

Special Issue Reprint

Mineralogical and Geochemical Characterization of Geological Materials, 2nd Edition

Edited by
Teresa Pereira da Silva, Daniel P. S. De Oliveira and João Pedro Veiga

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**Mineralogical and Geochemical
Characterization of Geological
Materials, 2nd Edition**

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Guest Editors

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Basel • Beijing • Wuhan • Barcelona • Belgrade • Novi Sad • Cluj • Manchester

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Editorial

Editorial for Special Issue “Mineralogical and Geochemical Characterization of Geological Materials, 2nd Edition”

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The characterization of geological materials through advanced mineralogical and geochemical approaches remains a cornerstone of geoscientific research, underpinning our understanding of Earth systems, the distribution and accessibility of natural resources, environmental processes, and the preservation of cultural heritage. In an era marked by increasing demand for critical raw materials, growing environmental pressures, and the urgent need to support the energy transition, these analytical disciplines have become more important than ever.

As global challenges associated with resource security, environmental sustainability, resource efficiency, and climate change continue to intensify, high-quality characterization of geological materials is essential for informed decision-making across exploration, extraction, processing, and remediation activities. The development and application of innovative analytical methodologies, combined with multi- and interdisciplinary research frameworks, are therefore critical to generating the knowledge required to address these complex societal challenges. Such advances not only enhance our capacity to identify and responsibly develop strategic mineral resources but also contribute to environmental monitoring, circular economy initiatives, and the sustainable management of natural capital, reinforcing the pivotal role of geosciences in supporting a resilient and sustainable future.

Following the success of the first Special Issue, “Mineralogical and Geochemical Characterization of Geological Materials”, we are pleased to present this second edition. This collection brings together 12 contributions that highlight the evolving and increasingly strategic role of mineralogy and geochemistry in addressing some of the most pressing scientific, environmental, technological, and societal challenges of our time. Collectively, these studies demonstrate how advances in the characterization of geological materials are expanding our understanding of Earth systems, supporting the sustainable management of natural resources, enabling the identification and development of critical raw materials, and contributing to environmental protection and cultural heritage preservation.

Macchiarella et al. (Contribution 1) demonstrated that mineral precipitation patterns in the Trapani–Paceco saltworks are closely linked to pond typology and microbial activity, highlighting the sustainable reuse of the byproduct *mamma caura* as a valuable resource within the salt production cycle and supporting circular economy practices in traditional Mediterranean saltworks.

An integrated mineralogical, geochemical, and geostatistical approach was applied by Brime Barrios et al. (Contribution 2) to evaluate the critical raw material (CRM) potential of nine mining and metallurgical waste types from the Cartagena–La Unión Mining District

(SE Spain). The authors identified significant enrichments in Co, Ni, Cu, Ga, Nb, and rare-earth elements, controlled by lithogenic, sulfide-derived, and oxidation–adsorption processes. They also highlighted both the economic potential of residue reprocessing and its environmental benefits for the remediation of mining areas.

Keim et al. (Contribution 3) investigated floating mineral rafts from hypersaline coastal environments using advanced imaging and analytical microscopy techniques. They proposed that raft formation is driven by evaporation-induced supersaturation at the air–water interface, where reduced activation energy promotes mineral nucleation and subsequent crystal growth, providing new insights into carbonate precipitation processes in hypersaline systems.

The Special Issue further includes contributions focused on geoheritage, industrial heritage, and the conservation of geological and architectural materials. Salisid et al. (Contribution 4) demonstrated through a systematic review that geopolymers are promising, sustainable, and durable materials for the conservation of tuff- and coral rock-built architectural heritage structures, providing compatible alternatives to increasingly scarce original building stones. Geopolymer formulations, commonly based on metakaolin and alkaline activators, can be tailored to match the esthetic, chemical, physical, and mechanical properties of original heritage stones, while providing comparable durability under accelerated aging and long-term exposure conditions.

An integrated multi-analytical approach combining Raman spectroscopy, SEM–EDS, LA-ICP-MS, and ToF-SIMS was employed by Xie et al. (Contribution 5) to investigate Lower Cambrian phosphatic deposits from the Pedroche Formation (Spain). They revealed that phosphatization processes were strongly controlled by host lithology, pore-water chemistry, and microbial activity, with carbonate fluorapatite formation occurring under seawater-influenced suboxic conditions, preserving valuable information on early diagenetic mineralization during the Cambrian radiation.

Studies on lithium-bearing ores and pegmatite deposits contribute valuable knowledge regarding the mineralogical and geochemical characteristics of materials that are increasingly essential for the energy transition and the development of advanced technologies. Durjagina et al. (Contribution 6) demonstrated that the beneficiation efficiency of European lithium-bearing ores is strongly controlled by their microstructural characteristics, showing that coarse-grained zinnwaldite ores are more favorable for selective comminution than finer-grained lepidolite ores, thereby emphasizing the importance of integrating mineralogical and mechanical analyses to optimize lithium recovery and support sustainable European supply chains.

Several articles address the growing importance of critical raw materials and strategic mineral resources. Silva et al. (Contribution 7) studied the abandoned Preguiça mine (Portugal) and revealed a diverse assemblage of secondary minerals, as well as the first reported occurrence of massicot. Through XRD, SEM, and pXRF analyses, the authors documented significant enrichments in Fe, Ca, Zn, and Pb and highlighted the presence of vanadium- and arsenic-bearing minerals that may constitute potential critical raw materials. The study provides new insights into supergene mineral transformations and metal behavior in abandoned mining environments, while emphasizing the potential of legacy mining sites as valuable targets for sustainable resource recovery and strategic raw material assessment.

Zimanovskaya et al. (Contribution 8) demonstrated that the Alday rare-metal occurrence in East Kazakhstan hosts fault-controlled lithium-bearing albite–spodumene pegmatites formed through fluid–magmatic fractionation of the Kalba granite complex, establishing key geological, geochemical, and metasomatic indicators for the exploration of rare-metal mineralization enriched in Li, Ta, Nb, Be, and Sn.

The applicability of optical light microscopy combined with automated image processing for the classification of real coal mine dust particles was evaluated by Santa et al. (Contribution 9), demonstrating its potential as a rapid monitoring tool for occupational health protection, while identifying particle agglomeration and site-specific optical variability as critical challenges that require appropriate sample dispersion and local calibration to ensure accurate dust characterization.

The development of rapid in situ mineral identification procedures and improved data-processing workflows reflects the ongoing effort to increase analytical efficiency and accuracy in both laboratory and field environments. Gokuladas et al. (Contribution 10) developed an innovative in situ Raman spectroscopy methodology for underground mineral identification that combines dual excitation wavelengths, Shifted Excitation Raman Difference Spectroscopy (SERDS), and a deep learning-based U-Net model to produce fluorescence-free and quasi-noise-free spectra, significantly improving measurement reliability, acquisition speed, and mineral discrimination based on characteristic pseudo-Voigt peak positions and intensities.

Several studies reinforce the strong connection between geological resources and cultural heritage. Santo et al. (Contribution 11) demonstrated that serpentinites from the Monteferrato area are mineralogically and physically compatible with historically used stones in Tuscan monuments and therefore suitable for restoration purposes, although high chrysotile contents pose significant health risks that require strict safety measures and careful evaluation before their practical use in heritage conservation.

Environmental applications also represent a major theme of this collection. Stafilov and Šajn (Contribution 12) demonstrated that the distribution of uranium and thorium in North Macedonian soils is primarily controlled by geological formations and parent materials, with the highest concentrations occurring in areas dominated by Neogene and Paleozoic igneous rocks and mineralized zones, providing an important geochemical baseline for environmental assessment and soil monitoring.

The papers published in this second edition of “Mineralogical and Geochemical Characterization of Geological Materials” demonstrate the vitality, diversity, and interdisciplinary nature of current research in mineralogy and geochemistry. Together, they advance knowledge across a wide range of topics, including mineral resources, critical raw materials, environmental processes, geoheritage, and cultural heritage conservation. By integrating innovative analytical techniques with sustainability-oriented perspectives, these contributions highlight the pivotal role of geological materials characterization in supporting scientific discovery, resource security, environmental stewardship, and sustainable development.

As Guest Editors, we sincerely thank all authors for their excellent contributions, the reviewers for their rigorous evaluations and constructive comments, and the editorial team of *Minerals* for their continuous support throughout the publication process. We hope that this Special Issue will serve as a valuable reference for researchers, practitioners, and stakeholders working in the fields of mineralogy, geochemistry, and geological materials. By bringing together diverse case studies, innovative methodologies, and sustainability-oriented applications, it aims to stimulate further research and foster new advances in the characterization, management, and sustainable utilization of geological materials, supporting solutions to emerging scientific, environmental, technological, and societal challenges.

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

List of Contributions

1. Macchiarella, A.L.; Colli, A.; Pellegrino, L.; Merli, M.; Pastero, L. Mineralogical Characterization of the Trapani–Paceco Saltworks: Insights into the Valorization of a Byproduct “Mamma Caura” from Waste to Resource. *Minerals* **2026**, *16*, 681. <https://doi.org/10.3390/min16070681>.
2. Barrios, Á.B.; Alcolea, A.; Méndez, A.; Rodríguez-Pacheco, R. Geostatistical Assessment of Critical Raw Materials in Nine Mining and Metallurgical Waste Types from the Cartagena–La Unión District (SE Spain). *Minerals* **2026**, *16*, 477. <https://doi.org/10.3390/min16050477>.
3. Keim, C.N.; Rossi, A.; Farina, M. Floating Rafts from Coastal Hypersaline Environments in Brazil. *Minerals* **2026**, *16*, 445. <https://doi.org/10.3390/min16050445>.
4. Salisid, K.B.A.; Lucero, R.; Oros, R.; Villacorte-Tabelin, M.; Phengsaart, T.; Xue, S.; Zeng, J.; Mangaya-ay, I.C.A.; Arima, T.; Tabelin, C.B. + 3 authors. The Conservation of Architectural Heritage Structures Built with Tuff and Coral Rock: A Systematic Review and Bibliometric Analysis of Geopolymer Formulation, Application, Compatibility and Durability. *Minerals* **2026**, *16*, 426. <https://doi.org/10.3390/min16040426>.
5. Xie, Y.; Zhu, A.; Huang, T.; Jin, L.; Fernández-Remolar, D.C. A Multi-Analytical Approach to the Study of Phosphatic Materials from the Lower Cambrian of Spain. *Minerals* **2026**, *16*, 405. <https://doi.org/10.3390/min16040405>.
6. Durjagina, A.; Fransiskus, E.K.; Eitz, P.; Mezzetti, M.; Lieberwirth, H. Characterization of Li-Ores from European Deposits for Mineral Processing. *Minerals* **2026**, *16*, 395. <https://doi.org/10.3390/min16040395>.
7. Silva, T.P.; Morais, I.; Soares, S.; Rodrigues, I.; de Oliveira, D.P.S.; Mirão, J. New Contributions to Mineralogical and Geochemical Knowledge of Old Preguiça Mine, Beja, Portugal. *Minerals* **2026**, *16*, 348. <https://doi.org/10.3390/min16040348>.
8. Zimanovskaya, N.A.; Mataibayeva, I.E.; Orazbekova, G.B.; Nadine, S.; Amrenova, A.Zh. Geology, Mineralogy, and Age of Li-Bearing Pegmatites: Case Study of Alday Area (Eastern Kazakhstan). *Minerals* **2026**, *16*, 148. <https://doi.org/10.3390/min16020148>.
9. Santa, N.; Jaramillo, L.; Sarver, E. Assessment of Optical Light Microscopy for Classification of Real Coal Mine Dust Samples. *Minerals* **2026**, *16*, 15. <https://doi.org/10.3390/min16010015>.
10. Gokuladas, D.; Sohr, J.; Braeuer, A.S.; Freyer, D. A Raman Measurement and Pre-Processing Method for the Fast In Situ Identification of Minerals. *Minerals* **2025**, *15*, 1316. <https://doi.org/10.3390/min15121316>.
11. Santo, A.P.; Garzonio, C.A.; Pecchioni, E.; Salvatici, T. Petrophysical Characterisation and Suitability of Serpentinites from the Monteferrato Area (Tuscany, Italy) for Architectural Restoration. *Minerals* **2025**, *15*, 1105. <https://doi.org/10.3390/min15111105>.
12. Stafilov, T.; Šajin, R. Spatial Distribution of Uranium and Thorium in the Soils of North Macedonia. *Minerals* **2025**, *15*, 1063. <https://doi.org/10.3390/min15101063>.

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Article

Mineralogical Characterization of the Trapani–Paceco Saltworks: Insights into the Valorization of a Byproduct “*Mamma Caura*” from Waste to Resource

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Abstract

Saltworks are anthropogenic environments providing important ecosystem services ranging from biodiversity support to ecotourism. The traditional management of small Mediterranean coastal saltworks is slowly declining. Consequently, there is a need to deepen the study of these active evaporitic basins and valorize the byproducts of the production cycle. In accordance with circular economy principles, these byproducts are traditionally reused as essential ingredients for the purification of edible salt. The study area is a small Mediterranean saltwork, “Chiusicella,” located within the Trapani–Paceco Saltworks Nature Reserve (Sicily, Italy). Sediments from various ponds and a waste material used by salt workers, locally known as “*mamma caura*”, were analyzed using X-ray diffraction (XRD) and Scanning Electron Microscopy coupled with Energy-Dispersive X-Ray Spectroscopy (SEM-EDS). Additionally, brines from high-salinity ponds were used to analyze the precipitation sequence following total evaporation. Results demonstrate a clear relationship between the stability fields of mineral phases typical of evaporitic environments and the pond typologies. Furthermore, the interaction and synergy between bacterial activity in the water and the precipitating mineral phases appear more evident, thus outlining a clearer profile of the role of byproduct reuse within the saltwork’s annual production cycle.

Keywords: saltworks; mineralogical characterization; *mamma caura*; evaporitic minerals; valorization of byproduct

1. Introduction

Solar saltworks are anthropogenic ecosystems that provide a product of vital economic importance (NaCl, mineral halite) while offering significant ecosystem services, such as biodiversity maintenance, carbon sequestration, and ecotourism [1,2]. However, traditional small-scale saltworks in the Mediterranean have faced a sharp decline since the 1950s, leading to major shifts in salt production patterns. The higher efficiency of mechanized operations in industrial saltworks—better suited for large-scale production—has driven a trend toward increasing pond dimensions, with a consequent decrease in the number of saltworks, resulting in the progressive abandonment and economic failure of smaller, artisanal facilities [3,4]. This shift also led to the loss of traditional production practices, such as the use of the so-called ‘*mamma caura*’, a mixed-phase, fine-grained sediment derived from saltworks cultivation and traditionally seasonally reused. This dense, dark,

and muddy byproduct is reused in artisanal salt cultivation processes, aligning this ancient production method with the principles of the circular economy. Indeed, in modern or large-scale industrial saltworks, this sediment is typically disregarded and excluded from the production cycle, unlike in artisanal salt making, which relies on the maintenance and preservation of traditional methods.

Mineral extraction in saltworks relies on two fundamental resources: solar energy, which drives evaporation, and seawater, the primary source of salts. Seawater contains a complex suite of dissolved ions and metals, with major components including Cl^- , Na^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , K^+ , HCO_3^- and Br^- [5]. Among these, the bromide anion (Br^-) does not typically form its own crystalline phases during early evaporation but acts as a co-variant, substituting within the crystal lattice of halite by isomorphic replacement of chloride ion (Cl^-) at advanced stages of evaporation [6,7]. Other cations, such as Sr^{2+} , Fe^{2+} , and Al^{3+} , are minor components associated with rarer mineral phases [8,9]. Notably, many of these elements are classified as Critical Raw Materials (CRMs), representing strategic resources for the global energy transition [10]. The most common precipitates forming evaporite sequences are chlorides, sulfates, and calcium-magnesium carbonates. The three minerals constituting the bulk of evaporitic deposits are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), and halite (NaCl) [11]. K-Mg salts are rarer and precipitate at higher densities; these include sylvite (KCl), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), langbeinite ($\text{K}_2\text{Mg}_2(\text{SO}_4)_3$), kainite ($\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$), and polyhalite ($\text{K}_2\text{Ca}_2\text{Mg}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$) [12]. However, evaporitic crystallization is influenced by many factors: temperature and its variations, humidity, wind action and consequently evaporation and crystallization rate, depth of water, pH, local variations of the water composition [13], and biological activity [14,15]. Salt precipitation via evaporation is a polythermal process with daily and seasonal temperature fluctuations [13], and the precipitation mode is termed equilibrium crystallization when the salts remain in contact with the solution from which they precipitated [16]. The pioneering experiment on the complete evaporation of water (collected from the Mediterranean coast of France) at 40 °C to study the precipitation sequence was conducted by Usiglio (1849a,b) [17,18]. This study established a sequence inversely proportional to the solubility of the precipitated salts, known as the “Usiglio sequence”. Subsequent experiments and observations in marine saltworks [10–21] have repeated these findings, and all converge on the same results regarding the initial stages of precipitation:

1. First stage: Characterized by the precipitation of calcium carbonate (CaCO_3), whose stability field lies within the salinity range of approximately 35‰ to 140–200‰.
2. Second stage: When salinity exceeds ≈ 200 ‰, calcium sulfate precipitates as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Initially fine-grained, the crystal progressively coarsens; when individual crystals reach 2 mm in size, they are termed “selenites” [22].
3. Third stage: The gypsum stability field terminates when salinity reaches approximately 290–325‰, marking the entry into the halite (NaCl) stability field.

Beyond these first three stages, the sequence enters the stability field of potassium and magnesium salts, where differences exist for slightly different conditions of evaporation and chemical composition of the waters. Many studies converge on the precipitation of epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) as the salt following halite [23,24]. Valyashko (1962) [25] reports the following precipitation sequence from Black Sea waters: epsomite (which subsequently transforms into sakiite, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), followed by carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), and finally, bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) as the last phase. Furthermore, the study notes the presence of sylvite (KCl), which begins to precipitate with sakiite and disappears at the onset of carnallite precipitation. However, another study by Charuit and Genty (1980) [26] on Mediterranean bitterns at a temperature of approximately 28–35 °C reports a different sequence: epsomite alone, followed by epsomite with kainite ($\text{KMg}(\text{SO}_4)\text{Cl} \cdot 3\text{H}_2\text{O}$),

then kainite alone, and finally kainite associated with bischofite and/or carnallite. The theoretical evaporation of seawater proceeds until the so-called “eutonic point”, where the brine reaches an invariant composition and multiple solid phases co-crystallize in equilibrium [27,28]. The theoretical crystallization sequence was first established through solubility studies by Jacobus Henricus van't Hoff and numerical calculations based on the Pitzer model [29–32]. While new models yielding different sequences have subsequently been proposed, one of the reference theoretical precipitation sequences at a constant temperature of 25 °C, reported by Braitsch and Kinsman (1978) [33], is as follows:

1. Initial precipitation phases characterized by calcite, gypsum and halite;
2. Precipitation of Mg-sulfates or Na-Mg sulfates (without potassium);
3. Precipitation of Mg and K salts (specifically the sylvite field);
4. Precipitation of carnallite;
5. Precipitation of bischofite.

This study presents a characterization of the crystalline phases along the sediments of each pond and analyzes the crystalline phases that precipitate from the brines (known as *bittern*) after total evaporation in order to obtain a mineralogical characterization of the various environments and a precipitation sequence of the most soluble salts. The research focuses on the “Chiusicella” saltwork within the Trapani and Paceco Nature Reserve (Sicily, Italy), a site that still employs traditional harvesting methods. Another key objective of this work is the characterization of a strategic yet under-investigated byproduct locally known as “*mamma caura*”. Often described by traditional salt workers as the “salt yeast” or “mother lye”, this sludge is considered the essential ingredient for producing refined, high-purity salt for the food industry. While this material has been largely discarded in industrial-scale production, this study aims to scientifically validate its role as a natural bio-georeactor. We hypothesize that the synergistic action of the microbial communities and the specific mineral phases within the “*mamma caura*” allows it to adsorb and absorb impurities, effectively “cleaning” the final salt product. To achieve this, solid samples and sludge were subjected to a multi-analytical approach, including X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM-EDS), and Raman Spectroscopy, to reconstruct the geochemical and mineralogical evolution across the saltern system.

2. Study Area

Salt pans, also called salinas or saltworks, are considered an anthropogenic ecosystem, and for this reason, they are well-known to a restricted fraction of the scientific community. Saltworks are part of the cultural heritage of the Mediterranean, but in addition to economic production, they play an important role in maintaining biodiversity [3].

The samples were collected from the Chiusicella saltwork (also known as Salina Chiusa), located in the Nubia district of Paceco, Trapani, Sicily (Figure 1a). The site is situated within the “Saline di Trapani e Paceco” Nature Reserve, managed by the WWF. The traditional and little saltwork Chiusicella (Figure 1b) covers an area of $\approx 73.75 \text{ m}^2$ and is dedicated exclusively to the production of food-grade salt. The primary objective of the saltwork management is to ensure the maximum recovery of high-purity halite (NaCl) through a controlled fractional crystallization process. The saltwork is organized into four distinct types of ponds, each characterized by a progressively increasing range of salinity. This interconnected system acts as a natural laboratory, mirroring the classic evaporitic sequence described by Usiglio (1849a,b) [17,18].

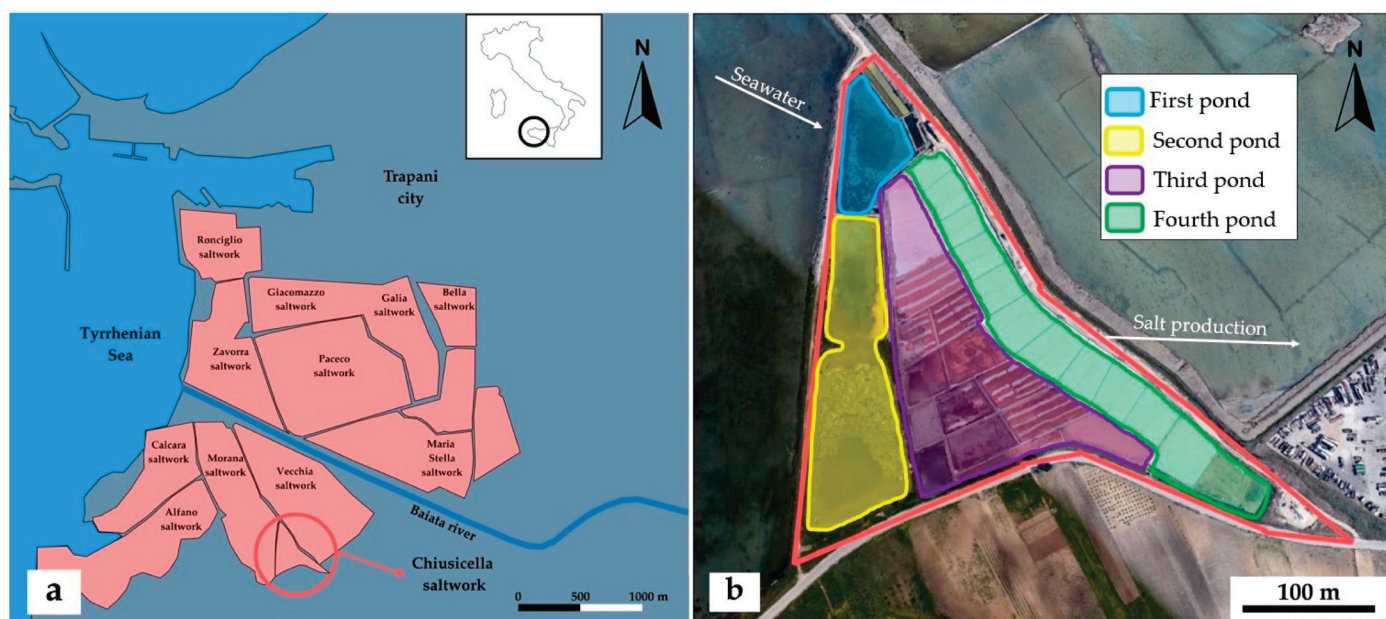


Figure 1. (a) Simplified map of the major saltworks of the Nature Reserve located near Trapani city. The study area, Chiusicella saltwork, is the small environment in the red circle on the south shore of the Baiata river. (b) Satellite image of the Chiusicella saltwork, in which it is possible to distinguish the four typologies of ponds inside, differentiated by colors and the flow of water from the seawater to the salt production.

Every solar saltworks consists of a variable number of interconnected ponds. In the Chiusicella saltwork, as well as in other saltworks, each pond can be classified into four main categories (Figure 1b), sequentially arranged along an increasing density gradient. Brine density has been traditionally described by salt workers using an empirical measurement dating back to 1768, known as the Baumé scale. The measured values ($^{\circ}\text{Bé}$) were converted to density (ρ , expressed in g/cm^3) using the standard conversion formula for liquids heavier than water at the reference temperature of $16\text{ }^{\circ}\text{C}$: $\rho = 145/(145 - ^{\circ}\text{Bé})$ ([34,35] see Tables 1–11). Based on this non-linear conversion, the starting seawater concentration of $3.5\text{ }^{\circ}\text{Bé}$ corresponds to an initial density of $1.025\text{ g}/\text{cm}^3$, while the halite saturation point at $26\text{ }^{\circ}\text{Bé}$ corresponds to a density of $1.218\text{ g}/\text{cm}^3$.

Each type of pond corresponds to an evaporitic stage, and the brines become progressively denser from the first basin to the last pond. The terms “cold” and “warm” are purely empirical and traditional: salt workers historically observed that the initial ponds, containing mostly raw seawater, are generally cooler than the highly concentrated brines in the ponds immediately preceding halite precipitation. Hence, the distinction between the “cold pond” and the “warm pond” is fundamentally based on brine density. They are defined as follows:

1. **Cold pond:** This is the initial basin where seawater is introduced via tidal action. These ponds are typically larger and deeper than the subsequent ones, with a density slightly higher than that of natural seawater, ranging from about $3.5\text{ }^{\circ}\text{Bé}$ to $5\text{ }^{\circ}\text{Bé}$ ($\approx 1.025\text{--}1.036\text{ g}/\text{cm}^3$). For simplicity, from now on, this pond will be referred to as the first pond.
2. **Second pond:** In this second stage, the salinity increases up to $12\text{ }^{\circ}\text{Bé}$ ($\approx 1.090\text{ g}/\text{cm}^3$).

Ecologically, these first two environments closely resemble coastal lagoons, hosting marine mollusks and gastropods; additionally, they are often utilized by locals for fish farming.

3. Warm pond: Here, the brine concentration reaches up to 26 °Bé ($\approx 1.218 \text{ g/cm}^3$), bringing the solution close to halite saturation. For simplicity, from now on, this pond will be referred to as the third pond.
4. Crystallizing pond: This is the final, shallowest basin where the food-grade salt precipitates and is ultimately harvested. For simplicity, from now on, this pond will be referred to as the fourth pond.

In the third and fourth ponds, compared to the first and second ponds, biodiversity decreases significantly due to hypersaline conditions and high temperature. The ecosystem hosts organisms adapted to these extreme conditions, such as unicellular green microalgae of the genus *Dunaliella*, particularly the species *D. salina*, which is characteristic of Mediterranean hypersaline environments and contributes to the water coloration ranging from pink to red due to the production of pigments such as carotenoids [36]. However, the water coloration is not entirely due to the production of secondary metabolites by algae, but primarily to halophilic bacterial communities and Archaea [37–39]. Prokaryotic diversity in highly saline ponds is dominated by extremely halophilic Archaea such as the genus *Halobacterium* (whose best-known species is *H. salinarum*) and *Haloquadratum*, as well as halophilic bacteria such as *Salinibacter ruber* and others of the genus *Halomonas* [40–42].

The salt cultivation cycle is annual, and the harvesting period varies locally between August and September. Salt workers explain that it is necessary to wait a few years from the start of cultivation for the saltworks to reach full capacity, which corresponds to the time required for the formation of “*mamma caura*”. At the end of each season, this sediment, which accumulates in the third ponds, is not discarded but rather preserved for use the following year. It is traditionally referred to as “salt yeast”, as its application acts as a biological primer that promotes the coloration of the brines. This coloration, in turn, increases the absorption of solar radiation, thereby accelerating evaporation. Furthermore, its use appears to be linked to the production of a cleaner and whiter artisanal salt. Finally, being a gypsum-rich sediment, it is also utilized to waterproof the ponds and their embankments.

3. Materials and Methods

Samples were collected in September, at the end of the saltwork’s production cycle and during the salt harvesting phase. Sediment samples were collected from each pond of the Chiusicella saltwork (Figure 2). Sediment cores were collected using a custom-made PVC manual corer (inner diameter $\approx 10 \text{ cm}$). The coring tube was manually driven into the salt pan sediments. To ensure full recovery and prevent sample loss during retrieval, the top of the tube was hermetically capped to create a vacuum. Once extracted, the sediment core was upwardly extruded using a custom-fitted piston. The core was then carefully sectioned at 1 cm intervals using a caliper to ensure high depth resolution. Each slice was immediately transferred into individual, uniquely labeled containers for subsequent analysis. Solid samples were immediately refrigerated and transported to the Department of Earth and Marine Sciences of the University of Palermo (Sicily, Italy). Each sediment centimeter was labeled with the corresponding pond ID and depth range (i.e., the first centimeter was labeled 0–1, the second 1–2, and so on). A total of 33 solid samples were collected: 6 cm from the first pond, 6 cm from the second pond, 11 cm from the third pond, 9 cm from the fourth pond and 1 sample of *mamma caura*. Concurrently, 1 L brine samples in contact with the sediments were collected from the fourth and third ponds, stored in polypropylene containers, refrigerated, and transported to the research laboratories. The solid samples were subsequently oven-dried at 40 °C for 48 h to remove pore water. This type of treatment induces the precipitation of residual salts in all samples due to the increase in supersaturation during the evaporation of the water solvent. Therefore, a rigorous quantitative XRD analysis of the highly soluble crystalline phases is not possible,

as it is affected by an overestimation of the concentrations of these salts. For this reason, the quantitative analysis for the first and second ponds was not considered reliable and was not performed. In the third pond, the analysis was carried out, but the overestimation (ranging between 0.54 and 3.24% as NaCl) of the more soluble phases due to evaporation effects must be considered. This overestimation can be quantified based on the known salinity of the water and the amount of water removed from the sample during the drying procedure. In the fourth pond, the overestimation is still present, but the quantitative analysis was not performed, as this pond was the most subject to anthropogenic intervention. All samples were promptly sent to the research laboratories of the Department of Earth Sciences at the University of Turin (Turin, Italy) for chemical and mineralogical analyses.

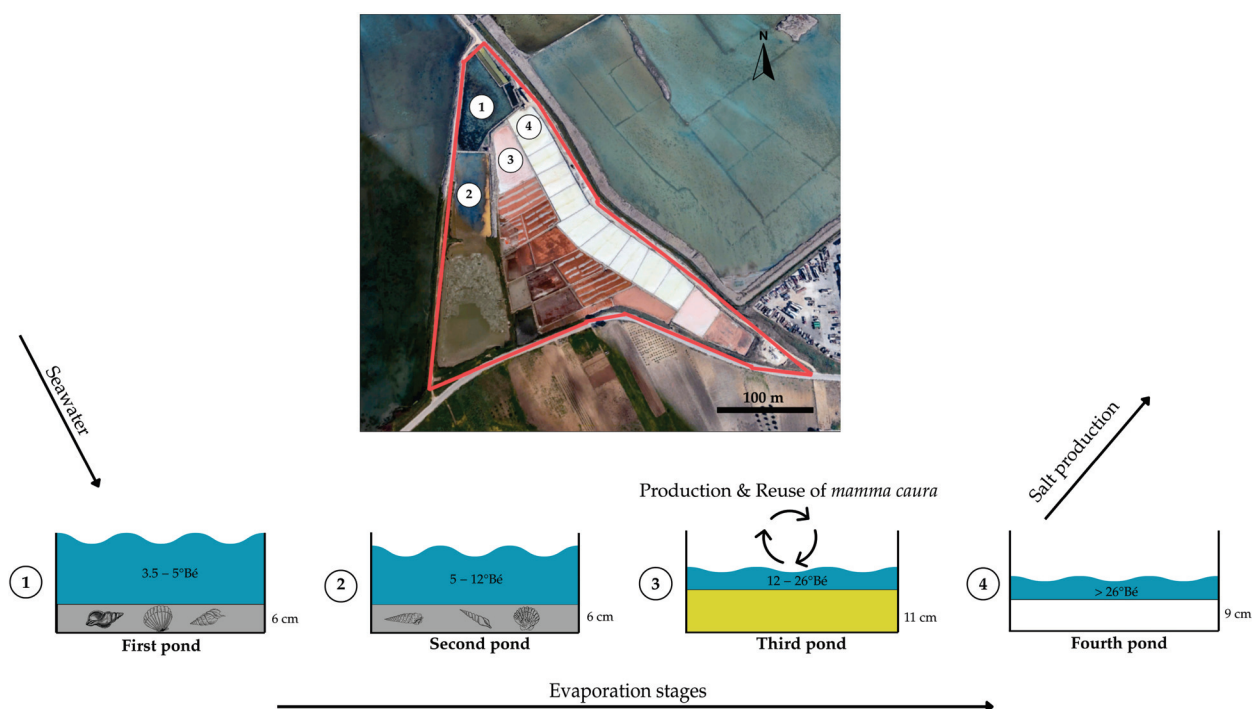


Figure 2. Satellite image of the “Chiusecella saltwork” (red perimeter) in which the numbers indicate the points of sampling, and they correspond to the four typologies of ponds. The diagram below illustrates the water flow from seawater to salt harvesting (black arrows). In the third pond, the “mamma caura” is produced, which will subsequently be used in the next production cycle. Additionally, the thickness of the sampled sediments and the number of samples are reported: 6 in the first pond, 6 in the second, 11 in the third, and 9 in the fourth. Note that the water level in the pond represents brine density.

A 50 mL aliquot of the residual brine was transferred into a 50 mL flask containing a glass slide placed at the bottom. The solution was evaporated to dryness at a constant temperature of 50 °C. Upon complete evaporation, the glass slide featuring the precipitated crystals was recovered, coated with a thin gold layer, and analyzed using a Tescan Vega Scanning Electron Microscope (SEM) (TESCAN ORSAY HOLDING a.s., Brno, Czech Republic) equipped with Oxford Instruments Xplore 15 EDS microanalysis (Oxford Instruments, High Wycombe, UK).

For all solid samples, mineralogical identification was performed via X-ray powder diffraction (XRD). Samples were finely ground using an agate mortar and spiked with a known amount of metallic silicon as an internal standard. This standard was employed to perform full pattern fitting and to calibrate peak shift corrections, ensuring high precision in d-spacing measurements.

Data were acquired using a MiniFlex 600 diffractometer (Rigaku Corporation, Tokyo, Japan) ($\lambda = 1.54 \text{ \AA}$, Cu-K α radiation) across a 2θ range of $2.0\text{--}100.0^\circ$, with a step size of 0.02° and a scanning speed of $0.6^\circ/\text{min}$. Phase identification was carried out using the Match! software (version 4.2) package [43] coupled with the Crystallography Open Database (COD) [44]. The Reference Intensity Ratio (RIR) method was selected for semi-quantitative analysis, as it proved more suitable than Rietveld refinement for these specific samples, which are characterized by complex multi-phase matrices (often exceeding four distinct mineral phases) and varying degrees of crystallinity and chemistry. Semi-quantitative analysis was performed only for the sediments of the third pond.

Morphological and micro-chemical investigations of the sediment were conducted by Scanning Electron Microscopy (TESCAN ORSAY HOLDING a.s., Brno, Czech Republic) equipped with an Energy-Dispersive X-ray Spectroscopy 230 detector (Oxford Instruments, High Wycombe, UK) (SEM-EDS).

To preserve the internal fabric and textural relationships and associated sediments, samples were embedded in epoxy resin (R&G Faserverbundwerkstoffe GmbH, Composite Technology, Waldenbuch, Germany). Once cured, they were sectioned and polished to expose a representative cross-section. Finally, the polished surfaces were carbon-coated to provide the necessary conductivity for high-resolution secondary electron imaging and quantitative EDS microanalysis.

Furthermore, Raman spectroscopy was employed to analyze the organic pigments present in the “*mamma caura*” sample. Measurements were carried out using a Horiba Jobin Yvon HR800 Raman spectrometer (Horiba Jobin Yvon, Longjumeau, France) equipped with grating (600 grooves/mm) and an air-cooled CCD detector (-70°C). The excitation sources consisted of polarized lasers: a red HeNe laser (633 nm wavelength, 20 mW power) and a solid-state green Nd laser (532 nm wavelength, 250 mW power). The system was fitted with Edge filters for the 633 nm and 532 nm laser lines, along with a series of interference filters. The spectral resolution with the 600 grooves/mm grating was 1.5 cm^{-1} for the red laser. The spectrometer is coupled to an Olympus BX41 polarized light petrographic microscope (Olympus Corporation, Tokyo, Japan), configured for reflected light observations.

4. Results and Discussion

4.1. Mineralogical Characterization

4.1.1. First Pond and Second Pond

X-ray diffraction (XRD) analysis performed on sediments from the first two ponds (first and second, see Figure 2) reveals a qualitatively similar composition, dominated by a terrigenous fraction and carbonates, with mainly quantitative variations. This similarity reflects the nature of these environments, which act as a bridge between the coastal marine environment (aragonite from the shells), detrital fraction (sand and clay such as quartz and kaolinite), and the first stage of evaporation within the carbonate stability field (inorganic calcium carbonate such as calcite). Diffractograms for all sediment horizons from the first and second ponds are available in the Supplementary Information File (Figure S1).

In the upper sediment layers of the first pond and second pond (0–1 and 1–2 cm), the coexistence of calcite and aragonite was detected. However, analysis of the vertical profiles highlights a distinctive trend: while calcite is persistent, aragonite tends to disappear in deeper layers (Figure 3a). This evidence is attributable to the predominantly biogenic origin of aragonite in this system, linked to the presence of bioclasts (fragments of gastropod and mollusk shells) that colonize the bottom of low-salinity ponds but are not present in the underlying horizons (Figure 3b,c).

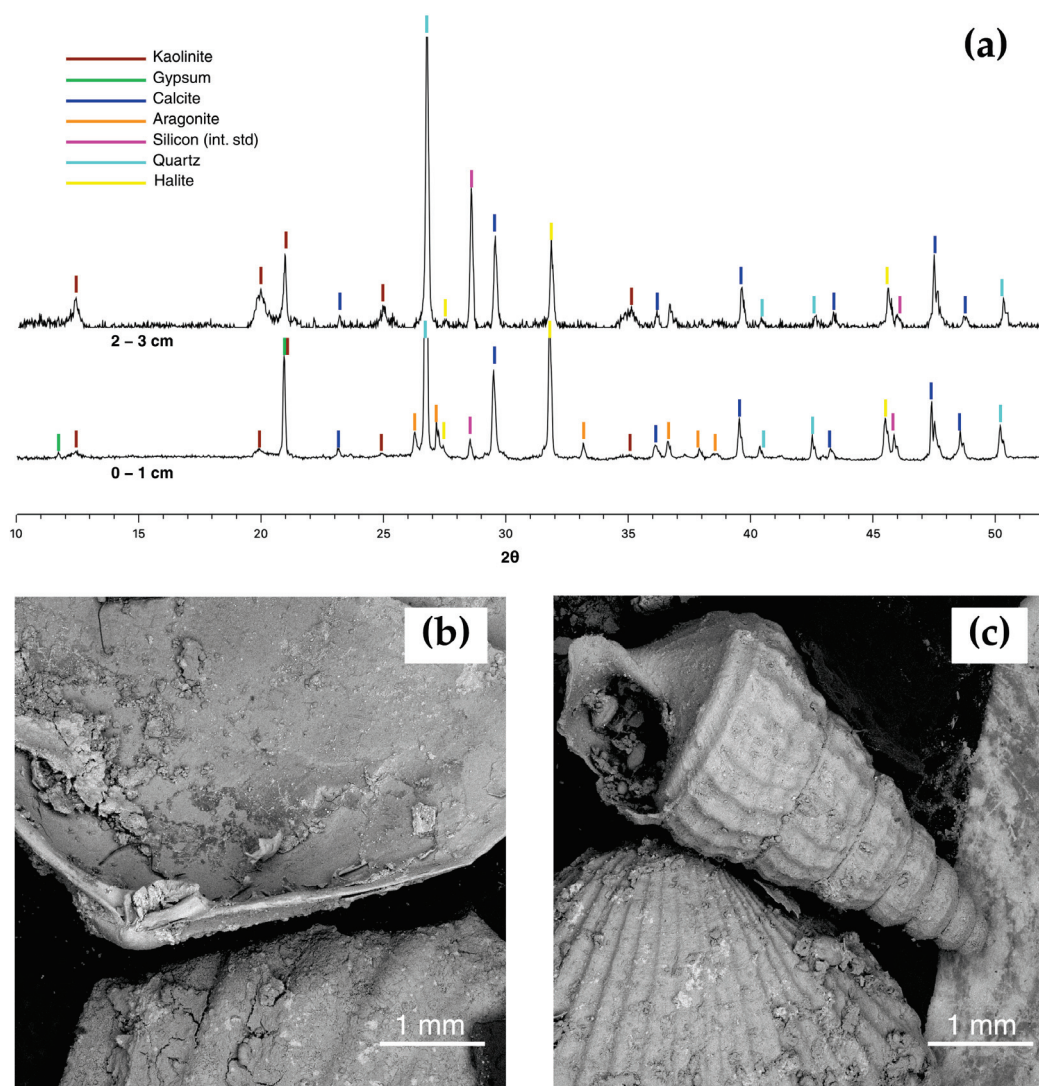


Figure 3. XRPD of the first centimeter of sediment from the first pond (bottom, 0–1) and the third centimeter of the same pond (top, 2–3), showing the identified phases. (a) The presence of aragonite (CaCO_3 , in orange) is evident in the first centimeter, whereas its main diagnostic peaks disappear from the third centimeter onwards. (b,c) SEM photomicrographs of gastropod and bivalve shells present in the first pond and second pond.

The silicoclastic component consists of quartz (sandy fraction) and phyllosilicates, such as kaolinite in this case. A rise in the background was also observed in the 12–20 Å range, probably indicating the presence of poorly crystalline smectites and disordered mixed-layer clays [45] (Figure S2). The origin of this detrital fraction is strictly connected to the geological setting of the area, characterized by the deposits of the Capo Plaia Synthem (Holocene), which constitutes the recent sedimentary cover of the Trapani and Paceco coastal plain [46]. Specifically, the saltworks are located on marshy and coastal plain deposits (AFL unit in the official geological cartography, specifically the “Xitta-Salina Grande” deposits), historically fed by the solid transport of the Baiata Stream and the local hydrographic system. These watercourses erode and transport coastalward the weathering products of the clayey-marly substrates of the hinterland (e.g., Terravecchia Formation), justifying the presence of clay minerals and quartz in the pond bottom sediments [46,47].

Finally, the presence of gypsum and halite does not represent primary precipitation from the water column (as the first ponds are still undersaturated) but is interpreted as secondary efflorescence resulting from the evaporation of interstitial water (pore water) during sample drying and preparation.

4.1.2. Third Pond and Fourth Pond

In the third pond and fourth pond, the physicochemical parameters of the brine shift significantly, entering the stability fields of sulfates and chlorides. The mineralogical assemblage of the third pond is primarily characterized by gypsum precipitation. However, a distinctive discontinuity is observed in the surface layer (0–1 cm), where halite prevails over sulfates. The presence of sodium chlorides at the very beginning of this sequence, theoretically reserved for calcium sulfates, stems from two fundamental factors. Firstly, changes in traditional saltworks management have led to the abandonment of an intermediate pond (historically known as Ruffiana) located between the second and the third pond. Its specific function was to monitor and regulate brine concentration through controlled dilution: by introducing less concentrated brines, this step prevented premature chloride supersaturation [48] before the final harvesting stage.

Secondly, the massive accumulation of halite in these horizons is a direct consequence of the brine density reaching and exceeding the halite saturation threshold (approx. 26 °Bé). In these advanced stages of evaporation, high-salinity conditions allow for the abundant crystallization of halite, which can synchronously co-precipitate with calcium sulfates. This co-precipitation is characteristic of natural highly evaporative environments, where specific chemical conditions allow multiple minerals to reach or maintain saturation simultaneously [49].

Below the surface crust, the mineralogical composition aligns with the expected evaporitic sequence. The gypsum content progressively increases with depth, reaching a peak concentration of approximately 91 wt% at the 5 cm horizon (Figure 4). Finally, a drastic shift occurs at the 8 cm depth, where the mineralogy reverts to the terrigenous-carbonates association typical of the initial ponds (see Section 4.1.1). This discontinuity marks the lithological boundary of the evaporitic sequence, between the 7th and 8th centimeters, identifying the horizon where the gypsum precipitation of the current annual production cycle began.

All diffraction patterns of the third pond and their semi-quantitative analysis are reported in the Supplementary Material (Figure S3 and Table S1, respectively).

The SEM-EDS investigation focused on the surface layers (0–3 cm) of the third pond to refine the mineralogical characterization. While the analysis confirmed the dominant presence of halite and gypsum (Figure 5a,b), the occurrence of minor phases in the 2–3 cm interval that were not clearly detectable by X-ray diffraction due to their low abundance (below the detection limit) is also highlighted. The EDS maps revealed phases of strontium and magnesium chlorides. Given the evaporitic context and the exclusive presence of Mg and Cl signals (e.g., absence of K), this latter phase is interpreted as likely bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) (Figure 5c,d). The strontium crystals exhibit an acicular to elongated morphology. While acicular celestite (SrSO_4) has been documented in several studies [50,51], in high-salinity environments, this habit also suggests the presence of a hydrated precursor phase, such as $\text{SrSO}_4 \cdot 0.5\text{H}_2\text{O}$ [52], rather than the typical tabular anhydrous celestite. Given the analytical limits of EDS in determining hydration states, both phases remain possible. Furthermore, due to the weak sulfur signal (<1%), the possibility that it is strontianite (SrCO_3) cannot be ruled out. Finally, although gypsum, which is abundantly found in these sediments (Figure 5a–d), may contain a certain amount of strontium [53], it is excluded as the strontium-bearing phase due to both the high concentration of strontium (~26%)

and the low calcium content (<1%). The presence of these phases suggests the existence of micro-environmental conditions locally reaching higher supersaturation degrees and enriched in strontium (Figure 5e,f).

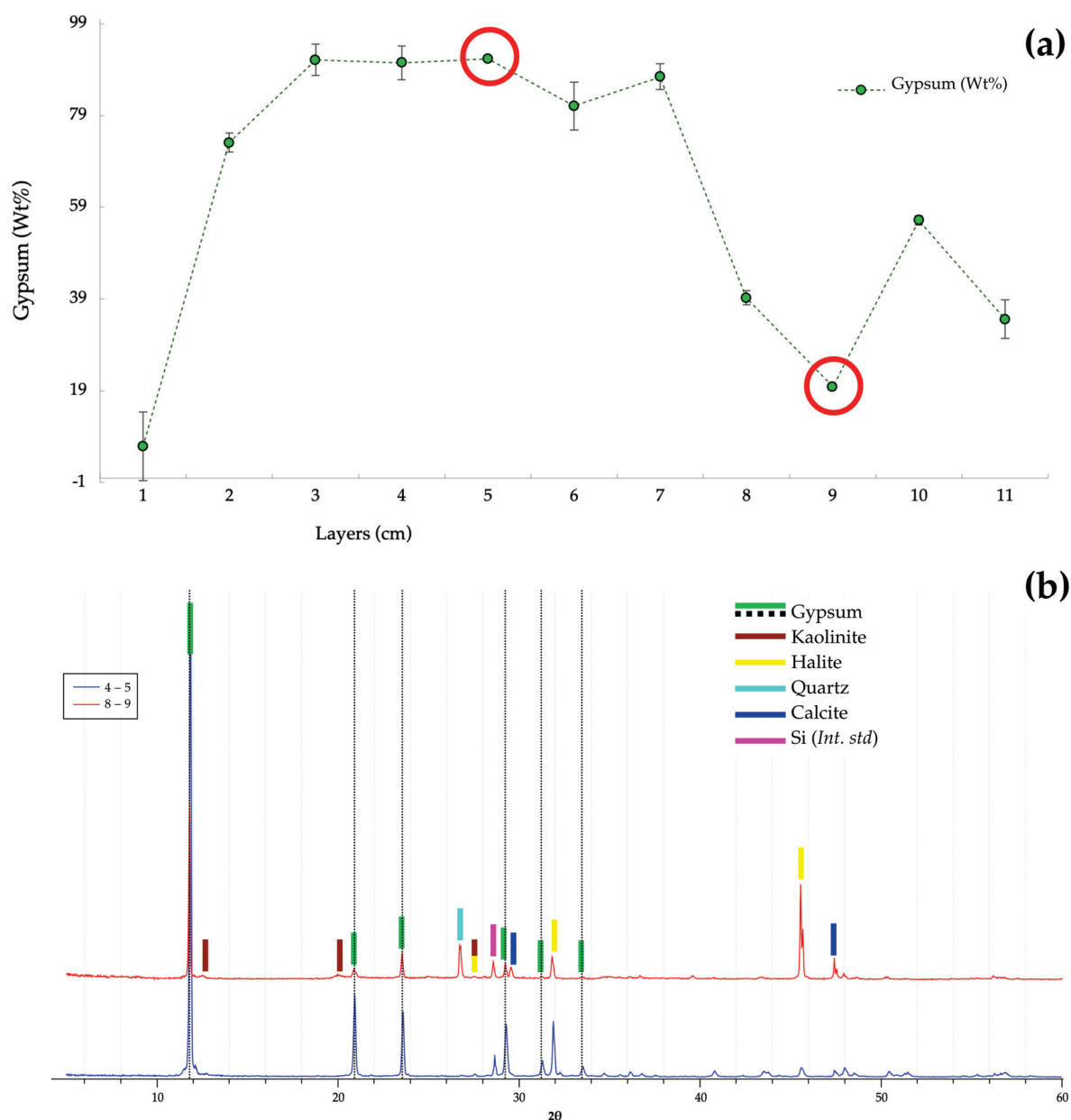


Figure 4. (a) The graph displays the trend of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) weight percentage throughout the third pond sediments. A sharp discontinuity is observed between the 7th and 8th centimeters, marking the boundary between the pond's authigenic precipitation and the allochthonous clayey and sandy substrate. Marked in red are the horizons, whose respective XRPD are shown below in (b). (b) XRPD of the 5th centimeter (in blue) and the 9th centimeter (in red) are shown. The peaks of the identified phases can be distinguished (by different colors shown in the legend), highlighting the progressive decrease in gypsum and the appearance of the other minerals, such as quartz, calcite, and kaolinite, in the deeper horizons.

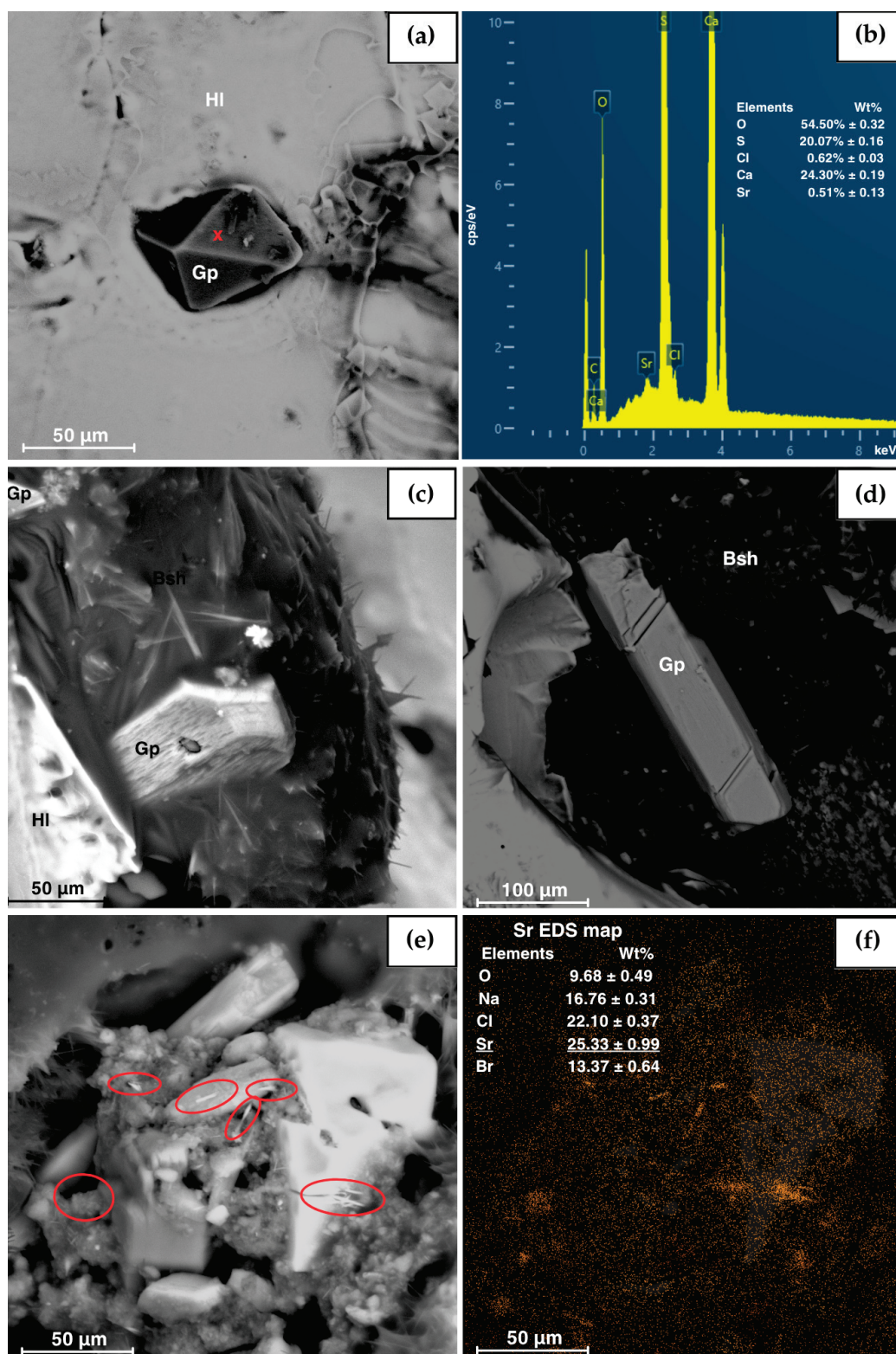


Figure 5. Scanning Electron Microscopy (SEM) photomicrographs of the top (0–1 and 1–2 cm) of the third pond sediments; chemical composition was determined via spot microanalyses and EDS mapping. (a) Gypsum crystal (Gp) surrounded by halite crystals (HI). Red cross represents the position of the EDS spectrum reported in (b). (c) Gypsum crystal (Gp) with several magnesium chloride crystals, presumably bischofite (Bsh). (d) Gypsum crystal (Gp) surrounded by magnesium chloride (Bsh) and halite (HI) crystals. (e) Small strontium salt needle crystals, highlighted in red, and relative EDS compositional map (f).

The characterization of the fourth pond reflects the operational conditions at the time of sampling, which coincided with salt harvesting operations. Consequently, the uppermost portion of the evaporitic sequence (the salt crusts intended for food use) is largely absent from the analyzed sedimentary record. Nevertheless, the first centimeter (0–1 cm) preserves the signature of the final precipitation phase, showing a mineralogy dominated by halite, which is clearly detectable by X-ray diffraction (XRD).

Below this superficial crust, the stratigraphy reveals a rapid transition. The second centimeter (1–2 cm) is predominantly enriched in gypsum. However, starting from the third centimeter, evaporitic purity decreases with the appearance of calcite and a quartz-rich sandy fraction, while the clay fraction reappears from the seventh centimeter downwards. The interpretation of this vertical profile suggests two distinct processes:

1. The presence of gypsum down to the fourth centimeter (0–4 cm), associated with low calcite concentrations, indicates authigenic precipitation (in situ) that occurred within the fourth pond during the early stages of supersaturation.
2. From the fifth centimeter downwards (5–9 cm), the concomitant presence of gypsum, calcite, halite, quartz, and clay minerals does not follow a natural depositional sequence but identifies the bottom horizon manipulated annually by salt workers during pond maintenance.

A crucial detail emerges from the morphological observation of the crystals: the gypsum crystals precipitated in this pond (transparent and clear) differ markedly from those precipitated in the third pond and constituting the “*mamma caura*”, which appear highly pigmented (see Section 4.2). All diffraction patterns for the fourth pond are available in the Supplementary Materials (Figure S4).

Only the dominant phases are reported in Table 1; these are the phases present in weight concentrations significantly higher (approximately >6 wt%) than the added internal standard.

Table 1. Lists the primary mineral phases identified by XRD in each centimeter of sediment from each pond. The Figure reports the main mineral phases identified by X-ray diffraction (XRD) that characterize each centimeter of the sediments from the respective ponds, present in significant concentrations (>6 wt%).

Layers	First Pond	Second Pond	Third Pond *	Fourth Pond *
0–1	Cal, Arg, Kln, Qz	Qz, Cal, Arg, Kln	Hl, Gp	Hl, Gp
1–2	Cal, Arg, Kln, Qz	Qz, Cal, Arg	Hl, Gp	Hl, Gp
2–3	Cal, Kln, Qz	Qz, Cal, Kln	Hl, Gp	Hl, Gp, Qz
3–4	Cal, Kln, Qz	Qz, Cal, Kln	Hl, Gp	Hl, Gp, Cal, Qz
4–5	Cal, Kln, Qz	Qz, Cal, Kln	Hl, Gp	Hl, Gp, Qz
5–6	Cal, Kln, Qz	Qz, Cal, Kln	Hl, Gp	Hl, Gp, Qz
6–7	/	/	Hl, Gp	Gp, Cal, Qz, Kln
7–8	/	/	Hl, Gp, Cal, Kln, Qz	Gp, Cal, Kln, Qz
8–9	/	/	Hl, Gp, Cal, Kln, Qz	Gp, Cal, Kln, Qz
9–10	/	/	Hl, Gp, Cal, Kln, Qz	/
10–11	/	/	Hl, Gp, Cal, Kln, Qz	/

* Soluble salt overconcentration estimated as described in Section 3.

