**23**	**32**	**13**	**1618**

While the focus of this thesis is on Critical Raw Materials as defined by the EU, it is important not to overlook non-CRM elements that may represent significant economic value and contribute to the feasibility of reprocessing projects. Base metals such as lead (Pb) and zinc (Zn) – which are not included in the 2024 EU CRM list – are present in substantial concentrations in several Sardinian mining waste deposits. For example, the Montevecchio Sanna tailings analyzed in this study contain up to 30.4 wt.% Pb and 14.5 wt.% Zn, values that are comparable to, or even exceed, those of primary ore deposits. These high-grade base metal fractions could serve as the primary economic driver for reprocessing operations, with CRMs being recovered as valuable by-products. In the Sardinian regional database developed in this study, Pb and Zn are systematically recorded as residual elements in waste deposits derived from the processing of MVT and hydrothermal vein-type ores. Therefore, any future assessment of the economic potential of Sardinian mining waste should adopt an integrated approach that considers both CRM and base metal resources, as the combined value may significantly improve project viability.

6.3 Methodological approach for the characterization of mining waste

An important methodological outcome of this research concerns the analytical approach adopted for the preliminary characterization of mining waste deposits. The results demonstrate that standard analytical techniques, such as portable X-ray fluorescence (p-XRF) combined with mineralogical analyses (XRD and SEM-EDS), are sufficient to obtain useful data on waste materials composition and to identify deposits potentially enriched in economically relevant elements.

This preliminary screening approach represents an efficient strategy for large-scale regional investigations, allowing the rapid identification of priority targets for more detailed studies.

More advanced analytical techniques, including bulk geochemical analyses (ICP-MS and XRF) and microanalytical investigations at the microscale or nanoscale (e.g., Raman spectroscopy, EMPA, LA-ICP-MS), become necessary only for those deposits showing particularly promising concentrations of CRMs (*Balaram, 2023; Zhu et al., 2019*). These techniques allow the identification of the mineral phases hosting strategic elements, such as rare earth elements (REEs), and the evaluation of their liberation characteristics within the waste materials.

In this way, analytical resources can be focused on the most relevant deposits, optimizing both time and costs in large-scale exploration programs.

6.4 Importance of volume estimation

One of the key challenges in evaluating the potential economic relevance of mining waste deposits concerns the estimation of their volumes. While the presence of economically relevant elements is a necessary condition for considering reprocessing scenarios, the overall resource potential strongly depends on the total volume of the waste materials. (*Edraki et al., 2014; Lottermoser, 2011*)

Accurate volume estimations are often difficult to obtain due to the irregular morphology of many deposits, the absence of historical records, and the progressive modification of dump geometries through erosion and reworking processes.

In mineral resource evaluation, the economic significance of a deposit ultimately depends on the relationship between grade and tonnage. Therefore, the presence of economically relevant elements in mining waste deposits must always be evaluated together with reliable estimations of the total volume of the stored materials.

For this reason, future studies should integrate detailed geomorphological surveys, high-resolution digital terrain models, remote sensing techniques, geophysical surveys, and target drilling campaigns in order to obtain more reliable volumetric estimations. (*Jandieri, 2023; Esposito et al., 2017*)

6.5 The Sardinian mining waste database: significance and limitations

One of the most significant outcomes of this doctoral research is the creation of the first regional-scale geodatabase dedicated specifically to Sardinian mining waste deposits. Through the integration of bibliographic sources, archival data, cartographic analysis and GIS interpretation, a total of 1887 individual waste dump bodies were identified, mapped and classified across the island.

This database provides a coherent spatial framework for future environmental investigations, mineralogical studies and resource assessment projects, representing an important step toward the systematic evaluation of mining waste deposits in Sardinia.

However, as with any first-generation inventory, the database inevitably presents certain limitations. The identification of mining waste deposits relied largely on available documentation and remote-sensing interpretation, and it is therefore likely that some smaller or poorly preserved dumps may not have been detected. Furthermore, the level of detail available for individual sites varies depending on the availability of historical and analytical data.

In order to facilitate the identification of mining waste deposits that may require further detailed investigation, a conceptual classification scheme was developed (Tab. 4). This approach integrates residual metal grades, CRM potential and environmental risk in order to provide a preliminary framework for prioritizing mining waste deposits for future studies.