4.1.3. Precipitation Sequence

Although X-ray diffraction (XRD) analyses performed on precipitates obtained from the isothermal evaporation of brine ($T \approx 50^\circ\text{C}$) indicate an absolute predominance of halite, micro-structural and chemical investigations (SEM-EDS) revealed a more complex and polyphasic mineral assemblage.

In the sample derived from the third pond (Figure 6a), the presence of halite crystals with well-developed octahedral faces is remarkable. The stabilization of the {111} form at

the expense of the cubic faces is a phenomenon attributable to the selective adsorption of organic molecules present in the biological matrix of the brine or to kinetic conditions of high supersaturation [54–58]. The formation of the {111} form may depend on the extent of thermal gradient during crystallization [55,56]; however, under identical thermal gradient conditions, only the halite precipitated from the third pond exhibits the {111}-octahedral form. This finding supports the hypothesis that, in this instance, organic matter is responsible for stabilizing octahedral faces [57,58]. Furthermore, chemical maps (EDS) (available in Supplementary Materials) confirm the accessory precipitation of potassium chlorides (sylvite, KCl) and calcium and magnesium sulfate hydrates (gypsum and hexahydrate).

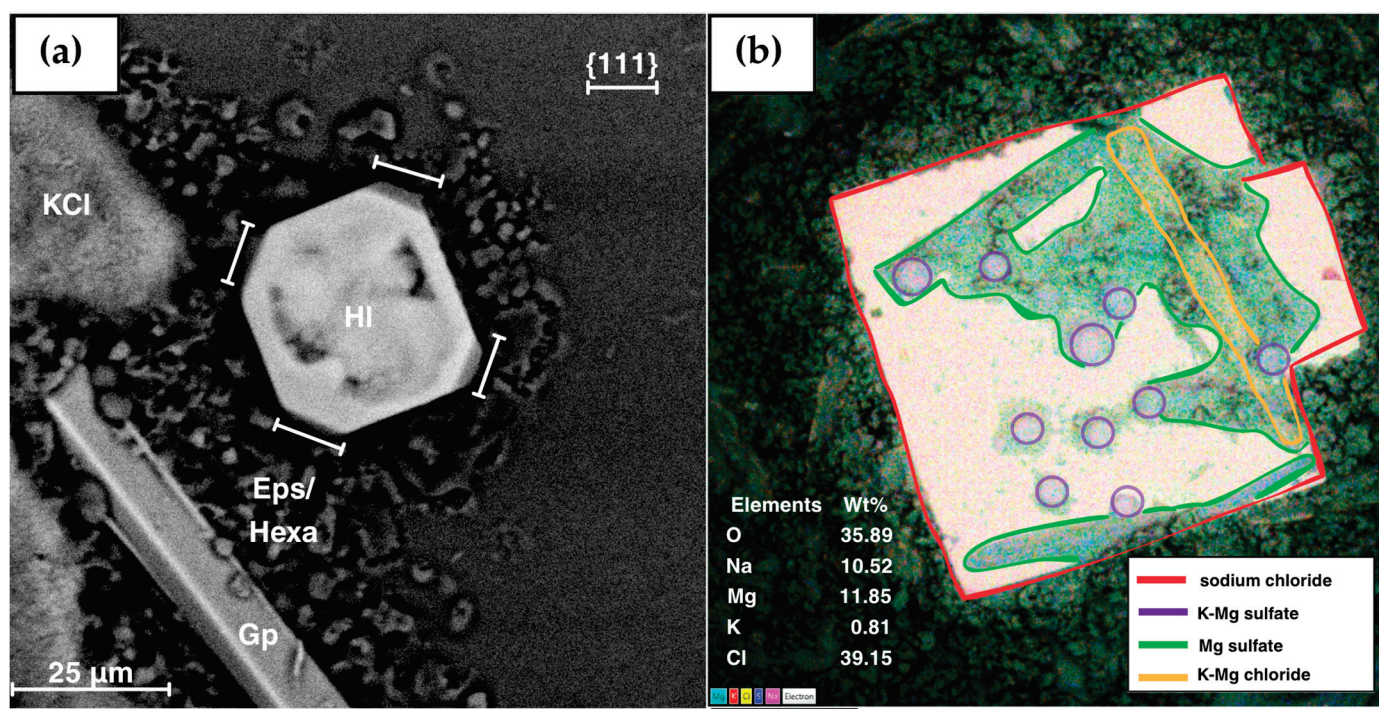


Figure 6. (a) SEM photomicrograph of precipitates from the “third pond” brines, displaying a halite crystal (HI) with distinct octahedral {111} form, surrounded by magnesium sulfate crystals (epsomite (Eps) and/or hexahydrate (Hexa), depending on the hydration state) and sylvite crystals (KCl). (b) EDS map of salts precipitated from the fourth pond brines, revealing a large halite crystal (in red) accompanied by K-Mg chlorides (in orange) and magnesium sulfates (in green), and small Mg-K sulfate crystals (in purple), presumably leonite or langbeinite.

From the fourth pond brine (Figure 6b), the mineral association evolves, reflecting a higher degree of concentration. Above the halite matrix, crusts of magnesium sulfates (epsomite or hexahydrate, respectively $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), K-Mg double chlorides (carnallite, $\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), and K-Mg double sulfates, chemically compatible with leonite or langbeinite (respectively $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$), are observed (Figure 6).

The absence of thermodynamically stable phases such as kainite or kieserite suggests that the experimental evaporation process followed a metastable path, kinetically controlled. The kinetic conditions induced by rapid evaporation inhibit the nucleation of kainite or kieserite in favor of other soluble salts [12,27,59,60]. It is crucial to note that, within the operational context of the saltworks, these highly soluble salts are not typically found in the ponds. This is because standard anthropogenic practices intentionally interrupt the natural precipitation sequence: salt workers actively drain the residual mother brines (bitterns) and harvest the halite before the brine reaches the eutonic point or dries up completely. This controlled discharge is necessary to prevent the co-precipitation of magnesium and

potassium salts, thereby avoiding the chemical contamination of the commercial sodium chloride harvest.

4.2. “Mamma Caura”

“Mamma caura” samples were collected from the exposed banks of the third pond. Macroscopically, the deposit exhibits a distinct vertical zonation: a bleached, oxidized surface crust overlies a dark, viscous layer (below 2 cm depth). The latter maintains higher temperatures, a phenomenon attributable to both thermal absorption by the dark substrate and the exothermic microbial decomposition of organic matter. This byproduct is described by salt workers as a material traditionally linked to salt production. Salt workers say its use is linked to the “good” production of clean, white salt, and that without it, the salt is gray or dirty.

XRD analysis reveals a mineralogical assemblage overwhelmingly dominated by gypsum, with subordinate amounts of halite and traces of calcite and quartz (Figure S6). The most striking feature, however, lies in the habit and color of the gypsum crystals. Unlike the transparent crystals of the fourth pond, the “mamma caura” crystals are intensely pigmented, displaying hues ranging from pink to brick-red and green (Figure 7a,b).

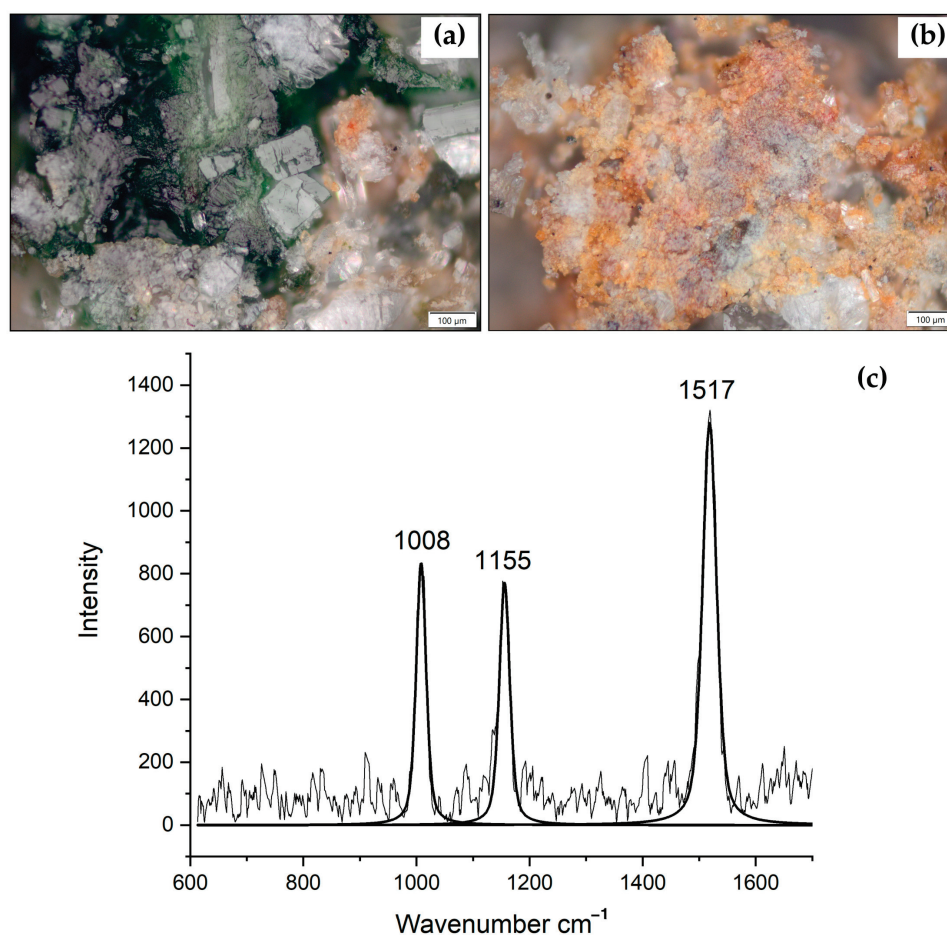


Figure 7. Photomicrographs of “mamma caura” crystals showing green (a) and orange (b) pigments; Raman spectrum of the orange pigment after background subtraction, showing three diagnostic peaks at 1517, 1155 and 1008 cm^{-1} (c).

This coloration is not superficial but due to the physical occlusion of biomass and metabolic products within the internal structure of the crystals during mineral growth. These occlusions provide evidence of endoevaporitic communities composed of halophilic bacteria, Archaea, and microalgae colonizing crystals. As widely documented in both

modern and ancient evaporites, gypsum crystals (selenites) act as an “optical window”: they offer physical protection against desiccation and UV radiation while allowing the light penetration necessary for photosynthesis, effectively creating an ideal intracrystalline photic zone [61–64].

The pigments responsible for the coloration are the metabolic products of these extremophiles, primarily identified as bacteriorhodopsins, retinal proteins characteristic of Halobacteria (Archaea); spirilloxanthins, carotenoids typically produced by anoxygenic photosynthetic purple bacteria; and carotenoids, antioxidant pigments produced by algae [38,64,65].

Raman spectroscopy performed on the pigmented crystals provided molecular confirmation of this biological activity. The Raman spectrum of the orange layer in the gypsum of the “*mamma caura*” crust was acquired using 633 nm excitation and contains a very strong fluorescence signal. In the spectrum, the strongest diagnostic bands are clearly visible, specifically at 1517, 1155, and 1008 cm^{-1} (Figure 7c). The fluorescent Raman spectrum without background subtraction and deconvolution operations can be found in the supplementary material in Figure S7. Generally, Raman bands at around 1515, 1155 and 1007 cm^{-1} are diagnostic of carotenoid pigments, and they are respectively attributed to ν_1 (C=C), ν_2 (C–C) stretching vibrations and to rocking modes δ (C=CH) of the CH_3 groups [66].

However, as reported by Edwards et al. (2005) [65], one typical carotenoid Raman band (at 1006 cm^{-1}) is often severely obscured by the strong sulfate stretching mode of the matrix (at $\sim 1008 \text{ cm}^{-1}$). Indeed, in our spectrum, the band observed around 1008 cm^{-1} perfectly overlaps with the ν_1 symmetric stretch vibration mode of the SO_4 tetrahedra of the embedding gypsum crystals (ν_1 at 1008 cm^{-1} for gypsum) [67,68].

The second Raman band at around 1155 cm^{-1} could be attributed to ν_2 (C–C) stretching vibrations of carotenoids.

However, the most important and reliable Raman band for our analysis is the ν_1 position (C=C stretching) at 1517 cm^{-1} , which is completely free from sulfate overlap. This band contains crucial information about the number of double bonds in the polyene chain (N) and is normally used for discrimination [39,63,64]. However, discriminating the exact biological source of this carotenoid based solely on the ν_1 value through spectroscopic analysis is difficult. The ν_1 value obtained for β -carotene in different biological systems is in the range of 1513–1531 cm^{-1} [69]. Nevertheless, our results are close to the values reported for salinixanthin extracted from *Salinibacter ruber* (at 1510–1513 cm^{-1} , N = 11) and spirilloxanthin extracted from *Ectothiorhodospira marismortui* (at 1509–1513 cm^{-1} , N = 13) in the study by Culka et al. (2022) [39].

The evidence of pigments found exclusively within the gypsum crystals of the “*mamma caura*” in the third pond provides crucial insights into the interactions between the bacterial component and gypsum mineralization processes [61–66]. This complex interaction suggests the existence of a bio-filtration mechanism driven by this predominantly gypsum-matrix geomaterial. This byproduct, far from being discarded, finds a fundamental reuse within the artisanal production cycle, ensuring a natural and effective filtration of the brines before their transfer to the final salt-harvesting ponds. Although salt workers have historically utilized this material on a purely empirical basis, observing that its application yields a visibly cleaner and higher-quality salt, these analyses now scientifically confirm its filtering power. This result allows for the definitive valorization of ancient traditional knowledge, demonstrating how biological efficacy supports and validates centuries-old artisanal practice.

5. Conclusions

Each pond in the saltworks system represents a distinct micro-ecosystem, although connected both mineralogically and hydrodynamically. The mineralogical characterization reflects the theoretical fractional precipitation stages: from the dominance of carbonates in the initial ponds (first and second), transitioning to calcium sulfates in the third pond, and finally to sodium chloride in the last pond. This zonation allows for the precise identification of stability fields for mineral phases relative to the salinity gradient.

A key finding is the dominant role of anthropogenic management in shaping the basin mineralogy. Stratigraphic analysis allowed for the identification of mineralogical discontinuities separating reworked bottom horizons from authigenic precipitation layers in equilibrium with the brines. In contrast, the stability field of soluble K-Mg salts is not represented in the natural ponds due to the artificial interruption of the precipitation cycle for harvesting. Laboratory experiments demonstrated that the formation of these highly soluble phases is strongly dependent on kinetic factors, which differ significantly between controlled laboratory conditions and the natural environment subject to thermal fluctuations. This suggests that future research should focus on the crystallization kinetics of bittern salts up to the eutonic point using different methodology.

Finally, this study provides the first analysis of “*mamma caura*”, a byproduct of artisanal salt production traditionally integrated into the production cycle. It clarifies and confirms its mineral composition, which consists primarily of gypsum and is rich in organic secondary metabolites produced by microorganisms living in the ponds and sediments, allowing it to be classified as a bio-mineral deposit. Specifically utilized in the third pond, this material acts as a bio-accumulator through the synergistic action of the mineral matrix and bacterial activity. This performs a crucial “filtering” function, explaining the underlying mechanisms of its longstanding empirical use to ensure the high purity of the salt harvested in the final ponds.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16070681/s1>, Figure S1: Mineralogical phases recognized by XRD: kaolinite (Kln), halite (Hl), calcite (Cal), aragonite (Arg), quartz (Qz); (Hl and Gp are considered artifacts resulting from sample preparation). (a) XRPDs of all horizons of the first pond; (b) XRPDs of all horizons of the second pond; Figure S2: Detail of XRPD of the 1st and 4th horizons of the second pond in which it is observed a rise in the background in the 12–20 Å d range; Figure S3: Mineralogical phases recognized by XRD: kaolinite (Kln), halite (Hl), gypsum (Gp), calcite (Cal), quartz (Qz) in the XRPDs from the 1st to 11th cm of the third pond; Table S1: Semi-quantitative analysis of the sediments of the third pond. Overconcentration of soluble salts was estimated as described in the Materials and Methods section of the main text; Figure S4: Mineralogical phases recognized by XRD: kaolinite (Kln), halite (Hl), gypsum (Gp), calcite (Cal), quartz (Qz), bassanite (Bss) in the XRPDs from the 1st to 11th cm of the third pond (Bss is considered artifact resulting from sample preparation); Figure S5: EDS compositional maps of precipitates from the third pond brine; Figure S6: XRPD pattern of *mamma caura* highlighting the characteristic diffraction peaks of gypsum (Gp), halite (Hl) and traces of calcite (Cal) and quartz (Qz); Figure S7: Original Raman spectrum with strong fluorescence signal of the orange pigment.

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Abbreviations

The following abbreviations are used in this manuscript:

Arg	Aragonite
Bsh	Bischofite
Cal	Calcite
EDS	Energy-Dispersive X-ray Spectroscopy
Eps	Epsomite
Gp	Gypsum
Hexa	Hexahydrite
Hal	Halite
Illt	Illite
Kln	Kaolinite
Qz	Quartz
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction

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Article

Geostatistical Assessment of Critical Raw Materials in Nine Mining and Metallurgical Waste Types from the Cartagena–La Unión District (SE Spain)

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Abstract

Mining and metallurgical residues represent one of the largest untapped secondary raw-material resources in Europe; however, their critical raw material (CRM) potential remains insufficiently quantified. This study applies a comprehensive mineralogical, geochemical, and geostatistical framework to evaluate nine distinct waste types from the Cartagena–La Unión Mining District (SE Spain), a historically exploited polymetallic system. A total of 79 samples were analysed using X-ray diffraction, wavelength-dispersive X-ray fluorescence, and advanced multivariate statistical techniques (correlation analysis, principal component analysis and hierarchical clustering) to identify geochemical associations controlling CRM distribution. The results reveal strong geochemical heterogeneity, with systematic enrichment in Co, Ni, Cu, Ga, Nb, and rare-earth proxies. Three dominant geochemical controls were identified: (i) a lithogenic silicate association governing Al–Si–Ti–Nb patterns, (ii) a sulphide-derived metalliferous association characterized by Cu–As–Sb, and (iii) an oxidation–adsorption association responsible for Ga–Y affinity. Several CRM concentrations approach or exceed typical global ore grades for secondary resources, particularly in flotation-derived and oxidation-rich residues. Geostatistical modelling confirms spatially coherent CRM hotspots, with base-metal enrichment linked to sulphide relics and Ga–Nb–Y controlled by Fe–Mn oxyhydroxides. Environmental assessment indicates potential metal mobility under acidic conditions, while also highlighting significant remediation benefits associated with residue reprocessing. Taken together, this study provides a robust and reproducible methodology for CRM assessment in legacy mining wastes and identifies priority residue types within the district with the highest strategic recovery potential.

Keywords: Critical Raw Materials (CRMs); mine tailings; metallurgical waste

1. Introduction

Mining and metallurgical wastes are increasingly recognized as strategic secondary sources of critical raw materials (CRMs) in the context of the European Union Critical Raw Materials Act (2023) [1] and the growing demand for secure and diversified mineral supply chains. Numerous studies have demonstrated the presence of cobalt, nickel, copper, rare earth elements, and other strategic commodities in tailings, metallurgical residues,

and process sludges [2]. Large-scale inventories, such as the USGS national survey of CRMs in mine wastes [3], highlight the need for systematic geochemical datasets to support circular-economy strategies [4].

Mining waste represents one of the largest industrial waste streams globally [5,6], and its volume continues to increase as ore grades decline and mineral demand rises. In the European Union, mining residues accounted for 26.2% of all waste generated in 2018, making them the second-largest waste stream after construction and demolition debris [1]. Globally, approximately 150 billion tons of rock are extracted annually, generating around 13 billion tons of sludge and 12.7 billion tons of tailings [7]. These materials represent both a significant environmental liability—due to risks of acid mine drainage, soil contamination, and erosion [8–10]—and a potentially valuable secondary resource for metal recovery.

Although many European mining wastes are classified as inert or non-hazardous, numerous facilities contain sulphide-rich deposits with elevated concentrations of metals and sulphates [10]. Spain, with more than 7000 inventoried waste deposits [11], hosts extensive volumes of flotation sludges, metallurgical residues, and tailings. These deposits, historically managed with limited environmental control, are now receiving renewed attention because their metal concentrations may approach those of primary ores [1]. Across Europe, more than 500 waste facilities are estimated to contain substantial quantities of valuable metals derived mainly from Cu–Pb–Zn–Ni sulphide ore processing [10].

In this context, the recovery of CRMs from mining and metallurgical wastes is gaining increasing strategic importance, particularly given the long development times for new mining projects—often exceeding 15 years between discovery and production [12]. Consequently, secondary sources such as legacy tailings, mine spoils, and metallurgical residues are increasingly considered key components of future mineral supply strategies. A wide range of technologies has been explored for CRM recovery, including flotation [1], magnetic separation [13], density- and size-based separation [14], pyrometallurgy [15], hydrometallurgy [16], and bioleaching [17]. However, the strong mineralogical heterogeneity, fine particle size, and chemical complexity of these wastes require site-specific approaches tailored to local geological and geochemical conditions [18,19].

Despite these advances, significant knowledge gaps remain. Many studies are restricted to individual sites, lack statistically representative sampling, or do not integrate geostatistical approaches capable of quantifying variability across multiple waste categories. While broader frameworks have emphasized the geopolitical and economic importance of waste valorisation [20], relatively few studies provide quantitative and statistically robust assessments linking CRM occurrence, mineralogical controls, and recovery potential within a unified framework.

The aim of this study is to address these gaps by applying an integrated mineralogical, geochemical, and geostatistical approach to nine mining and metallurgical waste categories from the Cartagena–La Unión Mining District (SE Spain). Specifically, this study (i) quantifies CRM concentrations, (ii) evaluates mineralogical and geochemical controls, (iii) identifies priority waste types for potential reprocessing, and (iv) proposes a reproducible framework applicable to other European mining districts.

2. Materials and Methods

2.1. Study Area

The study was conducted in the Cartagena–La Unión Mining District (CUMD), SE Spain, a ~100 km² region characterized by semi-arid Mediterranean conditions, with mean annual precipitation of 290 mm and an average temperature of 17 °C [21,22]. The district hosts stratiform Pb–Zn–Fe sulphide mineralization accompanied by gossans, stockworks,

and vein-type systems, and constitutes one of the most historically exploited polymetallic regions in Europe [23].

The studied waste materials originate from different historical mining periods, mainly spanning from the late 19th century to the late 20th century, reflecting changes in mining, beneficiation, and metallurgical practices. Some deposits correspond to early mining activities, whereas others are related to more recent operations or have been subject to reworking and weathering processes.

2.2. Waste Typology and Sampling Strategy

Nine categories of mining and metallurgical wastes were selected based on the classification proposed by [22], covering the full range of residues generated during historical open-pit mining, flotation, gravity concentration, and smelting activities: (1) open pit spoils, (2) post-flotation waste (on land), (3) post-flotation waste (on sea), (4) gravity concentration spoils, (5) mine spoils, (6) false gossan, (7) pre-concentration waste, (8) molten slag, and (9) well borings.

Table 1 summarizes the main characteristics of each waste type. Samples within each category were collected from multiple deposits and mining sites across the Cartagena–La Unión Mining District, ensuring that no category is represented by a single location. This sampling strategy was designed to capture spatial variability and avoid bias associated with site-specific conditions.

Table 1. Types of mining and metallurgical wastes modified from [22].

Number	Types of Mining and Metallurgical Waste	Description	No. of Deposit	Age	Surface Area (km ²)	Volume (10 ⁶ m ³)	No. of Samples
1	Open pit spoils	12 open pits	32	1953–1991	4210	135.99	5
2	Post-flotation waste (on land)	Tailing ponds	89	1940–1941	2180	22.89	26
3	Post-flotation waste (on sea)	Costal deposit	3	1956–1991	0.830	25.00	3
4	Gravity concentration spoils	Historical processing	119	1950–1991	0.650	3.73	21
5	Mine spoils	Waste dumps	176	1950–1991	0.480	3.01	13
6	False gossan	Oxidized zone	11	1953–1951	0.260	6.93	2
7	Pre-concentration waste	Early processing	1	≈1910	0.060	0.59	3
8	Molten slag	Smelting residues	19	≈1840	0.130	0.66	3
9	Well borings	Subsurface materials	1.902	≈1860	0.020	0.51	3
Total					8.820	199.43	79

A total of 79 composite samples were collected following a standardized and reproducible protocol. Each composite sample consisted of 5–8 increments collected from the upper 0–50 cm of exposed waste surfaces, selected to ensure representativeness and avoid recent disturbances. Field QA/QC procedures included duplicate samples every 10 samples and pre-cleaning of tools to minimize cross-contamination.

These wastes were generated from the lithological materials of the CUMD, shaped by the specific industrial processes to which they were subjected during exploitation [22], as illustrated in the diagram in Figure 1.

2.3. Sample Preparation Methodology

In the laboratory, samples were air-dried at temperatures below 40 °C to preserve mineralogical integrity, manually disaggregated, and homogenized. The material was then reduced using a riffle splitter to obtain a representative subsample of 200–300 g.

Subsamples were prepared for mineralogical (XRD and SEM–EDS) and chemical analyses (XRF and ICP–MS). This standardized preparation procedure minimizes particle-

size bias, reduces heterogeneity, and ensures analytical comparability across all waste categories (Figure 1, Table 1).

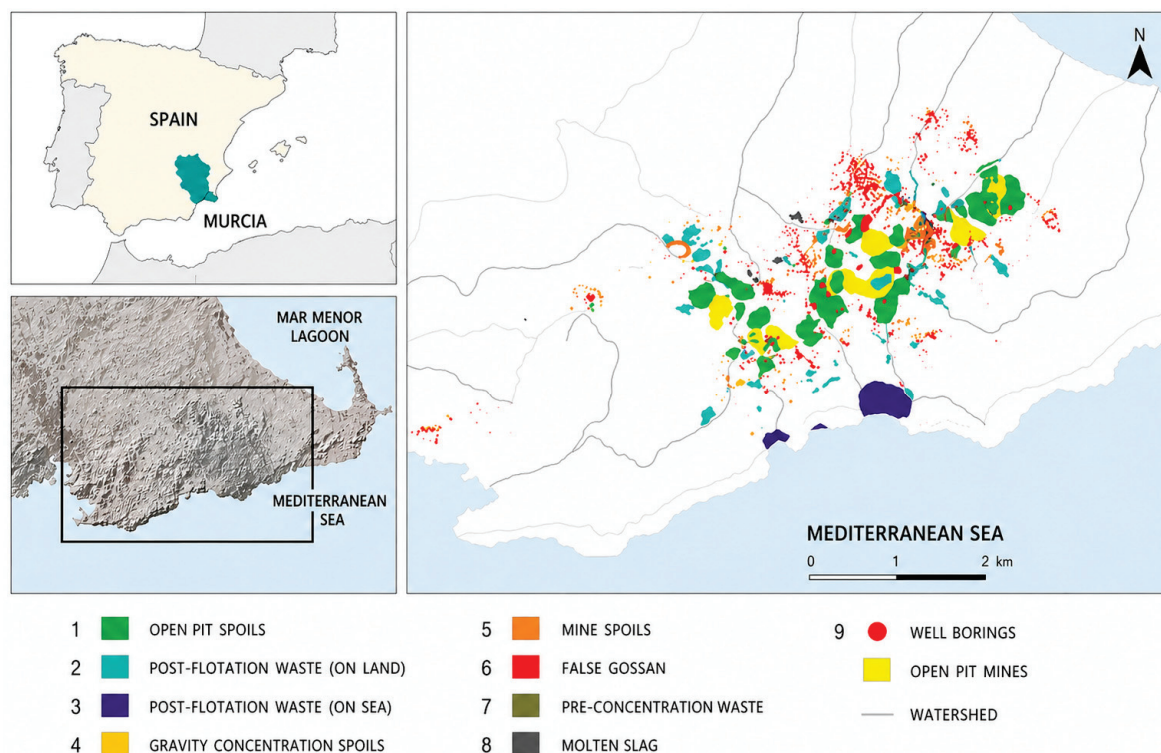


Figure 1. Spatial distribution of mining and metallurgical waste types in the Cartagena–La Unión Mining District (SE Spain), including location maps and detailed cartographic representation of the study area [21,22]. Colors and numbers (1–9) correspond to the classification of waste types defined in Table 1 and to the process-based scheme presented in Figure 2.

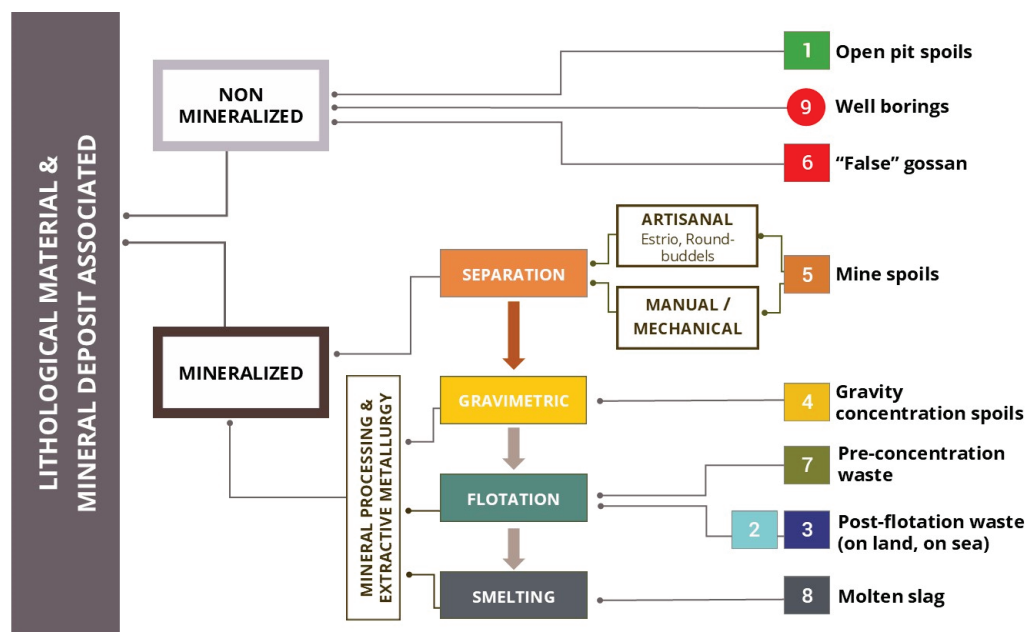


Figure 2. Simplified flow diagram of the waste generated from lithological material according to the industrial process it has undergone. The diagram illustrates the main pathways from non-mineralized and mineralized materials through separation and metallurgical processes, including gravimetric concentration, flotation, and smelting. Colors correspond to the waste categories defined in Figure 1, and numbers indicate the classification of waste types as listed in Table 1.

2.4. Physical–Chemical Characterization

pH measurements were performed on <2 mm fractions using a 1:2.5 solid-to-deionized-water ratio, following the [23] standard. Solids density was measured using a helium pycnometer [24], while dry bulk density was determined according to the [25] geotechnical standard.

2.5. Mineralogical Composition

X-ray diffraction (XRD) analyses were performed on <63 µm powdered samples using a Bruker D8 Advance diffractometer (CuKα radiation, $\lambda = 1.5406 \text{ \AA}$, 40 kV, 30 mA). Diffractograms were recorded over a 5–70° 2θ range, with a step size of 0.02° and a counting time of 1 s per step. Phase identification was carried out using the ICDD PDF-4+ database, and quantitative analyses were based on the relative intensity ratio (RIR) method.

Scanning Electron Microscopy coupled with Energy-Dispersive Spectroscopy (SEM–EDS) was used as a complementary technique to support mineralogical interpretation. Analyses were performed using a Zeiss instrument (ZEISS Group, Oberkochen, Germany) operating at 15 kV, with backscattered electron (BSE) and secondary electron (SE) imaging modes. Point analyses were quantified using ZAF-corrected EDS software (SmartEDS, version 6, ZEISS Group, Oberkochen, Germany).

SEM–EDS observations were consistent with the mineralogical phases identified by XRD and were used to validate mineralogical and geochemical interpretations, particularly for accessory phases and textural relationships.

2.6. Chemical Composition

The bulk chemical composition of the samples was determined using XRF and ICP–MS. Major elements (Si, Al, Fe, Mg, Ca, K, Na, Ti, Mn, and P) were quantified by wavelength-dispersive XRF on fused glass beads to ensure matrix homogenization and minimize mineralogical effects on analytical response. Trace and critical elements (e.g., Co, Ni, Cu, Zn, Ga, Nb, Y, and REEs) were analysed by ICP–MS following acid digestion using a HF–HNO₃–HClO₄ mixture in closed Teflon vessels and microwave-assisted heating to guarantee complete dissolution of refractory silicates and oxide phases. Analytical precision and accuracy were better than 5% RSD for most analysed elements, as validated through routine measurements of certified reference materials (CRMs). Sulphur content was determined by LECO combustion analysis, given its significance for evaluating sulphide abundance and the acid-generating potential of the waste materials.

2.7. Geostatistical Analysis

Geostatistical and multivariate analyses were applied to characterize data variability and identify geochemical controls on element distribution.

Descriptive statistics (mean, median, standard deviation, and coefficient of variation) were computed to assess data variability. Normality tests (Shapiro–Wilk and Anderson–Darling) were applied to evaluate distributional behaviour.

To improve normality and reduce skewness, a Box–Cox transformation was applied where appropriate:

$$y(\lambda) = (x^{\lambda} - 1)/\lambda \quad \text{for } \lambda \neq 0 \quad (1)$$

$$y(\lambda) = \ln(x) \quad \text{for } \lambda = 0 \quad (2)$$

where x is the original data and λ is the transformation parameter.

The Median Absolute Deviation (MAD) was used as a robust measure of variability:

$$\text{MAD} = \text{median}(|x_i - \text{median}(x)|) \quad (3)$$

Prior to multivariate analysis, all variables were standardized using z-score normalization. Principal Component Analysis (PCA) was applied to reduce dataset dimensionality and identify geochemical associations. A Varimax rotation was used to improve interpretability by maximizing variance of squared loadings.

For spatial analysis, experimental semivariograms were constructed using both omnidirectional and directional approaches. Spherical, exponential, and Gaussian models were fitted, with model selection based on leave-one-out cross-validation.

The bulk chemical composition is presented in oxide form together with loss on ignition (LOI) for descriptive purposes. However, multivariate analyses were performed on the original elemental dataset. The conversion to oxide form represents a linear transformation and does not significantly affect statistical relationships after standardization. LOI was not included in the PCA.

3. Results

3.1. Physical-Chemical Characterization of Mining and Metallurgical Waste

The nine mining and metallurgical waste types defined in Section 2 exhibit pronounced physical–chemical heterogeneity resulting from differences in ore mineralogy, processing history, and post-depositional weathering intensity [22]. Table 2 summarizes the pH and density ranges obtained for each category. Although mean values provide a useful summary, those corresponding to waste types with a limited number of samples ($n \leq 3$) should be interpreted with caution, as they may not fully capture intra-category variability.

Table 2. Density and pH range. Values in parentheses represent mean values. Ranges are provided to illustrate the variability within each waste type.

Number	Types of Mining and Metallurgical Waste	pH Range	Solids Density (g/cm ³)	Dry Density (g/cm ³)	No. of Samples Characterized
1	Open pit spoils	4.1–6.5 (4.60)	2.71–3.01 (2.83)	1.89–2.14 (2.00)	5
2	Post-flotation waste (On Land)	2.5–7.5 (5.20)	2.69–3.1 (2.88)	1.88–2.35 (1.90)	26
3	Post-flotation waste (On Sea)	2.3–7.5 (6.80)	2.71–3.02 (2.88)	1.65–2.14 (1.90)	3
4	Gravity concentration spoils	2.0–7.5 (3.80)	2.56–3.01 (2.86)	1.79–2.42 (2.00)	21
5	Mine spoils	6.1–7.5 (6.90)	2.62–3.41 (3.10)	1.85–2.35 (2.00)	13
6	Gossan	6.5–8.0 (7.25)	2.61–2.95 (2.70)	1.90–2.10 (2.00)	2
7	Pre-concentration waste	4.1–6.4 (4.90)	2.85–3.45 (3.20)	1.95–2.25 (2.00)	3
8	Molten slag	5.1–5.6 (5.40)	3.56–4.51 (3.76)	2.99–3.19 (3.00)	3
9	Well borings	5.1–6.1 (5.80)	2.95–3.34 (3.10)	1.80–2.20 (2.00)	3
Total					79

pH values show a broad range from strongly acidic conditions (pH $\approx$ 2.0) in gravity concentration residues to near-neutral to slightly alkaline conditions (pH $\approx$ 8.0) in gossan materials. This variation reflects differences in sulphide content, oxidation state, and buffering capacity. Acidic conditions (pH $\leq$ 3) are typical of residues rich in pyrite and secondary Fe-sulphates, whereas near-neutral values occur in carbonate-bearing materials with effective buffering capacity [8–10].

Solids density also shows significant variability (2.6–3.8 g·cm^{−3}), reflecting differences in mineralogical composition, including silicates, sulphates, oxides, and metallurgical phases. Slag samples display the highest densities, consistent with Fe-rich and smelting-derived phases, whereas gossan and mine spoils show lower densities due to the dominance of goethite and weathered silicate minerals.

Post-flotation tailings deposited in marine environments exhibit the widest pH variability (2.3–7.5), reflecting intense weathering, high sulphide reactivity, and prolonged exposure to marine aerosols. Fine-grained (<1 mm) textures favour rapid oxidation and acid generation, whereas mixing with carbonate fragments locally promotes neutralization processes [8,9].

In contrast, mine spoils and gossan materials exhibit higher pH values and moderate densities, indicating advanced oxidation stages and effective buffering by carbonates and Fe oxyhydroxides. Gravity concentration residues, which retain higher proportions of primary sulphides, show persistently acidic behaviour.

Collectively, these results indicate that the CUMD wastes form a highly heterogeneous multi-material system in which pH and density variations are controlled by the combined effects of primary mineralogy, processing history, and weathering processes. These parameters play a key role in controlling metal mobility, secondary mineral formation, and the spatial distribution of critical raw materials discussed in subsequent sections.

3.2. Mineralogical Characterization

The mineralogical composition of the nine waste types (Table 3) reflects the complex interaction between primary ore assemblages, mineral processing techniques, and long-term weathering under semi-arid Mediterranean conditions [22,26]. Mineral identification was performed using quantitative X-ray diffraction (XRD), complemented by scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM-EDS). These complementary techniques enabled the identification of both major mineral phases and fine-grained accessory minerals, as well as the verification of textural relationships and secondary mineral associations relevant for critical raw material (CRM) retention.

The reported values correspond to mean mineral contents, while variability within each waste type reflects differences in source material, processing history, and degree of alteration. This variability is consistent with the inherently heterogeneous nature of mining and metallurgical wastes.

Silicates. Silicate minerals constitute the dominant phase assemblage across most waste types, ranging from 50 to 98 wt.%. Quartz, feldspars, muscovite, chlorite, and clinocllore are widely distributed and reflect the strong lithological control of the host rocks. High proportions of silicates in open-pit spoils and gravity concentration residues indicate limited upgrading during early mechanical processing stages. The occurrence of kaolinite and talc in several samples reflects hydrothermal alteration and supergene weathering processes typical of polymetallic sulphide districts.

Oxides. Oxide minerals occur in proportions between 1 and 19 wt.% and include hematite, magnetite, goethite, and Fe–Mn oxyhydroxides. These phases originate both from primary mineralization and from the oxidative weathering of sulphides. Goethite-rich materials, particularly in mine spoils and gossan deposits, exhibit a high capacity for metal scavenging and play a key role in controlling CRM mobility and retention [8–10]. The presence of cassiterite (SnO₂) and magnesioferrite in selected samples indicates the contribution of high-temperature metallurgical residues.

Sulphates. Secondary sulphates are abundant in several waste categories (up to 20 wt.%), especially in oxidized mine spoils. Jarosite-group minerals (plumbojarosite, natrojarosite, and hydronium jarosite), together with gypsum, anglesite, and beaverite, indicate advanced sulphide oxidation under acidic conditions. Their formation is consistent with prolonged exposure to meteoric waters and the semi-arid climatic conditions of the study area [21,22]. These phases play a critical role in the immobilization of elements such as Pb, Zn, As, and other trace components.

Table 3. Mineralogical composition (wt.%) of the different waste types (1-9). Values represent mean contents, with [standard deviation/ranges] indicating variability within each category. Waste categories are defined in Table 1.

Mineral *	General Formula	1	2	3	4	5	6	7	8	9
Silicates		52	82	79	68	94	61	98	92	42
Quartz	SiO ₂	19	29	12	30	37	30	48		30
Muscovite	(K,Na)(Al,Mg,Fe) ₂ (Si _{3.1} Al _{0.9})O ₁₀ (OH) ₂	14	36	17	27	43		2		5
Clinochlore	(Mg,Fe) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	8	12	30	6	1			4	3
Chlorite	(Mg,Al) ₆ (Si,Al) ₄ O ₁₀ (OH) ₈	11	1			9		46		4
Edenite	NaCa ₂ Mg ₅ AlSi ₇ O ₂₂ (OH) ₂		2		3					
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄		1	10	1	4	25	2		
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂		1	6	1					
Magnesian fayalite	Mg _{0.3} Fe _{1.7} (SiO ₄)								88	
Greenalite	Fe ₆ Si ₄ O ₁₀ (OH) ₈			4			6			
Albite	Na(AlSi ₃ O ₈)									
Clinocrysotile	Mg ₃ (Si ₂ O ₅)(OH) ₄									
Sulphates		16	11	1	23	5	20	1	2	19
Gypsum	CaSO ₄ ·2H ₂ O	2	6	1	11	1	9			
Plumbojarosite	Pb(Fe ₃ (OH) ₆ (SO ₄) ₂) ₂	1	2		9	3	5			19
Hydronium jarosite	(H ₃ O)Fe ₃ (SO ₄) ₂ (OH) ₆	12	1		1	1				
Natrojarosite	NaFe ₃ (SO ₄) ₂ (OH) ₆		2		1			1		
Beaverite (Zn)	Pb(Fe ³⁺ ₂ Zn)(SO ₄) ₂ (OH) ₆		1							
Anglesite	Pb(SO ₄)						6		2	
Aluminite	Al ₂ (SO ₄)(OH) ₄ ·7H ₂ O				1					
Carbonates		20	2	11	1					32
Dolomite	CaMg(CO ₃) ₂	14		2						27
Calcite	CaCO ₃	1	2	5	1					1
Siderite	FeCO ₃			4						
Smithsonite	ZnCO ₃	5								5
Cerussite	PbCO ₃									
Zinc and aluminium hydroxide carbonate hydrate	(Zn _{0.65} Al _{0.35} (OH) ₂)(CO ₃)0.167(H ₂ O)0.499									
Oxides		10	4	5	6	1	19	1	2	7
Goethite	FeO(OH)	10	3	2	4	1	15	1		5
Magnesioferrite	MgFe ₂ O ₄		1	2	1					
Hematite	Fe ₂ O ₃			1	1		4			2
Cassiterite	SnO ₂								2	
Sulphides			1	3					4	
Sphalerite	ZnS		1	2						
Galena	PbS		1							
Pyrite	FeS ₂									
Elements		1			1					
Sulphur	S ₈	1			1					

* Phase minerals detected by powder X-ray diffraction in the nine types of mine and metallurgical waste analysed. Contents (wt.%) are semiquantitative estimates of the crystalline fraction of the sample, based on the relative intensity ratio (RIR) method.

Carbonates. Carbonate minerals range from 0 to 32 wt.% and include calcite, dolomite, smithsonite, and cerussite. Their presence indicates effective buffering of acid-generating reactions and the development of supergene Pb–Zn enrichment zones. Carbonate-rich domains correspond to neutralization fronts, explaining the higher pH values observed in Section 3.1.

Sulphides. Residual sulphides (0–4 wt.%) persist mainly as pyrite, sphalerite, and galena. These are particularly preserved in post-flotation tailings deposited in marine environments, where anoxic and saturated conditions limit oxidation. In contrast, terres-

trial tailings show significantly lower sulphide contents due to prolonged exposure to atmospheric oxygen. Despite their relatively low abundance, these sulphides remain the primary carriers of Cu, Ni, Co, Zn, As, and Sb.

Interpretation and link to CRM distribution. The mineralogical dataset confirms that the Cartagena–La Unión mining wastes form a highly heterogeneous multi-mineral system in which CRM distribution is controlled by several key mineralogical hosts. Silicate phases (Al–Si-rich minerals) are associated with the retention of Ga, Nb, and Y; Fe–Mn oxyhydroxides act as major sinks for As, Sb, V, and REE proxies through adsorption processes; jarosite-group sulphates and related secondary phases host Pb, Zn, Cu, As, and Sb under acidic conditions; and residual sulphides represent the primary sources of base metals such as Cu, Ni, Co, and Zn. These mineralogical controls provide the fundamental framework for interpreting the geochemical patterns observed in subsequent statistical and multivariate analyses.

3.3. Bulk Chemical Composition and CRM Distribution

The chemical composition of the nine mining and metallurgical waste types (Table 4) reflects the combined influence of primary ore mineralogy, beneficiation processes, metallurgical treatment, and secondary weathering processes. In agreement with the format adopted in Table 4, bulk compositions are expressed as major oxides (wt.%) together with loss on ignition (LOI), whereas trace and critical elements are presented separately in Table 5. The observed compositional variability is closely linked to waste typology, mineralogical hosts, and post-depositional alteration processes [22,26].

The major components are predominantly SiO_2 , Al_2O_3 , and Fe_2O_3 , although their relative abundance varies markedly among waste categories. SiO_2 reaches maximum values of 78.09 wt.% in open-pit spoils and remains high in several waste groups, reflecting the abundance of quartz, feldspars, muscovite, and chlorite identified in Section 3.2. Al_2O_3 attains values up to 23.18 wt.% in mine spoils and is mainly associated with clay minerals, micas, feldspars, and aluminosilicate alteration products. MgO and CaO are locally enriched in carbonate-bearing materials and Mg-rich silicates, whereas TiO_2 occurs consistently at low concentrations (≤ 1.02 wt.%), reflecting its association with resistant Ti-bearing silicates and oxide phases.

Fe_2O_3 is one of the dominant constituents in several waste categories and, in some residues, represents the principal oxide fraction. Mean values range from 24.87 wt.% in open-pit spoils to 62.94 wt.% in pre-concentration waste, with maxima exceeding 70 wt.% in selected samples. This enrichment reflects the abundance of goethite, hematite, jarosite-group minerals, ferruginous secondary phases, and residual Fe-bearing sulphides.

SO_3 exhibits significant concentrations, particularly in gravity concentration spoils (mean 8.17 wt.%; maximum 15.23 wt.%) and post-flotation land deposits (mean 7.79 wt.%), indicating the widespread occurrence of secondary sulphates such as gypsum, plumbojarosite, hydronium jarosite, and natrojarosite formed during sulphide oxidation under supergene conditions [22,26].

P_2O_5 , MnO, and other minor oxides occur at lower concentrations and are related to accessory phosphate minerals, Fe–Mn oxides, and lithogenic detrital inputs. LOI values range from 0.60 to 10.02 wt.% and mainly reflect the presence of structurally bound water, hydroxides, hydrated sulphates, minor organic matter, and carbonate decomposition during ignition. The highest LOI values occur in strongly weathered and sulphate-rich materials, consistent with intense secondary alteration.

Trace metals and critical raw materials (CRMs), as defined under the European Critical Raw Materials Act (2023) [1], are present across multiple waste categories (Table 5). Cobalt and nickel typically occur in the range of 0.004–0.02 wt.% and are associated with

Fe–Mn oxyhydroxides, secondary sulphates, and silicate matrices. Copper and zinc display significant variability, with locally elevated concentrations in flotation-derived residues, reflecting the presence of residual sulphides and their oxidation products. Gallium, niobium, and yttrium, although generally present at low concentrations (<0.12 wt.%), are consistently detected and are mainly associated with fine-grained silicates, Fe oxyhydroxides, and secondary sulphate phases. Barium and cerium occur more sporadically, reflecting contributions from accessory minerals such as barite and REE-bearing phases, as well as adsorption onto Fe–Mn oxides.

Table 4. Bulk chemical composition of the different mining and metallurgical waste types expressed as major oxides (wt.%) and loss on ignition (LOI). For each waste category, values are reported as maxim, minimum, mean, and standard deviation. No: number of samples. Waste categories are defined in Table 1.

WASTE		No.	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	ZnO	PbO	LOI
Open pit spoils	Max	5	5.16	16.60	78.09	0.11	4.97	1.70	1.79	0.53	1.27	27.25	2.55	0.47	5.89
	Min	5	0.21	1.98	2.80	0.02	3.42	1.22	1.51	0.03	0.74	21.76	1.39	0.93	5.21
	Mean	5	2.12	6.33	29.66	0.06	3.89	1.47	1.67	0.24	0.89	24.87	1.72	0.65	5.38
	SD	5	1.95	6.14	30.79	0.04	0.94	0.19	0.11	0.20	0.26	2.07	0.48	0.18	0.55
Post-flotation (land)	Max	26	3.71	18.28	34.80	0.33	8.94	2.53	9.79	0.73	1.68	53.02	1.97	1.30	9.10
	Min	26	0.23	1.88	10.80	0.04	6.39	0.01	0.95	0.11	0.55	26.75	1.23	0.54	5.25
	Mean	26	2.04	10.57	24.56	0.08	7.79	0.77	2.99	0.39	1.15	38.05	1.48	0.77	6.68
	SD	26	0.93	4.31	6.28	0.06	0.68	0.65	1.79	0.13	0.39	6.51	0.25	0.36	0.95
Post-flotation (on sea)	Max	3	4.58	15.70	36.81	0.14	6.42	1.65	6.11	0.35	1.38	47.43	2.12	0.70	6.10
	Min	3	2.90	5.35	29.22	0.09	2.60	0.80	3.15	0.23	1.23	34.80	1.56	0.33	5.90
	Mean	3	3.89	10.38	32.48	0.12	4.68	1.30	4.19	0.29	1.30	40.14	1.88	0.56	6.00
	SD	3	0.88	5.18	3.91	0.02	1.93	0.45	1.67	0.06	0.11	6.54	0.29	0.20	0.14
Gravity concentration spoils	Max	21	4.15	20.70	51.61	0.17	15.23	1.45	1.90	1.02	1.44	50.69	1.97	2.26	8.95
	Min	21	0.07	0.96	3.59	0.00	4.97	0.01	0.36	0.07	0.47	30.65	1.23	1.12	2.35
	Mean	21	1.19	8.18	23.05	0.09	8.17	0.32	1.22	0.42	0.94	41.30	1.21	1.78	6.04
	SD	21	1.17	5.72	14.48	0.05	2.10	0.33	0.42	0.27	0.32	5.52	0.27	0.33	1.84
Mine spoils	Max	13	6.10	23.18	64.02	0.17	6.99	1.25	2.64	0.91	0.11	38.40	1.47	1.10	9.20
	Min	13	0.41	10.20	25.90	0.08	3.20	0.04	0.55	0.48	0.02	21.74	1.32	0.27	5.69
	Mean	13	1.91	14.84	44.15	0.13	4.54	0.74	1.53	0.72	0.05	27.89	1.66	0.80	7.69
	SD	13	1.93	3.44	9.43	0.03	1.01	0.43	0.56	0.12	0.03	4.69	0.38	0.23	1.14
“False” gossan	Max	2	4.97	7.14	37.03	0.12	1.37	0.13	0.91	0.39	1.68	44.64	1.22	2.24	10.02
	Min	2	2.78	5.98	30.80	0.09	1.32	0.06	0.76	0.37	1.08	44.00	0.90	1.63	9.85
	Mean	2	3.88	6.56	33.91	0.10	1.35	0.10	0.83	0.38	1.38	44.32	1.06	1.93	9.94
	SD	2	1.55	0.82	4.40	0.02	0.04	0.05	0.11	0.02	0.43	0.45	0.23	0.43	0.12
Pre-concentracion waste	Max	3	6.14	15.31	47.85	0.20	5.97	0.54	0.92	0.59	2.12	70.52	0.72	1.26	4.98
	Min	3	1.74	2.53	26.50	0.05	4.87	0.04	0.55	0.27	0.26	57.46	0.45	1.06	3.86
	Mean	3	4.27	9.76	36.34	0.14	5.39	0.28	0.73	0.48	0.90	62.94	0.56	1.15	4.35
	SD	3	2.27	6.55	10.77	0.08	0.55	0.25	0.19	0.18	1.05	6.78	0.14	0.10	0.57
Molten slag	Max	3	3.53	5.74	29.41	0.09	5.94	0.75	1.66	0.38	1.38	62.32	1.98	2.91	2.10
	Min	3	0.74	5.12	23.23	0.07	3.70	0.30	1.09	0.22	1.06	52.84	1.56	2.14	0.60
	Mean	3	1.85	5.50	25.70	0.08	4.90	0.50	1.36	0.30	1.20	57.50	1.76	2.45	1.30
	SD	3	1.48	0.33	3.27	0.01	1.13	0.23	0.29	0.08	0.17	4.74	0.21	0.40	0.75
Well borings	Max	3	8.17	18.61	42.91	0.21	5.47	1.90	1.71	0.68	1.19	30.08	2.66	0.51	5.41
	Min	3	1.34	1.75	3.36	0.02	4.94	0.00	1.20	0.09	0.77	27.07	1.89	0.31	5.01
	Mean	3	5.14	8.78	23.54	0.10	5.14	1.04	1.41	0.39	0.98	28.42	2.35	0.40	5.20
	SD	3	3.48	8.77	19.79	0.09	0.28	0.96	0.26	0.30	0.21	1.53	0.41	0.10	0.20

Metalloids such as arsenic and antimony show strong spatial variability, consistent with their association with sulphide minerals (e.g., arsenopyrite and tetrahedrite-tennantite) and secondary sulphate phases. Elevated As concentrations in specific samples indicate advanced sulphide oxidation, followed by remobilization under acidic conditions and subsequent retention by Fe–Mn oxyhydroxides [8–10].

Table 5. Concentration of trace and critical elements in the different mining and metallurgical waste types (ppm). For each waste category, values are reported as maximum, minimum, and mean. No: number of samples. Waste categories are defined in Table 1.

Wastes	No.		V	Co	Ni	Cu	Ga	As	Sr	Y	Nb	Sb	Ba	Ce
1	5	Max	56	1160 *	100	467	0	2040	210	0	0	220	400	0
	5	Min	0	0	0	18	0	0	0	0	0	0	0	0
	5	Mean	31	268	20	282	0	550	107	0	0	66	80	0
2	26	Max	267	222	107	1190	33	3650	486	47	21	250	400	75
	26	Min	0	0	0	137	0	360	22	0	0	0	0	0
	26	Mean	91	67	26	331	8	1116	121	7	3	75	109	3
3	3	Max	46	42	26	300	0	817	900	0	0	110	120	0
	3	Min	0	0	0	123	0	100	56	0	0	0	0	0
	3	Mean	15	14	9	208	0	472	352	0	0	37	40	0
4	21	Max	170	118	55	1060	13	4690	252	0	25	1210	546	110
	21	Min	0	0	0	100	0	200	0	0	0	0	0	0
	21	Mean	79	46	14	372	2	1403	84	0	3	154	72	9
5	13	Max	180	81	51	459	29	1450	100	0	28	0	866	180
	13	Min	0	0	0	72	0	0	36	0	0	0	0	0
	13	Mean	121	26	26	220	9	523	66	0	14	0	267	14
6	2	Max	660	51	0	400	0	900	100	0	0	220	0	0
	2	Min	0	0	0	400	0	0	39	0	0	0	0	0
	2	Mean	330	26	0	400	0	450	70	0	0	110	0	0
7	3	Max	110	0	0	0	0	0	0	0	0	0	0	0
	3	Min	0	0	0	0	0	0	0	0	0	0	0	0
	3	Mean	70	0	0	0	0	0	0	0	0	0	0	0
8	3	Max	78	71	0	500	0	683	200	0	0	1100	5200	0
	3	Min	0	0	0	191	0	0	28	0	0	0	0	0
	3	Mean	40	36	0	320	0	228	132	0	0	367	1946	0
9	3	Max	89	50	223	413	12	2220	178	0	0	788	500	0
	3	Min	0	0	0	200	0	100	86	0	0	0	0	0
	3	Mean	30	25	85	289	4	1058	121	0	0	424	167	0

* The Co anomaly in waste 1 is due to the presence of an anomalous concentration of the sulphated efflorescence Hydroniojarosite (37%) which acts as a sink for divalent and trivalent metals and contains an important percentage of goethite (3%) Fe oxides with high adsorption capacity. It should also be noted that this is a sample that has not undergone any metallurgical process but is the result of manual separation [22].

A notable geochemical anomaly is observed for Co in sample B-EM23 (open-pit spoil), where concentrations are significantly higher than in the rest of the dataset. This enrichment correlates with the high abundance of hydronium jarosite (~37 wt.%) and subordinate goethite (~3 wt.%). Jarosite-group minerals are well-known sinks for divalent and trivalent metals, facilitating the incorporation and retention of Co, Ni, Zn, and Ga during advanced stages of sulphide oxidation [26,27]. The absence of metallurgical processing in this material likely preserves this geochemical signature, enhancing its distinctiveness.

Overall, the chemical dataset indicates that waste composition is controlled by the combined effects of primary mineralization and secondary geochemical processes. Primary ore assemblages (Pb–Zn–Fe sulphides and silicate gangue) define baseline concentrations of major and base metals, whereas secondary processes such as oxidation, dissolution–precipitation, and adsorption redistribute elements into oxyhydroxides, carbonates, and sulphates. This dual control explains the coexistence of a silicate-dominated matrix with localized enrichments in base metals and CRM proxies, providing the geochemical basis for the statistical and spatial analyses presented in subsequent sections.

3.4. Statistical Analyses

The statistical analysis reveals a well-defined geochemical structuring across the different waste types, reflecting the combined influence of primary mineralization, processing history, and secondary weathering processes.

To illustrate the statistical distribution of the dataset, histograms of representative elements (Si, Cu, As, and Ga) were constructed (Figure 3). These elements were selected to represent the main geochemical controls identified in this study, including lithogenic inputs, sulphide mineralization, and secondary adsorption processes.

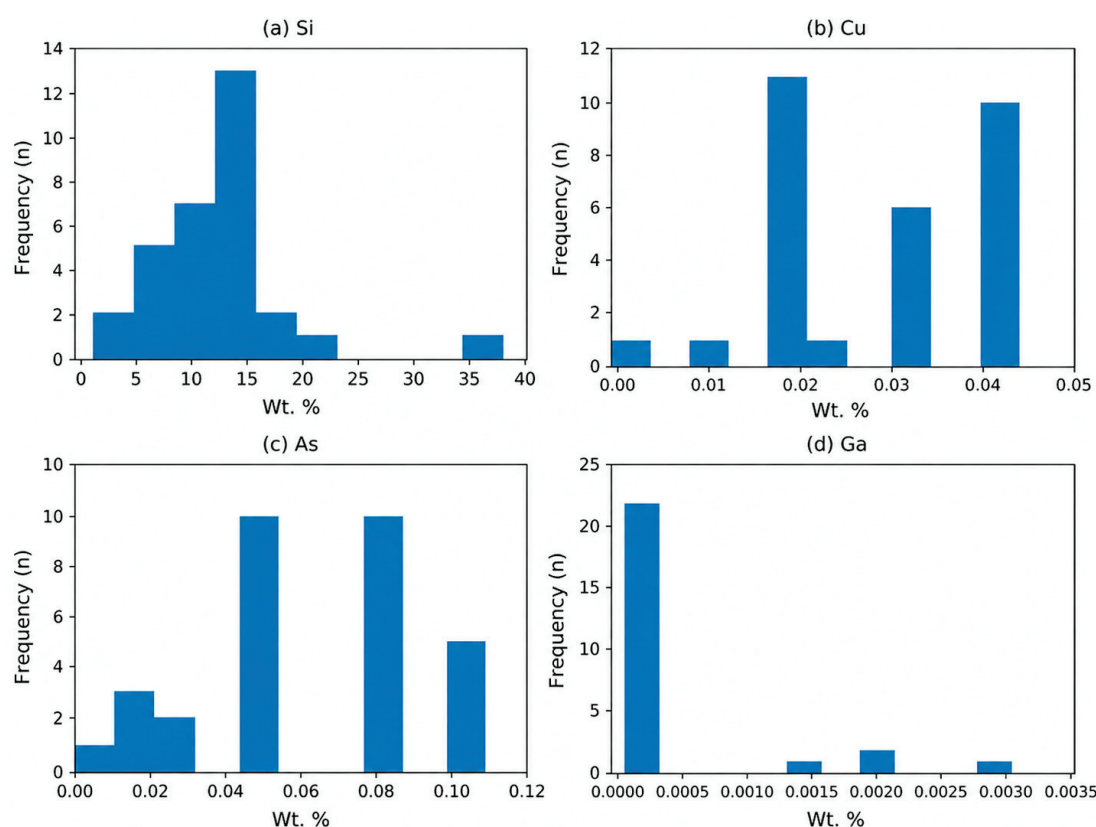


Figure 3. Histograms showing the frequency distribution of representative elements across the studied mine and metallurgical wastes: (a) Si, (b) Cu, (c) As, and (d) Ga. These elements illustrate the main geochemical controls identified in the statistical analysis, including lithogenic, sulphide-derived, and secondary enrichment processes.

Silicon (Si) exhibits a broad distribution, reflecting the heterogeneous contribution of silicate-rich materials and the variability of lithological sources across the different waste types. In contrast, Cu shows a more clustered distribution, with values concentrated within a relatively narrow range, indicating strong control by mineral processing and sulphide-derived phases.

Arsenic (As) displays a markedly skewed distribution with pronounced high-value tails, indicating localized enrichment associated with sulphide oxidation and secondary mineral formation. This behaviour highlights the presence of extreme values and supports the application of transformation techniques, such as the Box–Cox transformation, to improve data normality prior to multivariate analysis.

Gallium (Ga) exhibits a discontinuous distribution characterized by a high proportion of low or near-zero values, reflecting its selective enrichment and complex geochemical behaviour. This pattern is consistent with its association with secondary phases, particularly Fe–Mn oxyhydroxides, as identified in the PCA.

These distribution patterns confirm the non-normal nature of the dataset and justify the use of robust statistical measures, such as the Median Absolute Deviation (MAD), together with data transformation and standardization prior to multivariate analysis.

Correlation analysis indicates consistent associations between key elements, particularly among Cu–As–Sb and Fe–Mn-related trace elements, suggesting common mineralogical hosts and shared geochemical behaviour. These relationships are consistent with sulphide-derived phases and secondary Fe–Mn oxyhydroxides described in Section 3.2, which act as major sinks for trace elements through adsorption and co-precipitation processes [28,29].

Principal Component Analysis (PCA) further supports these patterns by identifying distinct geochemical associations corresponding to lithogenic, sulphide-derived, and secondary oxidation–adsorption processes (Table 6, Figure 4). The first components explain a substantial proportion of the total variance, indicating that a limited number of dominant processes control element distribution. PCA has been widely applied in geochemical studies to identify underlying controls in complex environmental datasets [29,30].

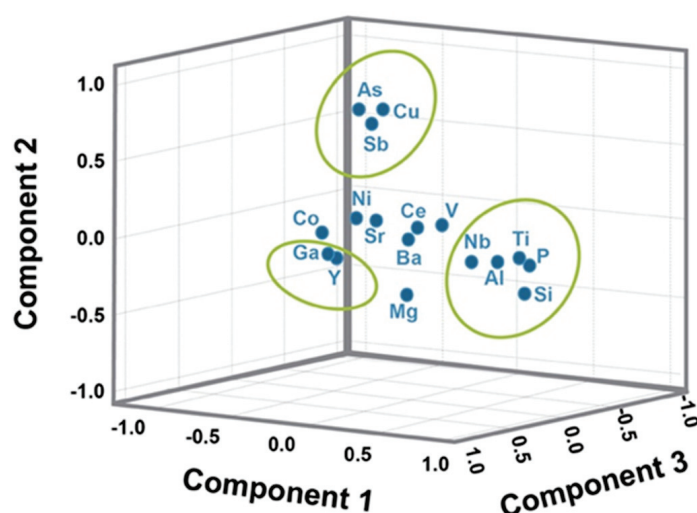


Figure 4. Principal Component Analysis (PCA) biplot showing the distribution of samples and elemental loadings along PC1 and PC2. The plot illustrates the main geochemical controls on element distribution, with separation between lithogenic (Al–Si–Ti), sulphide-derived (Cu–As–Sb), and Fe–Mn-related secondary associations. The first two components explain the majority of the total variance. Green circles indicate grouped samples with similar geochemical signatures, highlighting clusters associated with distinct waste types and geochemical processes.

Hierarchical Cluster Analysis (HCA) groups samples according to their geochemical affinity, broadly corresponding to different waste types and processing histories. These clusters reflect variations in mineralogical composition and degrees of alteration, reinforcing the interpretation of multiple geochemical controls [29].

The statistical results demonstrate that the distribution of critical raw materials is governed by the combined effects of lithological factors, sulphide mineralization, and secondary oxidation–adsorption processes. Similar patterns of compositional variability and heterogeneity have been reported in mine-waste systems, where geochemical distributions are controlled by depositional processes, mineralogical composition, and weathering intensity [31–33].

Table 6. Principal Component Analysis (PCA) loadings and percentage of explained variance. Only the most significant components (PC1–PC3) are shown, as they account for the majority of the total variance.

Element	PC1	PC2	PC3
Si	0.82		
Al	0.79		
Ti	0.75		
Nb	0.68		
Cu		0.76	
As		0.74	
Sb		0.71	
Fe			0.72
Mn			0.69
Ga			0.65
Y			0.63
% Variance	38%	22%	15%
Cumulative	38%	60%	75%

3.5. Correlation Matrix

The correlation matrix reveals well-defined associations between elements, reflecting common mineralogical hosts and shared geochemical behaviour across the different waste types.

Strong positive correlations are observed among Cu, As, and Sb, indicating their close association with sulphide-derived phases and their oxidation products. This grouping is consistent with the presence of primary sulphide minerals and secondary sulphates identified in Section 3.2. Similarly, significant correlations between Fe, Mn, and several trace elements highlight the key role of Fe–Mn oxyhydroxides as major geochemical sinks controlling the retention and redistribution of metals through adsorption and co-precipitation processes.

In contrast, elements such as Al, Si, and Ti show consistent positive correlations, reflecting their lithogenic origin and association with silicate mineral phases. These elements exhibit limited correlation with sulphide-related components, indicating a clear separation between lithogenic and metalliferous geochemical domains within the waste materials.

Other elements display weaker or more variable correlations, suggesting partial decoupling driven by secondary processes such as weathering, dissolution–precipitation reactions, and adsorption onto secondary mineral phases. This variability reflects the complex post-depositional evolution of the waste deposits and the superposition of multiple geochemical processes.

The correlation structure supports a multi-process control on element distribution, dominated by lithogenic inputs, sulphide mineralization, and secondary oxidation–adsorption processes. These relationships are consistent with the mineralogical observations described in Section 3.2 and provide the basis for the multivariate associations identified in the PCA (Section 3.6).

3.6. Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was performed to identify the main geochemical associations within the dataset (Table 7, Figure 4). A Varimax rotation was applied to improve interpretability by maximizing the variance of squared loadings within each component, thereby enhancing the separation of variables into distinct groups. This orthogonal rotation reduces overlap between components and facilitates a clearer identification of geochemical associations and underlying processes. In this study, the application of Varimax rotation enables the discrimination between lithogenic, sulphide-derived, and

secondary oxidation–adsorption controls, leading to a more robust and geologically meaningful interpretation of the PCA results [24,29].

Table 7. Rotated component matrix (rotation method: Varimax with Kaiser normalization). Only the first principal components are interpreted, as higher-order components explain a minor proportion of the total variance.

	Components						
	1	2	3	4	5	6	7
Mg	0.001	−0.446	−0.069	0.661	−0.354	−0.145	0.041
Al	0.856	−0.087	0.272	0.053	0.022	0.070	0.082
Si	0.753	−0.351	−0.128	0.013	0.097	0.145	0.011
P	0.849	−0.146	−0.026	−0.057	−0.117	−0.172	0.154
Ti	0.830	−0.094	0.042	−0.111	0.302	0.066	0.088
V	0.378	0.079	0.137	0.028	0.515	−0.244	0.024
Co	−0.409	−0.041	0.142	−0.389	0.294	−0.176	0.159
Ni	−0.102	0.105	0.269	0.801	0.212	−0.050	0.040
Cu	−0.109	0.769	−0.008	0.029	−0.112	0.194	0.345
Ga	0.091	−0.032	0.807	0.251	0.278	0.194	−0.001
As	−0.267	0.740	−0.015	−0.250	0.050	−0.230	−0.186
Sr	−0.086	0.045	0.079	0.004	−0.715	0.018	−0.041
Y	0.133	−0.069	0.784	−0.062	−0.338	−0.228	−0.069
Nb	0.666	−0.122	0.253	0.007	0.298	0.076	−0.239
Sb	−0.333	0.615	−0.215	0.336	0.031	−0.179	−0.182
Ba	0.074	−0.050	−0.004	−0.072	−0.098	0.872	−0.041
Ce	0.101	0.007	−0.043	0.012	0.077	−0.049	0.907

The PCA results show that the first three principal components account for most of the total variance (75%), indicating that geochemical variability is controlled by a limited number of dominant processes (Table 7). Higher-order components (PC4–PC7), which explain only a minor proportion of the variance, are interpreted with caution as they likely represent residual variability rather than meaningful geochemical controls.

The first principal component (PC1) is characterized by strong positive loadings of Al, Si, Ti, and Nb, reflecting a lithogenic control associated with silicate mineral phases. This component represents the influence of the host-rock composition on the waste materials.

The second principal component (PC2) shows high loadings of Cu, As, and Sb, indicating a sulphide-derived association linked to primary mineralization and its oxidation products. This component reflects the contribution of metalliferous sulphide phases and their subsequent geochemical transformation.

The third principal component (PC3) is mainly associated with Ga and Y, suggesting a strong influence of Fe–Mn oxyhydroxides and secondary adsorption processes. Although Fe and Mn are key constituents of these phases, their loadings are distributed across multiple components, reflecting their complex geochemical behaviour. In contrast, cobalt (Co) exhibits a partially decoupled behaviour in the PCA space. This can be explained by its multi-source geochemical affinity, as Co may be associated with primary sulphide phases, secondary sulphates (e.g., jarosite-group minerals), and Fe–Mn oxyhydroxides. This results in a more dispersed distribution and prevents a strict grouping with Ga and Y.

The PCA biplot (Figure 4) provides a clear visualization of the relationships between samples and elemental loadings. Samples are distributed according to their dominant geochemical signatures, showing a clear separation along PC1 and PC2. The projection of variables indicates that elements grouped in the same direction are positively correlated and share common mineralogical hosts, whereas opposite directions reflect contrasting geochemical behaviours, in agreement with the correlation matrix (Section 3.5).

Distinct geochemical domains can be identified in the biplot. Samples enriched in lithogenic elements (Al–Si–Ti) cluster along the positive side of PC1, reflecting a strong silicate control. In contrast, samples associated with sulphide-derived elements (Cu–As–Sb) are grouped along PC2, indicating the influence of primary mineralization and oxidation processes. A third domain, related to Fe–Mn oxyhydroxides, occupies an intermediate or orthogonal position, reflecting secondary adsorption processes and metal redistribution.

Overall, the PCA results demonstrate that the distribution of critical raw materials in the studied wastes is controlled by the combined influence of lithogenic inputs, sulphide mineralization, and secondary oxidation–adsorption processes, in agreement with the correlation analysis (Section 3.5) and mineralogical observations (Section 3.2).

3.7. Hierarchical Clusters

Hierarchical Cluster Analysis (HCA) was performed to classify the 79 samples into geochemically coherent groups. The analysis was conducted using z-score standardized variables, Euclidean distance, and Ward’s minimum variance method, which is well suited for multielement geochemical datasets as it produces compact and internally homogeneous clusters. Cluster robustness was assessed using the cophenetic correlation coefficient (0.86), indicating a good representation of the data structure.

Three major clusters were identified (Figure 5), each corresponding to distinct mineralogical and geochemical signatures consistent with the waste typology and processing history of the Cartagena–La Unión district.

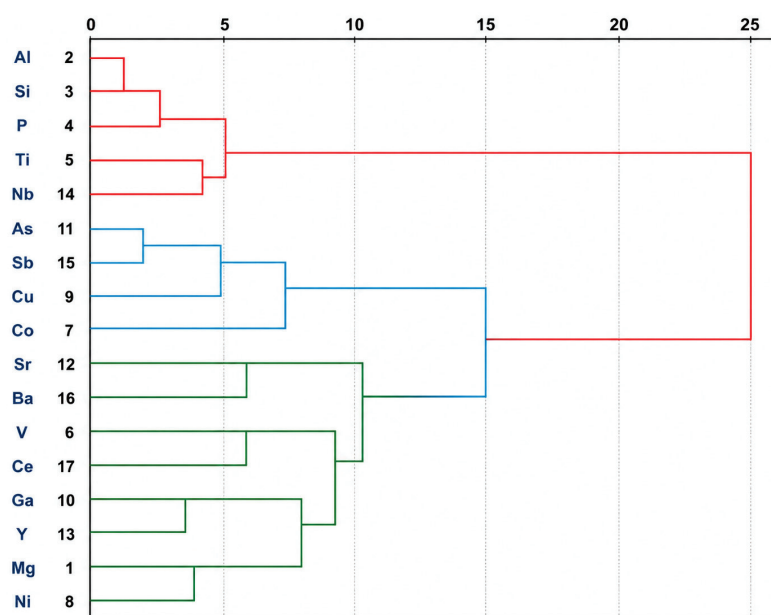


Figure 5. Hierarchical cluster dendrogram showing the grouping of samples based on multielement geochemical composition. The dendrogram highlights the separation into three main clusters corresponding to lithogenic, sulphide-derived, and oxidized transitional systems. Blue lines represent transitional systems, red lines correspond to lithogenic clusters, and green lines indicate oxidized transitional systems.

Cluster 1 comprises silicate-dominated lithogenic materials, including mine spoils, gossan, and mixed silicate-rich residues. These samples are characterized by high concentrations of Al, Si, Ti, Nb, and Y, and low contents of Cu, As, and Sb. The mineralogical assemblage is dominated by quartz, feldspars, muscovite, chlorite, and clay minerals such as kaolinite and talc. This group reflects materials largely controlled by host-rock composition and advanced weathering, with limited influence of sulphide mineralization.

Its geochemical signature closely corresponds to PCA Component 1, confirming a dominant lithogenic control and the retention of high field strength elements (HFSE) in silicate matrices and associated oxides.

Cluster 2 groups sulphide-derived and metalliferous residues, including flotation tailings, slag-related materials, and pre-concentration wastes. These samples are enriched in Cu, As, Sb, Co, Ni, and other chalcophile elements. The mineralogical assemblage includes residual sulphides (e.g., pyrite, chalcopyrite, galena, sphalerite), together with secondary phases such as jarosite-group minerals and Fe–Mn oxyhydroxides. This group reflects environments strongly influenced by sulphide mineralization and subsequent oxidation processes, including dissolution–precipitation and co-precipitation reactions. The strong correspondence with PCA Component 2 highlights this group as the most relevant in terms of critical raw material (CRM) enrichment and recovery potential.

Cluster 3 represents oxidized transitional materials, including partially weathered flotation tailings and carbonate-influenced residues. These samples show intermediate concentrations of Mg, Ca, Zn, Ga, Y, and locally Co, together with moderate levels of As and Sb. The mineralogical composition includes calcite, dolomite, smithsonite, cerussite, gypsum, jarosite, and Fe–Mn oxyhydroxides. This group reflects systems affected by neutralization processes and secondary mineral formation, where adsorption onto Fe–Mn phases plays a key role in trace element retention. The association of Ga and Y is consistent with PCA Component 3, supporting their linkage to secondary adsorption mechanisms.

4. Discussion

4.1. Quantitative Comparison Between Residues and Typical World Ore Grade

To evaluate the potential of the Cartagena–La Unión mining and metallurgical wastes as secondary raw-material resources, metal concentrations were systematically compared with representative global ore grades reported by the USGS (2022–2023) and recent international compilations of production and cut-off grades [3,18,34–41]. This comparison provides a robust benchmarking framework to assess the relative resource significance of the studied wastes in the context of both primary deposits and reprocessing operations.

For each element, mean, median, and maximum concentrations across the nine waste categories were normalized to wt.% to ensure consistency. The results demonstrate that several elements reach concentrations comparable to, or approaching, those of economically exploited ores and secondary resources.

Gallium (Ga) exhibits concentrations of up to 0.12 wt.%, significantly exceeding typical values reported for primary Ga sources (generally <0.01 wt.%). This enrichment highlights the strong potential of these residues as unconventional Ga resources. Similarly, yttrium (Y) and niobium (Nb) occur within the lower range of exploitable deposits (0.005–0.03 wt.%), supporting their relevance as secondary sources, particularly in fine-grained and oxide-rich materials.

Cobalt (Co) concentrations (0.004–0.02 wt.%) approach the lower bound of typical ore grades (0.01–0.10 wt.%). Although generally below primary deposit levels, these values fall within the range reported for tailings reprocessing and secondary recovery operations, reinforcing their potential economic relevance under optimized processing conditions.

Base metals such as Cu and Zn remain below typical primary ore grades (Cu: 0.3–1.0 wt.%; Zn: 3–10 wt.%), yet their concentrations are comparable to those currently processed in low-grade tailings reprocessing projects. This suggests that, while not viable as standalone targets, these elements may contribute significantly as by-products within integrated recovery flowsheets.

Elevated concentrations of As and Sb (0.02–0.6 wt.%) reflect the abundance of sulphosalt and sulphide-derived mineral phases. Although not primary economic targets, these

elements represent both a potential resource and a critical metallurgical and environmental constraint that must be addressed in any recovery strategy.

The observed enrichment patterns are consistent with the geochemical controls identified in Sections 3.4–3.7, where lithogenic inputs, sulphide mineralization, and secondary adsorption processes—particularly onto Fe–Mn oxyhydroxides—govern element distribution. The preferential association of Ga, Y, and Nb with fine-grained and secondary mineral phases explains their relative enrichment in specific waste types.

Overall, the comparison demonstrates that several waste categories contain concentrations of critical raw materials (CRMs) that are competitive within the context of secondary resource development. While most elements occur at sub-economic levels relative to primary deposits, their concentrations fall within ranges currently considered viable for reprocessing under favourable technological and economic conditions.

These results position the Cartagena–La Unión mining district as a promising secondary resource system, aligned with the objectives of the European Critical Raw Materials Act (2023) [1], which promotes the recovery of strategic elements from unconventional sources [1].

4.2. Economic Potential of CRMs in the CUMD

The economic potential of critical raw materials (CRMs) in the Cartagena–La Unión Mining District (CUMD) was evaluated by integrating concentration data, mineralogical controls, conceptual recovery pathways, and indicative market values. Although a full techno-economic assessment is beyond the scope of this study, this analysis provides a robust framework for assessing the relative economic relevance of Co, Ga, Nb, and Y as CRM proxies.

The studied residues exhibit concentrations of several CRMs that approach or exceed typical grades reported for secondary resources [36–39]. Gallium (0.008–0.12 wt.%) shows particularly significant enrichment, exceeding typical concentrations of primary Ga sources and comparable to those reported in Zn-processing residues and bauxite-derived materials. Yttrium (0.005–0.030 wt.%) and niobium (0.005–0.025 wt.%) occur within the lower range of exploitable secondary deposits, while cobalt (0.004–0.020 wt.%) approaches cut-off grades reported for tailings reprocessing in Cu–Co systems.

These concentration ranges are consistent with the geochemical patterns identified in Sections 3.4–3.7, where CRM enrichment is controlled by lithogenic inputs, sulphide mineralization, and secondary adsorption processes. In particular, the association of Ga, Nb, and Y with Fe–Mn oxyhydroxides and fine-grained silicate phases suggests preferential concentration in reactive secondary mineral assemblages, which are favourable for hydrometallurgical extraction.

The mineralogical framework described in Section 3.2 indicates that hydrometallurgical routes—such as acid leaching, selective precipitation, and solvent extraction—are more suitable than pyrometallurgical approaches for CRM recovery in the CUMD. Cobalt exhibits a more complex behaviour due to its multi-phase association with sulphides, secondary sulphates (e.g., jarosite-group minerals), and Fe–Mn oxyhydroxides, which may require selective or staged extraction strategies.

Based on representative market values (LME and USGS averages for 2023–2024) [37], Ga represents the highest-value element, followed by Co, Nb, and Y. Despite relatively low bulk concentrations compared to primary ores, conceptual recovery efficiencies in the range of 30–60% indicate that the potential metal value per tonne of residue may be significant, particularly when integrated into multi-metal recovery flowsheets.

The integration of geochemical, mineralogical, and spatial data (Sections 3.6 and 3.7) indicates that the highest CRM potential is associated with: (i) post-flotation tailings, partic-

ularly marine deposits enriched in Ga–Y–Nb, (ii) oxidized pre-concentration residues enriched in Co and Ga, and (iii) transitional sulphate–carbonate materials exhibiting favourable leaching behaviour. In contrast, mine spoils and false gossan materials show lower CRM concentrations and limited standalone economic potential, although they may contribute within blending or bulk processing strategies.

Several constraints must be considered. Elevated concentrations of As and Sb represent both environmental and metallurgical challenges, requiring careful management in processing schemes. In addition, fine-grained textures and heterogeneous mineralogy may reduce recovery efficiency and necessitate pre-treatment steps such as classification or attrition.

Despite these limitations, the large volume of residues, the enrichment of CRMs in reactive secondary phases, and the compatibility with hydrometallurgical processing routes highlight the strategic potential of the CUMD as a secondary resource system. The recovery of CRMs from these wastes is fully aligned with the objectives of the European Critical Raw Materials Act (2023) [1], which promotes the development of domestic supply chains based on unconventional resources [1,41].

Taken together, these results demonstrate that, while not all waste types are economically viable as standalone resources, the combination of metal concentrations, mineralogical controls, and recoverability supports a realistic and scalable potential for CRM-oriented reprocessing based on integrated multi-metal recovery strategies.

5. Conclusions

This study provides the first comprehensive and integrated mineralogical, geochemical, and geostatistical evaluation of 17 critical raw materials (CRMs) across nine mining and metallurgical waste types from the Cartagena–La Unión Mining District (SE Spain). The results demonstrate that CRM distribution is governed by three robust and consistent geochemical associations: (i) a lithogenic silicate–oxide system (Al–Si–P–Ti–Nb), (ii) a sulphide-derived metalliferous association (Cu–As–Sb), and (iii) an oxidation–adsorption system dominated by Ga and Y. The strong agreement between correlation analysis, PCA, and hierarchical clustering confirms the internal consistency and reliability of these geochemical controls.

Several waste categories, particularly terrestrial flotation tailings, gossan materials, and pre-concentration residues, exhibit enrichment in key CRMs such as Ga, Y, Nb, and Co, with concentrations comparable to those reported in secondary CRM resources worldwide. Mineralogical evidence indicates that CRM retention is controlled by silicates, Fe–Mn oxyhydroxides, and jarosite–sulphate assemblages, highlighting the suitability of hydrometallurgical approaches for potential recovery.

Although average grades are generally lower than those of primary deposits, the large volumes of accumulated waste and the presence of coherent enrichment patterns demonstrate that the Cartagena–La Unión district represents a significant secondary CRM reservoir. The consistent association of Y with Fe–Mn oxyhydroxides further suggests that the potential for rare earth element (REE) recovery may be underestimated and warrants further investigation.

From a strategic perspective, these findings support the role of legacy mining wastes as viable unconventional resources, fully aligned with the objectives of the European Critical Raw Materials Act (2023) [1]. The integration of mineralogical, geochemical, and statistical approaches presented in this study provides a transferable and reproducible framework for the evaluation of CRM potential in mining waste systems at both regional and international scales.

Overall, this work demonstrates that mining and metallurgical wastes can transition from environmental liabilities to strategic resource systems, supporting the development of circular economy approaches and enhancing the resilience of critical raw material supply chains.

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Article

Floating Rafts from Coastal Hypersaline Environments in Brazil

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Abstract

Floating rafts are thin, flat mineral layers that precipitate at still air–water interfaces. They are composed of calcite, aragonite, vaterite, gypsum, trona, carnallite, and/or halite. Floating rafts present a flat surface at the top in contact with air, and a rough surface at the bottom, which develops as they grow into the water. In this work, we describe floating rafts from hypersaline environments using imaging and analytical microscopy techniques. The four rafts studied consist of interconnected polycrystalline grains. Scanning electron microscopy (SEM) showed that the top surfaces were flat, whereas in the bottom surfaces, the grains protrude into the water. High magnification revealed nanoparticles arranged in stacks, suggesting growth through the organized agglutination of nanocrystals. Electron diffraction of two of the rafts indicates that they consist of aragonite. Accordingly, electron energy-loss spectroscopy (EELS) shows the C K-edges characteristic of carbonates, along with O and Ca edges. Energy-dispersive spectroscopy (EDS) in the SEM also revealed a few Ca sulfate crystals on the bottom surface. In addition, the presence of cubic shapes indicates the presence of halite. We hypothesize that the genesis of these rafts is driven by evaporation of still water, which increases supersaturation at the very surface, leading to mineral nucleation at the air–water interface, where the activation energy is lower.

Keywords: carbonate rafts; paper-thin rafts; cave rafts; hypersaline; authigenic minerals; evaporite; Lagoa Vermelha

1. Introduction

Floating rafts consist of thin, flat mineral layers that precipitate at the air–water interfaces of still water bodies [1–11]. They have also been called “calcite rafts” [4,6,9,12], “aragonite rafts” [12,13], “paper-thin rafts” [10], flocs [8], “cave rafts” [14], “calcite ice” [1], or simply “rafts” [5,7,15,16]. They float at the air–water interface due to the surface tension until they grow too large and/or are disturbed by mechanical perturbation, causing them to sink to the bottom [1,2,5,7–9,11,12,15]. They exhibit a smooth surface facing the air, and a rough surface extending into the water [3,4,7–11,13]. They are composed by pure calcite (CaCO_3) [9], low Mg-calcite ($\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$) [2,4], aragonite (CaCO_3) [10,12], calcite and aragonite [3,8,11,13], calcite, aragonite and vaterite (CaCO_3) [8], calcite and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [14], gypsum [17,18], trona ($\text{NaH}(\text{CO}_3) \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) [17–19], carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) [17–20], or halite (NaCl) [5,7,15–18,20–23].

Crystals in floating rafts nucleate at the air–water interface and grow into the water [1,4,7,8,10,11]. Depending on environmental conditions, Ca carbonate supersaturation

may be driven by (i) CO₂ degassing, which increases pH and carbonate ion concentration [3,4,9–11], (ii) by the high pH, which promotes dissolution of atmospheric CO₂ into the water and subsequent formation of carbonate ions that precipitate with Ca²⁺ [8], or (iii) by water evaporation, which concentrates ions such as Na⁺ and Cl[−], leading to halite precipitation [7,15].

Floating rafts are generally considered to originate from physical–chemical processes, with possible contributions from organic materials [2,8]. Some authors consider mineral nucleation in the rafts as homogeneous, whereas others propose heterogeneous nucleation involving dust particles or organic matter at the water surface. The air–water interface is negatively charged at a pH > 3–4.5 and this charge increases with pH [24–26], which may favor the concentration of cations for mineral precipitation.

Floating rafts have been described mainly in caves [1,2,4,6,11–14,23]. They have also been reported in ditches [9], springs [3,8,10], travertines, tropical streams, alkaline ponds, acid saline ponds [15], and evaporite systems [5,7,15,16,27]. Rafts from evaporite environments are composed of halite, gypsum, trona, and/or carnallite [5,7,15–23]. We have observed the development of rafts on still water surfaces of hypersaline coastal environments in Brazil; however, these are not composed of halite, gypsum, trona or carnallite.

In this work, we describe the structure and mineral composition of rafts formed in hypersaline waters using scanning electron microscopy (SEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), electron energy-loss spectroscopy (EELS) and energy-dispersive spectroscopy (EDS).

Field Description

There are several lagoons along the coast of Rio de Janeiro State (Figure 1). About 100 km east of the city of Rio de Janeiro, most coastal lagoons are permanently hypersaline due to seawater inputs combined with semi-arid climate, in which evaporation exceeds precipitation [28,29]. Several saltworks are still active in the region. They pump lagoon water into salt-producing ponds for evaporation, leading to the precipitation of NaCl [30].

Araruama Lagoon is the largest hypersaline lagoon in Brazil (Figure 1a,b). It is 40 km long, up to 13 km wide, and has an average depth of 3 m. A permanent channel to the east allows seawater to enter the lagoon [29]. Salinity ranges from 36.7 to 64.3‰, pH from 7.6 to 8.9, water temperature from 19.0 to 32.7 °C, and dissolved inorganic carbon (DIC) from 1678 to 2269 μmol kg^{−1} [31,32]. Ca–Mg carbonates in the sediments account for 2%–83% [31,33].

Vermelha Lagoon (Figure 1c) is much smaller, about 4.4 km long and up to 850 m wide, covering an area of 2.4 km². There is no surface drainage or runoff to the lagoon. Maximum water depth ranges from 1.0 to 1.70 m, depending on seasonal variations in precipitation and evaporation. Vermelha Lagoon is separated from both the Atlantic Ocean and Araruama Lagoon by sandbars [28]. Water salinity ranges from 43.5 to 97‰ [34,35], temperature 20 to 36.5 °C, and pH 7.3 to 9.4 [28,34–38]. Vermelha Lagoon has been extensively studied because it produces authigenic dolomite (CaMg(CO₃)₂) and contains Holocene stromatolites [28,35–46]. Sediments, microbial mats and stromatolites from Vermelha Lagoon produce abundant authigenic minerals characteristic of evaporitic environments, including calcite, Mg–calcites (Ca_{1−x}Mg_xCO₃; 0.07 < x < 0.46), dolomite, aragonite, gypsum, anhydrite (CaSO₄), and halite [28,36,38–46]. Water in the lagoon is supersaturated with respect to calcite, aragonite and dolomite [38].

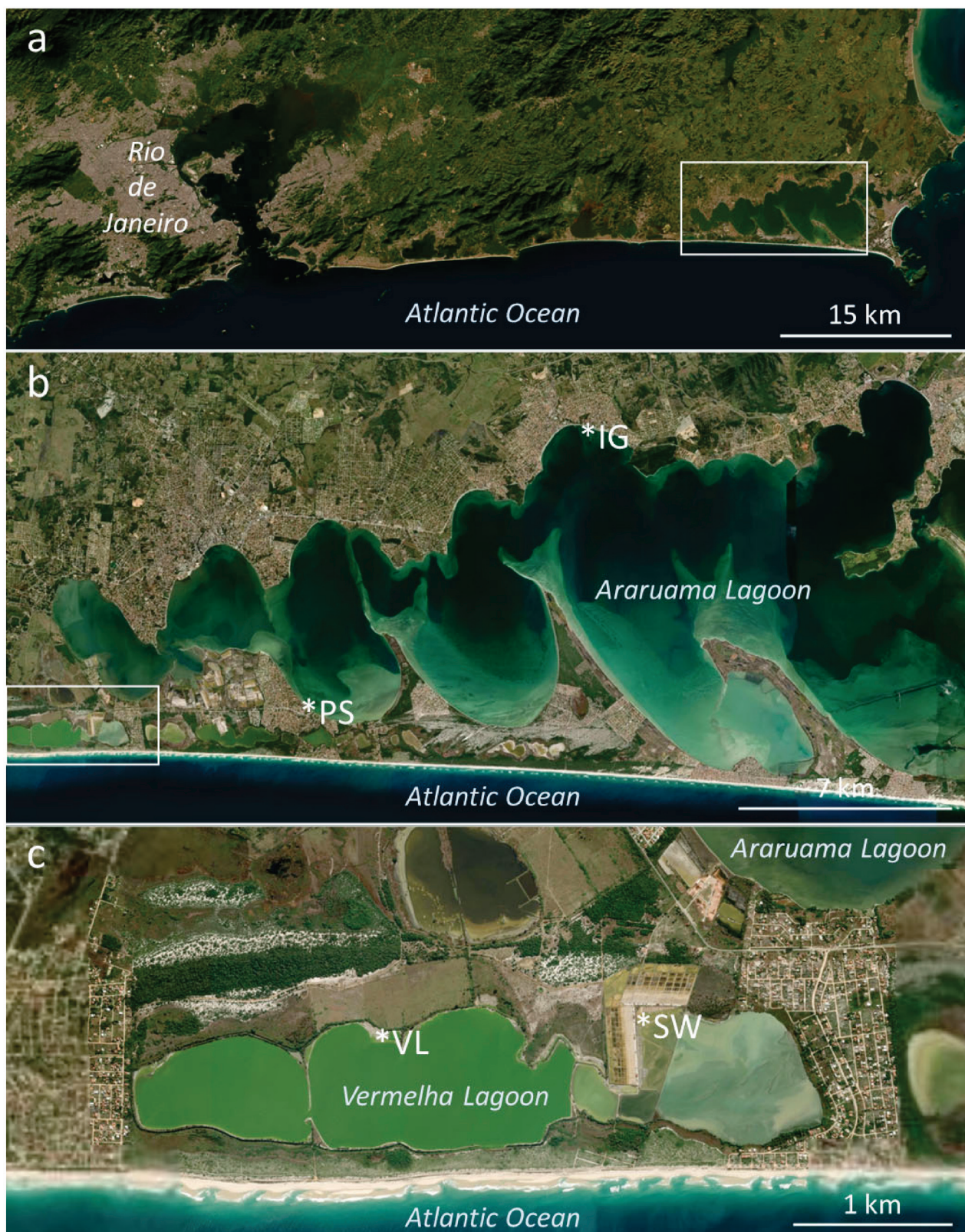


Figure 1. Satellite images of the sampling locations. (a) Portion of the coast of Rio de Janeiro State showing Rio de Janeiro City and the area enlarged in “b” (rectangle). (b) Araruama Lagoon and the two sites, “Praia Seca” (PS) and “Iguaba Grande” (IG) (asterisks). The rectangle indicates the area enlarged in “c”. (c) Vermelha Lagoon and the adjacent saltwork. Asterisks indicate the sampling sites for Vermelha Lagoon (VL) and saltwork (SW).

Water from these lagoons is pumped into artificial salt-producing ponds for evaporation (Figure 1c), leading to precipitation of halite [29]. Salt production is a traditional activity in the region. A saltwork located on the northern shore of Vermelha Lagoon has been operating since at least 1929. It covers an area of 0.87 km² [30] and uses water from Vermelha Lagoon. There is also a small channel that conveys water from Araruama Lagoon into Vermelha Lagoon and the saltwork. During field work, we observed several piles of halite and a few piles of gypsum in this saltwork (personal observation). Shiraishi et al. [38] reported that brine from this saltwork had a pH of 7.95, Na⁺ and Cl[−] concentrations about four times those of seawater, and was supersaturated with respect to calcite, aragonite, dolomite and gypsum. Microbial mats from this saltwork contain Mg-calcite, aragonite, gypsum and halite [38].

2. Materials and Methods

Floating rafts were collected from puddles located near the margin of Vermelha Lagoon (22°55'32" S, 42°22'58" W; Figure 1c). It was dry season, and the water level of the lagoon was low. Salinity was 69‰, and the pH was 8.6.

Water and sediment samples were collected for other purposes and left to stand in the laboratory. After a few weeks, some of them developed floating rafts at the water–air interface. The sample collected from a saltwork near Vermelha Lagoon (22°55'36" S, 42°23'21" W; Figure 1c) had a salinity of 110‰ and a pH of 7.6. It contained water and a piece of a microbial mat from a puddle. Samples collected from Araruama Lagoon included sites at Iguaba Grande (22°50'23" S, 42°13'01" W) and Praia Seca (22°55'13" S, 42°18'25" W) (Figure 1b). Water from Praia Seca had a salinity of 61‰ and a pH of 7.4. Both samples from Araruama Lagoon contained water and unconsolidated sediments.

The rafts were collected using glass slides, coverslips and/or plastic labware. They were observed under the light microscope Nikon Eclipse E200 equipped with a Nikon DS-Fi2 camera.

For scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), dry samples were washed in distilled water and mounted on aluminum stubs using carbon tape. Some samples were sputter-coated with gold using a Bal-Tec SCD 050 sputter coater to obtain high-resolution secondary electron images. Uncoated samples were observed using backscattered electrons and analyzed by EDS. Samples were examined using either a Jeol s125, a Jeol JSM-6490LV microscope equipped with a Noran EDS detector, or a Quattro S microscope equipped with an EDS detector (Thermo Fisher Scientific, Waltham, MA, USA).

For transmission electron microscopy (TEM), samples were embedded in Spurr resin and sectioned using an RMC PTX ultramicrotome (Boeckeler Instruments, Inc., Tucson, AZ, USA). Ultrathin sections were collected on lacey carbon-coated copper grids and observed in a JEOL 2100F instrument (JEOL, Tokyo, Japan) operating at an accelerating voltage of 200 kV and equipped with an electron energy-loss spectrometer (EELS-GIF Tridiem Gatan, Pleasanton, CA, USA). Images were acquired using a 16-megapixel CMOS One View digital camera (Gatan). Selected area electron diffraction (SAED) was used to investigate the crystalline phases of the samples. Line profiles of SAED patterns were obtained using the rotational averaging tool in the DigitalMicrograph v3 software, which averages radial intensity profiles from diffraction patterns. These profiles were then compared to the interplanar spacings of calcite, vaterite, and aragonite obtained from an X-ray diffraction database. EELS was acquired in scanning transmission electron microscopy (STEM) mode with a spot size of 0.7 nm and a spectrometer aperture of 5 mm. The energy resolution measured at the zero-loss peak was approximately 1.5 eV. The background was removed by fitting it to a power law. The EELS and SAED profiles were formatted using Origin 8 (OriginLab Corporation, Northampton, MA, USA).

3. Results

During fieldwork at the end of the dry season, it was observed that some puddles formed along the margin of Vermelha Lagoon contained white, floating rafts at the surface. Their surfaces appeared dry, and they were easily broken. Samples were brought to the laboratory and examined with scanning electron microscopy. They exhibited a flat surface at the top (the interface with the air) and a rough surface at the bottom (the interface with water) (Figure 2a). The bottom surface displayed interconnected globules $10.0 \pm 2.4 \mu\text{m}$ in diameter ($n = 54$) (Figure 2b). There were some euhedral crystals, as well as diatom remains deposited at the bottom surface (Figure 2b). EDS analysis showed that the rafts consisted primarily of Ca, O and C, indicating a Ca carbonate (Figure 2c). Minor elements included Na, Mg, and S (Figure 2c).

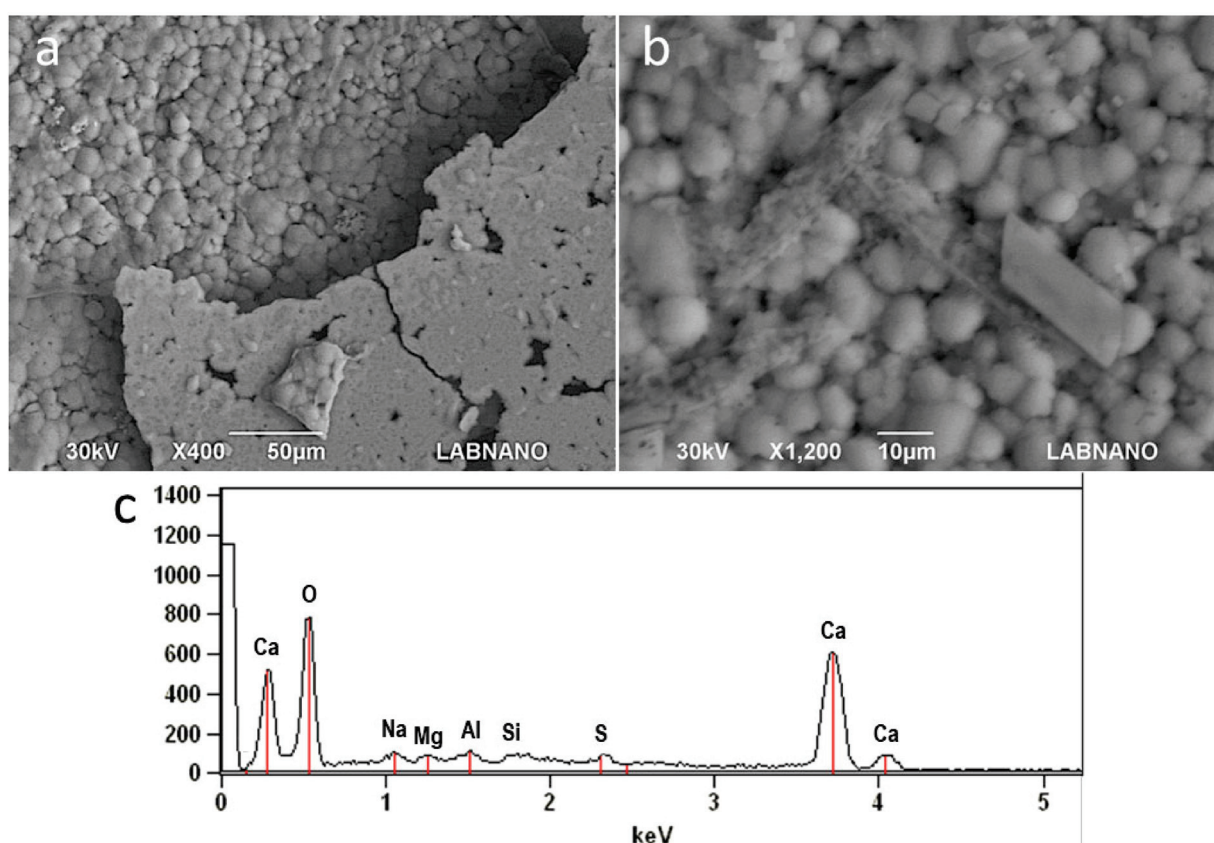


Figure 2. Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (EDS) data of floating rafts collected from a puddle at the margin of Vermelha Lagoon. (a) The flat upper surface (right) is superimposed on the rough bottom face (left) of the raft. (b) Higher magnification image of the bottom surface showing its globular morphology, along with diatom remains and a flat euhedral crystal. (c) EDS spectrum acquired from the flat upper surface, showing Ca and O peaks predominantly, indicating that Ca carbonates constitute most of the raft. Sodium, Mg, and S occur as minor components, whereas Al likely originates from the holder and Si from the Si(Li) detector. Backscattered electron images were obtained at 30 kV, and EDS analysis at 10 kV.

Rafts that formed at the air–water interface in samples from the saltwork maintained in the laboratory for other purposes were retrieved and analyzed. Polarized light microscopy and scanning electron microscopy (SEM) indicate that the rafts are composed of interconnected grains (Figure 3a,b). The grains were either rod-shaped or hemispherical (fan-shaped) (Figure 3a,b). They are $11.2 \pm 3.2 \mu\text{m}$ in diameter ($n = 35$), based on SEM images. EDS spectra indicate that Ca, C and O are the predominant elements in the rafts (Figure 3c), indicating predominance of Ca carbonate. Strontium and S occur as minor

elements. Strontium readily substitutes for Ca into the aragonite lattice due to its larger atomic radius [47] and is commonly found in natural aragonite (e.g., [48,49]). In contrast, S may be present in minor phases such as Ca sulfates (see below). Higher magnification revealed that both rod-shaped and hemispherical grains are composed of several strings of nanocrystals aligned parallel to each other (Figure 3d–g). In some cases, the nanoparticles are stacked in the helical pattern characteristic of aragonite twins. Organic materials occur both surrounding the grains (Figure 3d) and within them, among the nanoparticles (Figure 3g). Figure 4 shows the top surface of the raft from the saltwork sample, which is flat as expected. Backscattered electron images indicate that the grains grew radially, forming fans (Figure 4a). Higher magnification revealed stacks of nanocrystals extending parallel to each other over tens of micrometers (Figure 4b). Fans originate from discrete regions within these stacks and are responsible for the rounded morphologies of the grains (Figure 4b). Lateral growth ceased when adjacent grains came into contact (Figure 4a,b).

In some cases, additional minerals were observed on the bottom side of the rafts. In the sample collected from the saltwork, there were layered minerals that grew onto the Ca carbonates after their precipitation (Figure 5a,b). EDS spectra indicate that these minerals are composed mainly of Ca, S and O, consistent with a Ca sulfate (Figure 5c). Notably, the Ca sulfates gypsum and/or anhydrite have been reported in microbial mats from Vermelha Lagoon [46] and from the saltwork [38]. In addition, some Ca carbonate grains grew around cubic and chevron-shaped crystals (Figure 5d), which were subsequently dissolved, leaving voids with cubic, octahedral, and chevron morphologies. Similar features have been previously reported in halite rafts [5,7,16]. Given the high salinity of the water (110‰) and the occurrence of halite in microbial mats from the saltwork [38], it is likely that halite precipitated shortly after the onset of CaCO_3 precipitation. Thus, the saltwork rafts are composed predominantly of CaCO_3 , with minor amounts of halite and Ca sulfate, although the halite was dissolved during washing with distilled water in the sample preparation process.

Rafts also appeared at the air–water interface of samples from Praia Seca. Polarized light microscopy showed that they were composed of elongated grains, smaller than those observed in the saltwork sample (Figure 6a). Scanning electron microscopy revealed that the upper surface was flat, whereas the bottom surface was rough (Figure 6b), as in the other rafts. Measurements from SEM images show that the grains are $4.7 \pm 0.9 \mu\text{m}$ in diameter. EDS spectra showed predominantly Ca, C and O peaks, indicating a Ca carbonate (Figure 6c). Minor elements included Sr and S, as also observed in the saltwork rafts. At higher magnification, each grain was found to be composed of several euhedral prismatic crystals aligned parallel to one another (Figure 6d,e). Crystal size decreased progressively toward the tip of the grains (Figure 6e). The grains contained numerous sub-micrometric rounded holes (Figure 6b,d,e), which may have been produced by microboring cyanobacteria (e.g., [35,38]).

Figure 7 shows the upper surface of the Praia Seca rafts. Crystal arrangements included radial growth from multiple nucleation centers (Figure 7a), rosette-like structures (Figure 7b), and twinned crystals (Figure 7c). The nucleation centers were porous and contained columns of nanocrystals (Figure 7d), which presumably correspond to the mineralization front responsible for the growth of the larger euhedral crystals. A closer inspection indicates that the nanocrystals coalesced to form the euhedral crystals (Figure 7d).

As observed for the other rafts, those from Iguaba Grande exhibited a rough bottom surface (Figure 8a) and a flat top surface (Figure 8b). Closer inspection shows that each grain consists of a pack of long, thin crystals (Figure 8a). The grains contain numerous rounded pores, especially at their tips (Figure 8a). These pores are similar to those observed

in the Praia Seca rafts and likely were produced by microboring cyanobacteria. Each grain measured $9.7 \pm 2.3 \mu\text{m}$ in diameter ($n = 21$).

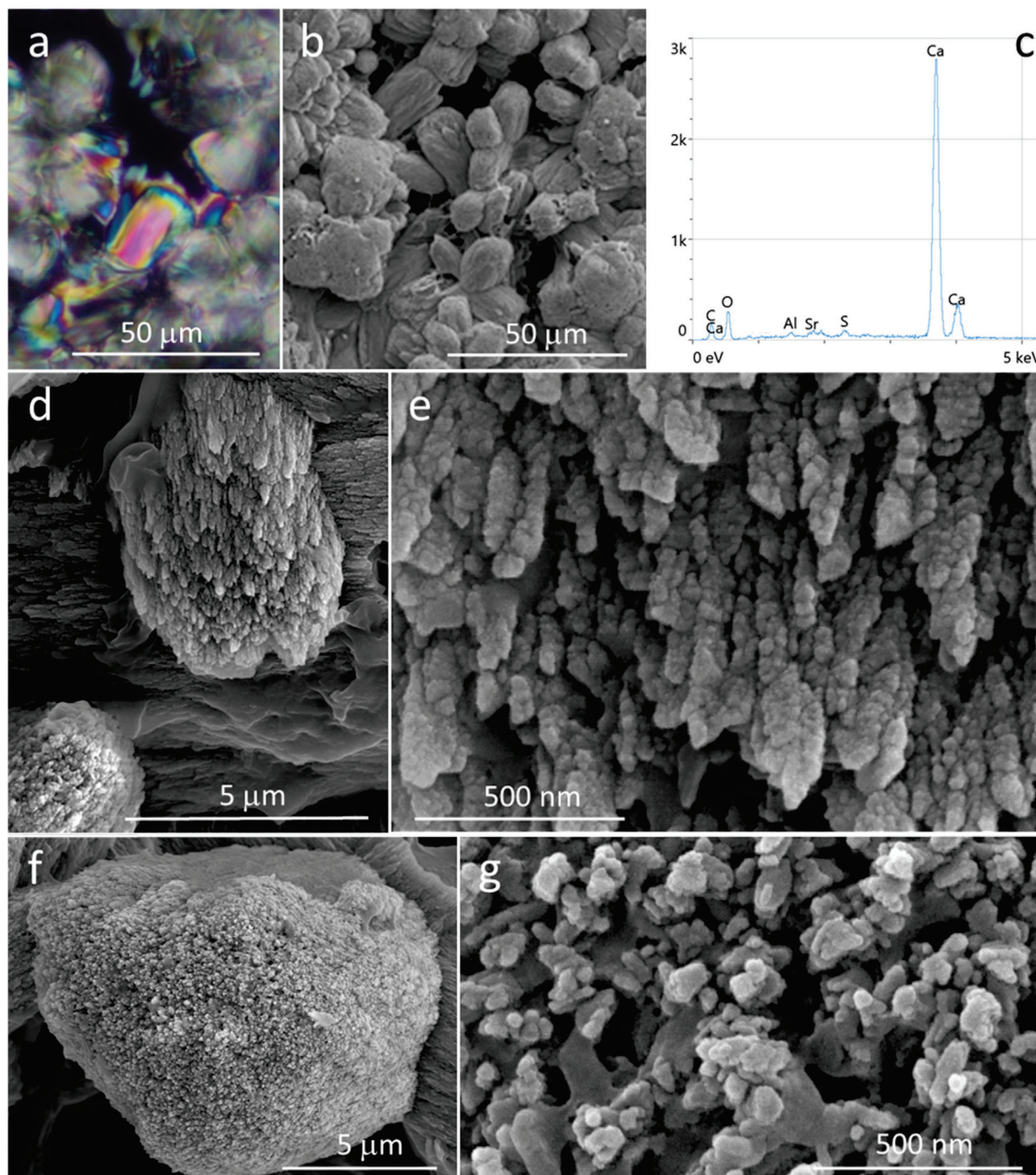


Figure 3. Microscopy images and EDS data of floating rafts that developed in a sample collected from the saltwork. (a) Polarized light microscopy image. Note the strong birefringence in the grain at the center, in the fan-shaped structure on the right, and at the margins of several other grains. (b) Low magnification SEM image of the rough bottom surface showing the intergrown grains that compose the raft. (c) EDS spectrum acquired in the SEM, showing Ca and O peaks predominantly, indicating a Ca carbonate. Minor elements in the sample include Sr and S, whereas the Al peak likely originates from the sample holder. (d) Side view of a grain that grew onto another grain. (e) Higher magnification image showing that it is composed of numerous stacks of nanocrystals. (f) Top view of a grain. (g) High magnification image showing in detail the packing of nanocrystals. Secondary electron images were obtained at 10 kV, and the EDS spectrum at 30 kV.

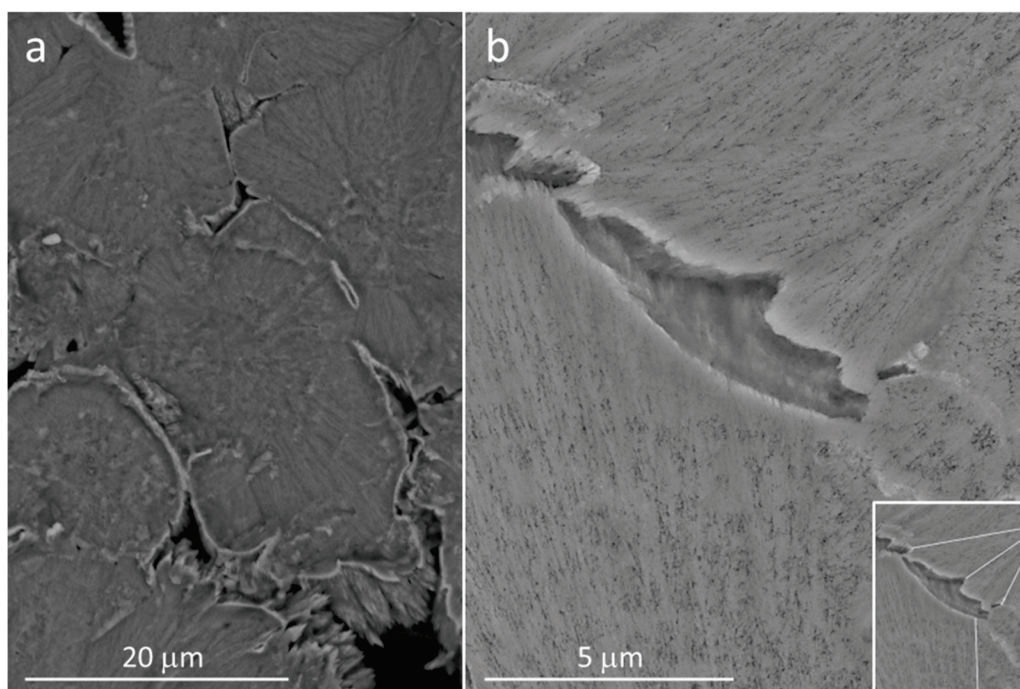


Figure 4. Backscattered electron images of the flat upper surface of rafts from the saltwork. (a) Several grains that grew until they came into contact with each other. (b) Higher magnification image showing straight lines corresponding to the growth pattern of the grains at the air–water interface. Note the presence of fan-shaped structures (see the map in the inset) originating from discrete points. Images were obtained at 10 kV.