Table 4. Conceptual framework for the prioritization of mining waste deposits for detailed investigation. The table illustrates an example of a classification scheme based on residual metal grade, potential CRM value and environmental risk, used to identify mining waste deposits that may require further detailed studies.

Type of waste	Residual metal grade	CRMs potential	Environmental risk
Flotation tailings	Moderate to high	High	High
Metallurgical waste	High	High	High
Waste rock	Low	Low to moderate	Moderate
Gravimetric tailings	Moderate to high	Potentially high	High

Despite these limitations, the database represents a fundamental starting point for future updates and refinements, which will progressively improve the completeness and accuracy of the regional inventory.

The results obtained in this study also suggest the possibility of developing synthetic indicators aimed at supporting the prioritization of mining waste deposits for further investigation. Based on the parameters recorded in the database, a conceptual multi-criteria framework (Conceptual Prioritization Matrix – CPM) is here proposed to support the preliminary prioritization of mining waste deposits for further investigation. The framework integrates four parameters: waste type (Wt, as a proxy for processing complexity and environmental impact), number of CRMs identified (CRMn), areal extent (Ad, as a proxy for volume), and environmental risk (Re). A simplified additive-multiplicative structure is used for illustrative purposes:

$$\boldsymbol{CPM}=(\boldsymbol{Wt}+\boldsymbol{CRMn}+\log(\boldsymbol{Ad}))\times\boldsymbol{Re}$$

where:

- *W_t = waste type weight (dimensionless), expressed on a scale from 1 to 10, based on data in Tables 2 and 4, where:*
  - *1–2 = waste rock and mixed waste;*
  - *3–4 = magnetic waste;*
  - *5–6 = gravimetric tailings;*
  - *7–8 = flotation tailings;*
  - *9–10 = metallurgical waste*
- *CRM_n = number of CRMs, derived from the database*
- *A_d = areal extent of the deposit, derived from the database and log-transformed to reduce scale effects and prevent dominance over the other variables*
- *R_e = environmental risk factor (dimensionless), expressed on a scale from 0 to 2, as defined in Table 4 and based on environmental data contained in the database (e.g., presence of erosion and transport of material within the waste deposit bodies, acid mine drainage, etc.), where:*
  - *0 = negligible risk;*
  - *0.5 = low risk;*
  - *1 = moderate risk;*
  - *1.5 = significant risk;*
  - *2 = high risk*

To test the applicability of the proposed framework on real case studies, the CPM was calculated for 17 mining waste sites that were sampled and characterized during this doctoral research. The selected sites cover the main waste typologies (flotation tailings, gravimetric tailings, mixed waste, metallurgical waste) and span the principal Sardinian mining districts investigated in this study. The results are reported in Table 5 and discussed below as a proof-of-concept, rather than as a definitive prioritization.

Table 5. Illustrative application of the Conceptual Prioritization Matrix (CPM) to selected mining waste sites sampled and characterized during this PhD. The CPM is a qualitative to semi-quantitative screening tool proposed to support preliminary prioritization of deposits for further investigation. Parameters are defined in Section 6.5. The ranking reflects the combined influence of waste typology, CRM endowment, deposit size and environmental risk. Values range from 47.10 (Montevecchio Levante, flotation tailings with high Pb-Zn-REE concentrations and active AMD) to 18.13 (Domus Nieddas, gravimetric tailings with limited CRM enrichment). The CPM is not intended as a definitive ranking but as a conceptual framework to guide discussion and future calibration.

Mining site	Type of waste	Wt	CRMn	log(Ad)	Re	CPM
Montevecchio Levante	Flotation tailings	8	10	5.55	2	47.10
Montevecchio Sanna	Mixed waste	2	10	4.84	2	33.68
Montevecchio Telle	Mixed waste	2	10	4.47	2	32.95
S'Acqua Bona	Mixed waste	2	7	4.64	1.5	20.46
Santa Lucia	Flotation tailings	8	10	4.43	1.5	33.64
Su Zurfuru	Mixed waste	2	4	4.96	2	21.93
Campo Pisano	Flotation tailings	8	3	5.45	2	32.91
Barega	Gravimetric tailings	6	1	5.12	1.5	18.18
Tasua	Flotation tailings	8	1	4.41	1.5	20.12
Monte Onixeddu	Flotation tailings	8	1	4.39	2	26.78
Seddas Moddizzis	Flotation tailings	8	1	3.90	2	25.80
Domus Nieddas	Gravimetric tailings	6	2	4.09	1.5	18.13
San Leone	Magnetic waste	4	1	4.24	2	18.49
Perda Lai	Flotation tailings	8	2	4.15	1.5	21.23
Monte Narba	Gravimetric tailings	6	7	4.67	2	35.35
Corti Rosas	Flotation tailings	8	5	4.01	2	34.03
Su Suergiu	Metallurgical waste	10	3	4.24	2	34.49