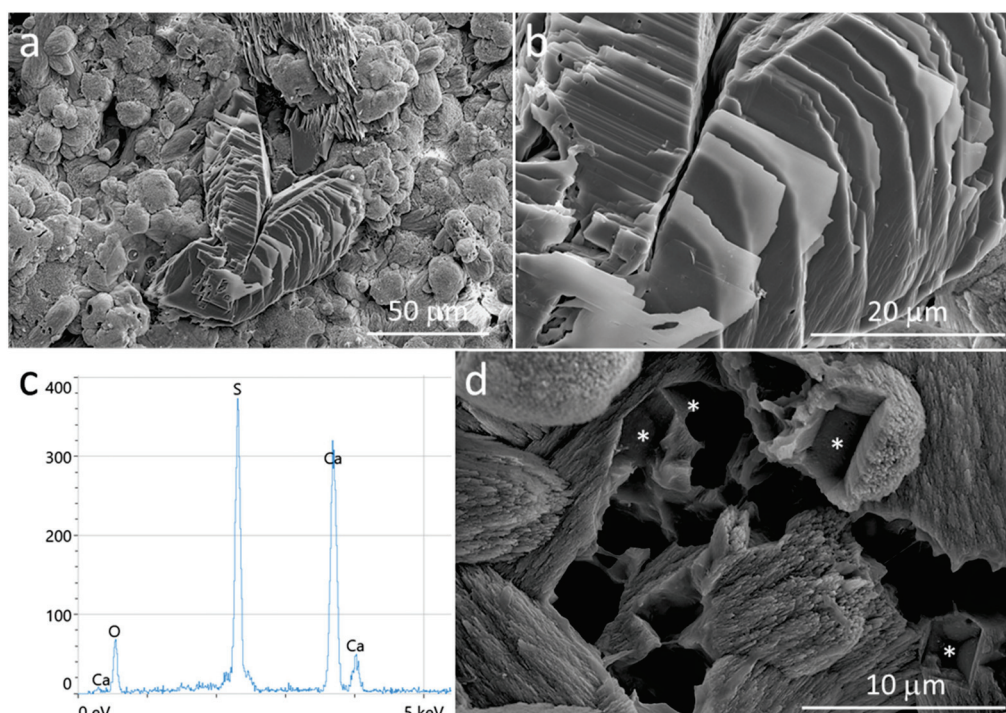


Figure 5. Scanning electron microscopy (SEM) and EDS data of additional mineral components present in rafts from the saltwork sample. (a,b) Layered minerals deposited on the bottom surface of the raft. (c) EDS spectrum acquired from this mineral, showing Ca, S and O, indicating a Ca sulfate. (d) Cubic- and chevron-shaped voids imprinted in some grains (asterisks) indicate that halite crystals were present during raft growth. Images were obtained at 10 kV, and the EDS spectrum was obtained at 30 kV.

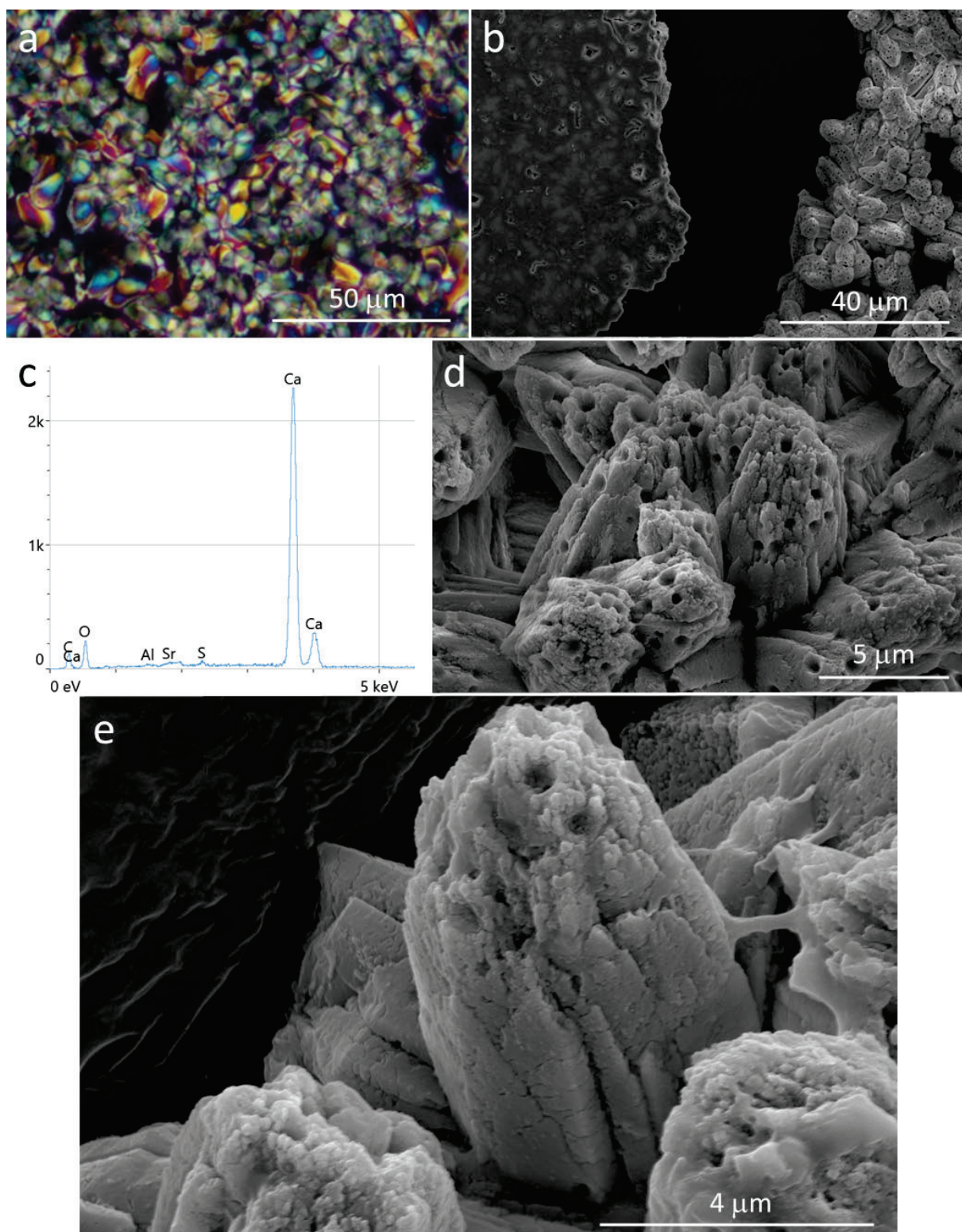


Figure 6. Microscopy images and EDS spectrum of floating rafts that developed in a sample collected at Praia Seca. (a) Polarized light microscopy image showing that most grains are birefringent. (b) SEM image showing the flat upper surface (left) and the rough bottom surface (right). (c) EDS spectrum acquired from the flat surface, showing mainly Ca, C and O peaks, indicating a Ca carbonate. Minor Sr and S peaks indicate impurities in the Ca carbonate and/or the presence of minor mineral phases. (d,e) Higher magnification images showing that the grains are polycrystalline. Crystals at the base appear more compact, whereas those at the top appear more loosely arranged. SEM images were obtained at 10 kV, and EDS spectrum was obtained at 30 kV.

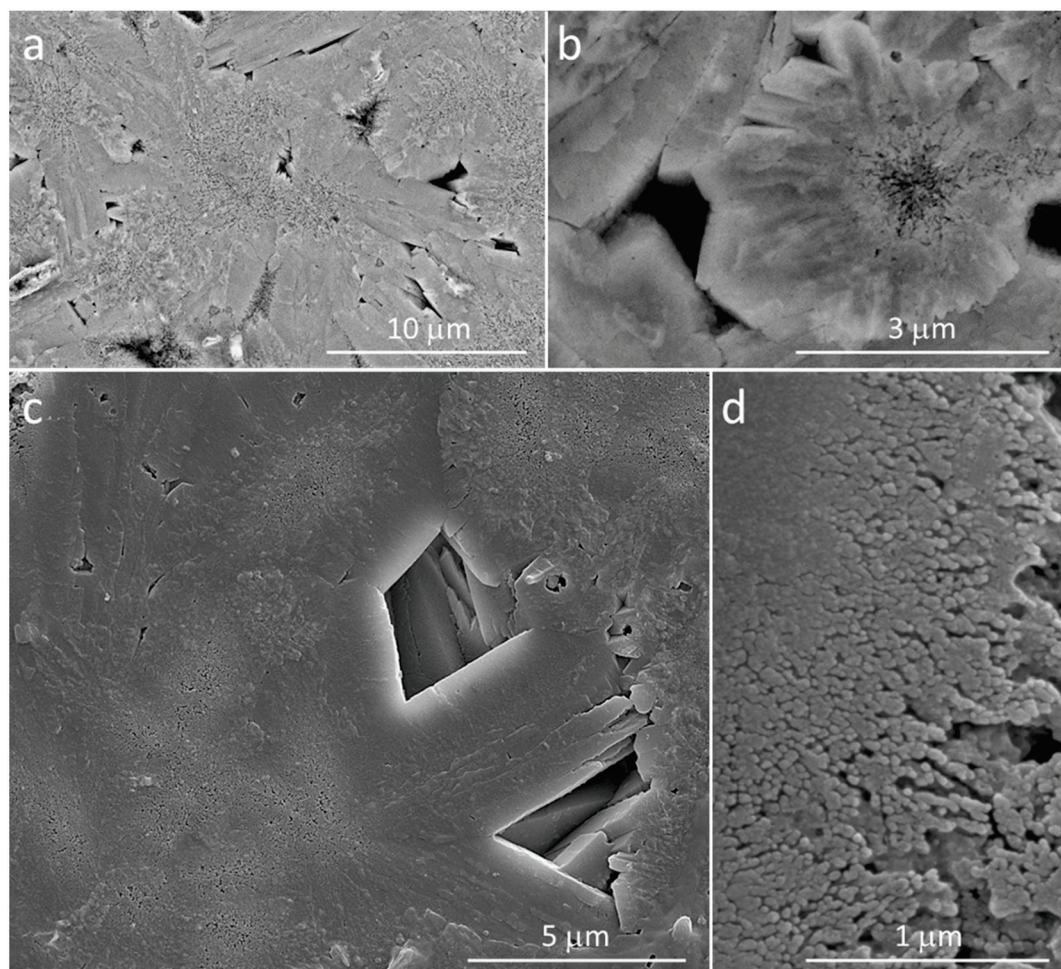


Figure 7. Scanning electron microscopy (SEM) images of the flat upper surface of rafts from the Praia Seca sample showing crystals growing radially from nucleation centers. (a,b) Backscattered electron images showing that microcrystals are constrained by the growth of neighboring crystals. (c,d) Secondary electron images. (c) Larger crystals grew to form twins. (d) Nanocrystals at the nucleation centers are organized in linear chains and coalesce as they grow. Images were obtained at 10 kV.

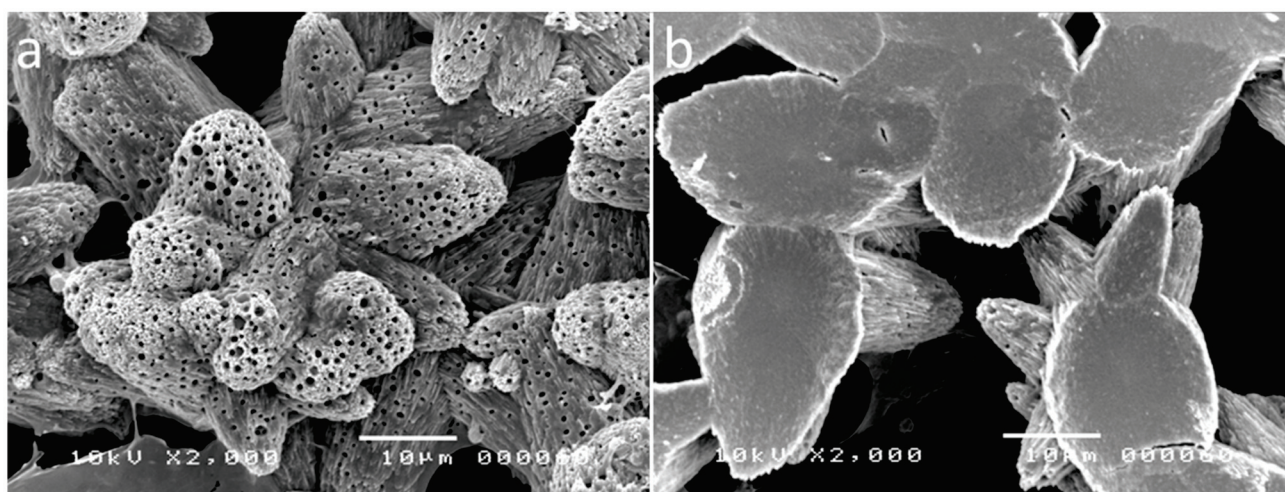


Figure 8. Scanning electron micrographs of rafts grown in samples from Iguaba Grande. (a) Rough bottom surface. Note that the interconnected grains are composed of fine crystals. Numerous pores are present, especially at the tips of the grains. (b) Flat upper surface. Note the outlines of the individual grains. Secondary electron images obtained at 10 kV.

Transmission electron microscopy (TEM) images of the Praia Seca and Iguaba Grande samples show an agglomeration of crystalline particles approximately 150 nm wide (Figure 9a,b). No morphological differences were observed between the Praia Seca and Iguaba Grande samples. SAED patterns were obtained from different regions of both samples using the same diffraction aperture (Figure 9c,d). Figure 10 presents the average radial intensity profiles from three different regions of the Praia Seca and Iguaba Grande samples and compares them with the most intense reflections of aragonite (red vertical lines), calcite (green vertical lines), and vaterite (blue vertical lines). The length of the vertical lines in Figure 10 is proportional to the X-ray diffraction intensity (data obtained from the X-ray database). A peak at approximately 3 nm^{-1} , observed in all diffractograms, coincides with the most intense peak of aragonite (111). A peak at approximately 3.7 nm^{-1} , observed in all profiles, corresponds to the (012) plane of aragonite. The most intense reflections of calcite and vaterite were not identified in any SAED pattern. These results indicate a strong predominance of aragonite crystals in both samples. Indeed, EDS spectra of Praia Seca rafts showed small amounts of Sr (Figure 6c), a common impurity in natural aragonite [48,49].

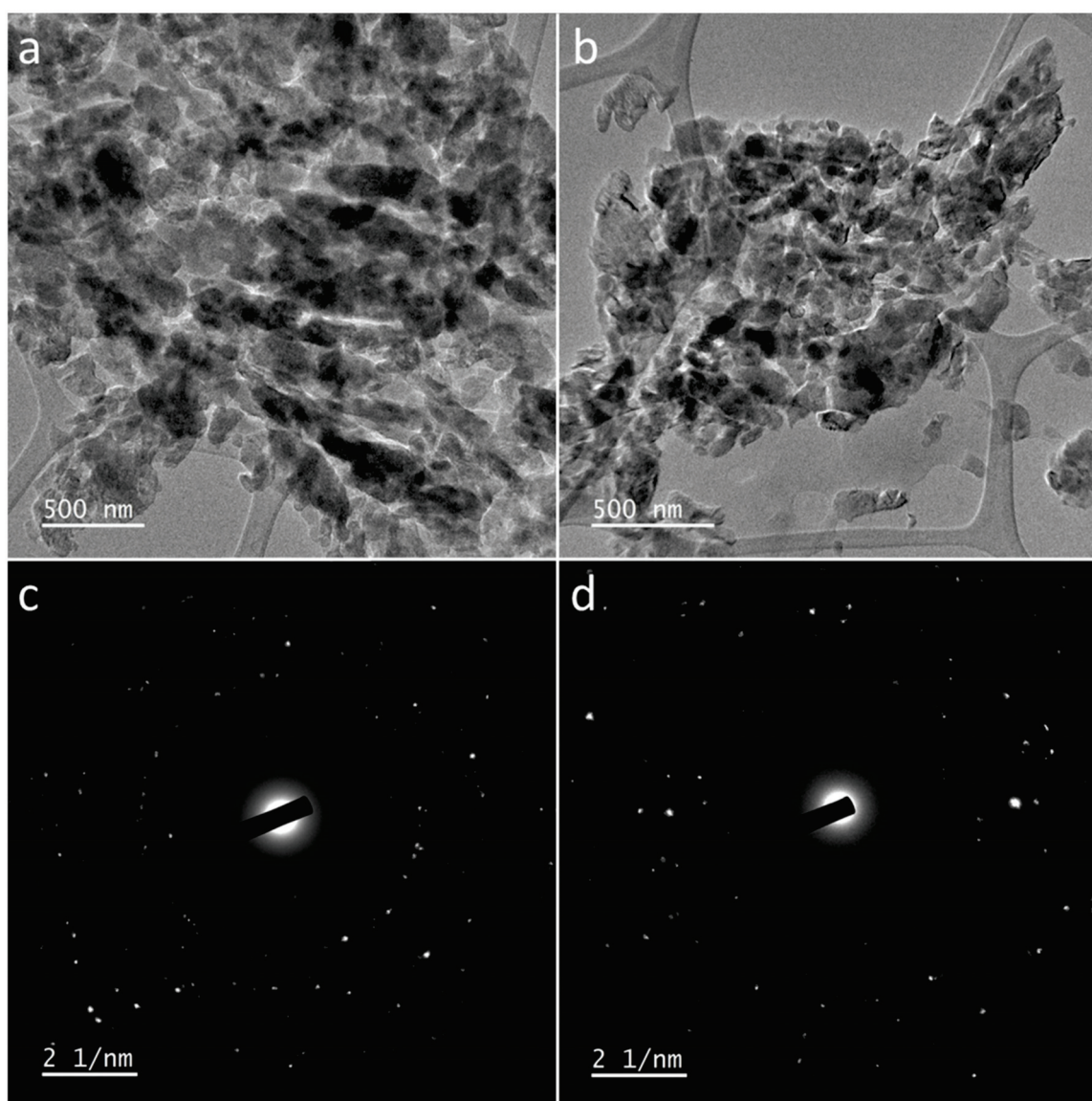


Figure 9. Transmission electron micrographs (a,b) and electron diffraction patterns (c,d) of samples from Praia Seca (a,c) and Iguaba Grande (b,d).

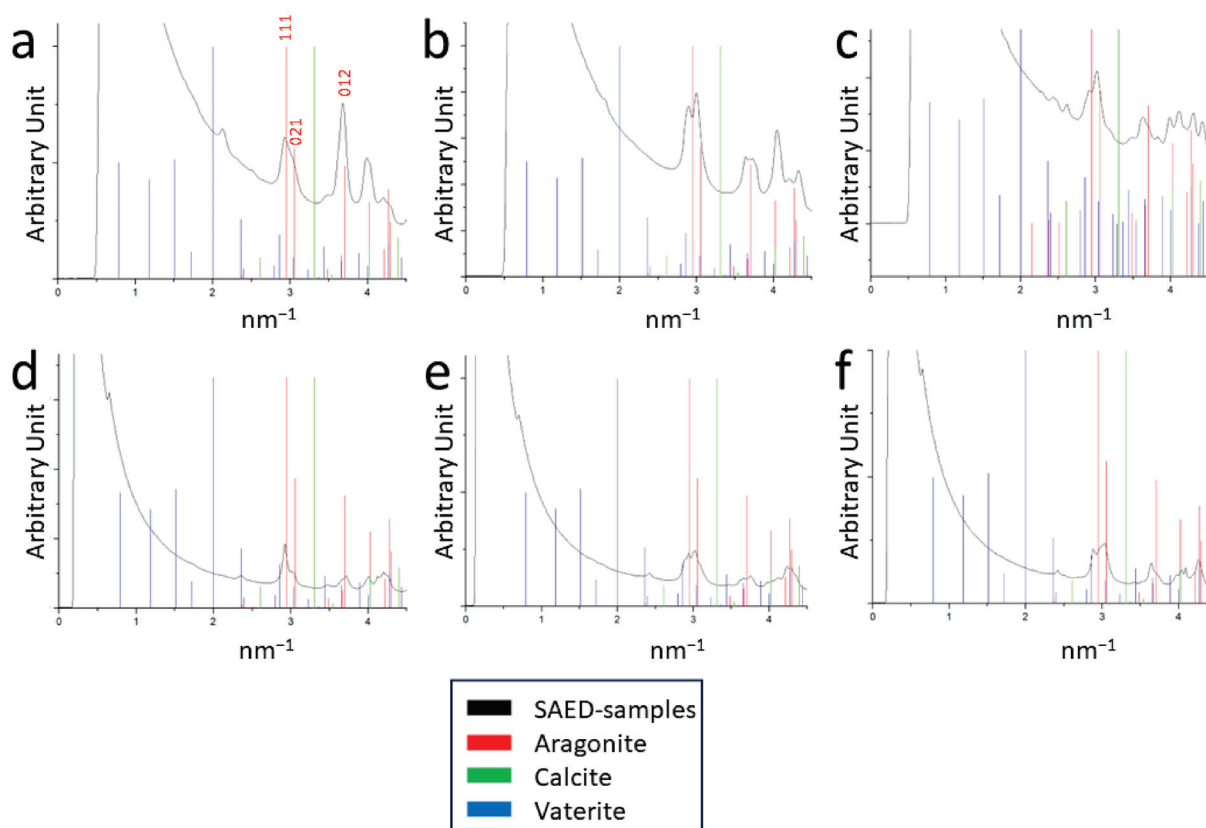


Figure 10. Average radial intensity profiles compared with the main diffraction lines of the Ca carbonates aragonite, calcite and vaterite. The main diffraction lines of aragonite are illustrated in (a). (a–c) Sample from Praia Seca. (d–f) Sample from Iguaba Grande.

Figure 11 displays the EELS spectra of the Praia Seca and Iguaba Grande samples. The spectra are similar and exhibit edges corresponding to the C K-edge (289 eV and 299 eV), the Ca $L_{2,3}$ -edge (346 eV), and the O K-edge (526 eV). The C peaks at 289 and 299 eV are assigned to C=O ($1s \rightarrow \pi^*$) and C–O ($1s \rightarrow \sigma^*$) bonds, respectively, of the carbonate group.

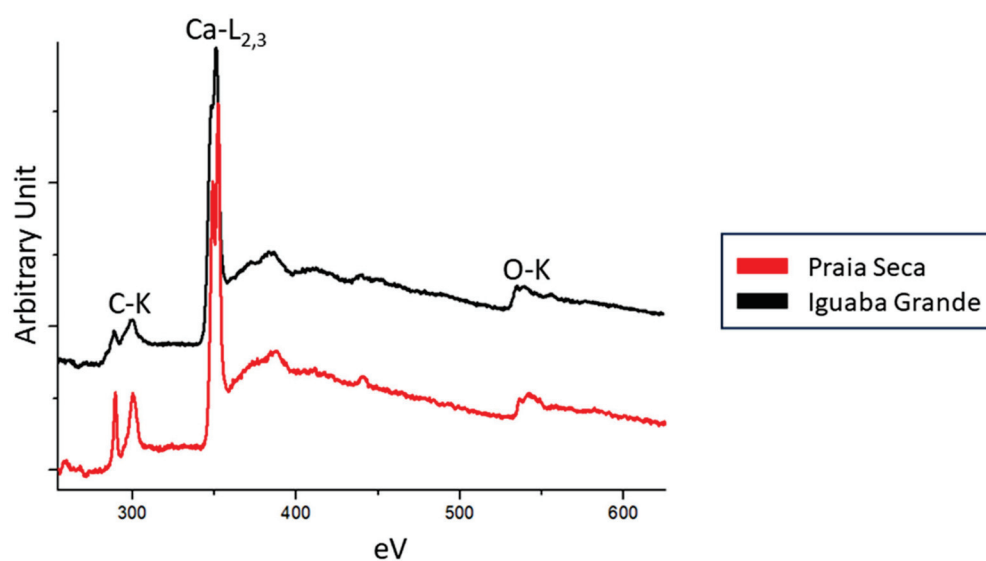


Figure 11. Electron energy-loss spectra of samples from Praia Seca and Iguaba Grande, showing the C and the O K-edges and the Ca $L_{2,3}$ -edge.

4. Discussion

Aragonite was identified in the two floating raft samples from Araruama Lagoon (Praia Seca and Iguaba Grande) by electron diffraction (Figure 9c,d and Figure 10). No diffraction spots indicative of calcite or vaterite were observed (Figure 10). Aragonite rafts have previously been reported in freshwater environments [12,38].

In all rafts described here, the upper surface is flat and the bottom surface is rough, as previously reported [3,4,7,9–11,13,18,27]. The morphology of grains on the bottom surface varied from hemispherical to rod-shaped (Figure 2a,b, Figure 3b,d,f, Figure 5a, Figure 6b,d,e and Figure 8a). Morphologically similar aragonite hemispheres have been described in rafts from freshwater travertines rich in organic matter and phototrophs such as diatoms or cyanobacteria [3,10].

The polycrystalline grains are composed of micrometric euhedral aragonite crystals, similar to those reported in the aragonite rafts from brackish waters [11] and/or apparently isometric nanoparticles comparable to those described in early stages of aragonite precipitation in microbial mats [50], corals and sponges [51]. These nanocrystals are aligned parallel to each other (Figure 3d,e,g, Figure 5d, Figure 6d,e and Figure 7d), resulting in a birefringence similar to that of single crystals (Figures 3a and 6a). Even in fan-shaped structures, the organization of the nanocrystals is maintained over several micrometers (Figure 4b). The alignment of nanocrystals to form larger composite units with different levels of crystallinity and purity is widespread among biominerals and synthetic minerals. This process results in faster growth, complex morphologies, and specific properties [52]. In this context, the similarity in shape and size of the grains within each sample, as well as among the four samples studied here, is remarkable. This suggests the presence of some kind of self-organization process in this system, possibly related to growth by aggregation of nanocrystals into mesocrystals, as proposed by Cölfen and Antonietti [52] and observed in synthetic aragonite [53].

It is important to note that the rafts studied here formed in natural waters spanning a range of salinities and pH values, and containing diverse microorganisms and complex organic matter (see Figures 2b, 3d, 3g and 6e), which may influence mineral precipitation. The environments from which the samples were collected are rich in organic matter [31,32,34,37], as appears to be the case for environments where similar aragonite rafts have been reported [3,10]. In contrast, rafts from cave environments, which are typically poor in organic matter, exhibit larger crystals and distinct crystal organization [2,4,11,13]. This contrast suggests that organic matter plays a role in shaping raft morphology by reducing crystal size and influencing their organization, ultimately controlling grain morphology. Natural environments contain a wide variety of organic molecules that can interact with inorganic ions and minerals. In some cases, these molecules promote nucleation, whereas in others they act as poisons to mineral growth [54]. Indeed, soluble organic molecules have been shown to regulate the polymorph precipitated, as well as the elemental composition, morphology and size of Ca carbonates [55–58]. Furthermore, Cölfen and Antonietti [52] highlighted the role of organic molecules in nucleation, crystal growth, and their aggregation into mesocrystals, thereby controlling the shape, size and properties of the material.

In addition to Ca carbonates, a Ca sulfate was also identified in the saltwork sample. Mixed rafts of calcite and gypsum have been found in a gypsum cave [14], although the morphologies of the Ca sulfate phases were distinct. The saltwork samples also contained voids with cubic shapes, chevron structures, and truncated octahedra, all characterized by 90° angles and consistent with halite. Halite rafts have been described in evaporite systems [5,7,15,17,18,20–23], and the crystal morphologies in these rafts are very similar to those observed in this work (see Figure 5d). Relics of sunken rafts composed of halite or gypsum have been identified in the geologic record of evaporite systems [17]. A few cubic

crystals and cubic voids were also observed on the bottom surface of Vermelha Lagoon rafts. Both the saltwork and Vermelha Lagoon are evaporite systems, where halite and Ca sulfates have been reported [38,46].

The lagoons and saltworks from which the samples were collected can be considered evaporite systems. As water evaporates, less soluble minerals such as Ca-Mg carbonates precipitate first, whereas more soluble phases such as Ca sulfates and halite precipitate later [17]. Authigenic Ca carbonates, including calcite, Mg-calcite and/or aragonite, have been reported in the sediments, stromatolites, and/or microbial mats of Vermelha Lagoon [28,38–40,43–46]. The relatively high abundance of these minerals in the sediments [28,39], together with supersaturation with respect to calcite, aragonite, and dolomite [38], indicates widespread precipitation of Ca-Mg carbonates in the lagoon. Indeed, Spadafora et al. [42] documented the precipitation of a Ca carbonate layer on stromatolite surfaces, later shown to consist of Mg-calcite, which also precipitates on shells [35,44]. Nucleation is likely the rate-limiting step for Ca-Mg carbonate precipitation in Vermelha Lagoon, and organic molecules may act as poisons to mineral precipitation directly from solution (e.g., [59]). In this context, the air–water interface may reduce the activation energy required for nucleation, similarly to solid surfaces. As proposed for halite rafts [7,15], evaporation from still water surfaces can increase supersaturation near the air–water interface and is likely the main driver of raft precipitation in Vermelha Lagoon and the other samples analyzed in this work.

5. Conclusions

The combined use of light and electron microscopy imaging, along with analytical techniques, was essential for generating data across multiple length scales, enabling the interpretation of the samples described in this work.

All rafts studied were composed of interconnected polycrystalline grains. The raft's top surfaces were flat, whereas the bottom surfaces were rough as a result of grain growth into the water. Each grain consisted of multiple groups of stacked nanocrystals, indicating that they form through hierarchical particle aggregation, i.e., they are mesocrystals.

The two rafts from Araruama Lagoon (Praia Seca and Iguaba Grande) consist of aragonite. In addition to Ca carbonate, the rafts from the saltwork also contained a Ca sulfate and probably halite.

Evaporation is probably a major driver of raft precipitation in Vermelha Lagoon and other hypersaline environments.

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The Conservation of Architectural Heritage Structures Built with Tuff and Coral Rock: A Systematic Review and Bibliometric Analysis of Geopolymer Formulation, Application, Compatibility and Durability

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Abstract

The conservation of tuff- and coral rock-built architectural heritage structures (AHS) is challenging because access to original tuff and coral rock has become difficult and severely limited due to urbanization, land reclamation, the depletion of stone quarries, anti-mining and anti-quarrying legislation. An emerging approach to address this issue is to create compatible “replacement” rocks via geopolymerization, a process that is more sustainable and greener than the use of conventional cement and concrete. To explore the potential of geopolymers for AHS conservation strategies, the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines were implemented; 103 eligible articles were identified and classified into geopolymers for AHS (34 articles), tuff-built AHS (60 articles), and coral rock-built AHS (9 articles). Tuff substrates in AHSs appear in a variety of colors (yellowish-brown, grayish-cream, reddish-brown, pale greenish-gray and pink hues), densities (1.0–2.5 g/m³), and compressive strengths (3–100 MPa). Meanwhile, coral rock substrates in AHSs appear in whitish-cream color and are coarse-pored (1–5 MPa), fine-grained (8–15 MPa), and calcarenite (50–60 MPa). In terms of geopolymer formulation, metakaolin was reported as the most popular main precursor or admixture, while NaOH and Na₂SiO₃ were used simultaneously as alkaline activators. Aggregates used in geopolymer formulations depended on local availability, including quartz sand, river sand, crushed stones, carbonate stones, volcanic rock, volcanic sand, tuff, brick, ceramic tiles,

and waste materials. Aesthetics, chemical composition, physical attributes, and mechanical properties have been identified as key criteria to ensure geopolymer compatibility for AHS conservation application. To date, geopolymers have been applied for AHS conservation as repair mortars, consolidants (i.e., grout and adhesives), and masonry strengthening (i.e., fiber-reinforced mortar). Finally, geopolymers formulated for AHS conservation have similar durability as the original substrate based on accelerated aging tests (i.e., salt mist, wet-dry, and freeze–thaw) and long-term outdoor exposure experiments.

Keywords: systematic literature review; architectural heritage structures; geopolymer; tuff; coral rock; architecture; heritage

1. Introduction

Architectural heritage structures (AHSs) are historical buildings, monuments, and sites constructed using natural stones or rocks which are being preserved for their cultural importance and significance [1]. Many of these AHSs were built using relatively soft rocks, with effective porosities of 20%–60%, bulk densities of 1.0–2.5 g/m³, and compressive strengths of 3–30 MPa [2–4]. Two natural rocks commonly used in AHSs are tuffs—a type of volcanic rock—and coral rock—a type of sedimentary rock—because they are locally available, soft enough to be worked with ancient tools, more durable than wood, and aesthetically beautiful [5–7].

A serious, inevitable problem associated with AHSs built from tuff and coral rocks is their high susceptibility to weathering, resulting in visible material loss and degradation after prolonged exposure to the environment. For example, Seigesmund et al. [8] reported that scaling and flaking on the surface of tuffs used in Mexican and Armenian AHSs were caused by swelling clay minerals that expand and contract during wet–dry cycles, inducing rock breakage and spalling due to internal tensile stresses. Similarly, Çelik and Sert [9] attributed the deterioration of tuff used in Turkish AHSs to salt crystallization, which was promoted by the high volume of micropores (<0.1 µm in diameter) serving as nucleation sites for rapid salt crystal growth.

In comparison, coral rocks are susceptible to water erosion and acid-promoted dissolution attributed to dissolved CO₂ in the air that lowers the pH of rainwater to around 5.8 [10], which gradually dissolves CaCO₃ in limestones and coral rocks. Manohar et al. [11], for example, investigated the deterioration mechanism of coral rocks used in Ramanathaswamy Temple, Remeshwaram Island, India, and found insignificant mass loss even after 15 cycles of salt weathering tests, which was attributed to the large pore size of the rock (~70% are >0.5 µm). However, visible damage to coral rocks was observed due to erosion from rainwater seepage and wind. Similarly, Urbina Leonor et al. [12] assessed the deterioration pattern of coral rocks used in the Port City of Veracruz, Mexico, using three artificial rain solutions, with pH of 5.0 (acid), 6.2 (non-acid), and 5.2 (global), consisting of [H⁺], [Na⁺], [NH₄⁺], [K⁺], [Mg²⁺], [Ca²⁺], [F[−]], [Cl[−]], [NO₃[−]], [SO₄^{2−}], [HCO₃[−]] or [CO₃^{2−}] and found that a high precipitation volume promoted higher deterioration of the coral rock regardless of its acidity.

Strategies to conserve weathered and degraded AHSs built from tuff and coral rocks follow strict rules to limit damage to the original structure and substrate material. According to the International Council on Monuments and Sites (ICOMOS, 2003), materials for AHS conservation must have visual and mechanical properties similar to those of the original materials to maintain historical authenticity and prevent damage. Traditional restoration techniques for AHSs use stones exploited from original historical quarries [13–15]. For

example, Siedel et al. [13] reported that Rochlitz tuff, obtained from active quarries in the Rochlitz Mountain, was still used to restore historical structures in Germany. As reported by Cárdenes et al. [15], three (3) active quarry areas in Arcuas have been exploiting stones for the restoration of heritage structures in the Canary Islands and Spain.

In recent years, however, urbanization, land reclamation, the depletion of stone quarries, and anti-mining and anti-quarrying legislations have limited access to original AHS materials. For example, the Cathedral Basilica of Aguascalientes, Mexico [16], was built using a light pink tuff called Barranca tuff, but because of the depletion of historical quarries, several restoration efforts have used Valladolid tuff. Similarly, the conservation of coral rock-built Spanish-era (16th to 18th century) churches and watchtowers in Bohol, Philippines, has become challenging because the entire island is a UNESCO Global Geopark, a designation that makes stone quarrying illegal.

An alternative approach to address this issue is to find replacement or substitute stones that have similar properties to the original rock substrate but are obtained from other quarry sites. Replacement stones have a similar visual appearance as the original substrate but their formation times differ, resulting in mismatched physico-mechanical properties and weathering behavior. For example, Blows et al. [17] reported that the currently unavailable Caen stone, a cream-colored, fine-grained French limestone formed during the Middle Jurassic period, used as a building material for AHS cathedrals in the United Kingdom, has often been replaced by Lepine stone, a whitish English limestone formed during the Upper Jurassic. Both stones were tested for salt weathering, and it was found that Lepine stone was less durable (14% mass loss) than the original Caen stone (4% mass loss) after 15 cycles of simulated salt weathering. These authors attributed the higher durability of Caen stone to its lower microcrystalline calcite content (50%) compared to Lepine stone (70%).

Similarly, Přikryl and Török [18] assessed the impacts of a new stone introduced to the Charles Bridge in Prague, Czech Republic, which was built using local sandstone that is now unavailable due to the closure of all sandstone quarries in Prague. The color, physical, mechanical, and weathering behaviors of the new stone differed from those of the original substrate, which likely accelerated the deterioration of the Charles Bridge. As countermeasures, both the original and replacement stones were investigated based on their petrophysical and mechanical properties to determine their compatibility, rather than solely relying on visual characteristics such as color, texture, and grain size. Rozenbaum et al. [19] also emphasized selecting replacement stone based on its aesthetic, physical, and mechanical properties. These authors noted that Saint-Maximin stone, a French limestone used in Le Mans Cathedral (11th–15th century), was incompatible with Romanian Limestone in terms of composition (SiO_2 of 12.5% and 0%; CaCO_3 of 87.4% and 97.1%), total porosity (38.0 and 27.0), and pore volume sizes (18 μm and 8 μm). In comparison to Garchy Stone, a limestone originating from south Paris, used in the cathedrals in Orleans, Nevers and Bourges (13th century) and its compatible replacement limestone in central Romania have a similar composition (SiO_2 of 0 and 1.7%, CaCO_3 of 99.6% and 97.5%), total porosity (19.7%, and 18.2%), and pore volume sizes of (1.3 μm and 1 μm). Meanwhile, Martínez-Martínez et al. [3] followed the recommendation of Rozenbaum et al. [19] and investigated other replacement tuff stones of the original rocks used in AHSs in Morelia from other quarries; they conducted compatibility tests based on petrophysical rather than solely aesthetic considerations.

In the absence of replacement stones or rocks, conservation activities for AHSs have historically relied on cementitious materials, such as cement- and concrete-based materials, due to their favorable mechanical properties and on-site applicability. In the 1950s, for example, concrete was used for the early restoration of Eger Castle in Hungary [20]. Concrete, however, promoted the formation of salt efflorescence, which led to severe

deterioration of the original stone substrate. According to Török et al. [20], the lower permeability of the concrete sealing the tuff walls of the Eger Castle not only introduced more rainwater into the tuff substrate but also prevented pore water evaporation, thereby enhancing salt efflorescence formation.

To improve compatibility, “artificial stones”, a type of concrete designed to mimic the natural physical and mechanical properties, including color and texture, of the natural stone by mixing local materials (e.g., natural pozzolana, crushed stones, local soils, sand) with white cement, superplasticizer, and inorganic-colored pigments, have recently been developed. For example, Stefanidou et al. [21] formulated an artificial stone to restore three (3) AHSs in Greece, namely the Ancient Agora of Pella, (5th–4th B.C.), the Ancient Theatre of Maronia (4th–3rd B.C.), and the Fortress of Saint Nicolaos of the Medieval City of Rhodes (15th century) built from marl limestone, limestone/marble, and sandstone, respectively; the result showed compatibility to natural stones attributed to texture, color, pore size distribution and compressive strength. Similarly, Menningen et al. [22] developed an artificial stone to mimic the aesthetic appearance and petrophysical properties of the original Armenian tuff for the restoration of cultural heritage, using cement, crushed original stones, and colored pigment. However, the drawbacks of artificial stone include the use of ordinary Portland cement (OPC), a major contributor to carbon dioxide (CO₂) emissions.

An emerging, more sustainable and greener alternative for cement- and concrete-based materials is geopolymers [23,24]. Geopolymers have been widely used as a sustainable alternative to OPC for reducing carbon emissions, providing high chemical resistance and mechanical strength under optimal conditions [25–27], and repurposing waste streams [28–31]. For example, Amar et al. [32] obtained a higher 7-day unconfined compressive strength (UCS) of 44 MPa for geopolymer concrete in comparison to OPC concrete (36 MPa), while at later stages of hardening (28 days), both have comparable UCS values of 51 MPa for geopolymers and 54 MPa for OPC.

Geopolymers have also been recently formulated to mimic the properties of natural rocks, a key development in the successful application of these materials for AHS conservation. For example, Peltz et al. [33] designed a synthetic sandstone, using metakaolin as the precursor and quartz sand as the aggregate, achieving an effective porosity (22.8%) and compressive strength (19.6 MPa) lower than those of natural rocks such as Berea sandstone at 13.1%, and 91.2 MPa and Flechtingen Sandstone at 5.8% and 129 MPa, respectively. Meanwhile, Simão et al. [34] utilized stone cutting waste from marble (80 wt%) and volcanic rocks (20 wt%), at 50 wt% and 75 wt% replacement for metakaolin, resulting in open porosity of 49.5% and 53.6% and a compressive strength of 28 MPa and 14 MPa, respectively. Meanwhile, Khater et al. [35] prepared a slag–metakaolin–granite composite (12.5 wt%–12.5 wt%–75 wt%) via hydraulic pressing at 30 MPa, 50 MPa, and 70 MPa, resulting in a compressive strength of 20.9 MPa, 35.8 MPa, and 13.3 MPa, respectively.

To explore in detail the formulations and properties of geopolymers applied to AHS conservation strategies, we employed a systematic approach to review the literature. Although several review papers about stone heritage conservation have been published, the majority did not focus on the application of geopolymers [36,37]. Among the few reviews that included geopolymers, the content and discussion were limited to functionalizing geopolymers as coating mortars [23] and reinforcing historical structures [24]. These previous review papers did not include compatibility criteria or issues between geopolymers and the original substrate of AHSs in terms of aesthetics, chemical composition, physical attributes, and mechanical properties. Moreover, the durability of geopolymers applied to AHS conservation has not yet been explored in detail. These knowledge gaps on geopolymer application for AHS conservation are addressed in this work, which is guided by the following research questions:

- i. What are the physical and mechanical properties of original tuff and coral rock substrates in AHSs?
- ii. What geopolymer formulations have been developed and applied for tuff-built and coral rock-built AHSs from 2013 to 2024?
- iii. What are the compatibility criteria used and properties measured in selecting geopolymers for the conservation of AHSs built from tuff and coral rocks?
- iv. How are geopolymers characterized, evaluated and applied in the conservation of AHSs built from tuff and coral rocks

2. Review Methodology

2.1. Search and Identification

This paper employed the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines [38] and the protocols recommended by Andrews [39] to review the conservation of heritage structures built with tuff and coral rock using geopolymers. Prior to the search, the protocol was pre-registered in the Open Science Framework (OSF) with registration DOI: 10.17605/OSF.IO/RQMJU. The search field remained within article title, abstract, and keywords and used the search string “geopolymer” OR (“coral” AND “rock”) OR “tuff” AND “heritage”, with publication dates restricted to 2013–2024, across the Scopus and Web of Science (WoS) databases and extracted during August 2025. A total of 487 items, 227 from Scopus and 260 from WoS, were retrieved, which were reduced to 368 after removing duplicates. Meanwhile, Google Scholar was used as a supplementary database with a similar search string, identifying 10 articles. The search, screening and article retrieval were conducted between June and July 2025.

2.2. Screening and Inclusion Criteria

Figure 1 illustrates the screening process, which excluded articles that did not focus on tuff, coral rocks, or geopolymers based on titles, abstracts, highlights, and keywords. These criteria removed 249 articles, resulting in 119 items for eligibility assessment. Based on the eligibility criteria, conference proceedings (13), inaccessible articles (2), review papers (1) and non-English studies (1) were removed. Full-text articles were also evaluated [40], and those not focusing on geopolymers for AHS conservation (9) were excluded. The PRISMA guidelines also allow for the inclusion of articles using other methods; thus, 10 articles were added using Google Scholar following the same screening criteria, and a total of 103 articles were classified for tuff-built heritage, coral rock-built heritage, and geopolymers applied to AHSs (Figure 2). Because this review focuses on geopolymers for AHS conservation, 34 papers containing experimental data sets were analyzed and summarized, while the remaining 69 articles about tuff-built and coral rock-built AHSs were included in this review because they had useful descriptive information about original substrate characterization and properties, assessment protocols and/or the extent of original substrate deterioration. The 34 geopolymer papers were further subdivided into different precursor materials used: metakaolin (12), fly ash (4), slag (4), volcanic ash (5), ceramic wastes (4), tuff waste (1), pumice (1), silica fume (1), local clay (1), and mine wastes (1).

2.3. Review Limitations

This review only focused on the formulation of geopolymers, including their compatibility and application for AHSs built from tuff and coral rocks. In addition, the discussion of geopolymer formulation was limited to the type of precursors, alkali activators, admixture, aggregate, and 28-day compressive strengths (unless specified). Meanwhile, material compatibility discussion focused on the use of aesthetic qualities as well as chemical, physical, and mechanical properties as criteria for selection. Aesthetic qualities were limited to color,

texture, and the presence of effloresce while chemical properties focused on microstructure and the release of ions from the substrate. Physical properties were limited to open porosity, water absorption, capillarity, and bulk density. Finally, mechanical properties focused only on important factors like adhesion, surface hardness, compaction, and compressive, tensile, and flexural strengths. Geopolymer application in AHSs was limited to the most common type of interventions, including repair mortar, consolidants, and masonry strengthening. In addition, the long-term behavior of the geopolymers was also reviewed, but limited to accelerated and long-term stability tests.

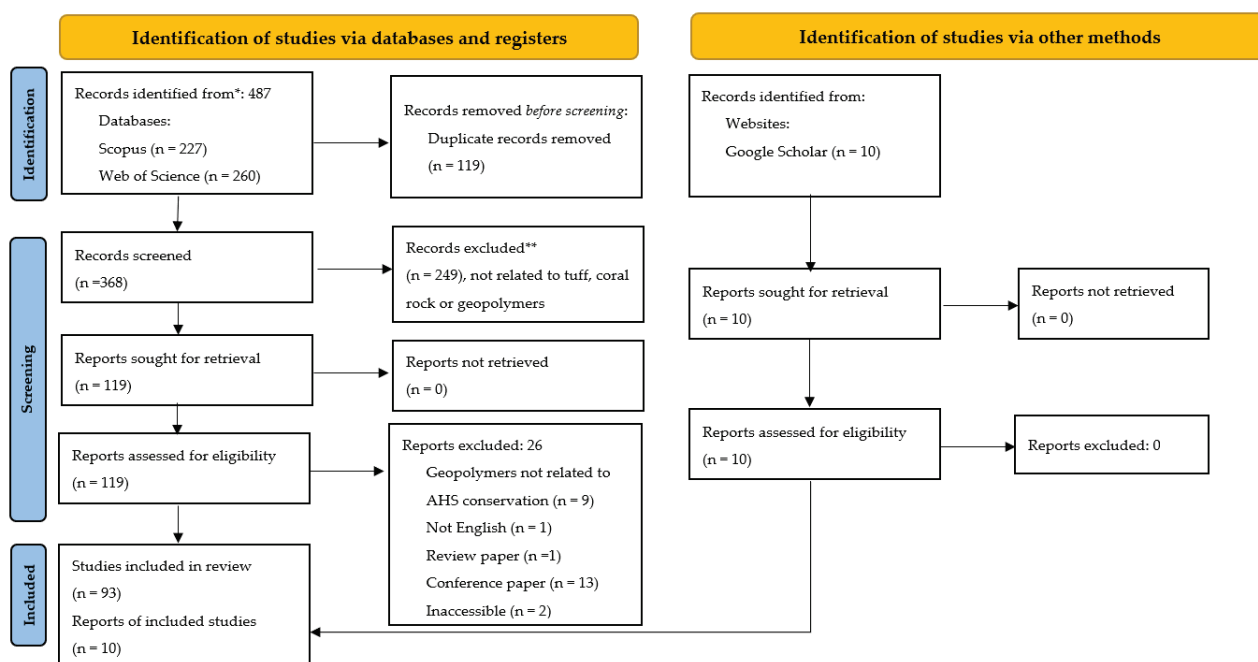
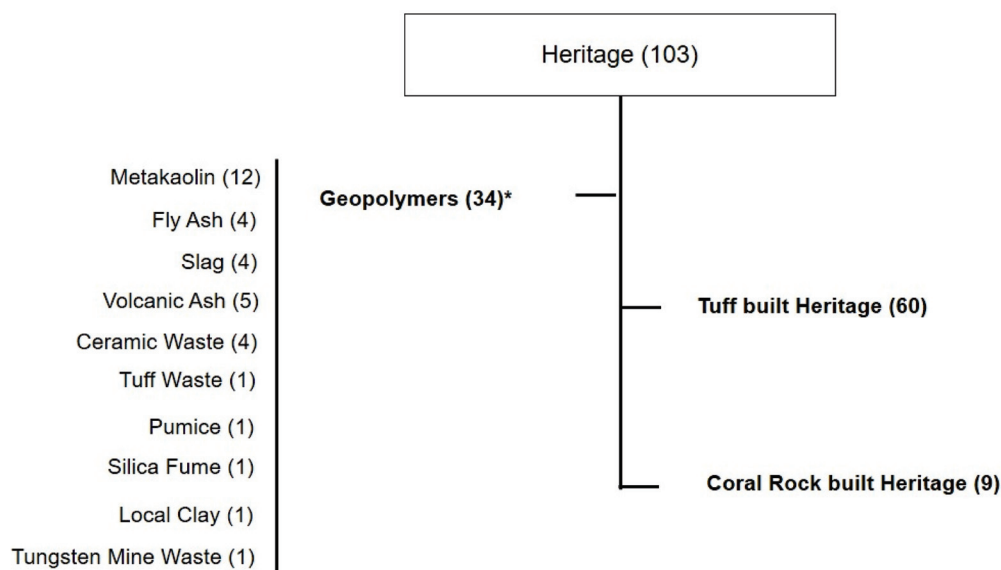


Figure 1. A schematic diagram of the article selection process following the PRISMA guidelines. * Reported the number of records identified from each database. ** Excluded by human, no automation tools used.



Note*: In cases of a combination of several precursors, the precursor with highest wt% is considered. For example, a binary mixture of fly ash-metakaolin-, wherein metakaolin is 10 wt%, of precursors, then geopolymer article is counted as fly ash.

Figure 2. Classification of eligible items related to AHS conservation analyzed in review.

3. Physical and Mechanical Properties of Original Tuff and Coral Rock Substrates of Architectural Heritage Structures

3.1. Tuff-Built Architectural Heritage Structures

Tuffs are rocks composed of pyroclastic materials (i.e., ash, rocks, and crystals) consolidated and naturally cemented with time due to extreme temperature and pressure generated during a volcanic eruption. Table 1 lists some tuff-built AHSs from different countries, along with their corresponding colors and physico-mechanical properties.

In general, tuffs exhibit a variety of colors, textures, and physico-mechanical properties depending on their location [2]. In Europe, tuff-built AHSs are found in Italy, Hungary, Spain, the Netherlands, Slovakia, and Germany (Figure 3). In Italy, for example, prominent AHSs such as the Ovo Castle, St. Elmo Castle, St. Domenico Maggiore Cathedral and St. Chiara were constructed during the 13th–16th century using Neapolitan Yellow tuff, a yellowish-brown, lightweight, and low-strength rock with a bulk density and compressive strength in the range of 1.0–1.3 g/m³ and 3–6 MPa, respectively [4]. Similarly in Hungary, a greyish-creamy to reddish-brown tuff with higher bulk density (1.6–1.8 g/cm³) and compressive strength (7–26 MPa) than Neapolitan Yellow tuff was used to construct the Sirok Castle, Eger Cathedral, and Ottoman Minaret during the 13th–19th century [5]. This tuff has a strength comparable to the greyish-beige tuffs used in cathedrals, churches, and historical buildings in the Netherlands, with compressive strengths ranging from 13 to 29 MPa [6,7]. In Rochlitz, Germany, a slightly higher strength tuff with a distinct deep reddish-brown color, with a similar appearance to a fired clay brick, was used to construct the Church of St. Maria in Mittweida, the Collegiate church in Wechselburg (Zchillen), and Portal of the church St. Kilian in Van Lausick, all of which were built around the 12th–15th centuries [13]. Two relatively high strength tuffs with compressive strengths ranging from 50 to 100 MPa have been reported in the literature. One was used in the Archaeological site of Mösne, Slovakia (16th–19th century; pale green-grayish rock) [14], while the other is known as the Arucas stones—with a dominant grey and a hint of yellow, blue, and red—from Canary Island, Spain, which was used in constructing the Church of San Juan Bautista [15,41].

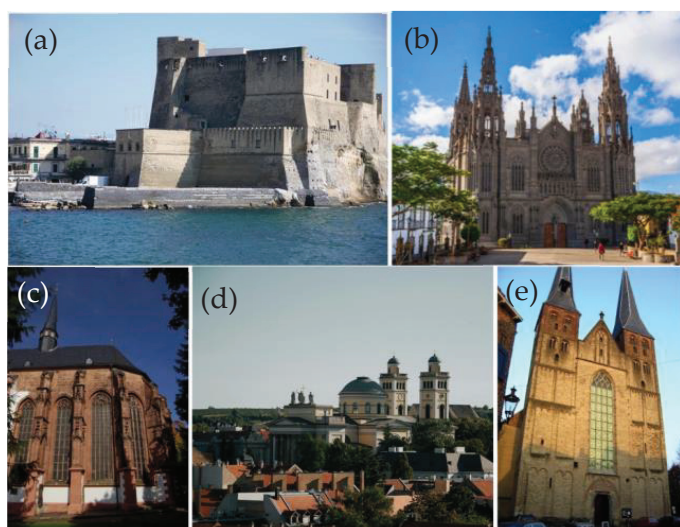


Figure 3. Examples of European tuff-built AHSs: (a) Ovo Castle, Naples, Italy (13th–16th century) (photo by Gmaiga from Pixabay), (b) Church of San Juan Bautista, Canary Islands, Spain (20th century) [15], (c) Church of St. Maria, Mittweida, Germany (15th century) [13], (d) Eger Cathedral, Eger, Hungary, (19th century) (photo by Molnár Tamás Photography from Pexels), and (e) Bergkerk, Deventer, Netherlands, (13th century) [7].

In North America, several AHSs were constructed in Mexico in the 16th century during the Spanish occupation and in Honduras during the Mayan civilization, dated 250–900 CE (Figure 4). In Mexico, there are a large variety of tuffs used in Spanish-influenced AHSs [42,43]; two of the most popular are the “Piera Vieja”, a pink-colored tuff with an effective porosity of 26.5%, bulk density of 1.8 g/cm³ and compressive strength of 30.8 MPa, and “Barranca Tuff”, with an effective porosity of 37.5% and bulk density of 1.5 g/cm³, which were used as building stones for Cathedrals in Morelia and Aguascalientes, respectively. Similarly, other colored tuffs were used, including the green-reddish colored “Loseros tuff”, with an effective porosity of 6%–17%, bulk density of 2.1–2.3 g/cm³, and compressive strength of 21–74 MPa and the white-colored “Tezoantla tuff”, with an effective porosity of 14.9%, bulk density of 1.9 g/cm³, and compressive strength of 50–67 MPa used in several historical sites of Guanajuato and Hidalgo, respectively, to construct historical churches, cathedrals, and government buildings in Mexico [3,16,44–46]. In Honduras, the famous Heritage Site, the Archeological Site of Copan, with a classic Mayan architecture, such as the Hieroglyphic Stairway, was built using Maya Tuff during 756 CE, a buff-greenish-colored stone with an effective porosity of 27%–28% [47,48].



Figure 4. Examples of representative tuff-built AHSs in North America: (a) Cathedral of Morelia, Mexico, (17th century) [42]; (b) Cathedral of Aguascalientes, Mexico (16–20th century) [16]; (c) Façade of Santa Veracruz Chapel of Mineral del Monte, Mexico (16th century) [46]; (d) Façade of Legislative office, Loseros, Mexico, 19th century [45]; and (e) Maya tuff stones, in Archeological Site in Copan, Honduras, (763 CE) [47].

In West Asia, several AHSs were built in Turkey and Armenia using tuff (Figure 5). In Turkey, there are various types of tuffs but those quarried in the Cappadocia region [49] like the cream-beige colored Döğler Tuffs in Afyonkarahisar (effective porosity of 42%, bulk density of 2.5 g/cm³, and compressive strength of 26.5 MPa) [9,50–53] and whitish-gray tuff in Malatya (effective porosity of 14.8%, bulk density of 1.8–1.9 g/cm³, and compressive strength of 12.9 MPa) [54] are the most notable. These tuffs were used to construct caravanserais—a roadside inn alongside the Silk Road with a central courtyard used by travelers for trade and commerce—mosques, and churches such as the Kayseri Castle (527–565 B.C.) in Kayseri, Döğler Caravanserai (1434) in Afyonkarahisar, and the 12th-century Battalgazi Mosque in Malatya. In Armenia, the tuff had a variety of colors, including black, red, golden, and grey brown, and was used in the construction of religious monuments and buildings like the Cathedral of Etchmiadzin (constructed around 301–303 A.D.) and the All Savior Church in Gyumri, which was rebuilt using black tuff [55].

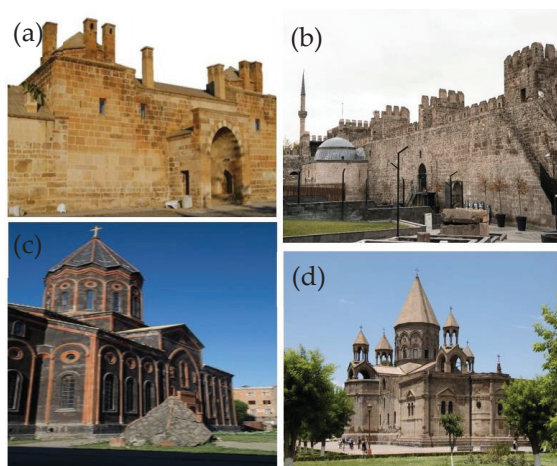


Figure 5. Examples of tuff-built AHSs: (a) Döğer Caravanserai, Afyonkarahisar, Turkey (1434) [51], (b) Kayseri Castle, Kayseri, Turkey, (527–565 B.C.) (Photo by Ahmed from Pexels.com), (c) All Savior Church, Gyumri, Armenia (1858–1872) [22], and (d) Cathedral of Etchmiadzin (301–303 A.D.), Armenia (photo by Areg Amirkhanian from worldhistory.org).

In East Asian countries such as China, Japan, and South Korea, tuff was used to construct platforms for temples, pagodas, shrines, and sculpted statues, which generally had a common grayish hue as a distinguishing characteristic (Figure 6). In China, for example, Guo et al. [56] characterized the stone platform used in Baoguo Temple, located in Ningbo, dated from 880–1013 C.E., with a light purple to grey color, which was similar to the tuff used in the Sanlao Stone chamber in Hangzhou, Zhejiang Province, with a grey-green color built in 1921 [57]. Meanwhile, in South Korea, the stones used in the five-story pagoda at Geumgolsan Mountain (Korean Treasure No. 529), in Jingdo-gun are estimated to have been constructed in 918–1392 CE and originally had a yellow to light gray color but now appear black and brown from weathering [58]. Meanwhile, the Oya Stone, a soft tuff in Japan, can appear grayish, brownish/creamy, or greenish, and was used to build the famous Oya-ji temple in 810 CE [59,60].



Figure 6. Examples of tuff-built AHSs in East Asia: (a) Baoguo Temple, Ningbo, China, (880–1013) [56], (b) Sanlao Stone House, Zhejiang, China (1921) [57], (c) Korean Treasure 529, Jingdo, S.Korea (918–1392 CE) (photo taken from Korean Heritage Service), and (d) Oya-ji Temple, Kanto, Japan (810 CE) [59].

Table 1. A list of notable AHSs around the world and the physical and mechanical properties of tuff used to build them.

Country	Heritage Structure, Region	Tuff Name	Color (Unweathered)	Effective Porosity (%)	Bulk Density (g/cm ³)	Unconfined Compressive Strength (MPa)	Date Constructed	Ref.
Italy	Ovo Castle, Naples							
	St. Elmo Castle, Naples	Neapolitan Yellow Tuff	Yellow-brown	50–60	1.0–1.3	3–6	13th–16th	[4]
Hungary	St. Domenico Maggiore Cathedral, Naples							
	St. Chiara Cathedral, Naples							
	Sirok Castle, Sirok	Eger, Demjén, Sirok, Bogács,	Greyish-cream	52.6	1.6	7.2		
	Eger Cathedral, Eger			41.8	1.5	10.4	13th–19th	[5]
	Ottoman Minaret		Reddish-brown	29.9	1.6	28.2		
				25.6	1.8	26.5		
Netherlands	St. Peter's church, Leiden	Römer Tuff, Weiberner, Ettringer Tuff	Greyish-beige	–	–	13–29	11th–15th	[6,7]
Germany	The Bergkerk, Deventer							
	The Deanery, Deventer							
	Church of St. Maria in Mittweida							
	Church St Kilian in Bad Lausick	Rochlitz Porphyry Tuff	Red	27.1	1.7–2.2	13.5–56	12th–15th	[13]
	Collegiate church in Wechelsburg							
Slovakia	Architectural site of Mósnyé	Peračica Tuff	Green	19.7–20.6	–	72–85.8	16th–19th	[14]
Spain	Church of San Juan Bautista, Canary Islands,	Rosa Silva, Piedra Azul, Piedra Amarilla, Rosa Silva, Lomo Tomas	Grey-blue, ochre	0.4–19.6	2.1–2.4	74–109		[15]
			Grey	3.2	2.4	67–69	20th	[40]
			Grey	22.0	2.1	51–60		
Mexico	Cathedral of Morelia	Piedra Vieja	Pink	26.5	1.8	30.8	17th	[3,42]
	Cathedral of Aguascalientes	Barranca Tuff	Pink	37.31	1.5	–	16th–20th	[16]
	Legislative Palace of Guanajuato,	Loseros Tuff	Green-red	6.8–17.4	2.1–2.3	21–74	19th	[43]
	Reloj Monumental (Clock Tower), Hidalgo	Tezoantla Tuff	White	14.9	1.9	50–67	1910	[44]
	Santa Vera Cruz Chapel, Hidalgo					1563–1578		
Honduras	Hieroglyphic Stairway, Copan	–	Buff-green	27–28	–	–	756 CE	[47,48]
Turkey	Kayseri Castle, Kayseri	Kuruköprü tuff	Greyish	22	1.9	52.5	527–565 BC	[49]
	Döğür Caravanserai, Afyonkarahisar,	Döğür Tuff	Cream-Beige	42	2.5	26.5	1434	[9,50–53]
	Battalgazi Heritage Mosque, Malatya	–	Greyish	14.8	1.8–1.9	12.9	12th	[54]
Armenia	All Savior's Church in Gyumri,	Gyri Black	Black	14.7	2.1	78.2	19th	[22,55]
China	Baoguosi Temple, Ningbo	–	Light-purple to grey	–	–	–	880–1013	[56]
	Sanlao Stone Chamber, Hangzhou	–	Grey-green	26	2.1	–	1921	[57]
South Korea	Five Stone Pagoda, Geumgolsan Mountain, Jindo-gun	–	Light gray	17.8	–	–	918–1392	[58]
Japan	Oya-ji Temple, and Stone Buddhas, Tochigi Prefecture, Kanto	Oya Stone	Gray, brownish/creamy, or greenish	40–45	1.4	10–15	810 CE	[59,60]

3.2. Coral Rock-Built Architectural Heritage Structures

Another type of rock widely used for AHSs is coral rock, also known as “coral stone” or “coral reef limestone”. Coral rock is a type of limestone with a white to cream-white color formed from coral reefs in ancient oceans, with an appearance similar to that of corals. They are formed when corals—produced by a multicellular organism called polyps—slowly develop a thick calcareous exoskeleton from sorbing abundant calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions in marine ecosystems. As these polyps die, their hard exoskeletons, consisting of calcium carbonate (CaCO_3), remain and, over millions of years, are buried, cemented, and compacted, transforming into coral rocks [11]. Meng et al. [61] reported four (4) categories of non-porous coral rocks—boulder, framework, gravel, and calcarenite—depending on the grain sizes. This variation in coral rock grain sizes could be attributed to the extent of dolomitization, cementation, erosion, and dissolution of coral skeletons over millions of years. For example, the calcarenite coral rock used in constructing the Ramanathaswamy Temple (India) had a bulk density of 2.21 g/cm^3 and a 50–60 MPa compressive strength [11].

When coral rocks have a reef-like appearance with visible pore structure, they can be classified into coarse-pore and fine-pore types, with annular and linear pore arrangements, respectively (Figure 7). Xu et al. [62], for example, employed a polarizing microscope and estimated pore sizes of 0.5–1 mm and 100–200 μm for coarse and fine coral rock, respectively. Wei et al. [63] also noted the lower compressive strengths (1.6–4.7 MPa) of coarse coral rock compared with fine coral rocks (7.6–15.1 MPa). Several examples of coarse coral rock are the Megalithic Temples of Malta, the Historical Houses of Jeddah in Saudi Arabia, the Historical Dome in Qeshm Island, Iran, and the Veracruz Port in Veracruz City, Mexico. In comparison, fine-pore coral rock was used in the Mosque in the Maldives, Historical Ruins in Kenya, Historical Houses in Tanzania, and Baroque Churches, government structures and Watchtowers during the Spanish Era in various islands and coastal regions in the Philippines. Table 2 summarizes some coral rock-built AHSs from the Maldives, Philippines, India, Mexico, Saudi Arabia, Iran, Kenya, and Tanzania. Like tuff, coral rocks come in several forms.

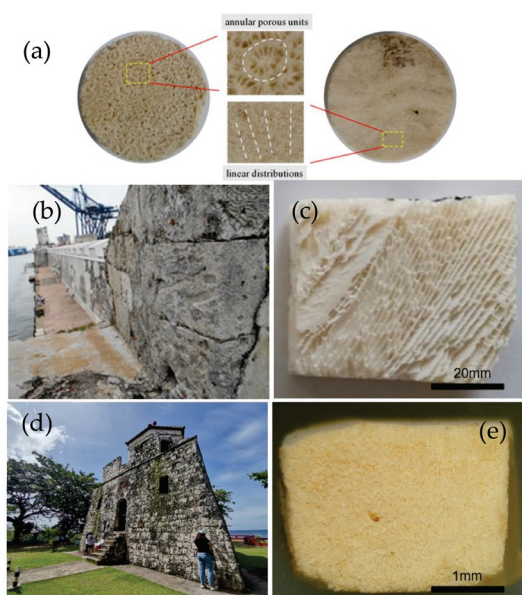
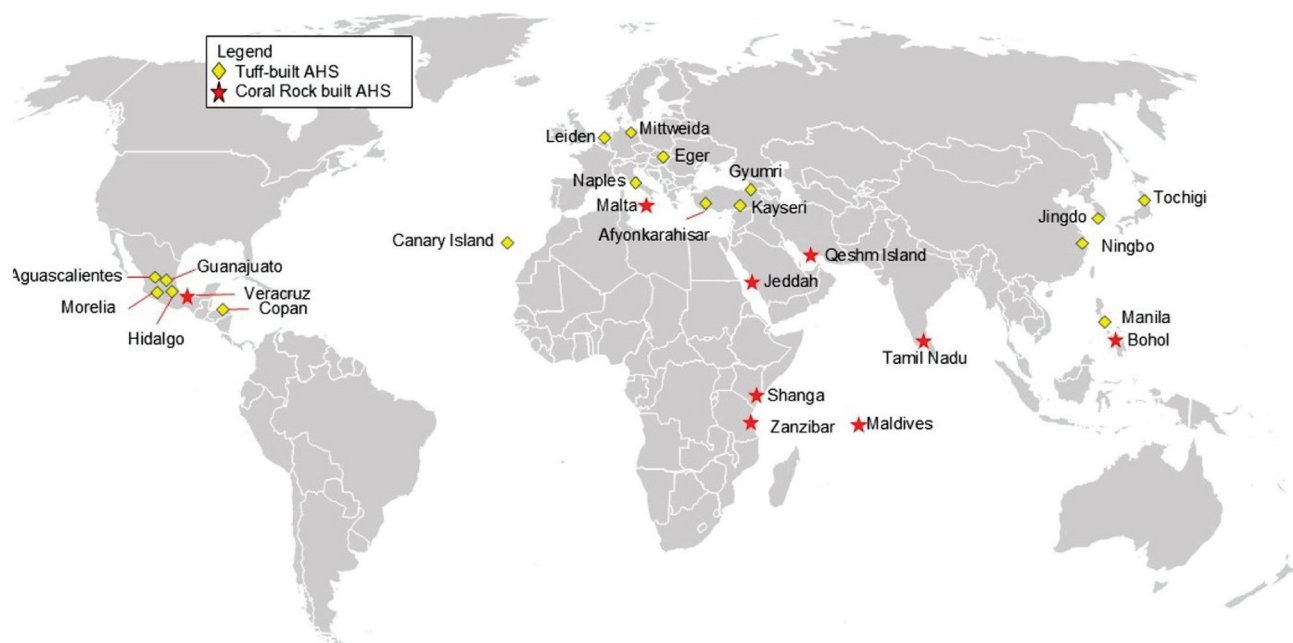


Figure 7. Different pore-structured coral rocks with a clear difference in pore structure: (a) coarse-pore coral rock and fine-pore coral rock [63], (b) coral rock used in the Port of Veracruz, Mexico, (c) a 5 cm cubic specimen of coarse-pore coral rock in Port of Veracruz, Mexico [12], (d) Maribojoc Watchtower, Bohol, Philippines, and (e) a 2 cm cubic specimen of fine-pore coral rock in Maribojoc Watchtower. Photos in (d,e) are from the authors.

Table 2. A list of notable AHSs built using coral rocks.

Country	Region	Coral Rock Type	Structure	Year	Ref.
Maldives	Several atolls	Fine-pored	Historical Mosque,	15th–17th	[64]
Philippines	Bohol	Fine-pored	Albuquerque Church, Dimiao Chapel, Maribojoc Church and Watchtower	17th	[65]
Kenya	Shanga	Fine-pored	Historical Ruins	10th–11th	[66]
Tanzania	Zanzibar	Fine-pored	Historical Residential Town	17th	[67]
India	Tamil Nadu,	Calcarenite	Ramanathaswamy Temple	13th	[11]
Mexico	Veracruz	Coarse-pored	Fortress of San Juan de Ulua and of the Portal de Miranda	16th–19th	[12]
Saudi Arabia	Jeddah	Coarse-pored; Calcarenites	Historical Residential Houses	646 AD	[68]
Malta	Malta Island	Coarse-pored	Megalithic Temples	4000–3000 BC	[69]
Iran	Qeshm Island	Coarse-pored	Historical Dome	800 AD	[70]

Figure 8 illustrates the locations of some AHSs constructed from tuff and coral rocks, indicating that most tuff-built AHSs are in areas with volcanoes, such as Japan, China, the Philippines, and Korea, all within the Pacific Ring of Fire. In addition, tuffs can be classified in terms of color depending on location, with tuffs found in South America (Mexico and Honduras) being light-colored, those found in Europe (e.g., Turkey) having grey to dark colorations, and those in Asian countries being characterized by intermediate (grey) to light colors. In comparison, AHSs made of coral rocks are situated in coastal regions (i.e., ports or islands) in tropical countries and can be further classified based on their physical property; that is, fine-pore coral rocks in AHSs are found in the Philippines, Kenya, Tanzania, and Maldives, coarse-pore coral rocks are common in AHSs in Mexico (South America), Jeddah, Iran (Middle East) and Malta (Europe), and non-pored coral rocks such as the calcarenite coral rock are common in India.

**Figure 8.** World map showing locations of some notable AHSs built from tuff or coral rocks.

4. Geopolymers in Architectural Heritage Structure Conservation

4.1. Publication Trends of Geopolymers in Architectural Heritage Structure Conservation

Figure 9 displays the trend of 34 articles on geopolymers for heritage conservation. The study of geopolymers for cultural heritage began in 2016, a year after the ratification of the United Nations Sustainable Development Goals (UN-SDGs), primarily focusing on developing sustainable repair mortars using metakaolin as a precursor material. In 2017, geopolymer composites with the addition of resins, mine waste, and fibers were reported, but the following year (2018), no publications on geopolymers for heritage conservation were found. In 2019, articles published focused on the repair of broken ancient tiles, while in 2020, there was a rapid increase in the use of pyroclastic deposits as geopolymer precursors and repurposing waste printed circuit boards. In 2021, waste bricks and stone waste were introduced as precursor materials and aggregate and mineral additives to improve the compressive strength of geopolymer mortar. The following year (2022), the addition of porcelain and tile wastes as a partial replacement for traditional metakaolin was evaluated, while silica fume was used as an alternative lime-based grout for historical masonry, and organic additives (polyvinyl acetate (PVA) and polydimethylsiloxane (PDMS)) were added to metakaolin-based geopolymers. In 2023, tuff and brick wastes were used as precursors and aggregates to develop geopolymers, ensuring characteristics similar to the original stone or materials, while in 2024, the apparent use of tile waste as repair mortar for suitability in historical brick masonry was attributed to its similar chromatic appearance.

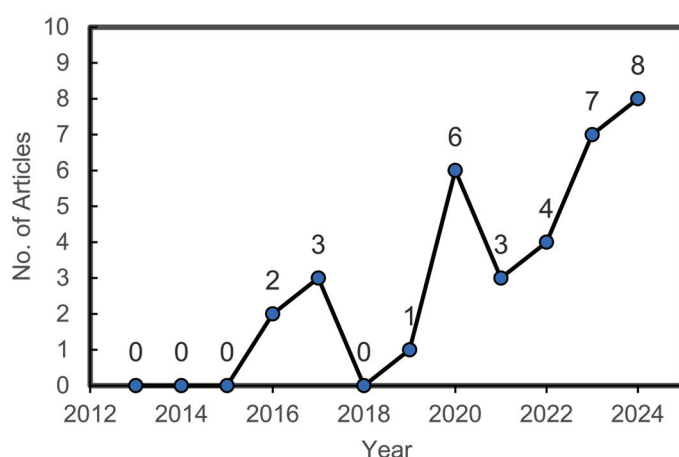


Figure 9. Number of articles published from 2013 to 2024 on geopolymers for AHS conservation.

4.2. Active Countries, Journals, and Institutions

Table 3 lists the countries where research on geopolymers for heritage conservation is active. Italy has the highest frequency on the list at 56%, followed by Portugal (12%), the Czech Republic (12%), and Turkey (6%).

Table 3. Countries with active publications from 2013 to 2024 on geopolymers for AHS conservation.

Country	Frequency	% (N = 34)
Italy	19	56
Portugal	4	12
Czech Republic	4	12
Turkey	2	6
India	2	6
Morocco	1	3
Philippines	1	3
China	1	3

Figure 10a shows the journals commonly publishing studies on geopolymer-based materials for heritage structures. Construction and Building Materials (21%), a Q1 journal based in the UK, has the highest publication rate, followed by Materials (11%), Ceramics International (8%), Journal of Building Engineering (8%), Crystals (5%), Polymers (5%), and Sustainability (5%).

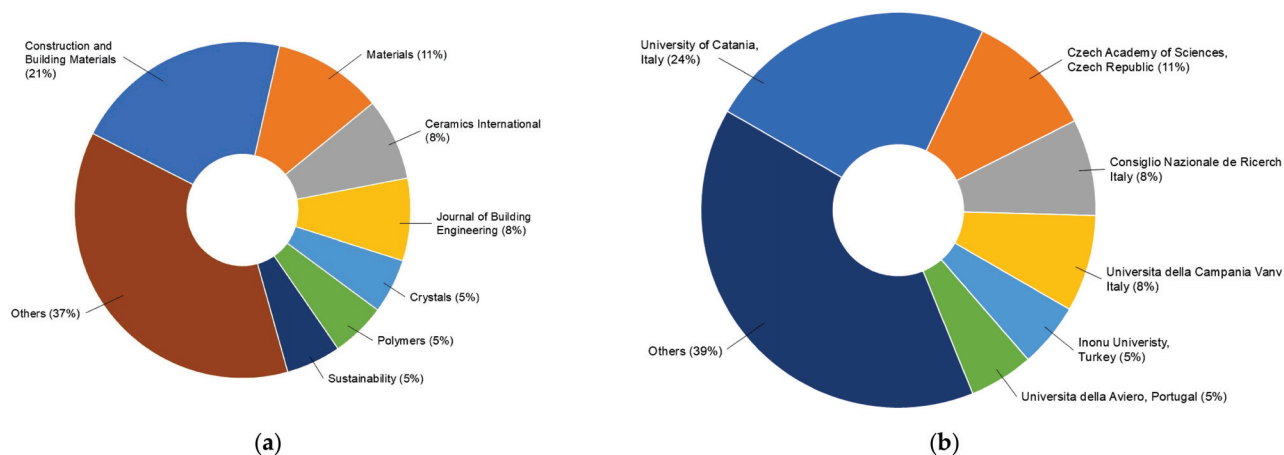


Figure 10. Active (a) journals and (b) institutions publishing on geopolymers for heritage conservation from 2013 to 2024.

Figure 10b displays the affiliation of authors by the number of publications, highlighting that most institutions are located in countries such as Italy, the Czech Republic, Turkey, and Portugal. The most active institution is the University of Catania (24%) in Italy, followed by the Czech Academy of Sciences (11%) in Czech Republic, then the Consiglio Nazionale de Ricerche (8%), and Universita della Campania Vanvitelli (8%) both in Italy, Inonu University in Turkey (5%) and Univerista della Aviero in Portugal (5%).

4.3. Active Authors

Table 4 summarizes the most active authors from 2013 to 2024, with Roberta Occhipinti (10.5%) being the most active, with four articles on the development of geopolymers using pyroclastic deposits (i.e., pumice, volcanic ash, volcanic soil). She is followed by Fugazzotto, M. (7.9%), with three papers related to the valorization of ceramic tile waste for geopolymers, and Perná, I. (7.9%), who focused on developing metakaolin-based geopolymers. Other notable authors include Ricciotti, L. (utilized ceramic tile waste and the addition of organic additives), Finocchiaro, C. (utilized pyroclastic materials, including volcanic ash and soil, using potassium activators), and Montinho, S. (focused on metakaolin-based geopolymers for repairing fragmented ancient ceramic tile facades).

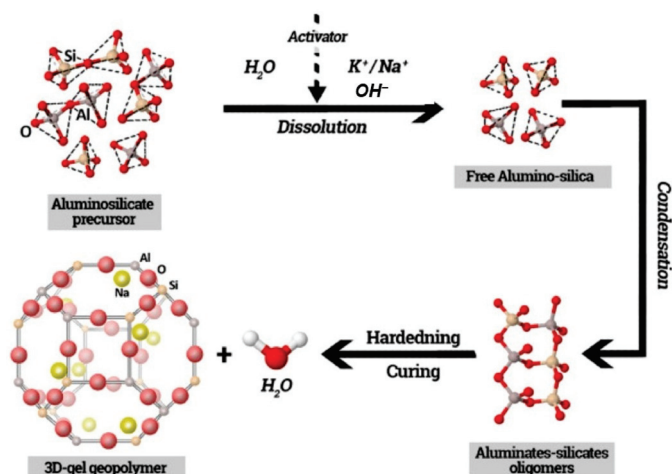
4.4. Definition and Formation Mechanism

Geopolymers are widely considered green alternative cementitious materials because of their low carbon emissions, high chemical resistance, and good thermal properties and mechanical performance [71,72]. This alternative material is formed by mixing geological (e.g., metakaolin, clays or volcanic ash) or industrial by-products/wastes (e.g., coal fly ash, palm oil fuel ash, silica fume, mine tailings, and slags) rich in aluminosilicate-bearing phases as “precursors” with alkali hydroxides (e.g., NaOH, KOH, and lime) and silicate solutions (e.g., Na_2SiO_3 and K_2SiO_3) as “activators” to form an amorphous to semi-crystalline structure with tetrahedral coordination of silica and alumina covalently bonded to oxygen, similar to the 3D arrangement of zeolitic materials, but with the presence of interstitial water and a porous structure [28–31].

Table 4. List of active authors, number of published studies, and country.

Author	Frequency	% (N = 34)	Country
Occhipinti, R.	4	12	Italy
Fugazzotto, M.	3	9	Italy
Perná, I.	3	9	Czechia
Ricciotti, L.	3	9	Italy
Finocchiario, C.	2	6	Italy
Moutinho, S.	2	6	Portugal
Tamburini, S.	1	3	Italy
Clausi, M.	1	3	Italy
Angelo, A.	1	3	Italy
Capasso, I.	1	3	Italy
Longo, F.	1	3	Italy
Vasanelli, E.	1	3	Italy
Rescic, S.	1	3	Italy
Maras, M.M.	1	3	Turkey
Kutlusoy, E.	1	3	Turkey
Baltazar, L.	1	3	Portugal
Beghoura, I.	1	3	Portugal
Allali, F.	1	3	Morocco
Kakria, K.	1	3	India
Gupta, V.	1	3	India
Dollente, I.	1	3	Philippines
Máková, P.	1	3	Czechia
Jin, G.	1	3	China

Figure 11 shows a simplified schematic illustration of geopolymerization, a process composed of three steps: (i) dissolution, (ii) condensation, and (iii) hardening. The dissolution step involves breaking the aluminosilicate bonds of precursor materials into aluminate and silicate species under alkaline conditions, while the alkali ions (Na^+ , K^+ , and Ca^{2+}) neutralize the negative charge on alumina and silica monomers. This is then followed by condensation or coagulation–polymerization involving the formation of a geopolymeric matrix composed of monomers of sialate bonds (Si-O-Al) and siloxo bonds (Si-O-Si), and polymerization to form polysialate ($-\text{Si-O-Al-O}-$), poly(sialate-siloxo) ($-\text{Si-O-Al-O-Si-O}-$), poly(sialatedisiloxo) ($-\text{Si-O-Al-Si-O-Si-O}-$), ferro-sialate ($-\text{Fe-Si-O-Al-O}-$), and aluminophospho ($-\text{Al-O-P-O}-$) bonds [23,24]. Finally, the matrix hardens to form an amorphous to semi-crystalline 3D gel structure similar to zeolite and water [25,26,31].

**Figure 11.** A schematic process diagram of geopolymerization (figure from Mabroum et al. [31]).

4.5. Metakaolin-Based Geopolymers

Metakaolin (MK), produced by calcining kaolinite at temperatures between 700 and 800 °C for 2–4 h, is the most commonly used precursor for geopolymers, with chemical composition typically around 50%–67% SiO₂, 31%–42% Al₂O₃, 0.3%–2% Fe₂O₃, 0.3%–1.3% K₂O + Na₂O, 0.2%–1.0% CaO + MgO, and 0.2%–2.2% TiO₂ with an SiO₂/Al₂O₃ ratio of 1–2. Table 5 summarizes that 27 of the 34 studies used metakaolin as the precursor; that is, 12 papers used it as the main precursor, while the remaining 15 used it as an admixture. Allali et al. [73], for example, developed an MK mortar to substitute CaCO₃ and Ca(OH)₂ as alternatives to traditional lime- and cement-based mortar in Moroccan heritage masonry to prevent salt efflorescence and improve flexibility. The MK mortar achieved a 7-day compressive strength of 77 MPa using sodium silicate and sodium hydroxide as activators, with the addition of calcitic sand (CaCO₃) containing quartz, dolomite, and muscovite at a lime substitution rate of 47%. This approach is economically advantageous in Morocco because MK is cheaper and more widely available in comparison to slaked lime (Ca(OH)₂). Similarly, Clausi et al. [74] developed an MK mortar with dolostone and sandstone as aggregates using the <0.5 mm particle fraction for dolostone and sandstone substrates. These authors formulated dense geopolymers with bulk densities of 2.7 and 3.0 g/cm³ and compressive strengths of 18 and 21 MPa, using dolostone and sandstone as aggregates, respectively. These dolostone and sandstone geopolymers resembled the original stones at a binder/aggregate ratio of 1 and a liquid-to-solid (L/S) ratio of 0.4, which could serve as replacements for natural dolostone and sandstone for restoration.

Table 5. Metakaolin-based geopolymer formulations and compressive strengths.

Country	Precursors SiO ₂ = 50%–67%, Al ₂ O ₃ = 31%–42%, Fe ₂ O ₃ = 0.3%–2% K ₂ O + Na ₂ O = 0.3%–1.3%, CaO + MgO = 0.2%–1.0%, TiO ₂ = 0.2%–2.2%	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Morrocco	Metakaolin	KS, KOH	Calcareous sand (CaCO ₃)	–	16–41 (7 d)	[73]
		SS, NaOH			63–77 (7 d)	
		KS, KOH	Ca(OH) ₂		7–10 (7 d)	
		SS, NaOH			2–40 (7 d)	
Italy	Metakaolin	SS, NaOH	–	Dolostone	18	[74]
				Sandstone	21	
				Quartz Sand	75	
Italy	Metakaolin	SS, NaOH	None	–	41	[75]
			Epoxy Resin		49	
Portugal	Metakaolin	SS, NaOH	–	–	0.6–1.0	[76]
Italy	Metakaolin	SS, NaOH	Bromothymol Blue (Organic Dye)	–	–	[77]
			Phenolphthalein			
			Cresol red			
			Methyl orange			
Portugal	Metakaolin	SS, NaOH	Zeolite	–	4.6	[78]
		NaOH	Ca (OH) ₂		1.0	
Czech Republic	Metakaolin	SS, NaOH	Waste Foam Glass	–	2.7–8.3	[79]
Czech Republic	Metakaolin (LO5)	KS, KOH	None	Quartz Sand	86.6	[80]
			Dolostone		72.7–87.7	
			Marble		73.8–75.7	
			Marlstone		78–80	
			Limestone		75–78	
			Feldspar		94–96	

Table 5. Cont.

Country	Precursors SiO ₂ = 50%–67%, Al ₂ O ₃ = 31%–42%, Fe ₂ O ₃ = 0.3%–2% K ₂ O + Na ₂ O = 0.3%–1.3%, CaO + MgO = 0.2%–1.0%, TiO ₂ = 0.2%–2.2%	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Italy	Metakaolin	SS, NaOH	None Polyvinyl Acetate Polydimethylsiloxane	–	40 38–42 37–42	[81]
Czech Republic	Metakaolin (LO5)	KS, KOH	Slag, Colored Pigments	Quartz sand		[82]
Czech Republic	Metakaolin (LO5)	KS, KOH	None	Quartz sand	75.5	[83]
China	Metakaolin,	SS, KS	Silica Fume	–	40–70	[84]

Note: “LO5”: in house calcination of kaolinite; “SS”: sodium silicate; “NaOH”: sodium hydroxide; “KS”: potassium silicate; “KOH”: potassium hydroxide; “–”: no data reported.

Meanwhile, Ricciotti et al. [75] incorporated epoxy resin into MK slurry to improve its compressive strength, workability, and thixotropic behavior—a decrease in viscosity under constant stress/stirring and an increase when undisturbed—for application as fixing mortar on stone substrates for detached tuff-built AHSs. These authors achieved higher compressive strength (49 MPa) than the control, a plain MK geopolymer without epoxy resin (41 MPa), which can then be easily added to inorganic-colored pigments during restoration to match the original stone color. In addition, Moutinho et al. [76] developed a low compressive strength MK-based geopolymer (0.6 and 1 MPa), which was achieved at a high H₂O/Na₂O ratio (18 and 17) and formulated as an adhesive for the repair of broken ancient ceramic tiles. The advantages of using an MK-based geopolymer include (i) its good compressive strength even as the lone precursor material and (ii) its initial pale white color that can be easily modified by adding colored pigments to match the color of the original material to be repaired [77]. However, the main drawback of metakaolin is the need for thermal treatment via calcination before use to remove chemically bound water (OH groups) and to convert naturally occurring kaolinite clay to metakaolin. Thus, its use is limited by supply and sustainability issues, unlike other precursors that can be recycled and repurposed (e.g., fly ash, blast furnace slag, sludge, and rice husk ash).

4.6. Fly Ash-Based Geopolymers

Fly ash (FA) is an industrial waste from coal fired power plants and biomass (e.g., wood, sugar cane bagasse, rice husk, tea dust and coconut shells), power plants, palm fuel oil industry, municipal waste incineration plants, and thermal power plants [28–30,85,86]; it has been widely used as partial replacement for OPC for greener construction materials due to its pozzolanic properties. More recently, FA has become a popular precursor for geopolymers because of its high surface area and high alumina and amorphous silicate contents [87] (Table 6).

Table 6. Summary of chemical and mineralogical composition of fly ash used in geopolymers.

Plant	Region, Country	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	Mineral Phases	Ref.
Neyveli thermal power plant	Tamil Nadu, India	52.2	25.8	3.6	3.0	2.2	0.6	1.3	Quartz (SiO ₂), Calcite (CaCO ₃), Hematite (Fe ₂ O ₃)	[88]
Calaca coal-fired power plant	Batangas, Philippines	79.3	—	4.0	5.6	4.4	1.6	0.08	Anorthite (CaAl ₂ Si ₂ O ₈), Quartz (SiO ₂), Goethite (α-FeOOH), Mullite (3Al ₂ O ₃ ·2SiO ₂)	[89]

Table 6. Cont.

Plant	Region, Country	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	TiO ₂	Mineral Phases	Ref.
CFBC, coal-fired power plant	Philippines	27.4	23.2	21.7	16.5	6.2	0.9	0.9	Quartz (SiO ₂), Calcite (CaCO ₃), Magnetite (Fe ₃ O ₄), Hematite (Fe ₂ O ₃), Maghemite (γ-Fe ₂ O ₃), Illite, Biotite	[90,91]
—	Italy	37.3	16.1	30.8	6.13	—	5.28	—	—	[92]
—	Italy	59.5	27.3	2.9	1.8	—	2.7	0.6	—	[93]

Note: “—”: no data reported, “CFBC”: circulating fluidized bed combustion.

Table 7 lists five studies that employed FA, of which four used it as the main precursor material. Previous studies have shown that FA is generally blended with other precursors (e.g., MK and slag) to increase the compressive strength of the resulting geopolymers. For example, Kakria et al. [88] repurposed the non-metallic fraction (NMF), a by-product of separating metallic and non-metallic components of printed circuit boards (PCBs), from sorting and achieved a 28-day compressive strength of 27–29 MPa using a mixture of 85 wt% FA and 15 wt% NMF in comparison to 55 wt% FA, 30 wt% MK, and 15 wt% NMF achieving 33–35 MPa with a binder/aggregate ratio of 0.33. Similarly, Dollente et al. [89] used FA mixed with silica fume, fiber, and fine aggregates as a restoration mortar for unreinforced historical masonry (URM), thereby increasing its tensile strength and improving its seismic competency. Out of the five (5) different types of fibers (i.e., polyvinyl alcohol (PVA), polypropylene (PP), stainless steel (STSL), chopped basalt (CB), and carbon fibers (CFs)) used in this previous work, PVA provided the highest increase in split tensile strength of 2.2 MPa in comparison to no fiber addition (1.6 MPa), while maintaining the compressive strength at around 12 MPa. Restoration of historical masonry was also reported by Longo et al. [92], who used FA with 5% MK and expanded glass aggregate as an inorganic matrix to create a fiber-reinforced cementitious material (FRCM), a composite composed of fiber mesh and mortar matrix, serving as reinforced plaster for historical masonry. This composite has a compressive strength of 6.0 MPa and a density of 1.03 g/cm³, with a lower thermal conductivity of 0.9 W/m²K^{−1} compared with the traditional natural hydraulic lime (NHL)-based matrix at 1.1 W/m²K^{−1} in tuff-built masonry. The advantages of using FA include its valorization, pozzolanic properties, and initially cement-gray color, which is quite helpful as a restoration material; thus, it is commonly used as a partial replacement for cement. To attain the desired strength, however, admixtures and careful adjustments of the concentrations of activators are required.

Table 7. Formulation of fly ash-based geopolymers and compressive strength.

Country	Precursors	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Italy	Fly ash	SS, NaOH	Metakaolin, Printed circuit board (non-metallic)	Sand	15.0–35.0	[88]
Philippines	Fly ash	SS, NaOH	Silica fume	Fine aggregate	12.6	[89]
Italy	Fly ash	SS, NaOH	Metakaolin	Expanded glass	6.0	[92]
Italy	Fly ash	SS, NaOH	Metakaolin	Expanded waste glass	7–10	[93]

Note: “SS”: sodium silicate; “NaOH”: sodium hydroxide.

4.7. Slag-Based Geopolymers

Slag, a by-product of the steelmaking industry, is generated when reducing and slagging agents (i.e., coke and limestone) are added to the iron ore to remove impurities. It is currently used as an alternative to Portland cement to develop sustainable construction materials, which are typically composed of 32.5%–35.7% SiO_2 , 9.94%–11.6% Al_2O_3 , 32.4%–42.1% CaO , and 7%–9.3% MgO . Table 8 summarizes four studies that used slag as the primary precursor and one article that used this material as an admixture. For example, Taburini et al. [94] developed a durable restoration mortar to strengthen ancient masonries by blending slag with other precursors (i.e., MK, wollastonite and sand) and achieved a 28-day compressive strength of 34.5 MPa, utilizing an MK/slag/aggregate ratio of 1/2/3.5 with 63% of the aggregate as sand and 37% as wollastonite fiber (composed of $\text{SiO}_2 = 46.5\%$, $\text{Al}_2\text{O}_3 = 0.96\%$, $\text{CaO} = 42.1\%$, $\text{Na}_2\text{O} = 0.15\%$, $\text{K}_2\text{O} = 0.47\%$, $\text{MgO} = 7.23\%$). Similarly, Maras et al. [95] achieved a comparable 28-day compressive strength of 33 MPa in a mixture of slag with the addition of slaked lime ($\text{Ca}(\text{OH})_2$) at 5 wt% and brick powders (0–2 mm) with 8 M NaOH, used as restoration material for Turkish Heritage structures. Notable results were also reported by Gupta et al. [96], who produced colored geopolymers by utilizing colored stone processing waste and slag, mixed at a 1:1 ratio, and hydraulically pressed. These authors reported pink, yellow, and white geopolymers with compressive strengths ranging from 15 to 25 MPa. Meanwhile, Kutlusoy et al. [97] used similar precursor materials as Maras et al. [95], but with higher amounts of slaked lime at 48% of precursors (slag/brick powders/slaked lime) and the addition of sodium silicate and sand to be used as joint mortar for heritage masonry, showing a 28-day compressive strength of 30.6 MPa. These results suggest that slag-based geopolymers high in lime (CaO) exhibit better mechanical properties, reaching a compressive strength of at least 30 MPa after geopolymerization, which could be attributed to the dense formation of calcium–aluminosilicate–hydrate (CASH) and calcium–silicate–hydrate (CSH), similar to products found in hardened Portland cements. Slag is waste collected from blast furnaces in the steel industry and can be used for repair due to its cement-like properties: it hydrates readily and provides relatively high compressive strength.

Table 8. Formulations of slag-based geopolymers for heritage conservation and their compressive strength.

Country	Precursors $\text{SiO}_2 = 32.5\%–35.7\%$, $\text{Al}_2\text{O}_3 = 9.94\%–11.6\%$, $\text{Fe}_2\text{O}_3 = 0.32\%–1.25\%$, $\text{CaO} = 32.5\%–42.1\%$, $\text{MgO} = 7\%–9.3\%$	Activators	Admixture	Aggregate	28-Day Compressive (MPa)	Ref.
Italy	Slag	SS, NaOH	Metakaolin, Wollastonite	River Sand	34.5	[94]
Turkey	Slag	NaOH	$\text{Ca}(\text{OH})_2$, waste brick powder	—	25–33	[95]
India	Slag	SS, NaOH	Dholpur Stone Jaiselmer Stone Kota Stone Makarana Stone	Sand	15 24 25 25	[96]
Turkey	Slag	SS, NaOH NaOH KOH	Slaked lime Brick powder	River Sand	18.1–30.6 11.5–26.2 11.1–27.1	[97]

Note: “SS”: sodium silicate; “NaOH”: sodium hydroxide; “KOH”: potassium hydroxide; “—”: no data.

4.8. Pyroclastic Material-Based Geopolymers

Table 9 lists five studies that utilized volcanic ash (VA) as a precursor for geopolymerization, collected from a single location in a village on the eastern flank of Mt. Etna,

Italy, during the volcanic eruption in 2013. This material is composed of amorphous phases attributed to the presence of volcanic glass (>60 wt%) and phases of plagioclase ((Ca,Na)Al₂Si₂O₈), augite (Ca(Mg,Fe)Si₂O₆), forsterite (Mg₂(SiO₄)), and Fe/Ti-oxides, with a lime (CaO) content of 10.5 and Si/Al > 2. For example, Finocchiaro et al. [98] achieved a 21-day compressive strength of 71 MPa by mixing VA with 20 wt% MK with potassium-based activators (potassium silicate and potassium hydroxide), while Na activators (sodium silicate and sodium hydroxide) achieved a lower compressive strength of 51 MPa. Meanwhile, Occhipinti et al. [99] only achieved a 28-day compressive strength of 45 MPa with VA and 20 wt% MK with Na activators, which decreased to 39 MPa after adding VA aggregates (0.075–2 mm). Similarly, Finocchiaro et al. [100] achieved a 28-day compressive strength of 25 MPa using Na activators containing 80 wt% VA and 20 wt% MK, which increased to 34 MPa upon incorporation of 2% slaked lime.

Another aluminosilicate-rich geological material promising for geopolymer applications is volcanic soil. Volcanic soils (VSs) are formed by the weathering of pyroclastic materials, such as lava, ash, and rock, and the accumulation of organic matter [101,102]. Table 9 lists a total of four studies that utilized volcanic paleosoil (Ghiara) collected from the south slope Quarry of Mt. Etna, with a yellow-reddish color tone, amorphous with phases of anorthite, forsterite, hematite, augite, corundum and magnetite with Si/Al > 2, and repurposed to be used as restoration material in historical building in Mt. Etna areas. For example, Finocchiaro et al. [98] achieved a 21-day UCS of 89 MPa by blending 20 wt% MK into K solution, compared with 51 MPa using Na solution. Meanwhile, Occhipinti et al. [99,103] only achieved a 28-day UCS of 25 MPa using a Na solution, but the addition of volcanic paleosoil aggregates resulted in a lower strength value of 21 MPa.

Meanwhile, pumice—a silica-rich geological material formed when silica-rich magma rapidly cools, releasing gases that form visible vesicles—from Aeolian Island, Sicily, Italy, was used by Occhipinti et al. [104,105]. This volcanic rock had a pale gray tone, was highly amorphous, and contained phases of corundum and plagioclase, with a high SiO₂ content (70%) and SiO₂/Al₂O₃ > 5. It was used as a precursor to restore building materials in Baroque Architecture in Sicily, originally built from Sicilian limestone. The pumice-based mortar developed in this work achieved a 28-day compressive strength of 12.7 MPa with the addition of 30 wt% MK, an activated with sodium silicate (Na₂SiO₃)/sodium hydroxide (NaOH) ratio of 1.19, and a liquid-to-solid ratio (L/S) of 0.61, showing comparable strength to western Sicilian limestones, which have a compressive strength ranging from 0.5 to 20 MPa; the geopolymer has a lower modulus ratio according to the Deere–Miller diagram compared with Sicilian limestone, which according to the authors is an ideal restoration material as it is less rigid than the original material, avoiding induced stress.

Table 9. Formulations and mechanical properties of pyroclastic-based geopolymer mortars.

Country	Precursors In Molar Ratio: VA: Si/Al = 2.5 VS: Si/Al = 2.2 PM: Si/Al = 3.1	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Italy	Volcanic ash	SS, NaOH	Metakaolin		18–50 (21 d)	[98]
	Volcanic soil				17–51 (21 d)	
	Volcanic ash	KOH, KS			29–71 (21 d)	
	Volcanic soil				30–89 (21 d)	
	Volcanic ash	SS, NaOH	Metakaolin	Volcanic rock	39	[99]
				None	45	
	Volcanic soil			Volcanic soil	21	
			None	25		

Table 9. Cont.

Country	Precursors In Molar Ratio: VA: Si/Al = 2.5 VS: Si/Al = 2.2 PM: Si/Al = 3.1	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Italy	Volcanic ash	SS, NaOH	Metakaolin, Ca(OH) ₂ Metakaolin	None	34 25	[100]
	Volcanic ash	SS, NaOH	Metakaolin	None Volcanic rock	45 39	
	Volcanic soil			None Volcanic soil	25 21	[103]
	Volcanic ash Volcanic soil Pumice	SS, NaOH	Metakaolin, Aluminum Powder	–	– – –	
	Pumice	SS, NaOH	Metakaolin		7.2–12.7	[105]

Note: “SS”: sodium silicate; “NaOH”: sodium hydroxide; “KS”: potassium silicate; “KOH”: potassium hydroxide; “VA”: volcanic ash; “VS”: volcanic soil; “–”: no data.

4.9. Ceramic Waste-Based Geopolymers

Table 10 summarizes five studies that used ceramic waste as precursors for geopolymer production. This waste has a similar chemical and mineralogical composition to MK, thus showing potential as an MK substitute. Ceramic wastes are typically composed of 57% SiO₂, 33% Al₂O₃, 3.5% Fe₂O₃, 1.4% K₂O, 0.8% Na₂O, and 0.8% CaO, with quartz (SiO₂), mica (KAl₂(AlSi₃O₁₀)(F,OH)₂), feldspar (K,N,Ca)(Al,Si)₄O₈, and hematite (Fe₂O₃) as their major mineral components [106]. Several ceramic wastes, such as porcelain stone wares, raw pressed tiles, and bricks, or mixed ceramic waste are incorporated with MK for geopolymer application. For example, Ricciotti et al. [107] utilized wastes from porcelain stoneware and ceramic tiles manufactured in Vicenza, Italy, and achieved promising results by using calcined raw pressed ceramic waste at 750 °C for 5 h and blending it with MK at 11.6 wt%, achieving a compressive strength of 41 MPa; porcelain waste showed a compressive strength of 30 MPa, and mixed ceramic waste achieved 38 MPa. These authors conducted a preliminary investigation for conservation and restoration wherein the slurry had good workability, making it easy to spread and model the slurry in tuff substrate as a fixing paste. The ease in producing a colored product with the addition of a water-based pigment should be noted, resulting in various types of colored MK geopolymers. Fugazzotto et al. [108–110] used tile waste to develop a brownish-red geopolymer product. For example, Fugazzotto et al. [108] blended tile waste with MK and hydraulic lime in small amounts to promote binding, resulting in a compressive strength of 14.3 MPa when cured at room temp in comparison to curing for 24 h at 65 °C, which resulted in 9.79 MPa, attributed to the crystallization of crypto-efflorescence which inhibits gel formation at higher temperature, lowering its compactness and resistance, coinciding with the results showing an increase in the effective porosity; this serves as a promising result in terms of ambient application. Therefore, in their recent case studies, these authors developed a reintegration mortar to apply on site to the deteriorated brick masonry of the Roman Odéon at Catania, due to its similar color tones to the brick elements. The test mortar was formulated using (i) tile waste or (ii) brick waste with MK and lime, and blended with aggregates such as carbonate sand, volcanic aggregates, and marble powder, depending on in situ availability, color, and fineness. After application, the test mortar was monitored for 7 days and 28 days and had good adhesion to the substrate, negligible efflorescence, low shrinkage and less visible cracks; the brick waste formulation showed higher similarity to the substrate in comparison to the tile waste formulation. Thus, it was not considered ethical due to intervention

recognizability, since during restoration the intervention material must still be recognizable. In another formulation by Fugazzotto et al. [110], various aggregates, including carbonate sand, silica sand, and tile waste, were evaluated, and the highest compressive strength of 32 MPa was achieved with carbonate sand as the aggregate and mixing waste tiles with 20 wt% MK. In addition, Capasso et al. [111] used brick waste blended with 20 wt% fly ash (FA) and achieved a compressive strength of 13.4 MPa, which is suitable as an alternative restoration mortar to traditional restoration materials such as lime mortar, OPC mortar, crushed bricks, sand, magnesian mortar, and natural limestone.

Table 10. Formulations and properties of ceramic waste-based geopolymers.

Country	Precursors SiO ₂ = 57.3, Al ₂ O ₃ = 32.7, Fe ₂ O ₃ = 3.5, K ₂ O = 1.4, Na ₂ O = 0.78, CaO = 0.83, with Quartz, Mica, Feldspar, and Hematite	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Italy	Porcelain and stoneware waste, Raw pressed ceramic waste, Calcined Raw pressed ceramic, Gypsum Mixed	SS, NaOH	Metakaolin	—	30 25 41 4 38	[107]
	Ceramic tile waste	SS, NaOH	Metakaolin, lime		3.5–14.3	
	Tile waste or Brick Waste	SS, NaOH	Metakaolin, lime	Carbonate sand, Volcanic aggregate marble powder	— — —	[109]
	Ceramic tile waste	SS, NaOH	Metakaolin	None Carbonate sand Silica sand Tile waste	14–27 18–32 6–7 6–16	
	Brick waste	SS, NaOH	Fly Ash None	Brick waste	13.4 5.3	[111]

Note: “SS”: sodium silicate; “NaOH”: sodium hydroxide; “—”: no data.

4.10. Geopolymers Formulated from Other Materials

Table 11 lists one study that utilized tuff waste obtained from the natural stone processing industry. Capasso et al. [111] repurposed tuff waste consisting of a mixture of Neapolitan yellow tuff and Viterbo red tuff as restoration material for Italian heritage structures, and it was mixed with FA at 10 and 20 wt%, resulting in compressive strengths of 1.48 and 1.34 MPa.

Table 11. Geopolymers formulated from wastes and local clays.

Country	Precursors	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Italy	Tuff waste (SiO ₂ = 58.8%, Al ₂ O ₃ = 31.82% Fe ₂ O ₃ = 2.99% CaO = 3.10% Na ₂ O = 3.44% MgO = 1.11% K ₂ O = 9.34% TiO ₂ = 0.53%)	SS, NaOH	Fly ash		1.3–1.5	[111]
			None	Tuff waste	0.8	
Portugal	Silica fume waste (SiO ₂ = 97% Al ₂ O ₃ = 0.15% Fe ₂ O ₃ = 0.03% CaO = 0.2% Na ₂ O = 0.05% MgO = 0.30% K ₂ O = 0.80%)	SS, NaOH	Polycarboxylate-based superplasticizer		10–12	[112]
			None	—	14–15	

Table 11. Cont.

Country	Precursors	Activators	Admixture	Aggregate	28-Day Compressive Strength (MPa)	Ref.
Portugal	Tungsten mine mud waste (SiO ₂ = 46.7% Al ₂ O ₃ = 17.0% Fe ₂ O ₃ = 15.7% CaO = 0.69% Na ₂ O = 0.85% MgO = 4.83%)	SS, NaOH	Portland cement, glass, metakaolin	Expanded Cork	10–19.5	[113]
Italy	Santena clay (Smectite- Montmorillonite, Kaolinite, Illite, quartz, feldspars)	KOH, KS	—	—	Not conducted	[114]

Note: “SS”: sodium silicate; “NaOH”: sodium hydroxide; “KS”: potassium silicate; “KOH”: potassium hydroxide; “—”: no data.

A silica fume (SF)-based geopolymer was formulated by Baltazar et al. [112] as an alternative for traditional natural hydraulic lime (NHL) by mixing SF with superplasticizer to improve its fluidity, resulting in a compressive strength of 10–12 MPa, which was slightly lower in comparison to that without the addition at 15 MPa.

Table 9 also summarizes a notable study by Beghoura et al. [113] that proposes re-purposing tungsten mine tailings as a potential historical restoration material in Portugal. Mortar was formulated by blending mine waste, glass, MK, and Portland cement with expanded cork and was activated with sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH), resulting in a maximum compressive strength of 19.5 after 28 days. The application of aluminum powder and hydrogen peroxide as foaming agents also resulted in volume increases of 358% and 141%, respectively, providing a lightweight material for restoration.

Meanwhile, Rescic et al. [114] utilized Santena clay mixed with alkaline activators potassium hydroxide and potassium silicate that stabilize plasters for use as earthen-based plaster in architectural heritage; the mixture was then subjected to several durability tests like thermo-hygrometric cycling (an accelerated aging test for earthen material to assess durability caused by swelling) and shrinking testing in a Climatic Chamber (heating first at 50 °C and 30% relative humidity for 6 h and then cooling at 20 °C at 90% relative humidity for 6 h, which is repeated 50 times). The results showed negligible weight loss of 0.30% for the stabilized plaster, identical to the original unstabilized plaster at 0.29%, indicating that the durability of the stabilized material was not significantly affected.

5. Compatibility Criteria in Using Geopolymers for Architectural Heritage Structure Conservation

According to the International Council on Monuments and Sites (ICOMOS, 2003), compatibility is critical for the structural conservation of AHSs; that is, the restoration (new) material and existing (old) material should have negligible negative impacts on the historical materials, especially in technical (chemical and mechanical), aesthetic, and historical (physical) aspects. In addition, Legislative Decree no. 42 of 22, 2004, of the Ministry of Cultural Heritage and Activities (Ministero per i beni e le attività culturali, Rome) known as the “Code of Cultural Heritage and Landscape” defines restoration (in Art. 29, paragraph 4) as “the direct intervention on the property through a complex of operations aimed at the material integrity and recovery of the property itself at the protection and transmission of its cultural values” which also include structural upgrading in properties at risk of earthquakes [115]. Meanwhile, in the Philippines, Republic Act No. 10,066 (National Cultural Heritage Act of 2009) defines restoration as “the action taken

or the technical intervention to correct deterioration and alterations” [116]. This section provides an overview of the compatibility criteria used for geopolymers applied in the restoration and conservation of heritage structures, which are categorized in terms of (i) aesthetic, (ii) chemical, (iii) physical, and (iv) mechanical compatibility.

5.1. Aesthetic Compatibility

The aesthetic compatibility criteria govern the visual appearance of structures, which is primarily perceived by the naked eye, to determine the similarity between the intervention and the original material in terms of color, efflorescence formation, and texture.

5.1.1. Color

To maintain the aesthetic appearance of the original material when using a geopolymer, colorimetric analysis is conducted to assess the similarity of geopolymers with original materials. Color analysis is conducted using a spectrophotometer with a spot diameter of around 6 mm, measured at least six times on different areas of the material, and reported in terms of the CIELab (a color coordinate space developed by Commission Internationale de l'Éclairage in 1976 to describe the color visible to the naked eye). The CIELab provides each chromatic coordinate— L^* , a^* , and b^* —to determine the color difference (ΔE), following the formula in Equation (1), where L^* denotes the lightness and ranges from 0 (total absorption or black) to +100 (white), while a^* and b^* denote the green/red and blue/yellow values, respectively, both ranging between -60 and 60 . The value of ΔE indicates the color similarity between two objects, with $\Delta E = 3$ defined as the perceptibility limit; that is, values of $\Delta E > 3$ indicate color differences readily perceptible to the naked eye [105,112].

$$\Delta E = \sqrt{(L_{\text{new}} - L_{\text{reference}})^2 + (a_{\text{new}} - a_{\text{reference}})^2 + (b_{\text{new}} - b_{\text{reference}})^2} \quad (1)$$

Table 12 lists the colorimetric analytical results reported in recent studies to assess color differences. For example, Clausi et al. [74] determined the chromatic difference between original stones (i.e., sandstone and dolostone) and the metakaolin-based geopolymer binder with ornamental stone aggregates (i.e., sandstone and dolostone), yielding ΔE values of 5 and 11 for dolostone and sandstone, respectively. These authors attributed the high value to changes in the degree of lightness of sandstone at $\Delta L = -10$, resulting in a paler tone compared to natural sandstones, allowing for similar but recognizable color differences after restoration. Similarly, Fugazzotto et al. [110] formulated ceramic tile-based geopolymers with the addition of either carbonate sand, siliceous sand, or tile waste as aggregates. The ceramic tile-based geopolymer for Messina bricks, which were used during 2nd–3rd B.C. in the ancient urban city of Zancle-Messana, had the lowest observed ΔE of 6 using tile aggregates and 10 wt% MK, while the highest ΔE of 21 was obtained using silica sand and 20 wt% MK. Meanwhile, the ceramic tile-based geopolymer for Gela Bricks, a reproduction of ancient bricks, achieved the lowest ΔE of 6.5 (10 wt% MK + silica sand) and 13 (10 wt% MK + tile waste), attributed to the different types of aggregate. In addition, Fugazzotto et al. [109] conducted a case study for on-site application using tile waste-based and brick waste-based geopolymers as restoration mortars for the brick walls of Roman Odéon of Catania (2nd century A.D.), and after 3 months of monitoring, although no color difference (ΔE) was measured, a general visual comparison was conducted, indicating an indistinguishable color difference using the brick waste geopolymer compared to the tile waste geopolymer as restoration mortar for ancient brick walls.

Table 12. Colorimetric analytical results of geopolymer mortars.

Binder Composition	Alkali Activator Ratio (NS/NaOH)	Aggregates	Reference Color (L _{ref})	Color Difference (ΔE)	Change in Color Coordinate			Ref.				
					ΔL	Δa	Δb					
MK	In molar ratio	Dolostone Sandstone	Dolostone Sandstone	4.7 10.9	−1.1 −10.8	1.1 −0.52	4.4 1.6	[74]				
Tile + 10 wt% MK	1	SS	Messina Bricks (Ancient Brick)	19								
		CS		9								
		CER		6								
Tile + 20 wt% MK	1	SS		21								
		CS		12								
		CER		14								
Tile + 20 wt% MK	2.3	SS	−		−		[110]					
		CS	12									
		CER	18									
Tile + 10 wt% MK	1	SS	6.5									
		CS	12									
		CER	13									
Tile + 20 wt% MK	1	SS	8.5									
		CS	8.3									
		CER	10									
Tile + 20 wt% MK	2.3	SS	−									
		CS	7									
		CER	8									
Tile + 10 wt% MK Brick + 10 wt% MK	1	CS	Odéon Bricks (Ancient Brick)	Recognizable Very Similar	−							[109]
Pumice + 20 wt% MK	1.33	None	Raw Pumice	1.3	0.5	0.25	1.16					[105]
Pumice + 30 wt% MK	1.19			3.2	−2.9	0.24	1.2					
Santena Clay	1 (KS/KOH)	None	Raw Clay	11.09	−9.49	−2.16	−5.32	[112]				
Tile + 10 wt% MK	1	SS	Raw Ceramic Tile	12		−		[110]				
		CS		4								
		CER		6								
Tile + 20 wt% MK	1	SS		3.2								
		CS		9.2								
		CER		9.5								
Tile + 20 wt% MK	2.3	SS		−						−		
		CS		5								
		CER		1.5								
VA + 20 wt% MK	n.v.	None	Prior to Weathering	1.87		−		[99]				
VA		2.49										
VS + 20 wt% MK		None		7.10								
		VS		6.19								
Santena Clay	1	None	Prior to Weathering	2.09	2.05	0.36	0.23	[112]				

Note: “−”: no data; “MK”: metakaolin; “SS”: silica sand; “CS”: carbonate sand; “CER”: tile waste; “VA”: volcanic ash; “VS”: volcanic soil; “NS”: sodium silicate; “NaOH”: sodium hydroxide; “KS”: potassium silicate; “KOH”: potassium hydroxide.

Meanwhile, some studies conducted colorimetric analysis to obtain different pseudo-colors for each formulation, compared with raw pumice, due to its original whitish color, which can be easily adjusted to match the color of Sicilian limestones in UNESCO-listed Sicilian baroque cities. For example, Occhipinti et al. [105] evaluated the pseudo-colors of each pumice-based geopolymer mortar formulation and achieved the best ΔE values of 1.3 (20% MK) and 3.2 (30% MK), compared with the original pumice, highlighting the significant effects of precursors on the resulting color. Similarly, Fugazzotto et al. [110] evaluated the pseudo-colors of formulations containing different types of aggregates (i.e., carbonate sand and ceramic tiles) compared with the original ceramic tile waste. These authors reported ΔE of 1.5 using tile aggregates with 20 wt% MK and a high Na₂SiO₃/NaOH ratio of 2.3, suggesting that high amounts of Na₂SiO₃ in the mixture had a strong effect on the final color. The results of Fugazzotto et al. [110] were consistent with those of Occhipinti et al. [105], who reported that increasing Na₂SiO₃/NaOH from 0.33 to 2.67 decreased the ΔE values from 6.4 to 2.3, respectively, leading to a higher yellow component. Rescic

et al. [112] evaluated the color difference between the original raw clay and the geopolymer plaster for stabilizing earthen cultural heritage, resulting in a ΔE of 11.1 (prominent darkening, negative ΔL), but after subjecting it to thermo-hygrometric cycles, the ΔE decreased to 2.09.