The CPM values obtained for the 17 sites show a coherent ranking that aligns with mineralogical and geochemical field and laboratory observations. The highest value (47.10) is obtained for Montevecchio Levante flotation tailings, which combine a high number of CRMs (CRM_n= 10), a large areal footprint ($\log(A_d)$= 5.55) and a high environmental risk factor (R_e= 2). At the opposite end of the ranking, gravimetric tailings from Domus Nieddas and Barega yield the lowest CPM values (18.13 and 18.18, respectively), reflecting their limited CRM presence. Intermediate values are recorded for Santa Lucia flotation tailings (33.64) and Su Zurfuru mixed waste (21.93), consistent with their specific enrichment in Ba-F and Bi-Sb, respectively. The high CPM values obtained for Monte Narba and Corti Rosas (35.35 and 34.03, respectively) reflect the documented enrichment in Sb, As and Ag in the Sarrabus-Gerrei district, confirming that the index captures district-scale metallogenic signatures. These results confirm that the CPM captures the combined effect of resource potential and environmental pressure, although its current formulation remains conceptual and requires further calibration.

It is emphasized that this formulation is qualitative and conceptual, intended to stimulate discussion rather than to provide a definitive ranking. The weightings and mathematical structure require calibration and validation on a larger dataset before

any operational application. Future work should focus on developing a statistically grounded index, possibly through multi-criteria decision analysis (MCDA) techniques. It should, however, be noted that mining waste deposits often display a high degree of heterogeneity, both in terms of waste typology and mineralogical–geochemical composition. This variability reflects the diversity of ore deposit types historically exploited and the different mineral processing and metallurgical techniques applied in the various Sardinian mining districts. As a consequence, different mineral processing and metallurgical treatment routes would likely be required for the effective recovery of valuable elements. For this reason, large-scale geochemical, mineralogical and geometallurgical characterization—possibly carried out at the scale of mining districts or according to deposit typology—would represent an essential step to better constrain processing strategies and to support the design and calibration of suitable mineral processing and metallurgical plants.
Notably, the parameters required for the construction of such an index are already included in the database developed within this study. The proposed CPM is a conceptual to semi-quantitative tool intended to guide future prioritization; its parameters and weightings would require further calibration and validation through dedicated studies before operational use. Beyond its role as a static inventory, the geodatabase provides a spatially explicit framework to guide future geophysical surveys (e.g., electrical resistivity tomography, ground-penetrating radar) and targeted drilling campaigns, which are essential to constrain dump geometries, estimate waste volumes, and ultimately evaluate the economic potential of secondary raw materials. Furthermore, the regional geodatabase developed in this study should be considered a dynamic tool that can be progressively improved through integration with existing international mining databases, such as those developed by ISPRA (Italian Institute for Environmental Protection and Research) in Italy or those developed by the BRGM in France or the USGS in the United States. The integration of these datasets would allow further refinement of the inventory and support more comprehensive regional assessments of mining waste deposits and their potential relevance for both environmental management and secondary resource recovery. This could represent a basis for future methodological developments.

6.6 Future technologies for mapping and characterizing mining waste deposits

One of the current limitations in assessing the full potential of mining waste deposits is the difficulty in mapping and characterizing micro-deposits or areas hidden under dense vegetation, which are often missed by traditional remote sensing and field surveys. Future technological developments may help overcome this limitation. In particular, the use of Unmanned Aerial Vehicles (UAVs) equipped with LiDAR (Light Detection and Ranging) sensors can penetrate vegetation canopies and generate high-resolution digital terrain models, allowing the detection and delineation of waste deposits even in densely vegetated areas. Furthermore, hyperspectral sensors mounted on UAVs or satellites can capture reflectance spectra that are diagnostic of specific minerals, including secondary sulfates, iron oxyhydroxides, and carbonate phases commonly associated with mining waste (*Grita et al., 2026*). The integration of hyperspectral imaging with machine learning algorithms could enable rapid, non-invasive mineralogical mapping of large waste dump areas, significantly reducing the need for extensive field sampling. The application of such technologies in the Sardinian context – where many mining sites are now covered by Mediterranean maquis vegetation – would greatly enhance the completeness of the regional database and support more accurate volumetric and grade estimations.