Furthermore, colorimetric analysis has been conducted to determine color changes in geopolymers after exposure to environmental factors. For example, Occhipinti et al. [99] evaluated the color changes of VA- and VS-based geopolymers with or without 6 months of outdoor exposure, resulting in insignificant color changes ($\Delta E = 1.9\text{--}2.5$) for VA-based geopolymers but with noticeable color differences for VS-based geopolymers ($\Delta E = 6.2\text{--}7.1$). Similarly, Rescic et al. [112] mixed earthen Santena clay material with K_2SiO_3 and KOH for stabilization, resulting in ΔE of 2.09 after subjecting the stabilized earthen materials to accelerated weathering via thermohydrometric cycle tests.

Several authors also developed colored geopolymers to achieve the desired product color using various methods. For example, Perná et al. [82] applied an on-site application protocol using inorganic pigments to match the original color of ceramic tiles during the renovation of churches in the Czech Republic. Similarly, Angelo et al. [77] developed a colored MK-based geopolymer using organic dyes (e.g., Bromothymol blue, phenolphthalein, cresol red, methyl orange), resulting in a blue, purple, violet, and brown-colored geopolymer. Meanwhile, Gupta et al. [96] developed a colored brick by adding colored waste stone powder from stone processing industries, resulting in pink, light yellow, and white colored geopolymers.

5.1.2. Presence of Efflorescence

The formation of efflorescence on AHS substrates not only deteriorates the durability of historic materials but also their aesthetic properties. Figure 12 illustrates a schematic diagram of how efflorescence forms in geopolymers, typically manifesting as white salt-like deposits on the surface or subsurface, gradually damaging the material. Recently, several authors monitored the presence of efflorescence; that is, the surface precipitation of white salt-like deposits composed of soluble sodium carbonates such as trona ($Na_3HCO_3 \cdot 2H_2O$), thermonatrite ($Na_2CO_3 \cdot H_2O$), natrite (Na_2CO_3), and natron ($Na_2CO_3 \cdot 10H_2O$) on the surface of geopolymers, a process promoted by the movement of excess alkali activators through the porous network into the surface and then reacting with atmospheric CO_2 [23]. For example, Occhipinti et al. [99] evaluated the effects of atmospheric exposure for 6 months on VA- and VS-based geopolymers in Catania and found the presence of trona ($Na_3H(CO_3)_2 \cdot 2H_2O$), natrite (Na_2CO_3), and natron ($Na_2CO_3 \cdot 10H_2O$) on unexposed mortars, with Trona and Natron present on the surface and in bulk. Moreover, these authors reported the formation of natrite (Na_2CO_3) covering two-thirds of the external surfaces of both VA-based mortar and binder, whereas for the VS-based geopolymers, only one-quarter of the external surface was covered in mortar and one-fifth in binder. The presence of natrite was attributed in this previous work to the leaching of natron and trona by rainwater, while natrite precipitated during dryer conditions. Similarly, Fugazzotto et al. [108] characterized the salt-like powdered deposits formed by scratching the surface of a ceramic-based geopolymer with a scalpel; they were characterized by X-ray diffraction (XRD) and identified as thermonatrite ($Na_2CO_3 \cdot H_2O$) and trona ($Na_3(CO_3)(HCO_3) \cdot 2H_2O$) in cured samples (65 °C for 24 h) but not in samples cured under ambient conditions. Meanwhile, Clausi et al. [74] prevented the formation of efflorescence using aggregates rich in aluminum (sandstone) and calcium (dolostone). This was confirmed by the absence of new crystalline phases in the XRD results after 90 days, including a reduction in FTIR bands around 1400 cm^{-1} , related to the carbonate stretching vibration of natron.

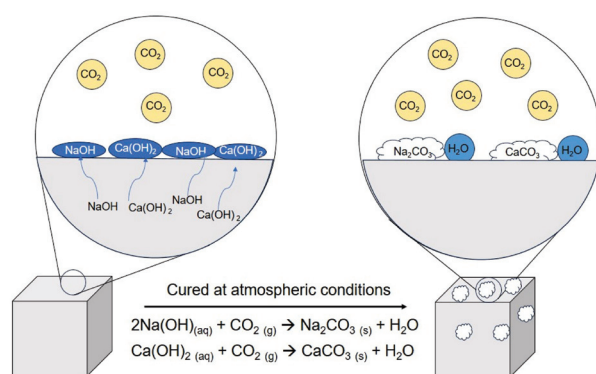


Figure 12. A schematic diagram of salt efflorescence formation [23].

Other researchers have prevented the formation of efflorescence by subjecting the geopolymer paste to a desalination process involving a series of washes or baths to leach excess alkalis. For example, Geraldès et al. [117] investigated controlling salt efflorescence formation by monitoring the electrical conductivity (EC) of the baths using either NaOH or KOH as alkaline activators and drying at 21 °C and 40 °C. These authors reported that the lowest EC was found when NaOH was used as the alkaline activator and dried at 40 °C, resulting in electrical conductivity (σ) of 5000 $\mu\text{S}/\text{cm}$ in the initial water bath consisting of 3.5 g of geopolymer paste in 50 g of distilled water; the other formulation reached approximately 8300 (NaOH at 21 °C), 9000 (NaOH at 21 °C) and 13,000 (KOH at 40 °C attributed to the increased curing temperature and smaller cation size of Na^+ , which easily leached in the surface. After the second and third baths, the EC reached approximately 500 and 0 $\mu\text{S}/\text{cm}$ (NaOH at 40 °C) and 1200 and 100 $\mu\text{S}/\text{cm}$ (NaOH at 21 °C), respectively, indicating that soluble salts can be easily removed by immersion.

5.1.3. Texture

It is important to maintain a surface texture similar to that of the original stone. This property is evaluated through macroscopic investigation depending on the type, distribution, and sizes of aggregates used in the restoration mortar to mimic the original stone. For example, Clausi et al. [74] utilized natural stones as aggregates with a particle size distribution of less than 0.5 mm and a binder/aggregate ratio of 1:1. Similarly, Occhipinti et al. [105] incorporated natural volcanic rocks as aggregate at 30 wt% of binders as restoration mortar with varied size distribution at 32.5% ($2 < \varnothing < 1 \text{ mm}$), 31.5% ($1.0 < \varnothing < 0.5 \text{ mm}$), 29% ($0.5 < \varnothing < 0.125 \text{ mm}$), 6% ($0.125 < \varnothing < 0.075 \text{ mm}$), and 1% ($\varnothing < 0.075 \text{ mm}$), while Capasso et al. [111] incorporated tuff waste with an aggregate size of 0.3 to 4 mm at an aggregate/binder ratio of 0.5; however, they did not conduct a macroscopic investigation, focusing on repurposing materials, which is common for geopolymers due to their infancy in AHS applications.

Unlike geopolymers used as restoration mortars, other studies developed artificial stone mortars (ASMs), with the distribution, type, and size of aggregates carefully designed to maintain similarity to stone; however, the drawback is their sustainability due to the use of OPC as the binder. Several studies have analyzed the difference in texture through microscopic [19,55] and macroscopic analysis [21] between original and new stone, assessing textural properties (i.e., grains, phenocrysts, and matrix). An on-site approach to achieve an antique appearance involves scraping the mortar to expose the aggregates [109]. For example, Stefanidou et al. [21] designed an artificial stone to replicate an old marl limestone in the archeological site of Pella, Greece; they recycled the old stone by crushing into 0–2 mm, with the addition of 0–2 mm and 2–4 mm sand and dry soil, binding with cement, pre-casting, curing for 14 days, and grooving with a chisel to resemble the surface

of original stone. Similarly, Menningen et al. [22] crushed the original tuff into fine and coarse aggregate ranging from 0 to 8 mm, bound it with cement, colored it with an inorganic pigment to match the matrix color, and macroscopically compared it with the original tuffs. The results showed satisfactory results as the addition of natural stone maintains the fine-grained glassy matrix, mimicking the original volcanic tuff. Another notable challenge in synthesizing black tuffs is the difficulty of replicating the original color of the natural rock, as cement pastes tend to lighten during setting and hardening.

5.2. Chemical Compatibility

5.2.1. Microstructure

Figure 13 shows scanning electron microscopy (SEM) photomicrographs collected to evaluate the microstructural differences between the original substrate and the restoration mortar. Ricciotti et al. [75,81,107], for example, observed through microstructural analysis a homogenous and continuous phase in the interface between the geopolymer and substrate (i.e., ceramic, tuff, and concrete) with no presence of microfractures and voids, indicating high chemical compatibility and good adhesion. Similarly, Fugazzotto et al. [105] conducted SEM analysis and found that the interface between the geopolymer and ancient brick substrates was well established, with no visible cracks or microcracks.

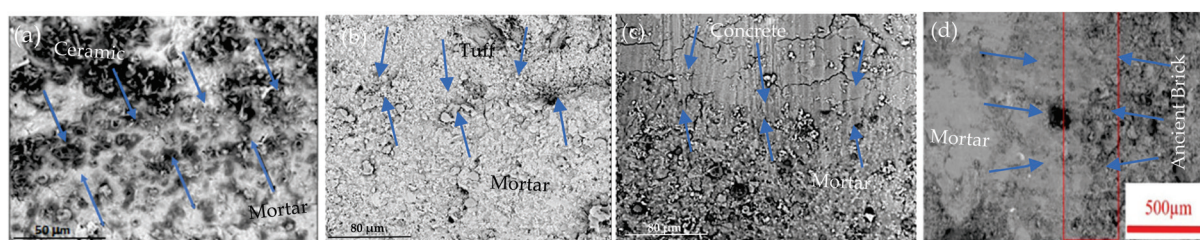


Figure 13. Interface transition zone (marked by blue arrows or red lines) between geopolymer and (a) ceramic, (b) tuff, (c) concrete, and (d) ancient bricks (figures from Ricciotti [75,81,107], MDPI, 2017, 2022, and Fugazzotto [105], reprinted with permission from Taylor & Francis (2024)).

5.2.2. Ionic Release

Ionic release is evaluated to measure the quantity of ionic species released from restoration mortars, enabling us to assess the potential formation of soluble salts that can further degrade ancient stones. For example, Ricciotti et al. [75] evaluated the chemical compatibility by measuring the release of ionic species when in contact with water to determine the soluble salt content with respect to thickness; their results showed trace concentrations of sodium ions (Na^+) after the initial wash using ultrapure water at around 6.7 and 5.5 mg/g sample for 3 mm and 6 mm thicknesses, respectively. Then, following a second wash, the sodium ions (Na^+) decreased to 1.7 mg/g sample (3 mm) and 1.6 mg/g sample (6 mm), while the third wash resulted in 1.3 mg/g (3 mm) and 1.1 mg/g (6 mm) and the final wash resulted in comparable ionic release of 0.7 mg/g (3 mm) and 0.7 mg/g sample (6 mm). The pH was maintained at 10–11, thus indicating a comparable difference regardless of the thickness of the sample.

5.3. Physical Compatibility

Table 13 summarizes the physical characteristics of restoration material, specifically porosity, water absorption, capillary absorption, and density compared with the properties of the original substrates, enabling us to determine the similarity based on the percent change. For example, Clausi et al. [74] produced a mortar with porosity and density ($2.7\text{--}2.9\text{ g/cm}^3$) similar to those of natural stone, providing an alternative for substitution or as a repair mortar compatible with the original material. Similarly, Capasso et al. [111]

reported a high similarity of the open porosity capacity of tuff waste (39%–42%) and brick waste (27%–34%) geopolymers compared with traditional mortars (30%–40%) and bioclastic limestone (24%–30%); they also maintained similar water absorption through capillarity between tuff waste ($20\text{--}33\text{ mg/cm}^2\text{ s}^{-1/2}$) and brick waste ($19\text{--}26\text{ mg/cm}^2\text{ s}^{-1/2}$) geopolymers in comparison to traditional mortars ($28.5\text{ mg/cm}^2\text{ s}^{-1/2}$) and natural bioclastic limestone ($31.3\text{ mg/cm}^2\text{ s}^{-1/2}$) used in stone heritage and found high similarities in these properties between the geopolymers and original materials. Meanwhile, Occhipinti et al. [105] reported the importance of a lightweight pumice-based geopolymer, with an average density of 1.4 g/cm^3 and an open porosity of 35%–37%, employed to prevent additional stress on Western Sicilian limestone used in Sicilian AHSs, with compressive strength ranging from 0.5 to 20 MPa during restoration. Meanwhile, Baltazar et al. [112] compared the open porosity and density of traditional lime-based grouts with those of geopolymer grouts and reported a lower density of approximately 1.35 g/m^3 for the former and 1.2 g/cm^3 for the latter. In contrast, open porosity was around 50% for lime-based grouts and 20%–40% for geopolymer grouts.

Table 13. Physical properties of geopolymers in comparison with reference material.

Property	Geopolymer Type	Geopolymer Value	Reference Material	Reference Material Value	Percent Change (%)	Similarity	Ref.
Open Porosity (%)	Pumice + MK	36.5	Sicilian Limestone	—	—	—	[105]
	MK + dolostone	17.8	Dolostone	—	—	Similar (from author) High	[74]
	MK + sandstone	14.1	Sandstone	2–6	57–85		
	FA	20–40	Natural Hydraulic Lime	50	20–60	Very High to High	[112]
	Tuff	39.4–42.3	Aerial Lime Mortar	25.9	52–63	High	[111]
			Natural Hydraulic Lime	23.5	67–80	High	
			OPC	18.8	113–128	Medium	
			Repair Mortars	26.2	50–61	High	
			Historical Magnesian Mortar	30–40	6–31	Very High	
			Natural Limestone	24–30	39–40	Very High	
	Brick	26.2–34.2	Aerial Lime Mortar	25.9	1.1–23	Very High	[111]
			Natural Hydraulic Lime	23.5	11.5–45.5	Very High	
			OPC	18.8	39.4–81	Very High	
			Repair Mortars	26.2	0–31	Very High	
			Historical Magnesian Mortar	30–40	12.7–15	Very High	
			Natural Limestone	24–30	8.3–13	Very High	
Water Absorption (%)	Tuff	26.7–31.0	n.d.	—	—	—	[111]
	Brick	15.7–19.8	n.d.	—	—	—	
Capillarity Absorption ($\text{mg/cm}^2\text{ s}^{-1/2}$)	Tuff	20.9–33.4	Aerial Lime Mortar	13.9	50–140	Medium to High	[111]
			Natural Hydraulic Lime	9.40	122–225	Medium	
			OPC	3.4	514–882	Very Low	
			Repair Mortars	24.2	13.6–38.01	Very High	
			Historical Magnesian Mortar	28.5	17–27	Very High	
			Natural Limestone	31.3	6.7–33	Very high	
	Brick Based	19.5–26.6	Aerial Lime Mortar	13.9	40–91	High	[111]
			Natural Hydraulic Lime	9.40	107–183	Medium	
			OPC	3.4	473–682.3	Low	
			Repair Mortars	24.2	10–19	Very High	
			Historical Magnesian Mortar	28.5	6.6–31	Very High	
			Natural Limestone	31.3	15–37	Very High	
Bulk Density (g/cm^3)	MK + dolostone	2.8	Dolostone	2.7	3.7	Very High	[74]
	MK + sandstone	2.9	Sandstone	2.9	0	Very High	
	Pumice + MK	1.43–1.46	Sicilian Limestone	—	—		[105]
	Silica Fume	1.0–1.2	Natural Hydraulic Lime	1.35	11–25	Very High	[112]
	Tuff	1.35–1.4	-	—	—		[111]
	Brick	1.73–1.76	-	—	—		

Note: “—”: no data. Similarity = Very High (0–50), High (50–100), Medium (100–300), Low (300–500), and Very Low (>500).

5.4. Mechanical Compatibility

5.4.1. Adhesion

Baltazar et al. [112] developed a silica fume (SF)-based geopolymer mortar as grouting for historical masonry. To assess the adhesion strength—defined as the bond strength between the restoration material and the substrate—of silica fume mortar compared to traditional lime-based mortar, an adhesion test is typically conducted. The adhesion test is a quantitative method for measuring the bond strength between the restoration material (e.g., mortar, grout, adhesive) and the original substrate (e.g., stone, tiles, ceramics, bricks) by developing several hybrid specimens. Based on the study of Baltazar et al. [112], silica fume-based geopolymers had higher flexural strength (0.6–0.9 MPa) compared with traditional natural hydraulic lime grout (0.1 MPa), an increase of around 90% (Figure 14a). Meanwhile, Tamburini et al. [94] conducted a pull-off test on fiber-reinforced slag–MK geopolymer mortar applied to ancient and modern construction clay bricks and reported good adhesion (0.9–1.7 MPa) to the ancient bricks, with failures observed in the original substrate (Figure 14b). In comparison, failure in the modern geopolymer bricks occurred at the reinforcement layer, with slightly higher adhesion of around 1.2–2.81 MPa. Similarly, Fugazzotto et al. [110] conducted an adhesion test with a “sandwich” specimen (Figure 14c) using two ancient bricks and reported poor adhesion with sand aggregates and a ceramic-based geopolymer, attributed to fracture at the interface, but no quantitative values were presented.

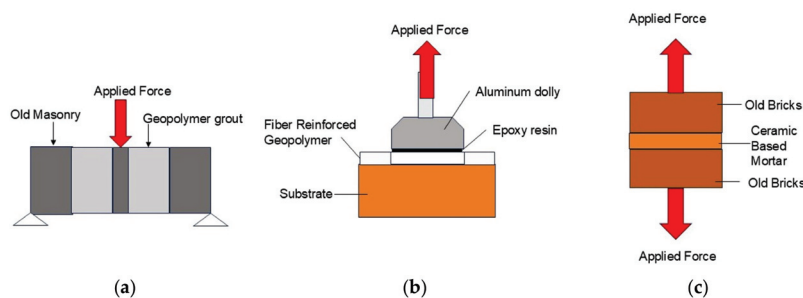


Figure 14. Different adhesion tests conducted for (a) grout from Baltazar et al. [112], (b) plaster from Taburini et al. [94], and (c) adhesive from Fugazzotto et al. [110].

5.4.2. Surface Hardness

Maras [95] employed an in situ non-destructive technique (NDT) to evaluate the surface hardness of historical mortars and geopolymer mortars and reported a medium level of similarity based on the rebound hardness test. Also, Capasso et al. [111] conducted a surface hardness test using the Shore-D hardness test but did not compare the results to the original materials.

5.4.3. Compactness

Compactness is measured using ultrasonic pulse velocity (UPV), another in situ NDT method used to determine the degree of damage in the material; it depends on the material’s density and modulus of elasticity, which can result in a degree of deterioration. For example, Maras [95] evaluated the compactness of geopolymers and original mortars and found a higher value for geopolymers, with an increase of 50% compared to the in situ joint historical mortars.

5.4.4. Compressive Strength

Occhipinti et al. [105] compared the mechanical properties of a pumice-based geopolymer and traditional limestone using Miller diagrams and showed similarities to low-strength limestone (Figure 15). Meanwhile, Capasso et al. [111] compared tuff and brick waste geopolymers with conventional materials in cultural heritage, showing similarities to the original

materials, with the tuff waste geopolymer (0.81–1.34 MPa) and brick waste geopolymer (5.34–13.4 MPa) matching natural limestone (10.1 MPa). Similarly, Baltazar et al. [112] also reported a higher compressive strength for a silica fume-based geopolymer (10–15 MPa) than for traditional lime-based mortar (8 MPa). However, Dollente et al. [89] compared the compressive strength without (12.6 MPa) and with the addition of fibers (1.81–12.1 MPa), finding a similar compressive strength depending on the type of fiber added to the mixture.

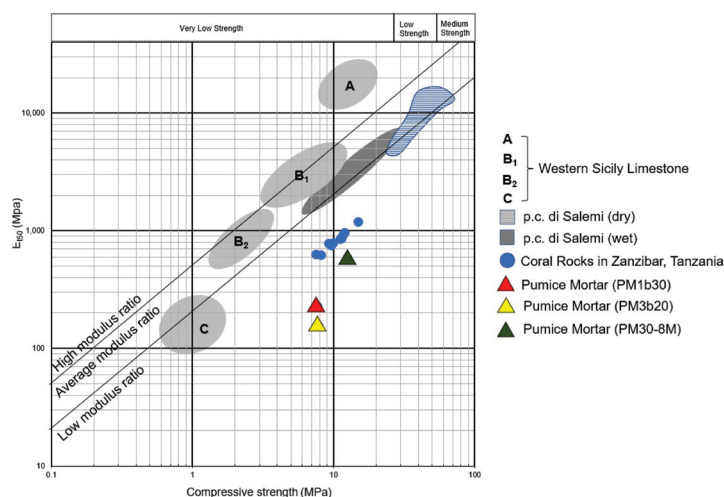


Figure 15. Redrawn and modified Deer–Miller diagram from Occhipinti et al. [105]. Comparing mechanical properties of geopolymers and limestones in Sicily, Italy, and coral rocks in Zanzibar, Tanzania (data from Ali et al. [67]).

5.4.5. Tensile Strength

Dollente et al. [89] incorporated five types of fibers (polyvinyl alcohol, chopped basalt, copper-coated stainless steel, polypropylene, and carbon fiber) into a fly ash–silica fume geopolymer mortar to enhance tensile strength while maintaining competent compressive strength, potentially improving the earthquake resistance of historical masonry. The results showed that the addition of PVA, stainless steel, and chopped basalt fibers achieved a comparable compressive strength of 12.0, 12.1 MPa, and 9.9 MPa, respectively, from a 12.6 MPa control mortar, while the increase in tensile strength was 2.2, 1.64, and 1.8 MPa in comparison to 1.58 MPa of control mortar. Meanwhile, Tamburini et al. [94] developed a slag–MK geopolymer with river sand as aggregate and fibrous wollastonite as filler, resulting in 28-day compressive and tensile strengths of 34.5 MPa and 4.8 MPa, respectively; the geopolymer was used as a mortar matrix for fiber/mesh-reinforced cementitious composites.

5.4.6. Flexural Strength

Flexural strength is defined as the ability of a material to resist bending under load, as measured by the stress prior to fracturing. It is important to determine the susceptibility of a reinforcement material to resist deformation and cracking, with a similar resistance compared to the original material (i.e., traditional mortars or rocks). For example, Capasso et al. [111] compared the flexural strength of traditional tuff and brick waste stone-based geopolymers and found a high degree of similarity for the tuff waste-based geopolymer, while the brick waste-based geopolymer showed low to high similarity to traditional mortars (Table 14). Meanwhile, the silica fume-based grout in Baltazar et al. [112] had a higher strength at 1.0–1.5 MPa than traditional natural hydraulic lime (NHL) mortars at 0.2 MPa, attributed to the reaction of silica fume in alkali activators forming an aluminosilicate gel in the microstructure. Similarly, Clausi et al. [74] obtained MK geopolymers that had the highest flexural strength of 3.2–3.6, but did not conduct a comparison with the original stones (i.e., dolostone and sandstone).

Table 14. Mechanical properties of geopolymers applied to AHSs in comparison with reference materials.

Property	Geopolymer Type	Geopolymer	Reference	Ref. Material Value	Percent Change%	Similarity	Ref.
Adhesion (MPa)	Silica fume	0.6–0.9	NHL	0.1	500–800	Very Low	[112]
	Slag + MK	0.89–1.65	SM Bricks (substrate 1)	–	–	–	[94]
	Slag + MK	1.21–2.81	EM Bricks (substrate 2)	–	–	–	
Surface Hardness	Slag	31–39	Historical Mortars	10–20	95–210	Medium	[95]
	Tuff	26.5–53	In situ Mortar	–	–	–	[111]
	Brick	31.2–75.8	In situ Mortar	–	–	–	
Compactness (m/s)	Slag	3000–4000	In situ Mortar	2000–3000 m/s	50	Very High	[95]
Compressive (MPa)	Pumice	3–6 MPa	Type A WSL	8–20 MPa	62–70	High	[105]
			Type B ₁ WSL	3–10 MPa	0–40	Very High	
			Type B ₂ WSL	1–3 MPa	0–200	Very High to Medium	
			Type C WSL	0.5–1.5 MPa	100–1100	Medium to Very Low	
			NHL	9 MPa	11–77	High to Very High	
	Tuff	0.81–1.48	Aerial Lime Mortar	0.5	62–196	Medium to High	[111]
			NHL	3.7	78–60	High	
			OPC	24.8	94–96	High	
			Repair Mortars	3.5	57–77	High	
			Historical Magnesian Mortar	–	–	–	
	Brick	5.3–13.4	Natural Limestone	10.1	85–92	High	[74]
			Aerial Lime Mortar	0.5	960–2580	Very Low	
			NHL	3.7	43–262	Medium to High	
			OPC	24.8	46–75	High to Very High	
			Repair Mortars	3.5	51–282	Medium to High	
	MK	18	Historical Magnesian Mortar	–	–	–	[89]
			Natural Limestone	10.1	47.5–32.7	Very High	
			Dolostone	–	–	–	
			Sandstone	–	–	–	
			Plain Mortar	12.5	0–86	High to Very High	

Table 14. Cont.

Property	Geopolymer Type	Geopolymer	Reference	Ref. Material Value	Percent Change%	Similarity	Ref.
Tensile (MPa)	FA	0.6–2.2	Plain Mortar	1.6	37.5–62.5	High to Very High	[89]
	Slag + MK	4.8	None	n.d.	–	–	[94]
	Silica Fume	0.2	NHL	1.0–1.5	80–86	High	[112]
Flexural (MPa)	Tuff	0.4–1.23	Aerial Lime Mortar	0.24	66–412	Medium to High	[111]
			NHL	1.00	23–60	Very High	
			OPC	4.70	74–91	High	
			Repair Mortars	–	–	–	
			Historical Magnesian Mortar	–	–	–	
	Brick	2.85–4.58	Natural Limestone	–	–	–	[111]
			Aerial Lime Mortar	0.24	1087–1808	Very Low	
			NHL	1.00	185–358	Low to Medium	
			OPC	4.70	2–39	Very High	
			Repair Mortars	–	–	–	
			Historical Magnesian Mortar	–	–	–	
			Natural Limestone	–	–	–	
	MK	3.2	Dolostone	–	–	–	[74]
	MK	3.6	Sandstone	–	–	–	

Note: “WSL”: Western Sicilian limestone; “NHL”: natural hydraulic lime; “OPC”: ordinary Portland cement; “–”: no data. Similarity = Very High (0–50), High (50–100), Medium (100–300), Low (300–500), and Very Low (>500).

6. Recent Applications of Geopolymers in Architectural Heritage Structure Conservation

Recent AHS conservation research has commonly formulated geopolymer-based repair mortars to restore or patch degraded parts of the original stone substrate, followed by the application of consolidants to fill cracks and fix loosened material. In addition, masonry strengthening has been studied as a retrofitting technique to improve its resistance against seismic activity; however, the majority of these studies only presented potential for restoration and a preliminary on-site evaluation. A few studies have also reported the successful on-site application of the material, prioritizing ceramic tiles and bricks, while studies related to on-site application on natural rocks have been well reported. Table 15 summarizes recent applications of geopolymers in cultural heritage, indicating the type of geopolymer, purpose, and original substrate.

6.1. Repair Mortars

Repair mortars are applied to the original material as an alternative to restoring large patches of degraded original material. For example, Allali et al. [73] developed an MK-based geopolymer with Ca-rich components (lime and calcareous sand) as additives to maintain chemical compatibility with traditional materials for Moroccan AHSs instead of traditional lime-based mortars and concrete, which easily form salts that are dense and have low flexibility; the developed geopolymer showed a 7-day compressive strength ranging from 16 to 77 MPa (CaCO_3) and 2 to 40 MPa (Ca(OH)_2). Similarly, Maras [95] developed a slag-based geopolymer as repair mortar for Turkish AHSs because the use of traditional low-strength mortars resulted in visible cracks post earthquake episodes; the geopolymer had a 7-day compressive strength of 10–20 MPa. Meanwhile, the 28-day compressive strength of repair mortars for Italian AHSs using metakaolin and pumice were 18–21 MPa and 7 to 12 MPa, respectively [74,105]. In addition, Kutlusoy et al. [97] aimed for structurally competent masonry by utilizing a high-strength slag-based geopolymer with a 7-day compressive strength ranging from 20.7 MPa to 36 MPa.

6.2. Consolidants

Consolidants are adhesives or grouts used to fill small gaps and cracks and fix broken original ceramics and natural stones. For example, Moutinho et al. [76,78] used an MK-based geopolymer as consolidants to fix broken ceramic tiles, resulting in a 7-day compressive strength of 0.6 MPa to 3 MPa, whereas Baltazar et al. [112] utilized it as grout for old stones in historical masonry and achieved a 28-day compressive strength of 10–12 MPa (with superplasticizer) and 14–15 MPa (control). Meanwhile, Ricciotti et al. [75] applied an MK-based geopolymer with epoxy resin as a fixing paste for tuff and concrete substrates, resulting in a 28-day compressive strength of 40–50 MPa.

6.3. Masonry Strengthening

Furthermore, strengthening historical masonry with high-strength geopolymer mortars reinforced with fibers to withstand seismic vibration has been explored. For example, Dollente et al. [89] applied an FA-based geopolymer mortar with added fiber to unreinforced historical masonry, resulting in tensile strengths of 0.6 MPa to 2.2 MPa, compared to the control value of 1.6 MPa. Meanwhile, other studies aimed to provide seismic reinforcement for historical masonry. For example, Tamburini et al. [94] focused on fiber mesh-reinforced mortar, for which the adhesion strength was measured by conducting pull-out tests on the original substrate (clay bricks), resulting in 0.9 to 1.65 MPa in historic bricks and 0.9 MPa in the control, and 1.6 to 2.8 MPa in modern bricks and 2.7 MPa in the control. Similarly, Longo et al. [92] found a tensile strength of 868 MPa.

6.4. Others

Finally, the remaining studies did not discuss applications for AHSs but showed potential for restoration through the development of colored geopolymers [77,96] without the addition of commercial colored pigments. For example, Gupta et al. [96] formulated slag-based geopolymer bricks with the addition of colored-stone processing waste, resulting in pink, yellow, greyish, and white-colored bricks with a compressive strength of 15–25 MPa. Meanwhile, Angelo et al. [77] developed colored MK-based mortar using the adsorption Bromothymol blue, methyl orange, cresol red, and phenolphthalein, resulting in blue, yellow, violet, and purple geopolymers, respectively.

Another notable result is the effects of maturation in different environments on the potential for restoration of MK-based geopolymers. Perná et al. [83], for example, reported different 28-day compressive strengths of geopolymers allowed to mature in air (86.5 MPa), demineralized water (79.3 MPa), and seawater (87.2 MPa). Meanwhile, MK–silica fume combined with sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3) resulted in a 7-day compressive strength of 30 to 58 MPa [84], while an MK–fly ash geopolymer with expanded waste glass aggregates achieved a 48-day compressive strength of 10 MPa [93].

Recently, on-site applications in restoration have been slowly rising. For example, Fugazzotto et al. [109] applied a ceramic-based geopolymer mortar to ancient bricks as a substrate, resulting in a similar chromatic difference. Similar to Perná et al. [82], the application of geopolymers for fixing historical ceramic tiles and sandstones has been shown. However, further developments are needed to enable application to highly weathered ancient stones and to develop a sustainable material that enhances the long-term preservation of stone architectural heritage structures.

Table 15. Current application of geopolymers for AHS conservation.

Country	Geopolymer	Purpose/Application	Original Materials	Architectural Heritage Structure	Ref
Morocco	Metakaolin	Repair mortar	Lime-based mortar	Moroccan Historical Monument	[73]
Italy	Metakaolin	Repair mortar	Sandstone and dolostone	Not specified	[74]
Turkey	Slag	Repair mortars	Low strength mortars	Turkish Historical Masonry	[95]
Italy	Volcanic ash Volcanic soil	Repair mortars/binders	Not specified	Catania Architectures	[98]
Italy	Volcanic ash Volcanic soil	Repair mortars/binders	Not specified	Catania Architectures	[99]
Italy	Volcanic ash Volcanic soil	Repair mortars/binders	Not specified	Catania Architectures	[103]
Italy	Volcanic ash, Volcanic soil, Pumice	Repair mortars/binders	Not specified	Not specified	[104]
Italy	Volcanic ash,	Repair mortars	Mosaics	Cathedral of Monreale, Sicily	[100]
Italy	Pumice	Repair mortars	Sicilian limestones	Sicilian Baroque Cities	[105]
Italy	Tile waste or Brick waste	Repair mortars	Ancient bricks	Cathedral of Messina, Sicily, and Archeological Ruins in Gela, Caltanissetta	[110]
Italy	Ceramic tile waste	Repair mortar	Ancient bricks	Roman Odéon of Catania	[109]
Italy	Brick waste	Repair mortar	Limestone, lime mortars	Not specified	[111]
Italy	Tuff waste	Repair mortar	Limestone, lime-based mortars	Not specified	[111]
Portugal	Tungsten mine waste	Repair mortar	None	Not specified	[113]
Italy	Metakaolin	Consolidant	Tuff, concrete, ceramic	None	[75]

Table 15. Cont.

Country	Geopolymer	Purpose/Application	Original Materials	Architectural Heritage Structure	Ref
Portugal	Metakaolin	Consolidant	Ceramic tiles	None	[78]
Portugal	Metakaolin	Consolidant	Ceramic tiles	None	[76]
Italy	Metakaolin	Consolidant	Ceramic artworks	None	[85]
Czech Republic	Metakaolin (LO5)	Consolidant	Ceramic tiles	None	[82]
Italy	Porcelain stoneware Waste	Consolidant	Ceramic artworks	None	[107]
	Raw pressed ceramic				
	Calcined raw pressed ceramic				
	Gypsum				
	Mixed				
Portugal	Silica fume	Consolidant/Grout	Hydraulic lime	Non specified	[112]
Italy	Local clay	Consolidant/Plaster	Local clay	Earthen Architectures	[114]
Turkey	Slag	Strengthening historical masonry	Ceramic brick masonry	Turkish Historical Architectures	[97]
Italy	Fly ash	Strengthening historical masonry	Tuff and brick masonry	Not specified	[92]
Philippines	Fly Ash	Strengthening historical masonry	Unreinforced stone masonry	Not specified	[89]
Italy	Slag	Strengthening historical masonry	Ancient and modern brick masonry	Not specified	[94]
Czech Republic	Metakaolin	Valorization	None	None	[79]
Czech Republic	Metakaolin (LO5)	Valorization	None	None	[80]
Italy	Ceramic tile waste	Valorization	None	None	[108]
Italy	Fly ash	Valorization	None	None	[88]
Italy	Metakaolin	Colored geopolymer	None	None	[77]
India	Slag	Colored geopolymer	None	None	[96]
Czech Republic	Metakaolin (LO5)	Investigation of maturation environment	None	None	[83]
China	Metakaolin,	Investigation of modified activators (Na ₂ SiO ₃ and K ₂ SiO ₃)	None	None	[84]
Italy	Fly ash	Investigation of lightweight Aggregates	None	None	[93]

Note: “LO5” means in-house calcination of clay at 750 °C for 4–5 h.

7. Long-Term Durability of Geopolymers for Architectural Heritage Structures

Another crucial property of geopolymer-based replacement materials for tuff- and coral rock-built AHS conservation is their durability. In this section, the durability and performance of geopolymers under (i) accelerated aging and (ii) long-term outdoor exposure are discussed.

7.1. Accelerated Aging

This type of durability or weathering test is conducted under cyclic conditions to assess the durability of geopolymers by subjecting the material to simulated long-term degradation under extreme environmental conditions within a relatively short time. Some tests categorized under accelerated aging applied to geopolymers are (i) salt mist environment [76], (ii) wet–dry cycles [114], and (iii) freeze–thaw cycles [76,78,94].

7.1.1. Salt Mist Environment

Moutinho et al. [76] conducted a salt mist environment test to evaluate the behavior of an MK-based geopolymer by subjecting it to an artificial environment in a climatic chamber with salt spray (fog), following ASTM B117-03, including a 3.5% salt solution, for 14, 28, and 60 days at 30 °C. The results showed no visible presence of salts, but XRD analysis identified the formation of halite (NaCl) in the specimen with higher water content ($\text{H}_2\text{O}/\text{Na}_2\text{O} = 18$) and finer precursor particle size ($D_{50} = 1.5 \mu\text{m}$).

7.1.2. Wet–Dry Cycle

Rescic et al. [114] conducted thermo-hygrometric cycles on earthen plasters, formulated using local Santena clay, a common material used in the construction of earthen architecture in Italy. The plaster was subjected to 50 °C and 30% RH for 5 h in a climatic chamber, followed by 20 °C and 90% RH for 5 h as one cycle and repeated 50 times. The results showed a change in color (ΔE) from 11.1 to 2.09, while the weight loss was low at 0.33 compared with the untreated material (0.29), inferring that a loss of cohesion of the conservation material to the substrate was negligible.

7.1.3. Freeze–Thaw Cycle

Moutinho et al. [76] conducted freeze–thaw cycles of MK-based geopolymers used as consolidants for ceramic tiles in a climatic chamber with 29 summer/winter cycles. Summer conditions consisted of 10 °C at 40% RH, then 60 °C at 95% RH. Winter conditions included -10 °C at 95% RH and 30 °C at 100% RH, with each cycle divided into four series, each lasting 7 h, with 8 h of drying, giving each cycle a total of 36 h. The results were visually inspected to identify the formation of cracks or a loss of adhesion on the substrate; after the first cycle in winter, visible cracks on the specimen with a low water content ($\text{H}_2\text{O}/\text{Na}_2\text{O} = 17$) and precursor particle size ($D_{50} = 6.0 \mu\text{m}$) were observed. Meanwhile, the tenth summer cycle showed a loss of adhesion of both geopolymers, and after nineteen cycles, no new cracks or material loss was observed. Meanwhile, mass loss at the second cycle was 16% for geopolymers with a high water content and 10% for geopolymers with a low water content. After the fourth cycle, mass loss was 18% and 14%, respectively. Additionally, Moutinho et al. [78] formulated metakaolin with the addition of zeolite, observing a mass loss of 10% and loss of adhesion to the substrate after 10 cycles. Meanwhile, Taburini et al. [94] conducted 50 freeze–thaw cycles over 12 h between 20 and -20 °C, with specimens placed under water at 20 °C; after the geopolymer had aged for one year, no cracks or surface loss was observed, weight loss was 0.67%, and residual compressive strength ranged from 40.2 MPa to 45 MPa.

7.2. Long-Term Outdoor Exposure

In contrast to accelerated aging tests that require special “climate” chambers, long-term outdoor exposure, as the name suggests, takes advantage of the natural environment. Although simple and cheap, this approach is tedious because constant monitoring of environmental parameters like temperature, relative humidity, and rainfall is required. For example, Occhipinti et al. [105] formulated volcanic ash- and volcanic soil-based geopolymers obtained from pyroclastic residues from Mt. Etna, Catania, Italy. After the mortars were cured for 28 days, they were exposed on a rooftop in Catania city center for six months (July 2020–January 2021) with a mean temperature of 19.6 °C and mean relative humidity of 75%. The results showed good stability of the geopolymers under outdoor conditions with no cracks, no visible efflorescence, no color difference and higher compressive strengths.

Meanwhile, Fugazzoto et al. [109] formulated ceramic brick waste geopolymers and applied them as ancient brick substrates in the walls of Roman Odéon monuments in Catania, Italy, with a mean temperature of 26.5 °C and 60% relative humidity. Post-monitoring was conducted after three months and visual inspection showed good adhesion, no visible efflorescence, cracks and shrinkage, while maintaining high chromatic similarity to the original brick substrate.

8. Summary and Future Perspectives

The conservation of AHSs built with tuff and coral rock is challenging because it requires restoration materials that are environmentally acceptable and sustainable while maintaining their compatibility with the original substrate. Recently, geopolymers have become a popular alternative restoration material to conventional OPC in AHS conservation due to their low carbon footprint, reduced energy consumption, and favorable physical, mechanical, and aesthetic properties. Although several geopolymers have shown potential application for AHS conservation, their compatibility with the original materials remains unclear.

This work provided a systematic and comprehensive review of the different geopolymers applied to the conservation of tuff- and coral rock-built AHSs, including the precursor materials, types of aggregates, composition of the admixture, and resulting physical, mechanical, and aesthetic properties of the material. In addition, the compatibility criteria for natural stones used in AHS conservation was reviewed, focusing on aesthetic, physical, chemical, and mechanical compatibilities with the original substrate. Furthermore, long-term durability test protocols and the performance of geopolymers under accelerated aging or long-term outdoor exposure were outlined. Specifically, the findings of this work are outlined below.

- Original tuff substrates of AHSs have variable properties, including color (yellowish-brown and grayish-cream to reddish-brown, with some portions showing pale greenish-gray and pink hues), density (1.0–2.5 g/m³), and compressive strength (3–100 MPa).
- Original coral rock substrates of AHSs typically have coarse–fine pores and compressive strengths of 1–60 MPa.
- Metakaolin was prominently identified as important in geopolymer formulations for AHS conservation, either as the main precursor or as an additive/admixture, due to its high reactivity and aluminosilicate content.
- Other materials used for geopolymer formulations include fly ash, slags, local clays, volcanic ash, volcanic soil, pumice, and wastes (ceramics, mining, and silica fume), all having high aluminosilicate contents.
- Sodium silicate and sodium hydroxide were the most commonly reported alkaline activators for geopolymers.
- Aggregates in geopolymers for AHS conservation depend largely on availability, so readily and locally available materials like quartz sand, river sand, crushed stones, carbonate stones, volcanic rock, volcanic sand, tuff, brick, and ceramic aggregates are commonly used.
- Compatibility criteria for AHS conservation include aesthetics (i.e., color and presence of efflorescence), physical attributes (i.e., porosity, water absorption, capillary absorption, and density), chemical composition (i.e., microstructure and ionic release), and mechanical properties (i.e., adhesion, surface hardness, compactness, compressive strength, flexural strength, and tensile strength).

- Geopolymer applications in AHS conservation vary from repair mortars for patching deteriorated stones, consolidants (e.g., adhesives or grouts), and strengthening mortars to replacement stones as substitutes for the original substrate.
- Key considerations for geopolymers when applied as repair mortars include breathability, adhesion, and surface finish identical to original substrate.
- Geopolymers as consolidants require appropriate viscosity to penetrate voids or cracks while maintaining cohesion between fragments to strengthen and reattach deteriorated/broken fragments of the original substrate.
- Key properties for geopolymers when used as strengthening mortars include high tensile and flexural strengths while maintaining considerable compressive strength to enhance resistance during seismic disturbances like earthquakes.
- When geopolymers as applied as replacement stones, they must have color, texture, compressive strength and weathering durability similar to the original substrate.
- Geopolymer durability for AHS conservation is tested using accelerated aging (i.e., salt mist, wet–dry cycle, and freeze–thaw cycle) and long-term outdoor exposure.
- Tuff- and coral rock-built AHSs are high susceptible to damage from earthquakes, so future works will likely focus on mortar strengthening strategies and seismic masonry resilience like fiber-reinforced geopolymer development.
- Modern-day pollution is rapidly accelerating the deterioration of tuff- and coral built-built AHSs, so developing compatible stone consolidants to retard weathering while maintaining the aesthetic appearance of the original substrate is crucial.

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Abbreviations

The following abbreviations are used in this manuscript:

AHS	Architectural heritage structure
ASM	Artificial stone mortar

CB	Chopped Basalt
CIELab	Commission Internationale de l'Éclairage-Lab
CF	Carbon fiber
EC	Electrical conductivity
FA	Fly ash
FRCM	Fiber-reinforced cementitious materials
ICOMOS	International council on monument and sites
MK	Metakaolin
NDT	Non-destructive technique
NHL	Natural hydraulic lime
NMF	Non-metallic fraction
OPC	Ordinary Portland cement
OSF	Open Science Framework
PCB	Printed circuit board
PDMS	Polydimethylsiloxane
PM	Pumice
PP	Polypropylene
PRISMA	Preferred Reporting Items for Systematic Reviews and Meta-analysis
PVA	Polyvinyl Acetate
SEM	Scanning electron microscope
SF	Silica fume
STSL	Stainless Steel
TEOS	Tetraethyl orthosilicate
UCS	Unconfined compressive strength
UNESCO	United Nations Educational, Scientific, and Cultural Organization
UN-SDGs	United Nations Sustainable and Developmental Goals
UPV	Ultrasonic pulse velocity
URM	Unreinforced masonry
VA	Volcanic ash
VS	Volcanic soil
WoS	Web of Science
XRD	X-ray diffraction

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Article

A Multi-Analytical Approach to the Study of Phosphatic Materials from the Lower Cambrian of Spain

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Abstract

Phosphatic deposits from the Lower Cambrian Pedroche Formation (Sierra de Córdoba, Spain) provide key insights into early diagenetic mineralization processes during the Cambrian radiation. This study applies an integrated multi-analytical approach combining Raman spectroscopy, SEM–EDS, LA–ICP–MS, and ToF–SIMS to investigate mineralogical, elemental, and molecular signatures of phosphatized bioclastic carbonates and associated siliciclastic facies from the Los Lagares-1 borehole. Results reveal a systematic phosphatization gradient from carbonate-dominated skeletal rims to phosphate-rich interiors composed of carbonate fluorapatite with variable carbonate and hydroxyl substitution. Trace-element systematics and REE patterns indicate seawater-influenced phosphogenesis under suboxic porewater conditions, coupled to iron reduction and early diagenetic clay mineral formation. In contrast, the siliciclastic siltstone facies preserves poorly crystalline phosphate phases associated with detrital aluminosilicates and chlorite, reflecting distinct porewater chemistry and crystallization kinetics. ToF–SIMS mapping demonstrates spatial coupling between fluorine and phosphate within fossil structures, confirming fluorapatite formation and localized organic matter entombment. These results highlight the strong control of host lithology on phosphate crystallization pathways and trace-element redistribution, and provide new constraints on microbially mediated phosphogenesis in restricted Early Cambrian reef–lagoon systems along the northern Gondwanan margin.

Keywords: phosphogenesis; carbonate fluorapatite; Lower Cambrian; Pedroche Formation; microbially mediated mineralization; REE geochemistry; LA–ICP–MS; ToF–SIMS; early diagenesis; reef–lagoon systems

1. Introduction

The Lower Cambrian represents a pivotal period in Earth’s history, characterized by unprecedented biological diversification and the establishment of complex marine ecosystems during the Cambrian Explosion [1,2]. This critical interval witnessed not only the rapid evolution of metazoan life but also fundamental changes in ocean chemistry and biogeochemical cycling that profoundly influenced the preservation and mineralization of biological remains [3,4]. Among the most informative records of this transition are phosphatic deposits, which provide crucial insights into the interplay between biological productivity, ocean chemistry, and early diagenetic processes that governed fossil preservation [5,6].

Phosphatic materials from Cambrian sequences have long attracted scientific attention due to their exceptional preservation of early skeletal and soft-bodied organisms [7], their significance for understanding ancient nutrient cycling [8], and their role as archives of paleoenvironmental conditions [9]. The formation of these phosphatic deposits involves complex interactions between primary biological productivity, microbial metabolism, redox conditions, and the availability of dissolved phosphate in seawater [10]. However, the precise mechanisms controlling phosphate mineralization during the early Cambrian, particularly the relative contributions of abiotic geochemical processes vs. microbially mediated mineralization pathways, remain poorly understood [10,11].

Spain's Lower Cambrian sequences, particularly those of the Pedroche Formation in the Sierra de Córdoba, offer exceptional opportunities to investigate these processes [12,13]. These deposits contain diverse phosphatic materials including nodular phosphorites, phosphatic fossil steinkerns, and phosphatized skeletal elements associated with calcimicrobial reef-lagoon systems [14,15]. Previous studies have established the broad stratigraphic and paleontological framework of these deposits [16–19], documenting their formation in the context of intense continental weathering [20,21], elevated nutrient fluxes [22], and the development of archaeocyath-calcimicrobial reef complexes [23]. However, detailed investigation of the mineralizing processes—particularly at the microscale where geochemical and microbial processes intersect—has remained limited [24].

This study employs a multi-analytical approach combining Raman spectroscopy, laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate phosphatic materials from the Lower Cambrian Pedroche Formation. The primary objectives are to: (1) characterize the mineral phases, elemental compositions, and microscale spatial distributions of phosphatic, carbonate, and Fe–Mg phyllosilicate components across lagoonal facies; (2) resolve REE fractionation patterns and partitioning pathways from Fe(III)-oxyhydroxides to porewaters and ultimately into carbonate fluorapatite (CFA) [25]; (3) evaluate the role of microbial Fe reduction and localized sulfate reduction in mediating phosphate release, CFA precipitation, chlorite formation, and pyrite development under suboxic to micro-anoxic conditions [26–28]; and (4) reconstruct the sequence of early diagenetic reactions controlling CFA nucleation, REE incorporation, and mineral replacement within skeletal and matrix domains [29–31]. Beyond lithological control, this study also evaluates the role of depositional setting—reef vs. lagoon facies—as a secondary influence on phosphatization pathways, porewater redox gradients, and trace-element redistribution.

2. Geological and Sedimentary Settings

2.1. Regional Geology

The Los Lagares-1 borehole is located in the Sierra de Córdoba (southern Spain), in the Las Ermitas area [32] (Figure 1A–C). Geologically, the Sierra de Córdoba forms part of the Ossa-Morena Zone of the Iberian Massif, a tectonostratigraphic domain that records the late Neoproterozoic–early Cambrian transition along the northern margin of Gondwana [33]. During this interval, the region evolved from Cadomian arc-related magmatism to an extensional regime associated with continental rifting and the onset of shallow marine sedimentation [34]. In the study area, Neoproterozoic volcanic and volcanoclastic rocks of the San Jerónimo Formation are unconformably overlain by Lower Cambrian sedimentary successions of the Pedroche Formation, recording the establishment of carbonate-dominated platform and reef–lagoon systems [12] (Figure 1B).

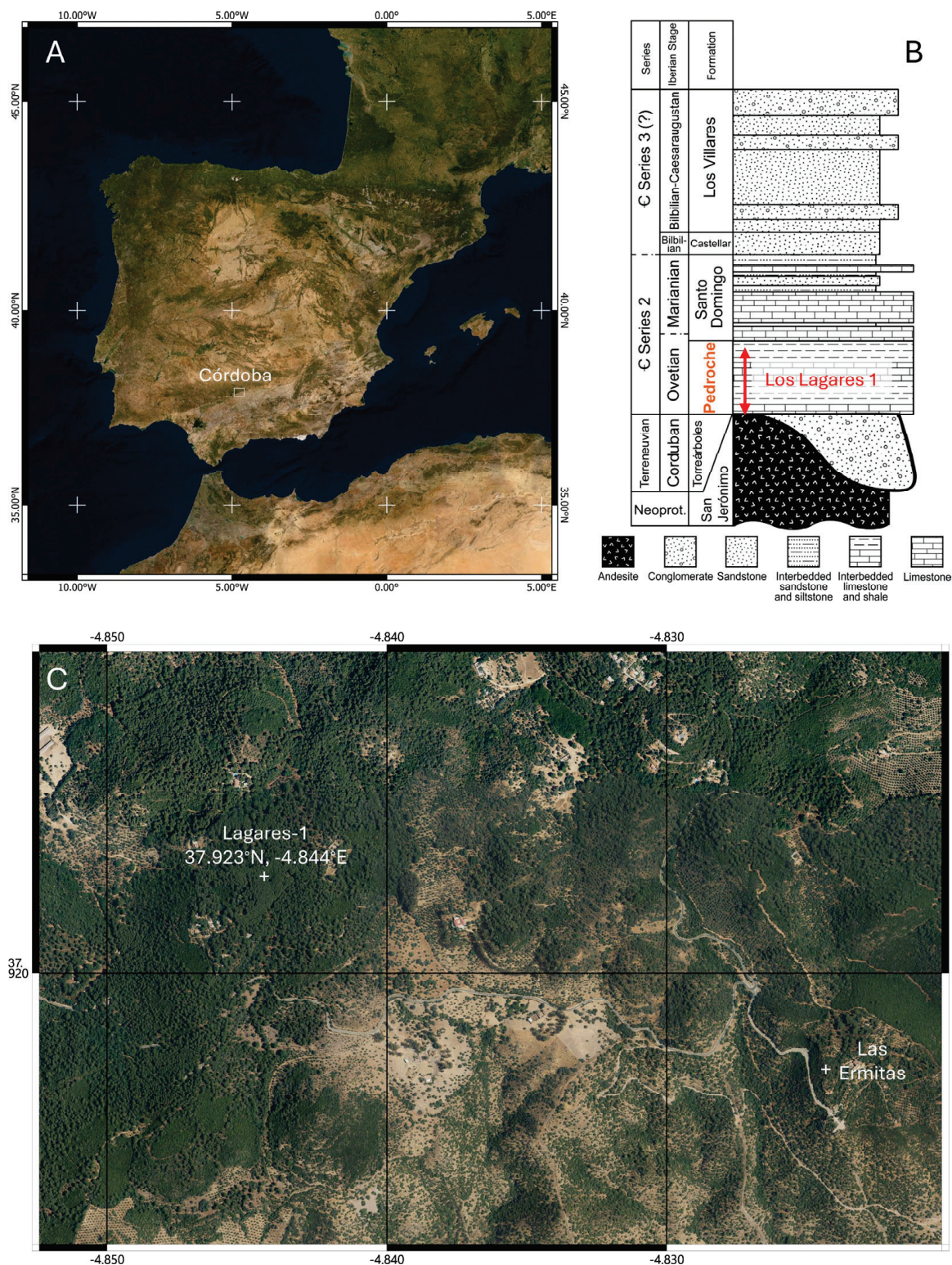


Figure 1. Geological setting and location of the Los Lagares-1 drill core. **(A)** Satellite image of the Iberian Peninsula showing the location of the study area near Córdoba in southern Spain (white rectangle). **(B)** Stratigraphic column of the Lower Cambrian succession in the Córdoba region, showing the position of the Los Lagares-1 borehole within the Pedroche Formation (red arrow). The succession comprises, from base to top: Neoproterozoic basement (San Jerónimo Formation), Terreneuvian Torreárboles Formation (Cordubán), and Cambrian Series 2 consisting of the Pedroche Formation (Ovetian) and Santo Domingo Formation (Marianian), overlain by Cambrian Series 3 deposits including the Castellar and Los Villares formations. **(C)** High-resolution satellite image showing the location of the Lagares-1 borehole (37.923° N, -4.844° E) and the nearby Las Ermitas locality.

The Los Lagares-1 borehole preserves a continuous subsurface record of approximately 290 m, with its lower portion penetrating altered andesitic rocks of the San Jerónimo Formation [32] (Figure 2). A sharp lithological boundary at 105.80 m depth marks the transition from this volcanic basement to the overlying sedimentary succession. Above this contact, the Pedroche Formation is dominated by carbonate-rich facies interbedded with fine-grained siliciclastic sediments, recording sustained Lower Cambrian deposition [35].

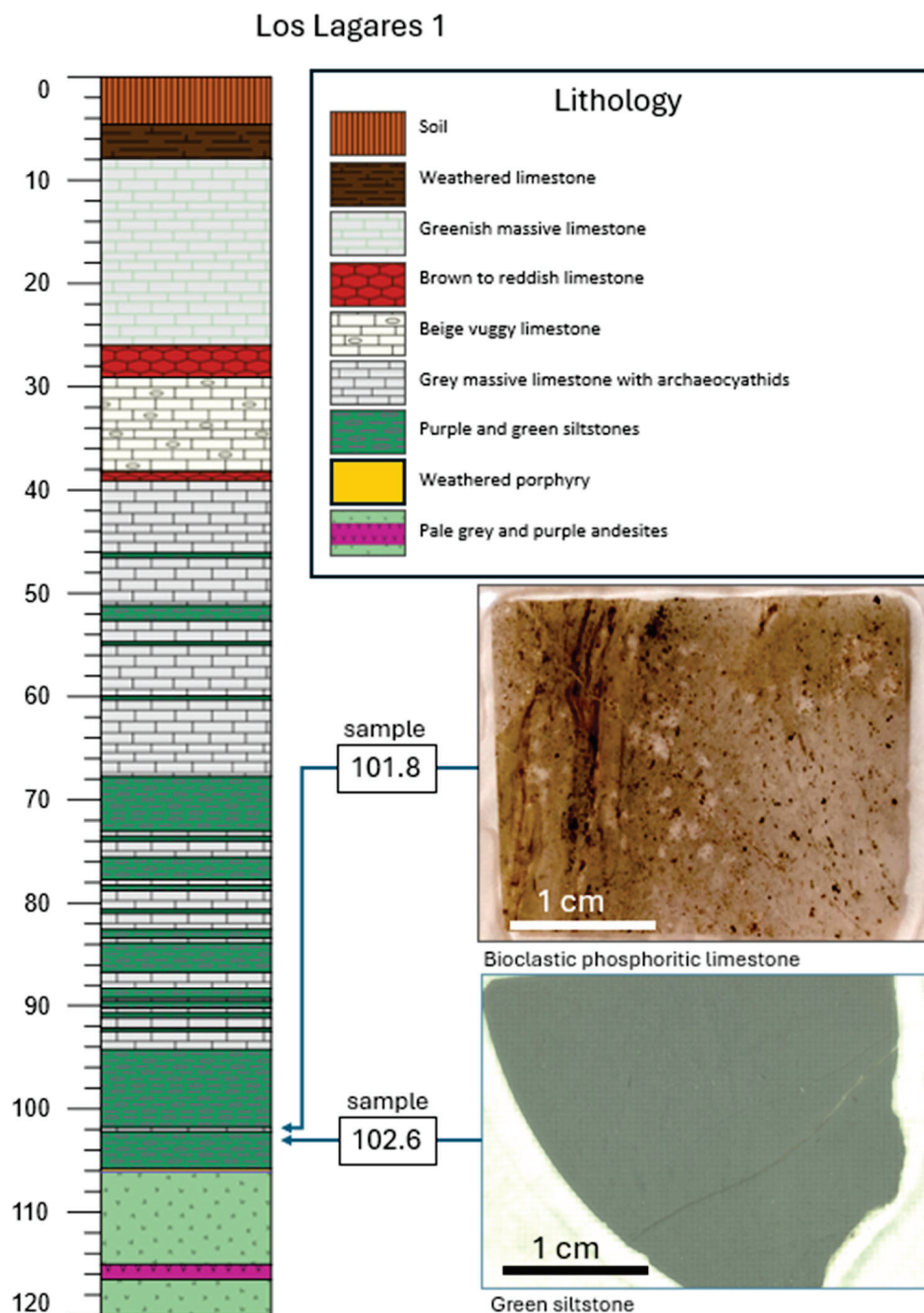


Figure 2. Simplified lithostratigraphic column of the Los Lagares-1 drill core showing the main lithological units and sedimentary facies of the Lower Cambrian Pedroche Formation. Polished slab photographs of the two analyzed samples are shown alongside the column: sample 101.8 m corresponds to a bioclastic phosphoritic carbonate; sample 102.6 m represents a greenish siltstone. The stratigraphic positions of the analyzed samples within the core are indicated by arrows.

2.2. Sedimentary Environments and Facies Interpretation

Sedimentation in the Los Lagares-1 section records the development of a shallow marine reef–lagoon system established on an irregular volcanic paleorelief [16,36]. The lower part of the sedimentary succession is dominated by green, purple, and ochre siltstones and marls, locally interbedded with nodular limestones, interpreted as lagoonal to marginal-lagoon deposits influenced by episodic siliciclastic input from adjacent continental areas [17].

Up-section, carbonate production increased significantly, leading to the development of nodular limestones and thick intervals of massive calcimicrobial limestone corresponding to reef-core and back-reef environments dominated by microbial communities and archaeocyathid frameworks [14,18,19]. The reef structures developed preferentially on elevated areas of the volcanic paleorelief and acted as semi-permeable barriers, partially isolating the lagoonal domain [37,38]. This geomorphological configuration restricted water circulation and favored the establishment of low-oxygen conditions within the lagoonal sediments [12] (Figure 2).

2.3. Phosphogenesis and Geochemical Context

The phosphatic deposits of the Pedroche Formation formed under the combined influence of elevated nutrient fluxes from continental weathering and microbially mediated diagenetic processes within the semi-restricted lagoonal environment [24,39]. Continental weathering under Early Cambrian elevated atmospheric CO₂ conditions delivered Fe(III)-oxyhydroxides bearing adsorbed phosphate to the coastal zone [20,22], where subsequent microbial iron reduction in suboxic porewaters released dissolved phosphate that precipitated as carbonate fluorapatite [26,27]. This study examines two contrasting facies from the Los Lagares-1 core: a bioclastic phosphoritic limestone at 101.8 m depth representing carbonate-dominated reef-lagoon sedimentation, and a greenish siltstone at 102.6 m depth representing siliciclastic-dominated lagoonal deposition [12,13].

2.4. Fossil Context and Geobiological Significance

The fossil assemblage recorded in the Los Lagares-1 sedimentary succession closely matches that documented in the Las Ermitas outcrops and reflects a diverse Lower Cambrian benthic ecosystem. Reefal facies are dominated by calcimicrobes and archaeocyathids, forming boundstones and bioherms that constitute the main framework of the reef system. Lagoonal and back-reef deposits host abundant small shelly fossils, including hyoliths, chancellorids, mollusks, and other problematic skeletal taxa, many of which are preserved as phosphatic internal molds [16,25,40,41] (Figure 3A,B). The release of phosphate into pore waters was critically mediated by microbial iron reduction, whereby iron-reducing bacteria facilitated the reductive dissolution of Fe-oxyhydroxides, liberating adsorbed phosphate and promoting its local supersaturation and subsequent precipitation as carbonate fluorapatite within decaying organic substrates [24,42].

The exceptional preservation of phosphatic steinkerns provides key insights into early Cambrian metazoan morphology and ecology and highlights the importance of biologically mediated phosphogenesis in shallow restricted marine settings. Together, the sedimentary, paleontological, and geochemical records of Los Lagares-1 document the strong coupling between paleotopography, reef development, nutrient cycling, and early diagenetic processes during the establishment of early Cambrian reef–lagoon ecosystems along the southwestern margin of Gondwana [24].

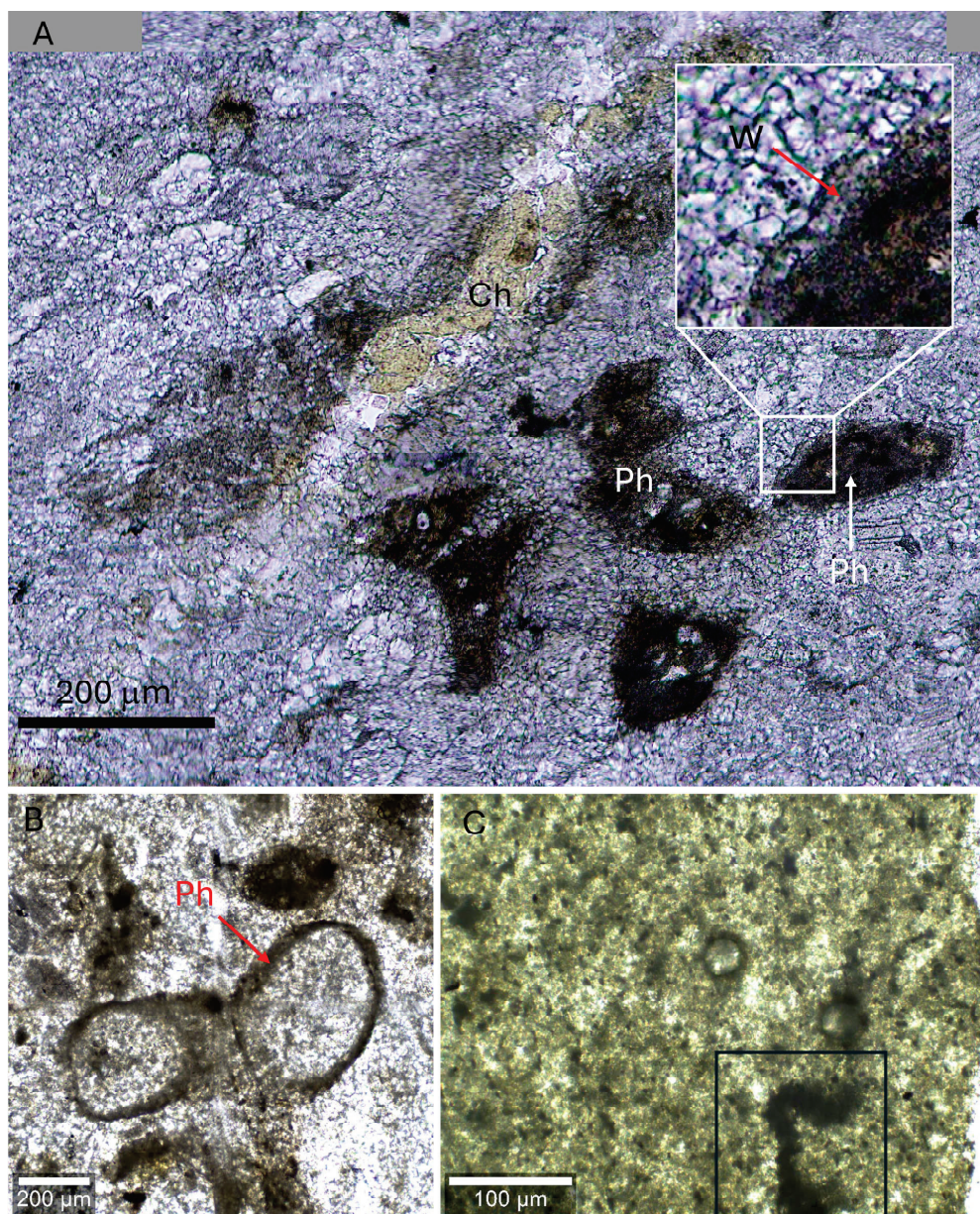


Figure 3. Thin-section photomicrographs of representative lithologies from the Los Lagares-1 borehole. (A,B) Sample 101.8 m, bioclastic phosphoritic limestone. Phosphate (Ph) occurs both as internal molds filling skeletal cavities and as replacive phases affecting skeletal walls (W). Chlorite (Ch) is present within skeletal structures. In (A), the inset (white square) shows a magnified view of a skeletal wall preserving remnants of original calcitic microstructure. (C) Sample 102.6 m, greenish siltstone, composed of fine-grained siliciclastic matrix. The outlined square highlights an organic structure preserved within the siltstone.

3. Materials and Methods

3.1. Sample Selection and Preparation

The samples analyzed in this study were obtained from the Los Lagares-1 borehole drill core, located in the municipality of Córdoba, Spain (37.923° N, 4.844° W; elevation 559 m) [32]. The borehole was drilled using rotary drilling techniques and reached a maximum depth of 292.5 m. Drilling operations were carried out between March 1981 and May 1982 within the framework of the Instituto Geológico y Minero de España (IGME), under the Ministerio de Industria y Energía, as part of the project “Investigación minera en la Reserva Estatal de Cerro Muriano (Fase II)”. The geological log and

stratigraphic column were prepared by INGEMISA, drawn by E. Velasco, and finalized in September 1982, at an original working scale of 1:200 (Plano N° 11-A-7) [32]. This continuous core provides a complete stratigraphic section through Lower Cambrian phosphatic deposits of the Pedroche Formation, offering exceptional preservation of mineralogical and paleontological features. Core samples were carefully extracted from specific intervals of interest identified during preliminary lithological logging, ensuring minimal contamination and preservation of primary textures [32].

The borehole intersects a complex volcano-sedimentary succession comprising alternating intervals of carbonates (limestones and dolostones), phyllosilicate-rich siltstones and shales, volcanoclastic deposits, and igneous rocks, locally affected by intense fracturing, brecciation, and hydrothermal alteration [24,36]. Carbonate units range from micritic to sparitic limestones, commonly brecciated and cross-cut by fracture-controlled calcite veins, and locally exhibit dolomitization, chloritization, and phosphatization, including phosphatized clasts and fossil fragments. Siliciclastic intervals are dominated by siltstones and fine-grained sandstones enriched in quartz, chlorite, and epidote, whereas volcanic and subvolcanic rocks are predominantly basaltic to andesitic, variably altered to low-grade hydrothermal assemblages of chlorite, epidote, albite, and calcite. Numerous fault zones, shear planes, and mineralized veins are recorded throughout the borehole, reflecting a prolonged history of tectonic reactivation and fluid circulation. All recovered core materials from the Los Lagares-1 borehole are archived and curated at the IGME Lithothèque (Litoteca del IGME), ensuring long-term preservation and accessibility of the borehole materials.

Selected core specimens from depths 101.8 and 102.6 m were prepared as standard petrographic thin sections (30 µm thickness) (Figures 2 and 3A–C), representing two contrasting lithologies within the Pedroche Formation: bioclastic phosphoritic carbonates and greenish siltstones [24]. Sample preparation followed conventional petrographic protocols. Specimens were vacuum-impregnated with low-viscosity epoxy resin to stabilize friable materials, mounted on glass slides, and ground and polished using progressively finer abrasives to achieve optical clarity. Thin sections intended for Scanning Electron Microscopy with Energy-Dispersive X-ray Spectroscopy (SEM-EDS) were carbon-coated or sputter-coated with platinum, whereas uncoated sections were used for optical microscopy and Raman spectroscopy.

Optical microscopy was conducted using a Leica upright transmitted-light microscope model DM2700P coupled to a Basler acA1920-40uc (ace series) USB 3.0 digital camera equipped with a Sony IMX249 CMOS sensor enabling detailed examination of microtextures, phosphatized skeletal elements, internal molds, and sedimentary fabrics (Figure 3A–C). This preliminary petrographic inspection played a critical role in identifying texturally and mineralogically representative areas of interest. Specific zones exhibiting phosphatic infillings, calcimicrobial lamination, organic-rich domains, or distinct diagenetic features were carefully selected and spatially documented prior to targeted high-resolution analyses. These microscopically defined regions subsequently guided SEM-EDS elemental mapping, LA-ICP-MS spot analyses, and ToF-SIMS molecular imaging, ensuring that advanced geochemical and molecular measurements were performed on petrographically constrained and contextually meaningful domains.

These two lithologies were selected because they constitute the dominant sedimentary facies within the studied interval and record contrasting depositional and diagenetic conditions. Sample 101.8 corresponds to a bioclastic phosphoritic carbonate characterized by abundant phosphatic components and frequent phosphatic internal molds [24] (Figures 2 and 3A,B). The fabric locally preserves fine laminar microstructures compatible with calcimicrobial accretion, indicating early phosphogenesis under carbonate-rich depositional conditions [24]. In contrast, sample 102.6 represents a greenish siltstone facies

composed of fine-grained siliciclastic sediment with low carbonate content and more homogeneous textures (Figures 2 and 3C), providing a distinct mineralogical and geochemical framework [24]. Together, these samples capture the principal pathways of fossil preservation and mineralization observed in the Los Lagares-1 succession. By targeting these two lithologies, the analytical dataset captures the principal compositional variability present in the section and allows for evaluation of the influence of lithology on phosphatization processes and elemental distributions.

3.2. Raman Spectroscopy

Thin sections were analyzed using confocal laser Raman spectroscopy (WITec alpha300 RA+, GmbH, Ulm, Germany) to identify mineral compositions and organic matter distributions [43] (Figures 4–6). The Raman system was equipped with a 532 nm Nd:YAG laser operated at 20 mW, coupled to a UHTS 300 spectrometer with 600 grooves/mm grating and Peltier-cooled CCD detector. The excitation wavelength was set at 532 nm, with the spectrum centered at around 1700 cm^{-1} . All images were acquired in reflected light mode using a Zeiss optical microscope (Zeiss, Jena, Germany) integrated with the Raman system. Single-point analyses were conducted with accumulation times of 10–20 s and integration times of 0.5 s per pixel to optimize the signal-to-noise ratio. Laser power was maintained at approximately 2–4 mW to enhance spectral signals while avoiding thermal damage or alteration to the samples.

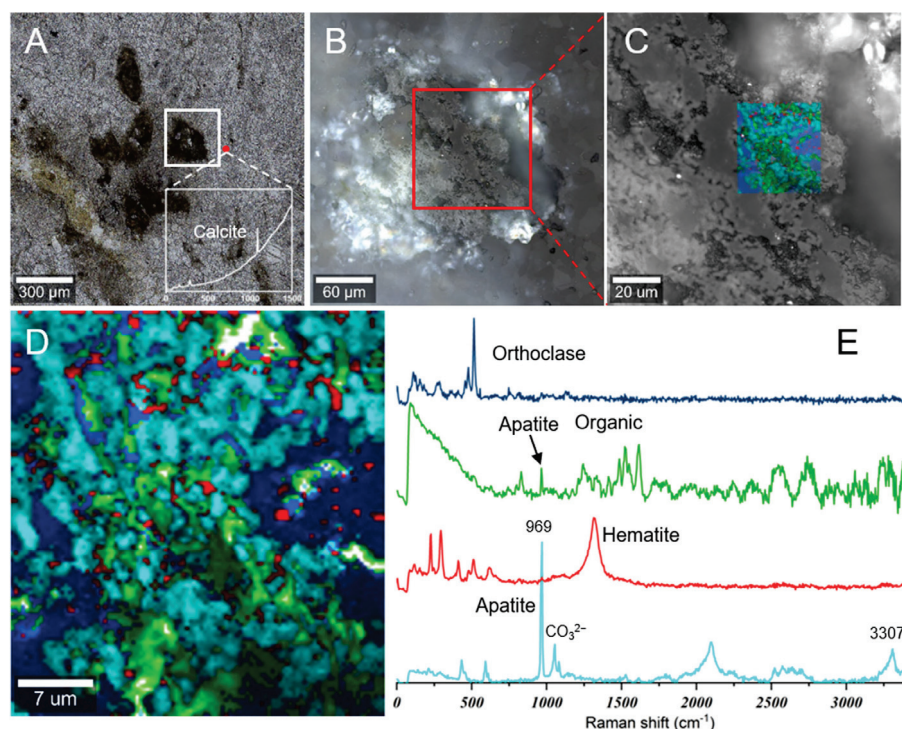


Figure 4. Raman mapping analysis of mineralized fossils from the phosphoritic bioclastic limestone at 101.8 m depth. (A) Transmitted light photomicrograph showing mineralized fossils within calcite matrix; the white rectangle indicates the area shown in (B) and the red square marks the location of the Raman spectrum displayed in (E). (B) Reflected light photomicrograph of the area outlined in (A); the red rectangle indicates the region shown in (C). (C) High-magnification image showing the spatial relationship between organic matter (green) and bioapatite (light blue). (D) False-color Raman map showing distribution of K-bearing silicate likely orthoclase (dark blue), apatite (blue), organic matter (green/red), and hematite (red). (E) Representative Raman spectra: K-bearing phyllosilicate, organic matter with apatite (peaks at 1243 , 1331 , 1485 , and 1615 cm^{-1}), hematite, and carbonate-substituted apatite ($\nu_1\text{ PO}_4^{3-}$ at 967 cm^{-1} , carbonate substitution peaks at 1055 and 1087 cm^{-1} , OH-related vibration at 3307 cm^{-1}).

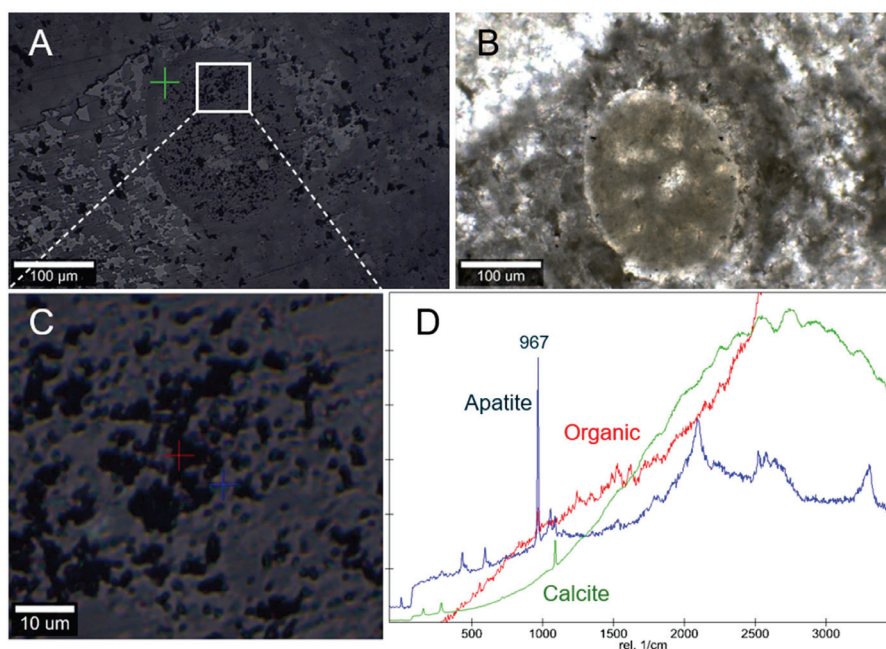


Figure 5. Raman spectroscopic point analysis of mineralized fossils from the phosphoritic bioclastic limestone at 101.8 m depth. (A) Reflected light photomicrograph showing mineralized fossils within carbonate matrix; green cross indicates analytical point, white rectangle marks area shown in (C). (B) Transmitted light photomicrograph of the same region. (C) High-magnification image showing locations of point analyses: red cross on organic-rich domain, blue cross on phosphatized region. (D) Raman spectra: apatite (blue) with ν_1 PO_4^{3-} peak at 967 cm^{-1} , organic matter (red) with peaks at 1246 , 1527 , 1617 , 2097 , 2525 , 2577 , and 3306 cm^{-1} , and calcite (green) from surrounding matrix.

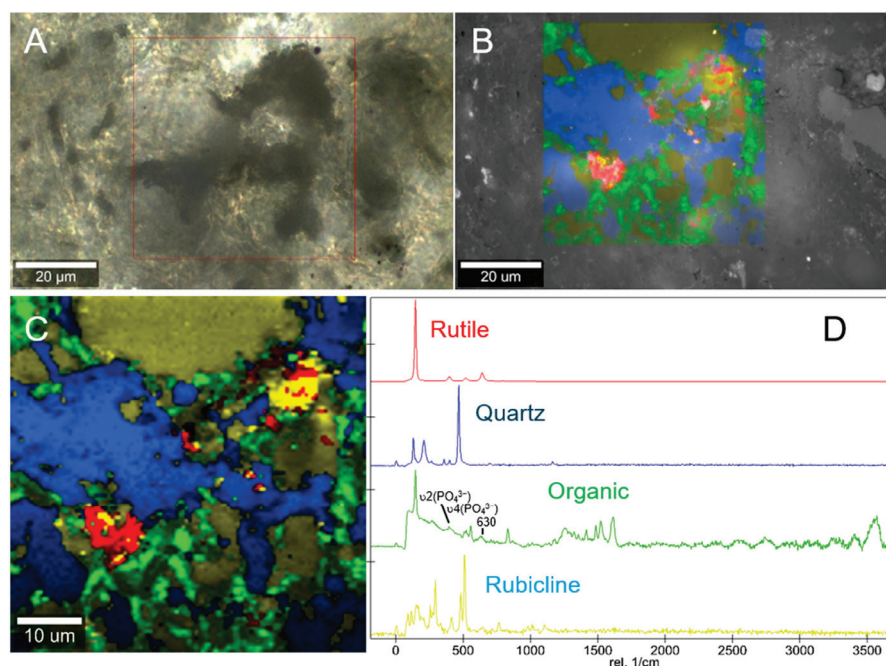


Figure 6. Raman mapping analysis of mineralized fossils from the siltstone at 102.6 m depth. (A) Transmitted light photomicrograph showing mineralized structures within quartz-dominated matrix; red rectangle indicates region selected for Raman mapping. (B) Reflected light photomicrograph overlapped with false-color Raman map. (C) False-color Raman map showing distribution of rutile (red), quartz (blue), organic matter (green), and rubicline (yellow). (D) Representative Raman spectra: rutile (TiO_2), quartz, organic matter with poorly crystalline phosphate (ν_2 PO_4^{3-} at 401 cm^{-1} , ν_4 PO_4^{3-} at 556 cm^{-1} , broadened ν_4 at 630 cm^{-1} , and organic peaks at 833 , 1257 , 1414 , 1487 , 1524 , and 1614 cm^{-1}), and rubicline [$\text{Rb}(\text{AlSi}_3\text{O}_8)$].

The instrument was calibrated using a silicon standard (520.7 cm^{-1}) before each analytical session. Spectral acquisition employed 200×200 -pixel grids using a $100\times$ objective (NA 0.9) and 500 nm step size for mapping analyses. Identical spectral parameters were employed for both single-point and large-area mapping analyses. Large-area scan data were processed using WITec Project FIVE software, version 5.3 (WiTec GmbH, Ulm, Germany). Cosmic ray artifacts and background noise were removed through automated filtering routines, and the spatial distribution of different mineral phases and organic components was visualized using false-color composite maps generated by the software.

3.3. Scanning Electron Microscope-Energy Dispersive X-Ray Spectrometry (SEM-EDS) Analysis

Thin sections of Los Lagares-1 samples were examined using a JEOL JSM-IT500 scanning electron microscope equipped with an Oxford Ultim Max energy-dispersive X-ray spectrometer at the State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology (MUST) (Figure 7). Samples were sputter-coated with a 10 nm layer of platinum before analysis to ensure conductivity and minimize charging effects. Mineralized fossils and microtextural features were characterized using secondary electron (SE) imaging and backscattered electron (BSE) imaging, acquired at an accelerating voltage of 15 kV, working distance of 8 mm, and probe current of approximately 1 nA. Elemental mapping was performed using EDS with silicon drift detectors and acquisition times of 100–300 s per field of view to confirm mineral compositions and spatial distributions of major and minor elements.

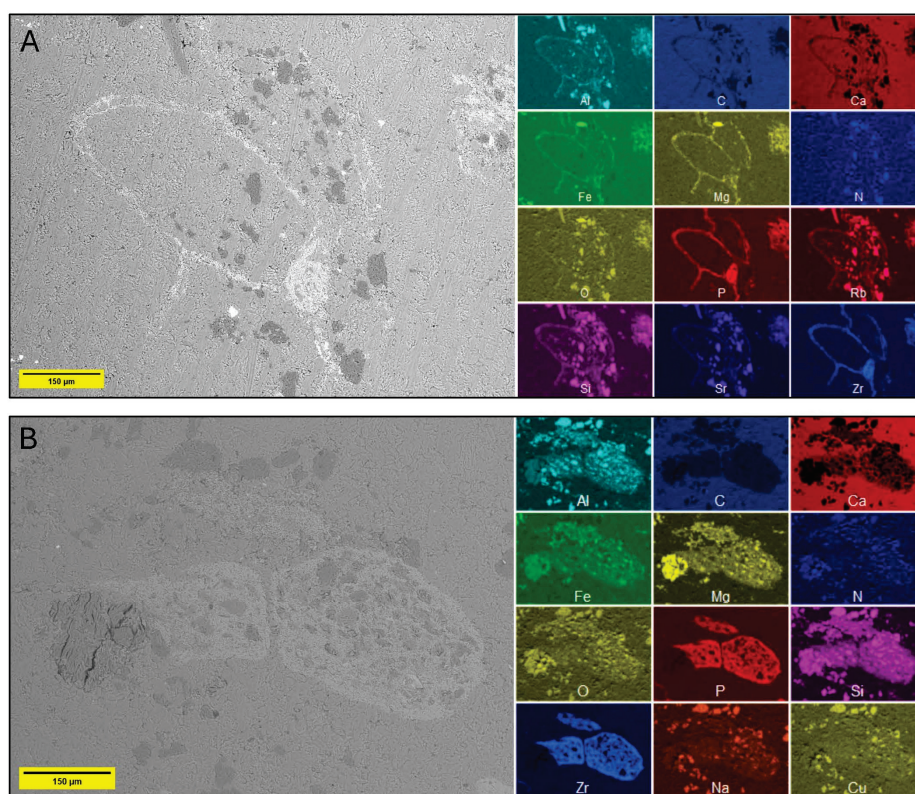


Figure 7. SEM-EDS elemental mapping of phosphatized bioclastic structures from the limestone at 101.8 m depth. **(A)** BSE image and elemental maps of a phosphatized bioclast showing distribution of Al, C, Ca, Fe, Mg, N, O, P, Rb, Si, Sr, and Zr. P is concentrated along bioclast walls; Ca-C association marks carbonate matrix; Fe-Mg-Si-Al co-localization indicates authigenic chlorite; Rb-Sr correlates with Si-Al-rich phyllosilicate domains. **(B)** BSE image and elemental maps of intensely phosphatized bioclastic aggregates showing similar element-mineral associations, with additional mapping of Na, Cu, and Al. Note that Na, Cu, and Al exhibit highly similar distribution patterns within the phosphatized structures. Scale bars = 150 μm .

3.4. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

In situ trace element analyses were performed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the State Key Laboratory of Lunar and Planetary Sciences, Macau University of Science and Technology (MUST) [44] (Figures 8–13). The analytical system consisted of a COMPex 4.0 ArF 193 nm (Coherent Corp., Saxonburg, PA, USA) excimer laser coupled with a GeoLas optical system and an Agilent 7900 ICP-MS (Agilent Technologies, Santa Clara, CA, USA). Laser parameters included a spot size of 32 μm , a repetition rate of 3 Hz, and an energy density of 4 J/cm². Each analysis comprised 45 s of background acquisition followed by 45 s of sample signal acquisition.

Signal intensities were calibrated using NIST SRM 610 and NIST SRM 612 glass standards as external references, without applying an internal standard correction. Data reduction was performed using ICPMSDataCal software [44]. Ablation spots were positioned in transects perpendicular to laminated structures, enabling the reconstruction of fine-scale geochemical variations across individual laminae and providing insight into temporal changes in depositional chemistry. A total of 30 spots were analyzed for each sample, distributed across compositionally distinct domains identified during preliminary petrographic examination.

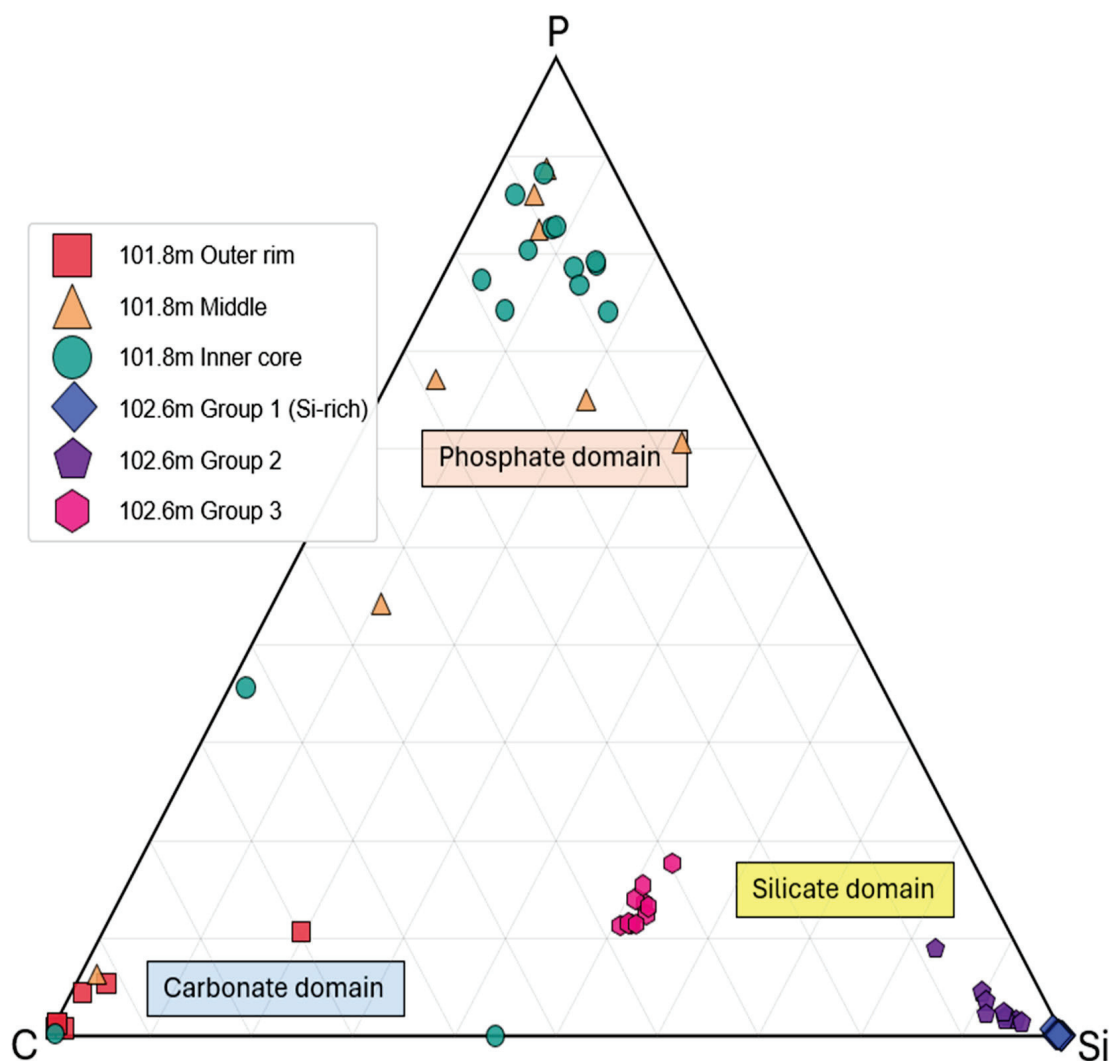


Figure 8. Ternary diagram showing relative proportions of P (phosphate), C (carbonate), and Si (silicate) for microdomains analyzed in samples 101.8 m and 102.6 m. Data normalized to 100%. Sample 101.8 displays compositional spread from carbonate-dominated outer rim toward phosphatic inner domains. Sample 102.6 clusters toward the Si apex, indicating dominantly detrital signature.

It should be noted that LA-ICP-MS is primarily optimized for trace element analysis, and major element concentrations derived from this technique carry higher uncertainties than trace element data due to matrix effects, elemental fractionation, and calibration uncertainties when using silicate glass standards for phosphatic and carbonate matrices (Figures 8–13). Accordingly, major element ratios reported in this study (e.g., Fe/Al, Mg/Al, Ca/P, Fe/Ti) are used as semi-quantitative compositional indicators to discriminate between mineral domains rather than as absolute concentration measurements, and should be interpreted with this limitation in mind.

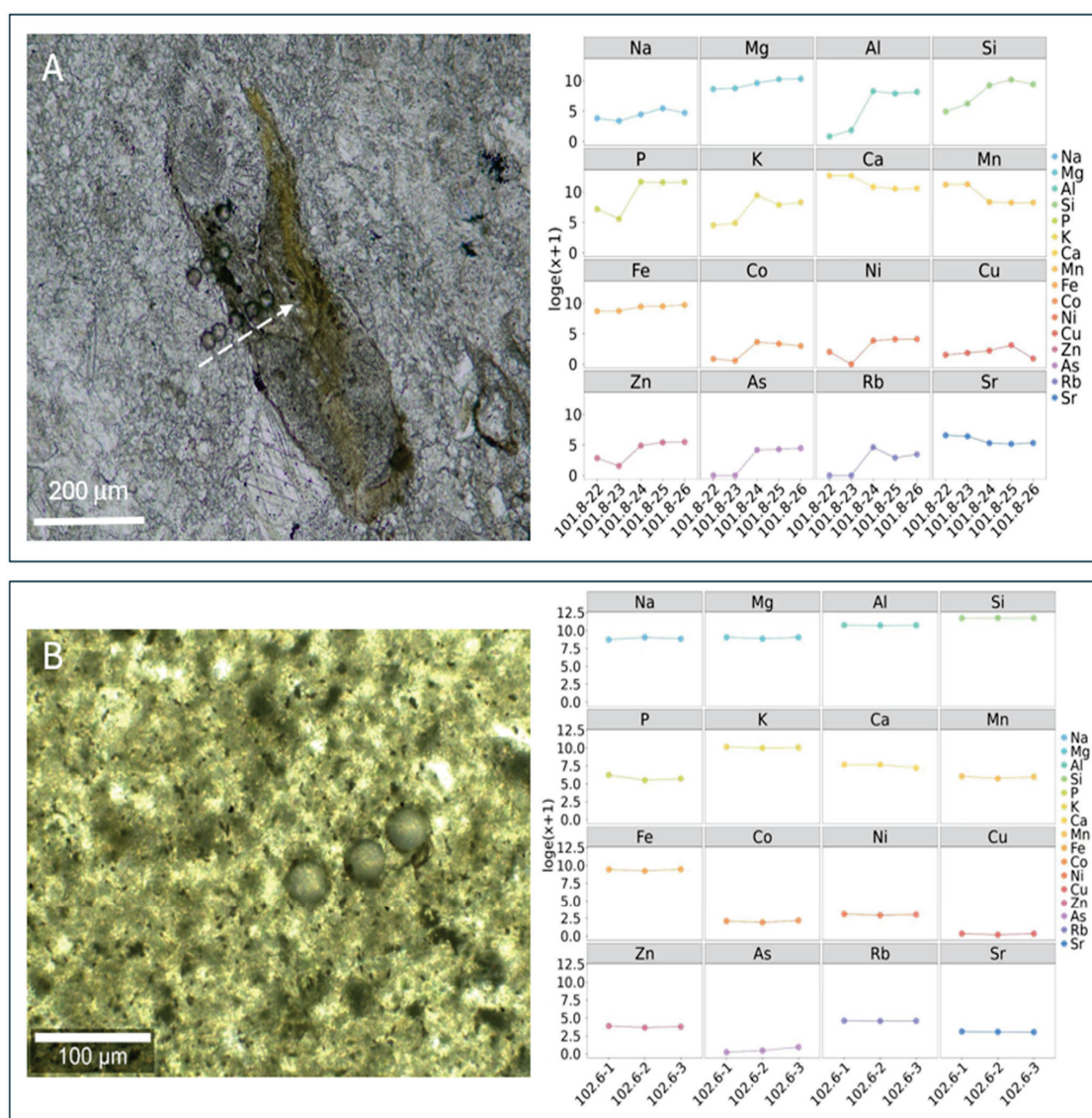


Figure 9. Petrographic context and LA-ICP-MS elemental variations for selected ablation spots in samples 101.8 and 102.6. **(A)** Thin-section microphotograph of the bioclastic phosphoritic carbonate (sample 101.8) showing a phosphatized skeletal fragment within fine-grained carbonate matrix. The arrow indicates a cluster of rounded microstructures associated with the phosphatized bioclast, highlighting localized textural heterogeneity and potential sites of enhanced phosphatization. Multi-plots display log-transformed elemental concentrations ($\log(x + 1)$) from LA-ICP-MS ablation spots (101.8-2 to 101.8-6). **(B)** Thin-section microphotograph of the greenish siltstone (sample 102.6) with dispersed rounded grains. Corresponding LA-ICP-MS spot analyses (102.6-1 to 102.6-3) show comparatively homogeneous elemental distributions with higher Si, Al, and associated lithophile trace elements.

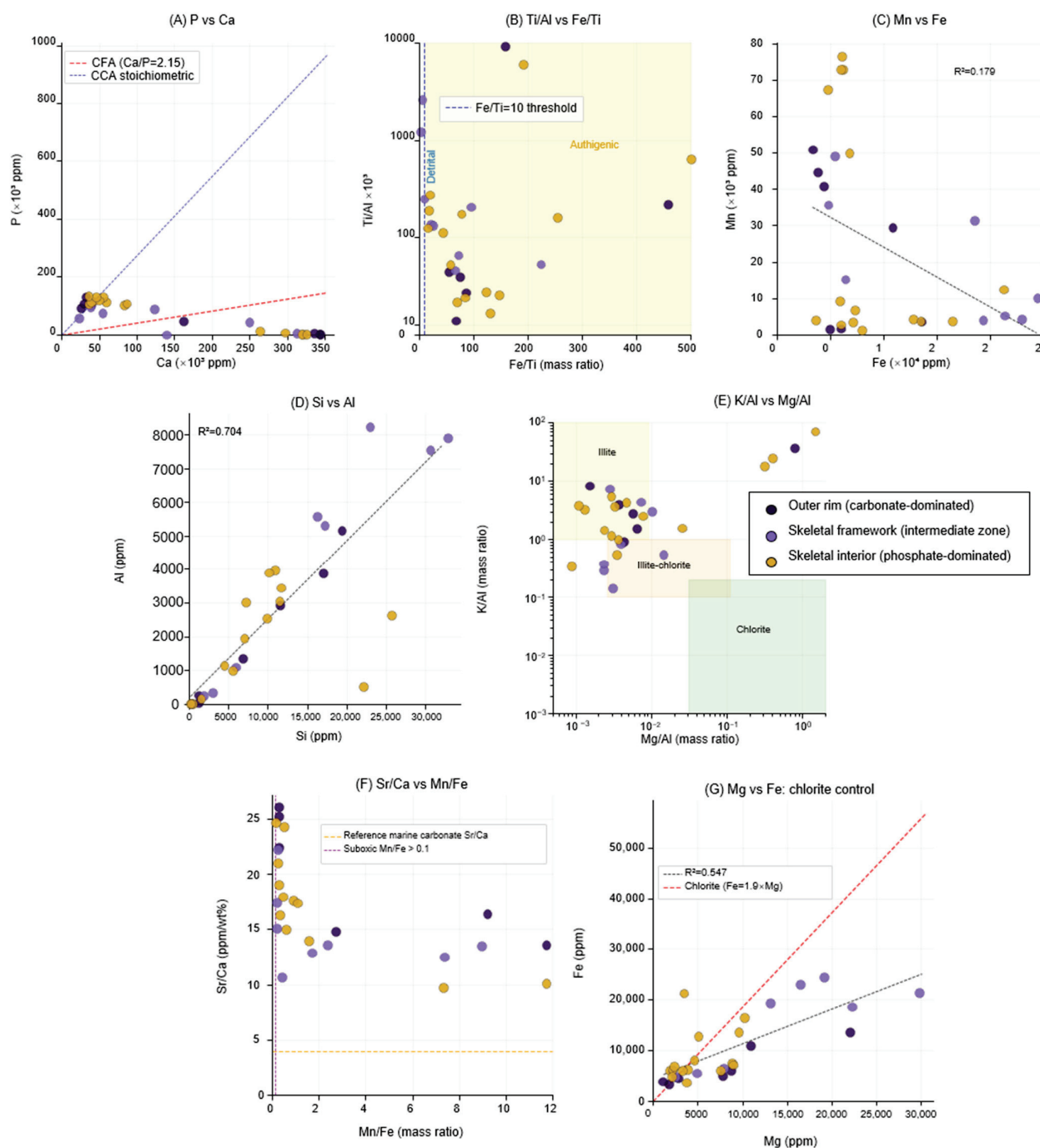


Figure 10. LA-ICP-MS major, minor, and trace element geochemistry of bioclastic phosphoritic limestone (sample 101.8 m). **(A)** P vs. Ca plot showing the phosphate–carbonate relationship relative to ideal carbonate fluorapatite stoichiometry (CFA; Ca/P = 2.15) and calcite (CCA stoichiometric) reference lines. **(B)** Ti/Al vs. Fe/Ti plot distinguishing detrital from authigenic iron components; the Fe/Ti = 10 threshold separates detrital (left) from authigenic (right) fields. **(C)** Mn vs. Fe plot showing weak negative correlation ($R^2 = 0.179$), indicating decoupled behaviour consistent with Mn mobility under suboxic conditions. **(D)** Si vs. Al plot demonstrating a strong positive correlation ($R^2 = 0.704$) consistent with a coupled aluminosilicate framework. **(E)** K/Al vs. Mg/Al plot discriminating clay mineral assemblages, with compositional fields for illite, illite–chlorite, and chlorite shown. **(F)** Sr/Ca vs. Mn/Fe plot for redox–diagenetic discrimination; reference lines indicate marine carbonate Sr/Ca and suboxic Mn/Fe threshold (> 0.1). **(G)** Mg vs. Fe plot showing moderate correlation ($R^2 = 0.547$) consistent with Fe–Mg-rich chlorite (Fe = 1.9 $\times$ Mg reference line). Outer rim (carbonate-dominated): dark purple circles; Skeletal framework (intermediate zone): light purple circles; Skeletal interior (phosphate-dominated): gold circles.

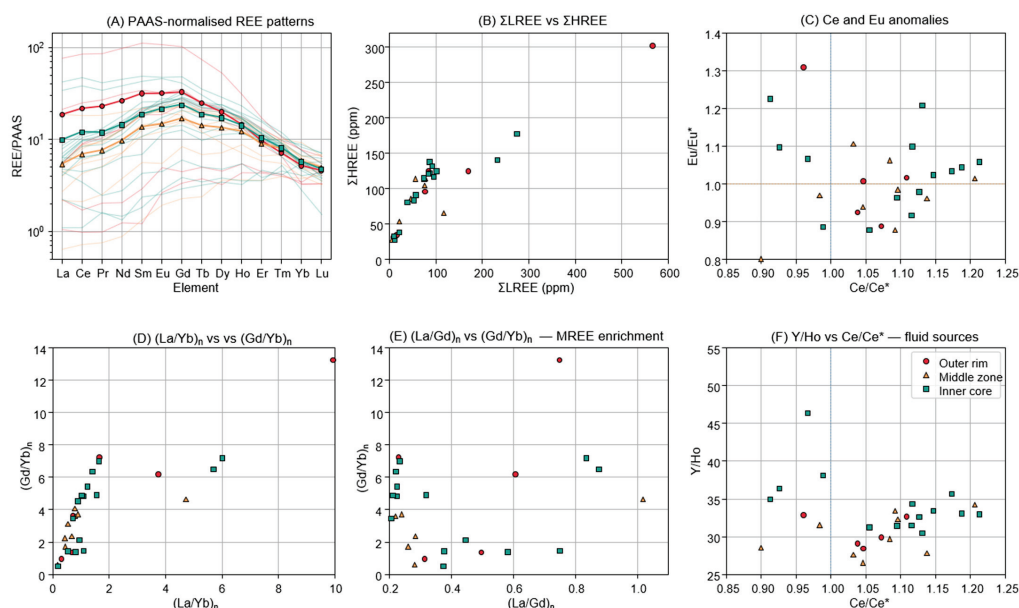


Figure 11. REE systematics of the limestone at 101.8 m (Los Lagares-1 borehole) showing geochemical variations across textural domains (outer rim, middle zone, inner core). **(A)** PAAS-normalized REE patterns. Thin lines represent individual analyses, whereas thick lines represent the mean PAAS-normalized pattern for each compositional domain displaying overall enrichment in LREEs relative to HREEs and subtle variations between domains, with slight negative slopes toward the heavy REEs. **(B)** Σ LREE vs. Σ HREE plot showing a positive correlation, indicating coupled behavior during diagenetic redistribution, with inner core samples tending toward higher total REE concentrations. **(C)** Ce/Ce* vs. Eu/Eu* anomalies illustrating predominantly near-neutral to slightly positive Ce anomalies and minor Eu variability, suggesting limited redox-driven fractionation. **(D)** $(\text{La/Yb})_n$ vs. $(\text{Gd/Yb})_n$ ratio plot showing variable REE fractionation, with inner core samples spanning the widest range of $(\text{Gd/Yb})_n$ values. **(E)** $(\text{La/Gd})_n$ vs. $(\text{Gd/Yb})_n$ plot highlighting middle REE (MREE) enrichment trends and differential fractionation across domains. **(F)** Y/Ho vs. Ce/Ce* ratio plot is used to infer fluid sources, showing values close to seawater signatures with minor deviations, suggesting a dominant marine influence with possible diagenetic modification.

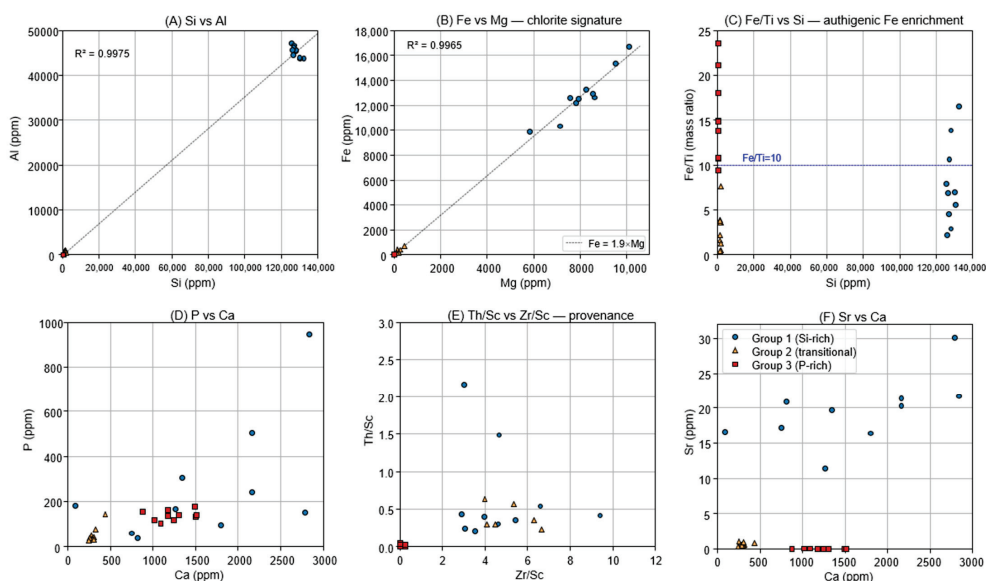


Figure 12. LA-ICP-MS major, minor, and trace element geochemistry of the greenish siltstone (sample 102.6 m) illustrating compositional controls, mineral associations, and provenance signatures across

three compositional groups. (A) Si vs. Al plot showing a strong linear correlation ($R^2 = 0.9975$), consistent with a dominant detrital aluminosilicate framework. (B) Fe vs. Mg plot displaying a tight correlation ($R^2 = 0.9965$) along the $\text{Fe} = 1.9 \times \text{Mg}$ reference line, indicative of Fe–Mg-rich phyllosilicates, interpreted as authigenic chlorite or chamosite. (C) Fe/Ti vs. Si plot highlighting authigenic iron enrichment; elevated Fe/Ti ratios (>10 threshold) in Si-poor samples indicate Fe addition beyond detrital input, whereas Si-rich Group 1 samples fall mostly below the threshold. (D) P vs. Ca plot showing decoupling between phosphorus and calcium, indicating that P is not primarily hosted in carbonate phases. (E) Th/Sc vs. Zr/Sc provenance discrimination diagram, with samples clustering in a field consistent with mixed felsic to intermediate detrital sources and limited sediment recycling. (F) Sr vs. Ca plot illustrating low Sr contents in most samples, consistent with the subordinate role of carbonate phases and dominance of siliciclastic material. Group 1 (Si-rich): blue circles; Group 2 (transitional): gold triangles; Group 3 (P-rich): red squares.

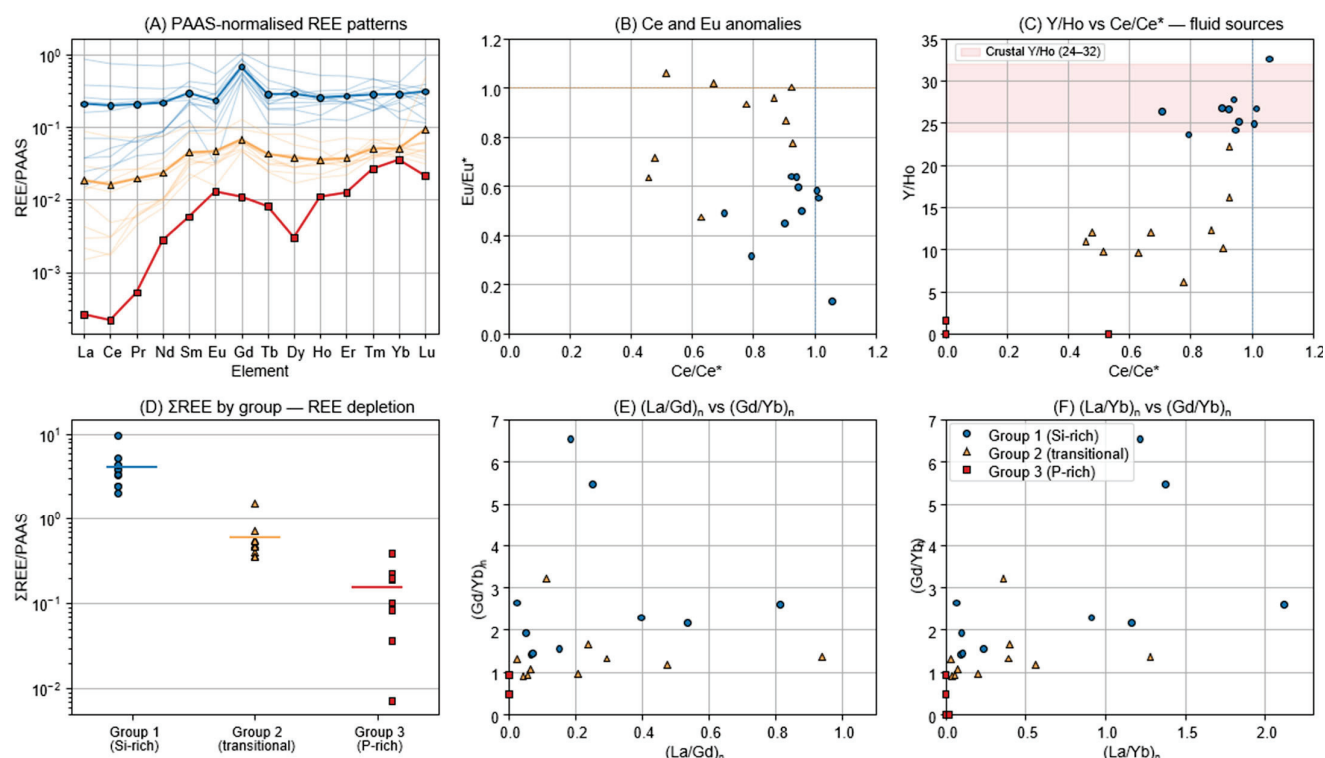


Figure 13. REE systematics of the siltstone at 102.6 m (Los Lagares-1 borehole) showing compositional differences among Si-rich (Group 1), transitional (Group 2), and P-rich (Group 3) samples and their implications for detrital control and fluid interaction. (A) PAAS-normalized REE patterns. Thin lines represent individual analyses, whereas thick lines represent the mean PAAS-normalized pattern for each compositional group showing overall low REE concentrations relative to PAAS, with Group 1 (Si-rich) displaying higher and relatively flat patterns, Group 2 (transitional) showing moderate enrichment, and Group 3 (P-rich) exhibiting strongly depleted REE contents. (B) Ce/Ce^* vs. Eu/Eu^* anomalies indicating predominantly negative Eu anomalies and variable Ce behavior, with most samples clustering around or below $\text{Ce}/\text{Ce}^* = 1$, suggesting limited redox-controlled Ce fractionation and absence of significant hydrothermal Eu input. (C) Y/Ho vs. Ce/Ce^* ratio plots highlighting fluid signatures, with Group 1 samples clustering near the seawater field (elevated Y/Ho), while Groups 2 and 3 show lower ratios consistent with dominant detrital control. (D) ΣREE distribution by group showing higher REE concentrations in Si-rich samples and markedly lower values in P-rich samples. (E) $(\text{La}/\text{Gd})_n$ vs. $(\text{Gd}/\text{Yb})_n$ plot illustrating middle REE (MREE) fractionation, with Group 1 displaying greater variability and occasional MREE enrichment relative to Groups 2 and 3. (F) $(\text{La}/\text{Yb})_n$ vs. $(\text{Gd}/\text{Yb})_n$ plot highlighting differences in LREE–HREE fractionation, with Si-rich samples showing broader variability and P-rich samples remaining consistently depleted. Shaded fields represent typical seawater Y/Ho ratios.

3.5. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analyses were performed using a TOF-SIMS IV instrument at the Service of Analysis and Characterization of Solids and Surfaces, Research Support Services, University of Extremadura, Spain [45,46] (Figures 14 and 15). The instrument was equipped with a bismuth liquid metal ion gun (LMIG) as the primary ion source and dual sputtering sources (oxygen and cesium ion guns) for depth profiling. Analyses were conducted under ultra-high vacuum conditions (2×10^{-9} mbar) using Bi_3^{++} cluster ions as the primary beam, operated in high-current bunched mode (HC-BUNCHED) to achieve optimal lateral resolution ($\sim 1 \mu\text{m}$). The primary ion gun was operated at 25 kV with an extractor voltage of 10 kV and an emission current of $1.00 \mu\text{A}$, resulting in a Bi_3^{++} beam current of approximately 0.21 pA. Both the primary ion gun and sputtering gun were positioned at 40° relative to the sample surface normal.

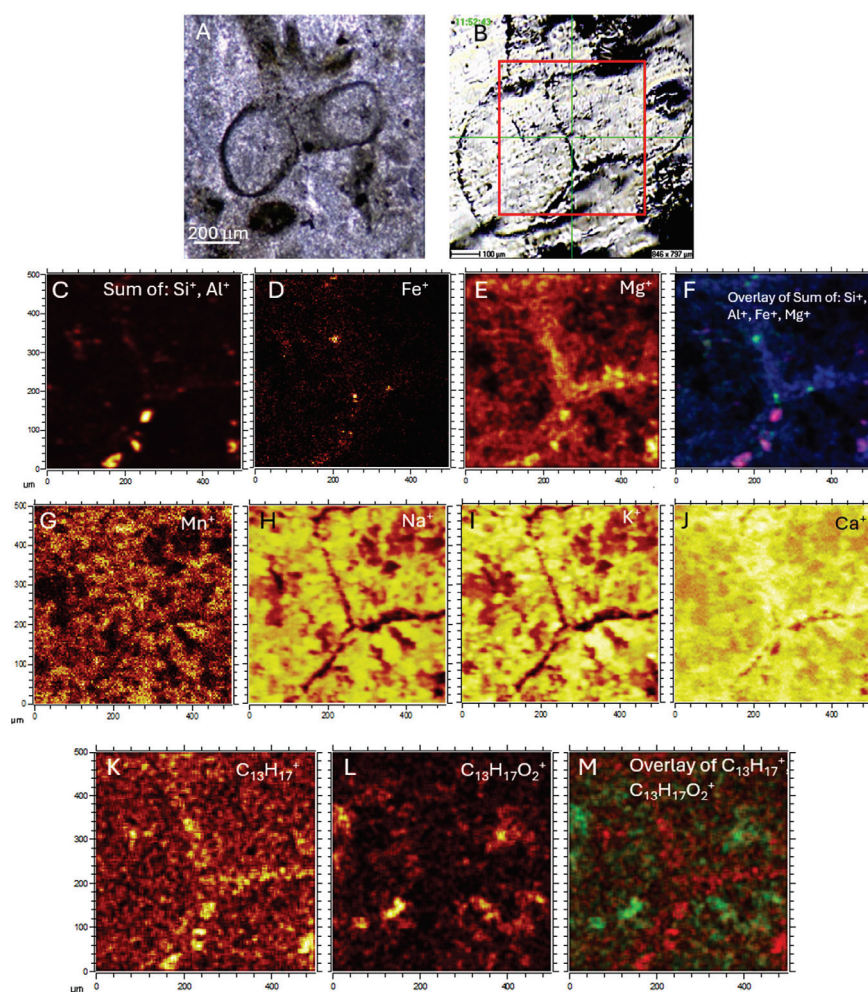


Figure 14. ToF-SIMS positive ion distribution maps of phosphatized skeletal structures from the Pedroche Formation, Los Lagares-1 core. (A) Transmitted light image; scale bar = 200 μm . (B) Total ion image of analyzed area ($548 \times 298 \mu\text{m}$); scale bar = 100 μm , where the red square marks the analyzed target area. (C–E) Major cations: (C) $\Sigma\text{Si}^+ + \text{Al}^+$ highlighting aluminosilicate-rich inter-skeletal matrix; (D) Fe^+ enriched along skeletal walls and filamentous structures; (E) Mg^+ strongly correlated with skeletal elements. (F) RGB overlay ($\Sigma\text{Si}^+ + \text{Al}^+$ blue, Fe^+ red, Mg^+ green). (G–J) Alkali and alkaline earth elements: (G) Mn^+ , showing localized enrichment within fossil cavity interiors; (H) Na^+ , which is relatively uniform; (I) K^+ , which is concentrated in matrix areas; (J) Ca^+ , which is associated with carbonate fluorapatite. (K–M) Organic fragments: (K) $\text{C}_{13}\text{H}_{17}^+$ and (L) $\text{C}_{11}\text{H}_{13}\text{O}_2^+$, which show different spatial distributions. (M) RGB overlay demonstrating spatial decoupling between aliphatic (fossil walls, green color) and oxygenated (matrix, red color) organic compounds.