7. Conclusions

This doctoral research establishes the first comprehensive regional assessment of mining and mining–metallurgical waste deposits in Sardinia, addressing a major knowledge gap in the characterization and spatial organization of historical mining residues on the island. By integrating geological, historical and spatial datasets, the study has produced a structured geodatabase containing 1887 georeferenced mining waste deposits distributed across the Sardinian territory, establishing a methodological framework for the systematic assessment of mining waste at a regional scale.

The spatial distribution of mining waste deposits largely reflects the main historical mining districts of Sardinia, with approximately 65% of the mapped deposits located in the Sulcis–Iglesiente district, confirming its dominant role within the regional mining framework. This is followed by Sarrabus–Gerrei (12%) and Montevecchio–Ingurtosu (7%), highlighting a strongly uneven spatial distribution that reflects both the geological controls on ore formation and the historical organization of mining activities across the island. Statistical analysis of dump surface areas reveals a strongly skewed distribution: out of 1887 mapped sites, 1736 are classified as waste rock deposits, confirming their clear numerical dominance. However, when surface area is considered, flotation tailings and mixed waste deposits account for a disproportionately large share of the total footprint, despite being far less numerous. This decoupling between deposit frequency and spatial extent reflects differences in mining and processing practices and identifies large flotation-related facilities, concentrated mainly in the Sulcis–Iglesiente district, as priority targets for both environmental remediation and the evaluation of secondary raw materials.

The classification of deposits according to mining and processing typologies highlights that different stages of the mining cycle are associated with distinct mineralogical signatures and spatial distributions, which can be linked to specific metallogenic districts. Flotation tailings and processing residues represent the most promising targets for the recovery of secondary raw materials. In the Sulcis–Iglesiente district, these deposits may host baryte–fluorite associations with potential enrichment in Cu, W and Sn, alongside base metals (Pb–Zn). In the Fluminese–Guspinese–Arburese district, similar deposit types are associated with baryte–fluorite mineralization and critical elements such as Ni, Co, Bi, As and LREE, in addition to Pb–Zn. In the Sarrabus–Gerrei district, processing-related wastes are mainly linked to fluorite mineralization with W, As and Sb, again associated with base metals. These differences underline the importance of a district-scale approach in prioritizing targets for secondary resource evaluation. The presence of minerals containing critical raw materials within several Sardinian ore systems suggests that historical mining waste deposits may represent an important secondary resource for base metals and for different critical elements in the context of the European transition toward a more circular and resilient raw materials supply chain. However, the effective valorization of these materials requires further detailed knowledge of their mineralogical and geochemical properties and their response to preliminary screening to assess economic feasibility and environmental implications.

Beyond its regional significance, this work demonstrates the importance of systematic inventories of mining waste deposits as a fundamental step toward the integrated management of mining legacies. The methodological approach adopted here, combining GIS-based mapping, historical reconstruction and statistical analysis, provides a framework that can be applied to other mining regions globally characterized by extensive historical mining activity. In this context, Sardinia can be considered a pilot region for the development of a national system of mining-waste databases that will progressively be extended to other Italian mining regions. The geodatabase developed in this thesis constitutes a new knowledge platform that can support future research, environmental monitoring programs and strategic evaluations of secondary mineral resources, contributing to the sustainable management and valorization of Sardinia's mining heritage.

By integrating geological, spatial, and geochemical data into a unified database, this research provides more than a static inventory; it establishes a scalable and replicable methodological framework for the systematic evaluation of mining waste as a dynamic secondary resource system. In this perspective, mining waste is redefined from an environmental liability into a strategic component of the raw materials supply chain, bridging the gap between traditional geological knowledge and data-driven resource assessment. A first application of the proposed Conceptual Prioritization Matrix (CPM) to 17 representative mining waste sites illustrates this potential: the highest scores are systematically associated with flotation tailings from polymetallic Pb-Zn-REE systems (e.g., Montevecchio Levante, CPM = 47.10), whereas low-grade industrial mineral wastes rank consistently lower. This alignment between the index and independent analytical data supports the use of the CPM as a preliminary screening tool, while emphasizing the need for future calibration through multi-criteria decision analysis. This work, therefore, represents a foundational step toward developing base models and decision-support tools for sustainable resource management in the context of the energy transition.

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METALLOGENIC MAP OF MINING WASTES OF SARDINIA

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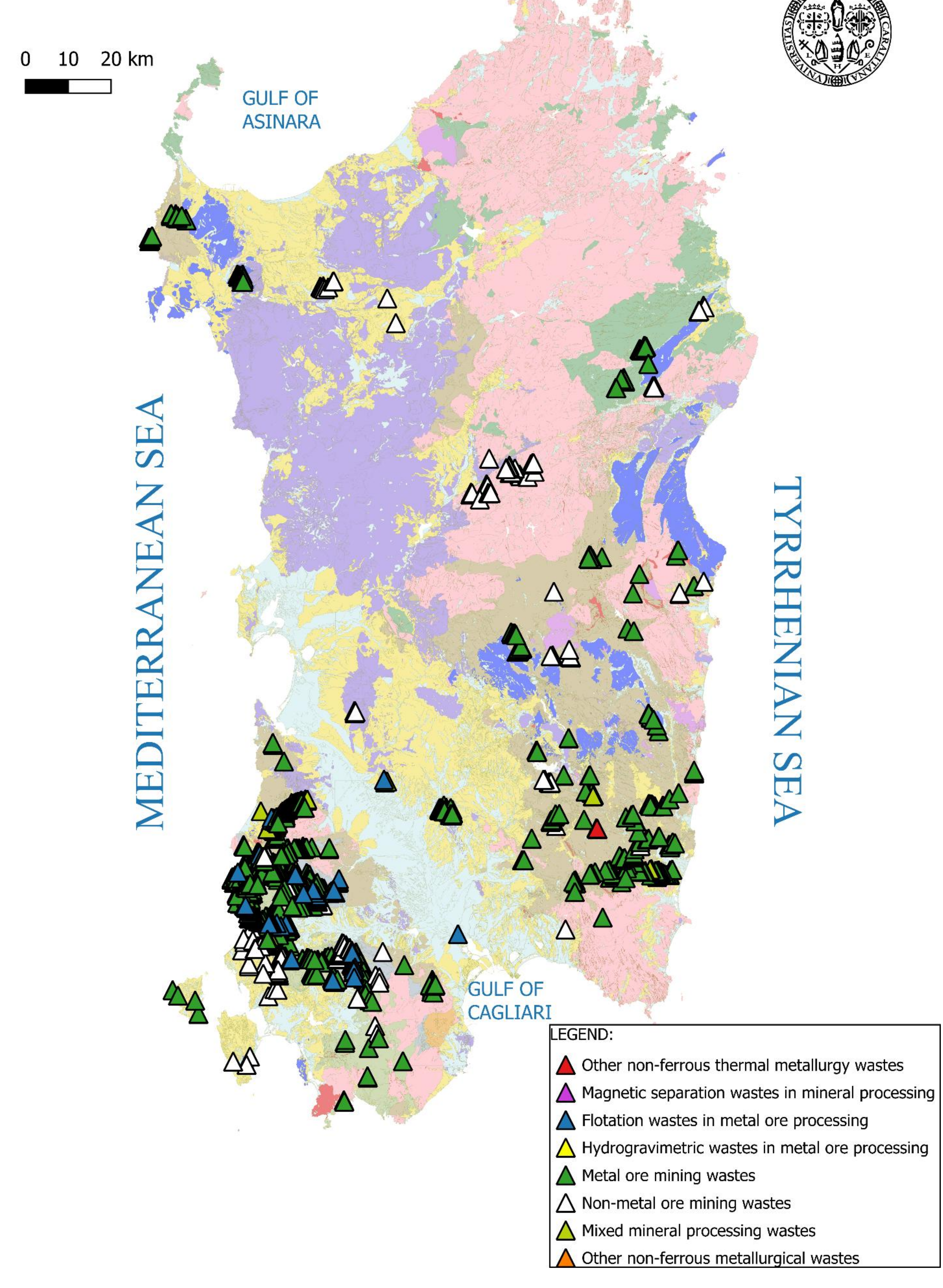

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