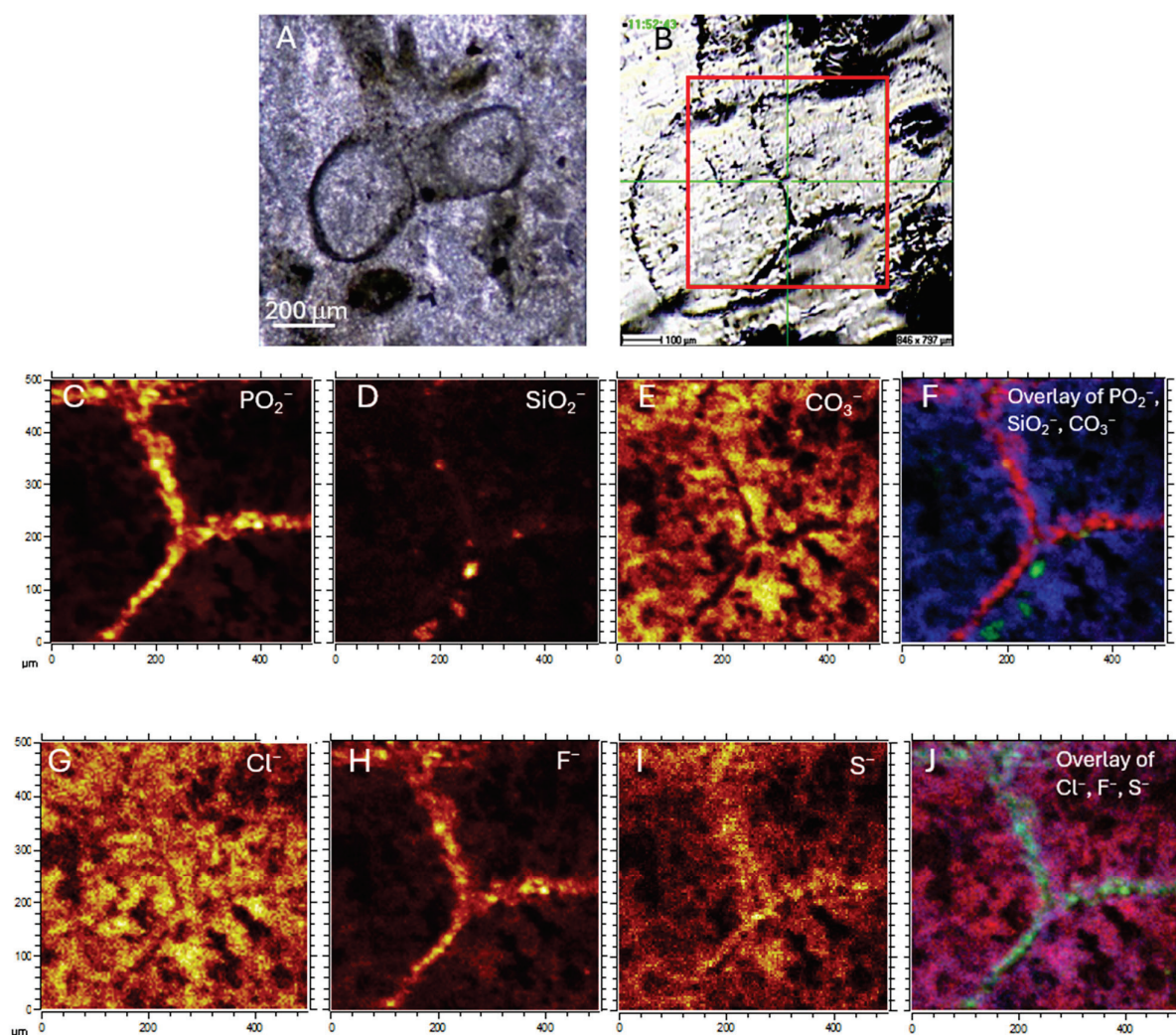


Figure 15. ToF-SIMS negative ion distribution maps of phosphatized skeletal structures from the Pedroche Formation, Los Lagares-1 core. (A) Transmitted light photomicrograph; scale bar = 200 µm. (B) Total ion image (548 × 298 µm); scale bar = 100 µm, where the red square marks the analyzed target area. (C–E) Major mineral phases: (C) PO_2^- , which is concentrated along skeletal walls; (D) SiO_2^- , which is enriched in inter-skeletal matrix; (E) CO_3^- , which is dominant in matrix. (F) RGB overlay (PO_2^- red, SiO_2^- green, CO_3^- blue) showing spatial separation of phosphate and carbonate domains. (G–I) Halogen and sulfur ions: (G) Cl^- , which is enriched along skeletal structures; (H) F^- , which is closely associated with phosphate-rich zones, confirming carbonate fluorapatite (francolite); (I) S^- , which is diffusely distributed with localized enrichment. (J) RGB overlay (Cl^- red, F^- green, S^- blue) highlighting halogen–sulfur relationships.

Mass spectra were acquired over a mass range of 0–12,000 u (unified atomic mass units) with a mass resolution of approximately 100 ns. Initial survey spectra were collected from analysis areas of 500 × 500 µm, 250 × 250 µm, or 25 × 25 µm at a pixel resolution of 128 × 128, with spectral acquisition continuing until an ion dose density of 1×10^{12} ions/cm² was reached to maintain static SIMS conditions and minimize surface damage. Cycle times of 105 µs or 120 µs were employed depending on the sample characteristics.

For depth profiling experiments, analyses were performed in non-interlaced mode with a sputtering time of 1 s, followed by acquisition of 2 analytical frames with no pause time between cycles. Sputtering was conducted using either the oxygen ion gun (for positive ion detection; Figure 14) or the cesium ion gun (for negative ion detection; Figure 15) at energies ranging from 250 to 2000 eV.

Positive ion mass spectra were calibrated using the following reference peaks: H^+ , H_2^+ , H_3^+ , C^+ , CH^+ , CH_2^+ , CH_3^+ , C_2H_3^+ , C_3H_5^+ , C_5H_5^+ , and C_6H_6^+ . Negative ion spectra were calibrated using H^- , C^- , CH^- , CH_2^- , O^- , OH^- , F^- , C_2^- , C_3^- , C_4^- , C_5^- , and C_6^- . Residual cesium contamination in the analysis chamber from previous profiling experiments resulted in detectable Cs-related peaks (e.g., $^{133}\text{Cs}^+$ at 132.91 u, Cs_2^+ at 265.8 u) in the acquired spectra, particularly in positive ion mode. These peaks were not considered in the primary calibration but can serve as additional high-mass reference points when necessary.

Specific analysis locations on each thin section were identified using the integrated optical camera system prior to ToF-SIMS analysis (Figures 14 and 15). Spectral processing and molecular mapping analyses were performed using SurfaceLab 6.7 software (ION-TOF GmbH, Münster, Germany). This software enabled comprehensive interpretation of the mass spectra, identification of molecular fragments, and generation of ion distribution maps to visualize the spatial heterogeneity of organic and inorganic compounds across the analyzed surfaces. All raw data files were archived for further analysis.

4. Results and Discussion

4.1. Mineralogical Framework from Raman Spectroscopy

4.1.1. Bioclastic Phosphoritic Limestone (101.8 m)

Raman spectroscopy of the bioclastic phosphoritic limestone at 101.8 m depth reveals a complex mineral assemblage dominated by carbonate fluorapatite within fossilized structures embedded in a calcite matrix (Figures 4A–E and 5A–D). The calcite constitutes the primary matrix component, with numerous organic structures exhibiting varying degrees of phosphate mineralization distributed throughout the carbonate groundmass.

Carbonate fluorapatite represents the dominant mineral phase within these fossilized structures, characterized by diagnostic peaks at 433, 595, and 967–969 cm^{-1} corresponding to the ν_2 , ν_4 , and ν_1 vibrational modes of the PO_4^{3-} tetrahedra [47–49] (Figures 4E and 5D). The presence of B-type carbonate substitution is indicated by peaks at 1055 and 1087 cm^{-1} , where CO_3^{2-} replaces PO_4^{3-} in the crystal lattice [50,51]. A peak at 3307 cm^{-1} is assigned to OH-related vibrational modes, indicating mixed carbonate–hydroxyl–fluorapatite composition typical of marine diagenetic environments [47,50]. The well-defined spectral features indicate relatively well-crystallized CFA, consistent with diagenetic maturation in a carbonate-dominated porewater system where Ca^{2+} and CO_3^{2-} activities were sufficiently high to promote crystal growth and Ostwald ripening [52–54].

The close spatial relationship between organic matter and apatite provides direct evidence for organically mediated phosphogenesis, where phosphate precipitation was driven by localized release of phosphorus during organic matter degradation [31,55] (Figures 4C,D and 5C,D). This pattern is characteristic of early diagenetic phosphatization, supporting models of microbially mediated phosphogenesis whereby bacterial decomposition releases dissolved phosphate that subsequently precipitates as apatite in the immediate vicinity of degrading organic substrates [27,28,41].

Accessory phases identified in the limestone include K-bearing phyllosilicates, likely glauconite rather than orthoclase, as authigenic K-feldspar precipitation is thermodynamically unfavorable under low-temperature diagenetic conditions [56–60]. Localized hematite (Fe_2O_3) is also present, indicating that strongly reducing, sulfidic conditions were not pervasive during phosphatization, consistent with phosphogenesis occurring within the suboxic zone above the sulfate–methane transition [26]. The predominantly authigenic mineral assemblage reflects a relatively quiet depositional environment where in situ diagenetic processes dominated over clastic sedimentation [61,62].

4.1.2. Greenish Siltstone (102.6 m)

Raman mapping of the greenish siltstone at 102.6 m demonstrates fundamentally different mineralogical characteristics reflecting the siliciclastic-dominated nature of this facies (Figure 6A–C). Quartz constitutes the primary matrix component, with phosphate mineralization within organic structures indicated by broader, less well-defined peaks at 401, 556, and 833 cm^{-1} , accompanied by a broad feature centered around 630 cm^{-1} [63]. These spectral characteristics are indicative of poorly crystalline or nanocrystalline apatite, representing an early stage of phosphogenesis where crystal ripening and Ostwald maturation have not progressed to completion [52,53].

The contrasting crystallinity between the two lithologies reflects the influence of host matrix composition on phosphate mineralization kinetics [64,65]. The silicate-dominated matrix provided fewer nucleation sites and different porewater chemistry compared to the carbonate-rich limestone, with lower Ca^{2+} and CO_3^{2-} activities potentially inhibiting crystal growth and maturation [66]. The poorly crystalline nature of the phosphate phases in the siltstone suggests that diagenetic conditions were less favorable for CFA precipitation, possibly due to limited Ca availability, different pH buffering, or shorter residence time in the phosphogenesis zone.

The mineral assemblage of the siltstone includes significant detrital components that provide constraints on sediment provenance. Rutile (TiO_2) is present, indicating derivation from medium- to high-grade metamorphic rocks in the source area [67,68] (Figure 6C,D). Rubicline [$\text{Rb}(\text{AlSi}_3\text{O}_8)$], a rare rubidium-bearing feldspar, was also identified, indicating derivation from highly evolved granitic or pegmatitic source rocks [69] (Figure 6C,D). The presence of these detrital minerals within organic-rich domains suggests that organic matter accumulation occurred concurrently with siliciclastic sedimentation, creating a mixed system where both detrital input and authigenic phosphogenesis contributed to the final assemblage [70,71]. The inverse relationship between clastic sedimentation rates and phosphogenesis efficiency is well documented: elevated detrital input typically dilutes porewater phosphate concentrations and reduces residence time at redox boundaries favorable for apatite precipitation [64].

4.2. Elemental Composition from SEM-EDS

SEM-EDS elemental mapping was concentrated on sample 101.8 because it exhibits substantially higher mineralogical and textural diversity than sample 102.6 (Figure 7A,B). Although phosphatic elements are present in the siltstone, the mineral assemblage observed at 102.6 m is fully represented within sample 101.8, whereas the latter additionally preserves a broader spectrum of phosphatic phases and multiple skeletal architectures with phosphatized walls and phosphatic internal molds. This expanded diversity provides a more complete geochemical framework to constrain phosphatization pathways and associated trace element redistribution.

The elemental mapping reveals two distinct modes of phosphate mineralization within the phosphoritic limestone. Along preserved bioclast walls, P concentrations correlate strongly with skeletal morphology, reflecting template-directed CFA precipitation on original organic substrates [41,72] (Figure 7A). The inverse relationship between P and C (carbonate) confirms progressive replacement of original calcitic shell material by phosphate phases during early diagenesis [73] (Figure 7A). Fe-Mg-Si-Al co-localization along skeletal features indicates contemporaneous formation of Fe-Mg phyllosilicates (chlorite/chamosite) with phosphate precipitation, suggesting both processes were controlled by the same redox gradient established during burial into the suboxic zone [40,74].

Phosphatic steinkerns filling internal molds show a different pattern, with P enrichment toward cavity centers and gradational decrease toward skeletal walls [11] (Figure 7B).

This distribution indicates centripetal precipitation from cavity-filling porewaters that became progressively enriched in dissolved phosphate during organic matter degradation within the enclosed microenvironment [31,55] (Figure 7B). The strong correlation between Fe, Mg, Si, and Al within specific domains confirms authigenic chlorite/chamosite formation [40,75], with the spatial association of these phyllosilicates with phosphatic phases reflecting their formation under similar suboxic conditions during microbial Fe(III) reduction [42,76].

The Rb-Sr association with Si-Al-rich domains rather than carbonate or phosphate phases contrasts with the typical Sr affinity for carbonate phases [77] (Figure 7A), indicating incorporation into clay mineral structures rather than carbonate lattices during diagenesis. Nitrogen is detected in localized patches within the phosphatized walls, with a distribution that partially overlaps with P-rich zones, potentially indicating nitrogen incorporation into the silicate mineral structures or the presence of nitrogen-bearing organic compounds associated with the clay minerals (Figure 7A,B). Zirconium shows a spatial distribution that correlates well with phosphorus, with elevated concentrations within the phosphatized skeletal structures rather than occurring as isolated detrital grains in the matrix (Figure 7A,B).

The elevated Fe concentrations associated with Si-rich domains support the iron reduction mechanism, with released Fe^{2+} sequestered primarily in authigenic chlorite rather than incorporated into the phosphate structure [42] (Figure 7A,B). The strong Fe-Mg-Si-Al correlation indicates that chlorite authigenesis accompanied phosphate precipitation regardless of the specific phosphatization mechanism, suggesting both processes were driven by the same underlying redox gradient established during early diagenesis [40,78].

4.3. Trace Element Geochemistry from LA-ICPMS

4.3.1. Compositional Domains and Sample Discrimination

The P-Si-C ternary diagram effectively discriminates compositional differences between samples and reveals systematic relationships between mineralogy and diagenetic history (Figure 8). Sample 101.8 displays a pronounced compositional gradient where middle zone samples under more reducing conditions during phosphate precipitation occupy intermediate positions with variable P and C contributions, and inner core samples cluster toward the P corner (60%–90% P), demonstrating progressive replacement of original carbonate shell materials by CFA during diagenesis. Outer rim samples show variable compositions, with several plotting toward the Si apex rather than the C apex, reflecting aluminosilicate-bearing domains within the bioclast rim [10,11] (Figure 8). This compositional trajectory documents active carbonate-to-phosphate replacement characteristics of early diagenetic phosphogenesis in carbonate-rich marine sediments [39].

In contrast, sample 102.6 plots entirely within the silicate domain near the Si apex. Group 3 approaches pure silicate composition (~95%–100% Si), while Groups 1 and 2 show slightly lower Si proportions (70%–90% Si) with minor P and C contributions, reflecting the quartz-dominated detrital matrix of the siltstone and fundamentally different diagenetic conditions compared to the phosphoritic limestone [64,65] (Figure 8). This clear separation demonstrates that primary lithology exerts fundamental control on diagenetic mineral assemblages [9].

4.3.2. Bioclastic Phosphoritic Limestone (101.8 m)

LA-ICP-MS trace element analysis of a phosphatized bioclast from sample 101.8 m reveals distinct compositional zonation across 30 analytical spots distributed among three spatial domains: the outer rim ($n = 7$, carbonate-dominated), skeletal framework ($n = 8$, intermediate zone), and skeletal interior ($n = 15$, phosphate-dominated) (Figures 9A, 10A–G and S1).

The elemental distributions demonstrate systematic variations reflecting progressive phosphatization of an originally carbonate bioclast.

The inverse relationship between Ca and P concentrations across compositional domains documents the centripetal phosphatization gradient. The outer rim preserves high Ca ($321,246 \pm 27,720$ ppm) and minimal P (3814 ± 4139 ppm), while the skeletal interior shows elevated P ($90,650 \pm 42,036$ ppm) and reduced Ca ($85,333 \pm 87,120$ ppm) [11,79] (Figure 10A). The preservation of a distinct carbonate-dominated outer rim indicates that phosphatization was arrested before complete replacement, possibly due to changing porewater conditions or establishment of a diffusion barrier [80]. The skeletal framework occupies intermediate compositions (P = $81,184 \pm 43,790$ ppm; Ca = $155,831 \pm 94,135$ ppm), recording the transition zone where active replacement occurred (Figure 10A).

Fe/Ti ratios consistently exceed the authigenic threshold (>10) across all domains, indicating secondary Fe enrichment beyond detrital contributions [81,82] (Figure 10B). This pattern directly supports active iron cycling during diagenesis, with Fe^{2+} released during microbial Fe(III) reduction available for incorporation into authigenic phases. Mn concentrations decrease dramatically from outer rim ($53,736 \pm 11,864$ ppm) to skeletal interior ($13,429\text{--}17,708$ ppm), reflecting preferential Mn incorporation into carbonate phases during progressive phosphatization [79,83] (Figure 10C). This Mn gradient is consistent with the crystal-chemical incompatibility of Mn^{2+} with the apatite structure and its favorable substitution for Ca^{2+} in the calcite lattice.

The strong Si-Al correlation ($R^2 = 0.704$) and preferential enrichment in phosphatized interior zones indicates that aluminosilicate phases formed contemporaneously with phosphate precipitation [74] (Figure 10D). K/Al vs. Mg/Al relationships suggest K-bearing phases consistent with illite or glauconite composition [84] (Figure 10E), while the spatial association between phosphate and phyllosilicate phases reflects shared geochemical controls during early diagenesis. Both phosphogenesis and glauconite formation are favored in suboxic marine sediments with slow sedimentation rates, and the co-occurrence of these phases documents the redox conditions prevailing during mineral formation [61,62].

Strontium and redox-diagenetic systematics provide complementary constraints on carbonate preservation and diagenetic alteration. Sr/Ca ratios are highest in the outer rim (19.0 ± 5.4) and decrease toward the skeletal interior (15.5 ± 5.5), consistent with preferential Sr retention in residual carbonate phases and progressive Sr loss during phosphate replacement of the original calcitic skeleton [79,80]. The co-variation of Mn/Fe ratios across compositional domains, with elevated values in the outer rim (5.66 ± 6.26) relative to the skeletal interior (4.26 ± 5.52), reflects the preferential partitioning of Mn^{2+} into carbonate over phosphate phases under suboxic conditions, supporting porewater Mn/Fe > 0.1 as a diagenetic indicator of suboxic mineralization [80] (Figure 10F). The Mg vs. Fe relationship across all compositional domains shows a moderate positive correlation ($R^2 = 0.547$) that tracks the chlorite stoichiometric reference line ($\text{Fe} = 1.9 \times \text{Mg}$), indicating that Fe and Mg mobility during diagenesis was largely controlled by authigenic chlorite or chamosite precipitation rather than by carbonate or phosphate phases (Figure 10G).

The REE systematics of sample 101.8 record the interplay between seawater-derived and diagenetically modified signatures. The PAAS-normalised REE patterns show MREE-enriched profiles across all three compositional domains, with the skeletal interior displaying the highest absolute concentrations (Figure 11A). Total REE concentrations (ΣREE) increase from the outer rim (925 ± 1084 ppm) to the skeletal interior ($2588\text{--}3321$ ppm), consistent with preferential REE incorporation into the CFA lattice during phosphatization [25] (Figure 11B). Ce anomalies evolve from slightly negative in the outer rim ($\text{Ce}/\text{Ce} = 0.91 \pm 0.08$), indicating inheritance from oxygenated seawater [85], to slightly positive in the interior ($\text{Ce}/\text{Ce} = 1.09\text{--}1.14$), recording more reducing conditions during

phosphate precipitation [86] (Figure 11C). However, given the large standard deviations in Ce/Ce^* within each compositional group, the difference between outer rim and interior values should be treated as a suggestive trend rather than a statistically robust distinction; both groups show considerable within-group variability and the confidence intervals overlap. Eu anomalies remain near unity across all domains ($Eu/Eu^* = 0.97\text{--}1.02$), indicating that suboxic conditions did not reach Eu^{2+} stability and that REEs were sourced from seawater-dominated fluids rather than high-temperature hydrothermal input [87] (Figure 11C).

The $(La/Yb)_n$ vs. $(Gd/Yb)_n$ diagram illustrates LREE depletion relative to MREEs across all compositional domains, with inner core samples showing the broadest range of $(Gd/Yb)_n$ values (Figure 11D). The $(La/Gd)_n$ vs. $(Gd/Yb)_n$ diagram confirms moderate MREE enrichment relative to both LREEs and HREEs, producing the bell-shaped pattern diagnostic of marine authigenic phosphates [25,86] (Figure 11E). Y/Ho ratios provide additional constraints on fluid sources, with the outer rim (36.5 ± 7.4) approaching seawater values ($\sim 44\text{--}74$) [88,89] and decreasing progressively toward the inner core (31.7 ± 4.6), documenting a transition from seawater-influenced conditions during initial carbonate precipitation to porewater-dominated conditions during phosphatization [90,91] (Figure 11F).

4.3.3. Greenish Siltstone (102.6 m)

LA-ICP-MS analysis of sample 102.6 reveals fundamentally different geochemical characteristics reflecting the siliciclastic-dominated nature of this facies. Hierarchical cluster analysis identifies three compositional groups based on Si, P, and associated trace elements: Group 1 (Si-rich, $n = 10$), Group 2 (transitional, $n = 10$), and Group 3 (P-rich, $n = 10$).

Silicon and Al exhibit exceptionally strong correlation ($R^2 = 0.9975$), establishing that virtually all silicate is structurally bound in aluminosilicate phases rather than occurring as free quartz [75] (Figure 12A). The near-perfect Mg-Fe correlation ($R^2 = 0.9965$) follows the chlorite reference line ($Fe = 1.9 \times Mg$), indicating syngenetic chlorite formation through coupled Fe^{2+} - Mg^{2+} incorporation during diagenesis [40] (Figure 12B). This exceptional correlation provides compelling evidence that Fe^{2+} released during iron reduction was efficiently captured by growing phyllosilicate crystals, representing a major sink for reduced iron that effectively coupled the iron and silicate cycles during early diagenesis.

Fe/Ti ratios (55–1034) far exceed the authigenic threshold (>10), demonstrating substantial secondary Fe enrichment independent of detrital Ti-bearing phases [81] (Figure 12C). This pattern is diagnostic of microbial Fe(III) reduction, which released Fe^{2+} from oxyhydroxides for subsequent incorporation into authigenic chlorite [24,27,28]. The magnitude of Fe enrichment relative to Ti documents the intensity of iron cycling within this facies. The inverse relationship between P and Ca (Figure 12D) further reflects the replacement of primary carbonate by authigenic phosphate, though it is less pronounced than in the limestone facies [12,79]. Provenance discrimination using Th/Sc vs. Zr/Sc ratios indicates sediment derivation from highly evolved felsic source rocks, consistent with upper continental crust compositions [92,93] (Figure 12E). The coherent clustering of all three compositional groups along the passive margin array suggests a uniform detrital source, with geochemical variability driven by diagenetic overprinting rather than changes in provenance. Sr concentrations remain low across all groups (Figure 12F), consistent with limited marine carbonate input and dominance of siliciclastic material [80].

The REE patterns of the siltstone preserve much stronger detrital signatures than the limestone. Pronounced negative Eu anomalies across all groups ($Eu/Eu^* = 0.028\text{--}0.136$) provide unequivocal evidence for derivation from felsic igneous rocks that underwent plagioclase fractionation [87,94] (Figure 13A,B). The magnitude of Eu depletion exceeds typical upper continental crust values, suggesting highly evolved granitic source rocks

consistent with the rubicline identified by Raman spectroscopy [69]. Importantly, the preservation of these negative Eu anomalies, even in samples with extreme authigenic Fe enrichment, demonstrates that syngenetic chlorite formation did not fractionate REEs, which remained hosted in resistant detrital accessory phases [93,95].

Near-chondritic Y/Ho ratios (24–32) closely match crustal values rather than approaching seawater signatures (~44–74) [90], demonstrating that REEs were overwhelmingly sourced from detrital minerals rather than seawater-derived authigenic phases (Figure 13C). This contrasts markedly with the elevated Y/Ho ratios in the limestone outer rim and indicates that seawater had minimal influence on REE budgets in this siliciclastic facies. The systematic 10-fold to 100-fold REE depletion from silicon-rich (Group 1) through transitional (Group 2) to phosphate-rich (Group 3) compositions, while maintaining similar pattern shapes, indicates dilution by REE-poor authigenic phases rather than selective fractionation [25] (Figure 13D). The $(La/Gd)_n$ vs. $(Gd/Yb)_n$ and $(La/Yb)_n$ vs. $(Gd/Yb)_n$ diagrams confirm that the REE pattern shape is preserved across all groups despite the order-of-magnitude concentration decrease, consistent with a common detrital source and REE immobility during diagenesis [92,93] (Figure 13E,F).

4.4. Molecular and Ionic Mapping from ToF-SIMS

ToF-SIMS analysis provides complementary molecular-scale information that confirms and extends the mineralogical interpretations from other techniques. The integration of positive and negative ion modes reveals mineral compositions and spatial relationships at sub-micrometer resolutions [45,96].

4.4.1. Positive Ion Distributions

The distribution of aluminosilicate components, represented by the sum of Si^+ and Al^+ signals (Figure 14C), reveals a heterogeneous pattern with elevated intensities concentrated in the matrix surrounding the phosphatized structures and along discrete domains at structural boundaries. Iron shows overall low abundance (Figure 14D) with localized enrichments that partially overlap with the Si-Al-rich domains. Magnesium (Figure 14E) displays enhanced signals particularly in matrix areas and along the boundaries of skeletal elements. The RGB overlay combining Si^+ / Al^+ , Fe^+ , and Mg^+ (Figure 14F) visualizes their co-localization in phyllosilicate-bearing domains occupying the spaces between and around phosphatized fossils. Manganese (Figure 14G) shows relatively uniform background levels with subtle enrichments tracing the structural outlines of the fossils. Sodium (Figure 14H) presents elevated signals in the surrounding matrix but notable depletion within the phosphatized skeletal interiors. Potassium (Figure 14I) shows moderate enrichment specifically in the aluminosilicate-rich domains. Calcium (Figure 14J) displays the highest intensities within the phosphatized skeletal structures, clearly delineating fossil morphology and confirming the calcium phosphate composition of these features. Aliphatic hydrocarbon fragments ($C_{13}H_{17}^+$; Figure 14K) show moderate enrichments along the phosphatized fossil walls, while oxygenated organic fragments ($C_{11}H_{13}O_2^+$; Figure 14L) reveal a more structured pattern correlating notably with the phosphatized skeletal elements. The RGB overlay of these two organic species (Figure 14M) confirms that organic molecular components are preferentially associated with the phosphatized domains.

The integrated cation distributions allow for identification of the principal mineral phases present. The Ca^+ enrichment sharply concentrated along the Y-shaped fossil wall (Figure 14J), combined with the PO_2^- and F^- distributions discussed below, unequivocally establishes carbonate fluorapatite (francolite) as the dominant phosphate phase [9,24]. The sharp, structurally controlled nature of this enrichment demonstrates template-directed precipitation nucleating preferentially on the original biological substrate [41,72,97]. The

Fe⁺ distribution (Figure 14D) reveals a complex dual iron mineralogy. Discrete hotspots showing spatial decoupling from the phosphate-enriched fossil walls reflect iron partitioning between multiple mineral phases [76]. The partial spatial correlation between Fe⁺, Mg⁺ (Figure 14E), and Si⁺/Al⁺ (Figure 14C), visible as co-enrichment zones in the RGB overlay (Figure 14F), strongly implicates chlorite-group minerals (chamosite) formed when Fe²⁺ released during microbial reduction of Fe(III)-oxyhydroxides interacted with aluminosilicate polymers under suboxic conditions [40,74,98]. Ferrous phyllosilicates form under suboxic conditions (Eh approximately −100 to +100 mV), while pyrite—confirmed by the Fe⁺/S[−] co-localization discussed in Section 4.4.2—requires more strongly reducing anoxic conditions [99].

This dual iron mineralogy reflects the redox-stratified nature of the early diagenetic environment, where microbial iron reduction released Fe²⁺ and PO₄^{3−} that precipitated as both phosphate minerals and ferrous phyllosilicates, with localized sulfate reduction producing pyrite where conditions became sufficiently anoxic [26,78,99]. The pronounced Mn⁺ enrichment within fossil cavity interiors (Figure 14G), rather than in phosphatized walls or external matrix, indicates that more reducing and possibly more acidic microenvironmental conditions prevailed within the decomposing organism during early fossilization [83]. Manganese oxides can serve as electron acceptors for microbial respiration under suboxic conditions, and restricted exchange between internal cavity fluids and external porewaters would have allowed Mn²⁺ to accumulate [83,100]. The minimal Na⁺ incorporation into apatite (Figure 14H) is consistent with the crystal-chemical constraints of the fluorapatite structure. The K⁺ enrichment in aluminosilicate-rich domains (Figure 14I) reflects K-bearing phyllosilicate phases, consistent with the glauconite and illite assemblages identified by LA-ICP-MS. The distinct spatial patterns of C₁₃H₁₇⁺ (Figure 14K) and C₁₁H₁₃O₂⁺ (Figure 14L) reflect two fundamentally different organic preservation pathways, as illustrated by the RGB overlay (Figure 14M). Aliphatic hydrocarbon fragments associated with the phosphatized fossil walls represent lipid-derived hydrocarbons from the fossilized organism's original biomolecules, which were rapidly encapsulated within the CFA mineral matrix before extensive microbial degradation [31,101]. Their preservation through phosphate encapsulation reflects the rapid kinetics of phosphate precipitation that effectively seal organic matter within an impermeable mineral barrier [102,103]. The oxygenated organic fragments enriched throughout the matrix (Figure 14L) represent predominantly microbial biomarkers from heterotrophic bacteria and fungi that colonized and degraded organic tissues during early diagenesis, which were preserved through adsorption onto phyllosilicate surfaces and incorporation into carbonate minerals rather than phosphate encapsulation [55,101]. This dual preservation mechanism creates a composite organic geochemical record that captures both the fossilized organism's original biochemistry and the diagenetic microbial ecosystem [31].

4.4.2. Negative Ion Distributions

The same target area was analyzed in negative ion mode (Figure 15A,B). The PO₂[−] distribution (Figure 15C) provides the clearest delineation of the phosphatized skeletal structures, with highest signal intensities along well-defined fossil outlines revealing an elongate tubular structure with distinct wall boundaries and preserved internal features. SiO₂[−] (Figure 15D) occupies domains spatially distinct from the phosphate-rich areas, with localized enrichments in the matrix rather than within the fossil structures. CO₃[−] (Figure 15E) shows moderate signal intensity across the analyzed area with enrichment in matrix domains surrounding the phosphatized structures. The RGB overlay (Figure 15F) demonstrates their complementary spatial relationships: phosphate (red) dominates the fossil structures while silicate (green) and carbonate (blue) phases concentrate in the sur-

rounding matrix with minimal overlap. Cl^- (Figure 15G) displays relatively uniform background levels with subtle enrichment along skeletal and filamentous structures. F^- (Figure 15H) presents the most striking correlation with the phosphate distribution, with highest signal intensities precisely tracing the fossil interiors and structural boundaries identified in the PO_2^- map. S^- (Figure 15I) shows a heterogeneous distribution with localized enrichments along organic-rich filaments that do not correspond directly to either the phosphate or silicate domains. The RGB overlay of Cl^- , F^- , and S^- (Figure 15J) illustrates the co-localization of F^- with the phosphatized structures, appearing as bright green domains mirroring the fossil morphology, while Cl^- and S^- are more diffusely distributed.

The negative ion distributions confirm and extend the mineral identifications made from the positive ion mode. The tight spatial correspondence between F^- (Figure 15H) and PO_2^- (Figure 15C) unequivocally confirms fluorapatite as the dominant phosphate phase [9,24]. The co-occurrence of CO_3^- with PO_2^- along the fossil walls—visible as purple zones in the RGB overlay (Figure 15F)—confirms significant carbonate substitution within the apatite crystal lattice, characteristic of carbonate fluorapatite precipitated from marine carbonate-rich porewaters [47,50]. The CO_3^- signal extending well beyond the phosphate-rich zones (Figure 15E) indicates additional calcite or Mg-calcite phases in the host sediment matrix. The strong spatial correlation between Fe^+ hotspots (Figure 14D) and S^- enrichment zones (Figure 15I) confirms pyrite (FeS_2) formation under localized anoxic microenvironments [26,78], while the diffuse S^- distribution along organic-rich filaments records early diagenetic sulfur cycling more broadly. The SiO_2^- distribution (Figure 15D) occupying domains distinct from the phosphate-rich areas, when combined with the Fe^+ - Mg^+ - Si^+ / Al^+ co-localization seen in the positive ion mode, confirms that silicon and aluminum are structural components of authigenic phyllosilicates rather than passive detrital matrix. The Cl^- enrichment along skeletal and filamentous structures (Figure 15G), co-localizing with F^- in the RGB overlay (Figure 15J), is consistent with phosphatized microbial templates where both halogens trace the original biological framework [41,72]. Multivariate principal component analysis of the negative ion mode data resolved six statistically independent components (Figure S5). Components 1 and 2 are dominated by signals sharply concentrated along the filamentous fossil fabric, with Component 1 loading strongly positive for both CNO^- and PO_2^- , and Component 2 capturing a spatial anti-correlation between these two ions—indicating that nitrogen- and phosphorus-bearing species occupy distinct sub-filament microenvironments, reflecting differential taphonomic preservation of phospholipid-derived phosphorus vs. proteinaceous nitrogen. Component 3 maps CO_3^- variance extending into the surrounding matrix, likely reflecting diagenetic carbonate phases associated with microbial activity. The diffuse F^- -dominated Component 5 suggests a disseminated fluorapatite phase distributed independently of the primary organic-rich structures.

4.4.3. Halogen Isotopes and Diagenetic Fluid Composition

ToF-SIMS analyses reveal halogen systematics that provide constraints on diagenetic fluid compositions. Chlorine is detected as ^{35}Cl and ^{37}Cl , with integrated peak areas of 503,961 and 154,714, yielding a $^{35}\text{Cl}/^{37}\text{Cl}$ ratio of ~3.26. Bromine is detected as both ^{79}Br and ^{81}Br with peak areas of 34,181 and 37,763, respectively. Both halogens are consistently observed within the carbonate matrix and are not confined to discrete accessory phases, with comparable isotopic distributions and relative signal intensities obtained across all analyzed areas.

The $^{35}\text{Cl}/^{37}\text{Cl}$ ratio of ~3.26 is close to the natural terrestrial value of ~3.13 [104,105], indicating a common crustal chloride source without extreme isotope fractionation, consistent with the absence of highly fractionated or exotic chloride reservoirs. Although

ToF-SIMS does not permit precise quantitative isotopic determination due to matrix effects, instrumental mass bias, and potential isobaric interferences—particularly $^{34}\text{SH}^-$ overlap with $^{35}\text{Cl}^-$ in sulfur-bearing systems [45,46]—the proximity of the measured ratio to natural abundance strongly argues against unusual fractionation. The consistent co-occurrence of Cl and Br, visible in the RGB overlay (Figure 15J), and the relative strength of the Br signal indicate that bromine-enriched saline fluids widely associated with evolved marine or connate brines were modified by evaporation or prolonged water–rock interaction during burial diagenesis [106–108]. Together, the near-natural chlorine isotopic distribution and appreciable bromine signal support saline diagenetic fluids of marine affinity, in agreement with established models for halogen behaviour in sedimentary basins [105,106,108].

5. Integrated Geochemical Model

5.1. Lithological Control on Phosphogenesis

The integrated datasets demonstrate that primary lithology exerted fundamental control on phosphatization pathways, producing distinct mineral assemblages and trace element signatures in the two studied facies [9,64]. These contrasting pathways reflect differences in substrate composition, porewater chemistry, and sediment permeability that directed diagenetic reactions along divergent trajectories.

The phosphoritic limestone at 101.8 m represents the optimal substrate for CFA precipitation [9,64]. High Ca^{2+} availability from carbonate dissolution, coupled with low siliciclastic dilution and slow sedimentation rates, allowed phosphate supersaturation to develop within porewaters during microbial Fe(III) reduction [10]. The centripetal replacement pattern—progressing from carbonate-dominated rim through intermediate framework to fully phosphatized interior—records the advancing reaction front where carbonate dissolution and phosphate precipitation occurred simultaneously [11] (Figure 10A). Template-directed nucleation on organic tissues facilitated exceptional preservation of fossil morphologies, with the phosphatized skeletal walls preserving original microstructural details [41,72] (Figures 7A and 14J). The REE geochemistry reflects seawater-influenced phosphogenesis with diagenetic modification [25,86] (Figure 11). Y/Ho ratios indicate mixed seawater–porewater signatures [88,91] (Figure 11F), while consistent LREE/HREE fractionation across compositional domains, as illustrated by the $(\text{La}/\text{Yb})_n$ vs. $(\text{Gd}/\text{Yb})_n$ relationships, suggests equilibration with homogeneous diagenetic fluids [109] (Figure 11B,D). The Ce anomaly evolution from negative (seawater-derived) to variable positive (porewater-modified) values records redox boundary migration as the zone of active phosphogenesis moved through the sediment column [85,86] (Figure 11C).

In contrast, the greenish siltstone at 102.6 m records a fundamentally different diagenetic pathway [65]. Lower Ca^{2+} availability, stronger geochemical buffering by aluminosilicates, and different porewater composition limited CFA crystallization efficiency, producing only poorly crystalline phosphate phases [63,65]. The silicate-dominated mineralogy focused diagenetic processes toward authigenic chlorite formation rather than phosphate precipitation [40]. The exceptional Mg–Fe correlation ($R^2 = 0.9965$) following the chlorite reference line documents efficient Fe^{2+} capture by growing phyllosilicate crystals, representing a major sink for reduced iron that effectively coupled the iron and silicate cycles during early diagenesis (Figure 12C). The REE systematics preserve much stronger detrital signatures than the limestone (Figure 13) where pronounced negative Eu anomalies inherited from felsic source rocks were not erased by diagenetic processes [110] (Figure 13B), and Y/Ho ratios cluster near chondritic values, indicating minimal seawater influence [90] (Figure 13C).

5.2. Redox Evolution and Microbial Mediation

The geochemical data record a consistent redox stratigraphy that controlled mineral formation and element redistribution during early diagenesis [78,82]. This redox evolution operated across three principal zones that developed within the upper sediment column. An oxic surface layer, where aerobic respiration maintained Fe(III)-oxyhydroxides stable, preserved seawater-derived REE signatures with minor negative Ce anomalies characteristic of oxygenated marine waters [85]. Below this, a suboxic zone represented the main phosphogenesis reactor where microbial Fe(III) reduction released both Fe^{2+} and adsorbed PO_4^{3-} into porewaters [27,28,39], driving the phosphate supersaturation necessary for CFA precipitation. At greater depth or in localized microenvironments within organic-rich zones, anoxic conditions allowed sulfate reduction to produce H_2S and promote pyrite formation [26].

Evidence for this three-tier redox zonation emerges from multiple independent proxies. Ce anomaly gradients record the transition from oxic (negative Ce/Ce) to suboxic-anoxic (positive Ce/Ce) conditions with depth [85,86] (Figures 11C and 13B). Mn/Fe ratio variations document the sequential reduction of Mn(IV) and Fe(III) oxides during progressive burial [82] (Figure 10F). Fe/Ti ratios exceeding authigenic thresholds (>10) in both samples demonstrate secondary Fe enrichment beyond detrital contributions, directly supporting the microbial iron reduction mechanism [82] (Figures 10B and 12C). The exceptional Mg-Fe correlation following chlorite reference lines confirms that released Fe^{2+} was captured by authigenic phyllosilicate precipitation rather than remaining mobile in porewaters [40] (Figure 12B). Discrete Fe-S hotspots in ToF-SIMS maps indicate that localized pyrite formation is restricted to specific microenvironments where sulfate reduction was particularly active [24,26], rather than basin-wide anoxia (Figures 14D and 15I).

An additional control on the observed heterogeneity in authigenic mineral assemblages may be due to temporal or spatial shifts in porewater gradient depth. Changes in the depth at which the suboxic-anoxic redox boundary is established—driven by variations in organic matter flux, bottom-water oxygen levels, or sedimentation rate—could produce differences in mineral assemblages between and within both lithologies without requiring differences in primary sediment composition alone. For example, a shallowing of the redox boundary would expose skeletal material to phosphate-supersaturated porewaters for a shorter duration, potentially explaining arrested phosphatization at the bioclast rim (Figure 10A), while deepening of the boundary could explain the spatial heterogeneity in pyrite distribution and Mn enrichment documented by ToF-SIMS [9,26] (Figures 14D,G and 15I).

5.3. Element Partitioning and the Fe-Oxyhydroxide Shuttle

LA-ICPMS trace element data reveal systematic partitioning governed by crystal-chemical controls on element incorporation. Three principal phases host trace elements: carbonate fluorapatite, calcite/Mg-calcite, and Fe-Mg phyllosilicates (chlorite/chamosite). Phosphorus concentrations increase systematically from the outer rim (3814 ± 4139 ppm) through the skeletal framework ($81,184 \pm 43,790$ ppm) to the skeletal interior ($90,650 \pm 42,036$ ppm) in sample 101.8, documenting the centripetal phosphatization gradient (Figure 10A). The REEs show similar enrichment patterns, with ΣREE increasing from 925 ± 1084 ppm in the outer rim to 2588–3321 ppm in phosphatized domains, consistent with preferential REE incorporation into the CFA lattice [25] (Figure 11B). The MREE enrichment characteristic of marine phosphorites ($(\text{Gd}/\text{Yb})_n = 2\text{--}8$) reflects preferential complexation of middle REEs by carbonate ions in seawater and their subsequent incorporation into the B-type carbonate substitution sites of the apatite lattice [25] (Figure 11E).

Manganese exhibits the most pronounced partitioning into carbonate phases, with outer rim concentrations ($53,736 \pm 11,864$ ppm) approximately four times higher than phosphatized interior values (13,429–17,708 ppm). This extreme Mn enrichment in the residual carbonate reflects the favorable substitution of Mn^{2+} for Ca^{2+} in the calcite lattice combined with Mn's crystal-chemical incompatibility with the apatite structure [79] (Figure 10C). Strontium similarly partitions preferentially into carbonate (994 ± 293 ppm in outer rim vs. 299–329 ppm in interior) (Figure 10F).

Continental weathering under Early Cambrian elevated atmospheric CO_2 conditions [20] produced Fe(III)-bearing oxyhydroxide complexes that scavenged phosphate and REEs from weathering fluids during fluvial transport to the shallow marine lagoon [24,39]. At the oxic water-sediment interface, these oxyhydroxides remained stable while FeOOH particles adsorbed additional PO_4^{3-} and scavenged dissolved REEs from seawater, concentrating these elements within the reactive iron pool [42]. Upon burial into the suboxic zone, microbial Fe(III) reduction destabilized the oxyhydroxide complexes, releasing both Fe^{2+} and adsorbed PO_4^{3-} into porewaters [9]. This coupled release drove phosphate supersaturation within carbonate-rich microenvironments where Ca^{2+} availability was high, promoting CFA nucleation on biological templates [72]. The REEs released during oxyhydroxide dissolution became available for incorporation into growing apatite crystals [25]. Simultaneously, released Fe^{2+} combined with silicate components and Mg^{2+} to form authigenic chlorite/chamosite under suboxic conditions [24,40]. This complete Fe-oxyhydroxide shuttle mechanism is summarized in Figure 16.

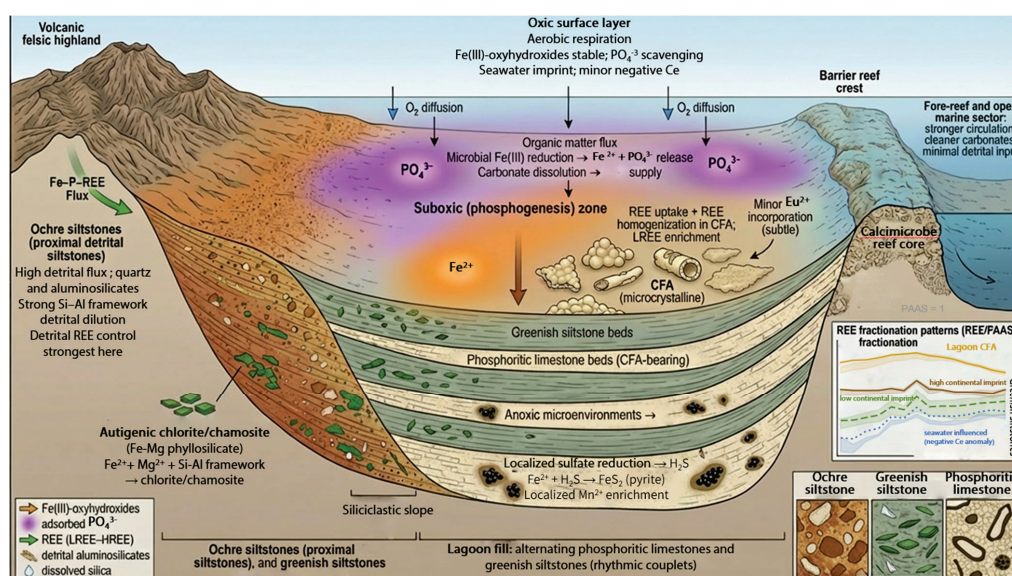


Figure 16. Conceptual model of lithology-controlled phosphogenesis in the Early Cambrian reef-lagoon system. Fe–P–REE flux from continental weathering of volcanic felsic highlands entered a restricted lagoon where microbial Fe(III) reduction in suboxic porewaters released PO_4^{3-} and Fe^{2+} , driving microcrystalline CFA precipitation in phosphoritic limestone beds and authigenic chlorite/chamosite formation in greenish siltstones. Anoxic conditions were confined to localized fossil-cavity microenvironments; basin-wide anoxia was absent. Blue arrows indicate O_2 diffusion from the water column, whereas black arrows represent geochemical fluxes and reaction pathways within the sediment. Colored shading highlights redox zonation and areas of PO_4^{3-} and Fe^{2+} enrichment associated with phosphogenesis. The inset shows PAAS-normalized REE fractionation patterns contrasting lagoon CFA (high continental imprint) with greenish siltstones (seawater-influenced, negative Ce anomaly). Lower-right photomicrographs illustrate the three principal facies: ochre siltstone, greenish siltstone, and phosphoritic limestone.

5.4. Provenance and Organic Matter Preservation

Both samples preserve coherent provenance signatures in immobile element ratios despite extensive diagenetic modification. The Th/Sc vs. Zr/Sc relationships consistently indicate felsic to intermediate source compositions [92,94], with most samples plotting within or near the felsic composition field characterized by elevated Th/Sc ratios (10–80) and moderate Zr/Sc ratios (5–35) (Figure 12E). The identification of rubicline [$\text{Rb}(\text{AlSi}_3\text{O}_8)$] by Raman spectroscopy in sample 102.6 directly supports derivation from highly differentiated granitic or pegmatitic source rocks [69] (Figure 6C,D). The detrital heavy mineral assemblage—rutile (TiO_2), quartz, and rubicline—provides additional provenance constraints, indicating derivation from medium- to high-grade metamorphic and highly evolved igneous rocks in the source area [67,68] (Figure 6C). The preservation of these detrital phases within the siltstone, in contrast to their virtual absence in the phosphoritic limestone, reflects the different depositional settings: proximal siliciclastic input to the siltstone vs. distal, clastic-starved conditions during limestone accumulation.

ToF-SIMS molecular mapping reveals multiple organic compound families preserved through different mineralization pathways, providing direct evidence for microbial involvement in phosphogenesis [31,101]. The spatial segregation between aliphatic hydrocarbon fragments ($\text{C}_{13}\text{H}_{17}^+$) concentrated along phosphatized fossil walls and oxygenated organic fragments ($\text{C}_{11}\text{H}_{13}\text{O}_2^+$) distributed throughout the matrix documents two fundamentally different preservation mechanisms (Figure 14K–M). The aliphatic compounds represent primary organismal lipids rapidly encapsulated within the CFA matrix before extensive microbial degradation, while the oxygenated compounds likely represent microbial biomarkers distributed throughout the diagenetic mineral matrix [55,101]. The N enrichment patterns detected by SEM-EDS suggest that nitrogen released during organic matter decomposition was partitioned between residual organic N preserved within phosphatized structures and NH_4^+ incorporated into authigenic phyllosilicates through K^+ substitution in interlayer sites (Figure 7A).

5.5. Implications for Early Cambrian Phosphogenesis

The Pedroche deposits demonstrate that Early Cambrian phosphogenesis was fundamentally controlled by microbial redox cycling operating within restricted platform environments, contrasting with modern upwelling-related phosphorites that develop under open-marine conditions with direct seawater signatures [9]. Several key implications emerge from this integrated study.

The strong lithological control on phosphatization efficiency and mineral texture explains the heterogeneous distribution of phosphatic facies within reef-lagoon systems. Carbonate substrates provided abundant Ca^{2+} and appropriate nucleation surfaces for well-crystallized CFA formation [64], whereas siliciclastic-dominated settings favored authigenic chlorite over phosphate precipitation [40] (Figures 10 and 12). This lithological control also influenced the association of exceptional fossil preservation with specific depositional environments [9,27] (Figure 3).

Beyond lithology, the depositional setting itself influenced phosphatization pathways through its control on redox gradients and porewater exchange. Shallow reefal facies likely maintained oxic bottom waters that pushed the zone of active phosphatization deeper into the sediment column, favoring phosphate mineral preservation [12]. Deeper lagoonal facies may have experienced transient water-column anoxia that could dissolve orthophosphates back into the overlying water, potentially inhibiting phosphatization within the sediment column [37] (Figures 16, 17 and S6).

Redox-Stratified Microbial and Geochemical Processes in Phosphoritic Limestone and Greenish Siltstone of the Early Cambrian Lagoon

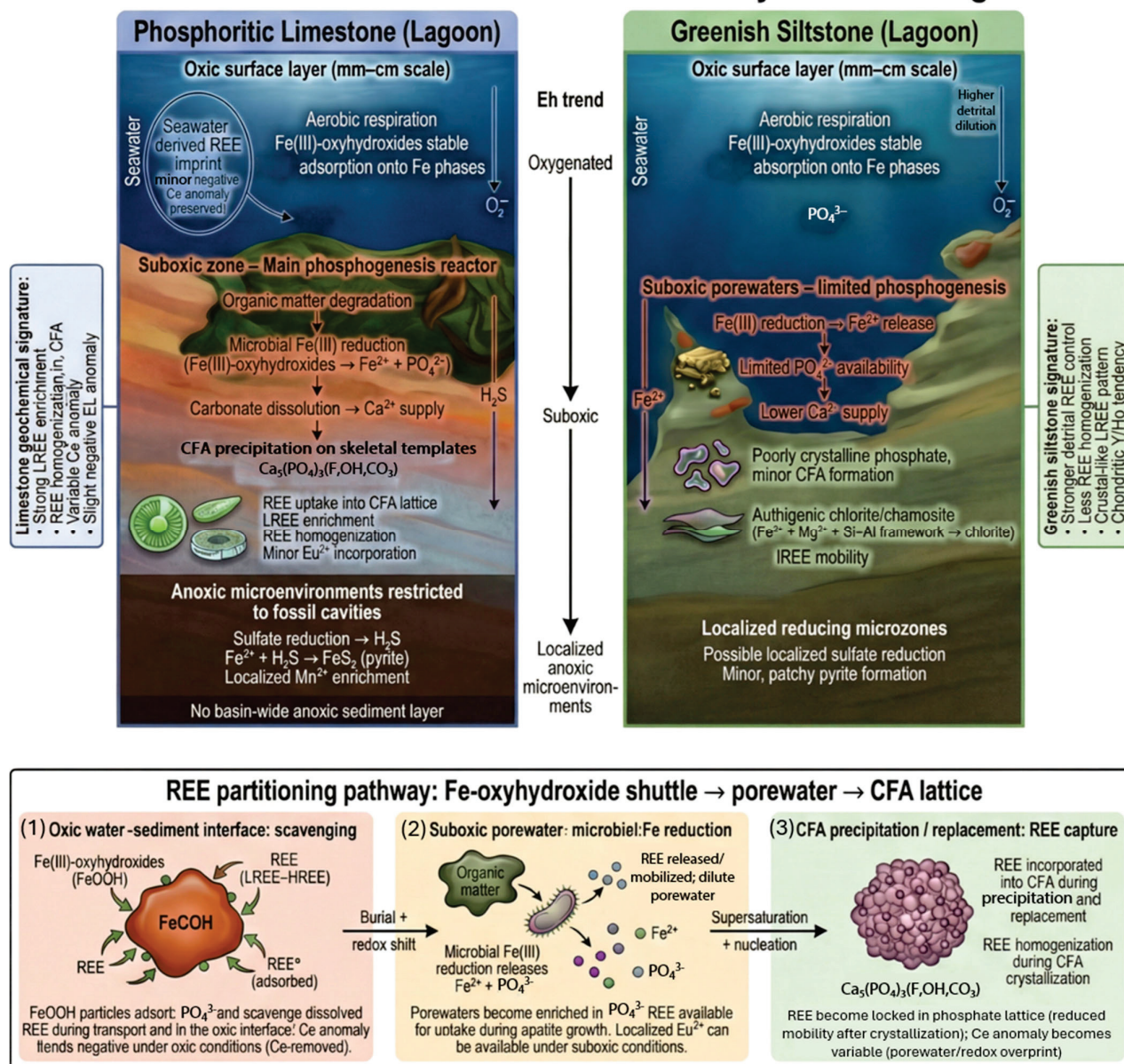


Figure 17. Redox-stratified microbial and geochemical processes controlling phosphogenesis in phosphoritic limestone and greenish siltstone of the Early Cambrian lagoon. In the limestone, a suboxic main phosphogenesis zone drove microbial Fe(III) reduction, carbonate dissolution, and CFA precipitation on skeletal templates, with REE uptake, LREE enrichment, and minor Eu²⁺ incorporation. Anoxic microenvironments were restricted to fossil cavities. In the siltstone, higher detrital dilution and limited PO₄³⁻ availability resulted in only poorly crystalline phosphate and dominant authigenic chlorite/chamosite formation. The lower panel illustrates the three-stage REE partitioning pathway: oxic Fe-oxyhydroxide scavenging → suboxic porewater mobilization → incorporation into the CFA lattice.

The multi-scale redox heterogeneity documented by this study—from basin-scale zonation through sediment-scale gradients to microenvironments within individual fossils [24,29]—emphasizes that Early Cambrian phosphogenesis operated through spatially and temporally variable processes rather than uniform basin-wide conditions (Figures 16, 17 and S6). This heterogeneity created diverse microenvironments for mineral

precipitation and organic matter preservation, contributing to the exceptional fossil record of this critical interval in Earth history [7,23,111].

6. Conclusions

The integrated mineralogical, elemental, and molecular datasets from the Los Lagares-1 borehole demonstrate that phosphogenesis in the Lower Cambrian Pedroche Formation was controlled by the interaction between host lithology, redox stratification, and microbially mediated nutrient cycling within a semi-restricted reef–lagoon system. The alternation of phosphoritic limestones and greenish siltstones records facies-dependent diagenetic pathways rather than a uniform phosphogenic environment.

The phosphoritic limestone at 101.8 m preserves centripetal replacement of skeletal carbonate by carbonate fluorapatite during early diagenesis. Raman spectroscopy confirms mixed carbonate–hydroxyl–fluorapatite compositions [47,50], and SEM–EDS and LA-ICP-MS analyses document systematic elemental redistribution from carbonate-dominated rims to phosphate-enriched interiors. Trace-element gradients and Mn/Fe systematics indicate suboxic porewater conditions consistent with microbial Fe(III) reduction as a principal mechanism for phosphate release [27,28,82]. REE patterns reflect initial scavenging by Fe(III)-oxyhydroxides, subsequent mobilization during iron reduction, and final incorporation into the CFA lattice, producing seawater-inherited signatures modified by early diagenetic equilibration [25,86].

In contrast, the greenish siltstone at 102.6 m records siliciclastic-dominated sedimentation with stronger geochemical buffering by aluminosilicates. Phosphate occurs as less crystalline and less pervasive phases [63], and REE systematics retain a more pronounced detrital influence [110]. Although microbial redox cycling operated in both facies, lithological differences controlled Ca availability, porewater chemistry, CFA crystallinity, trace-element partitioning, and the degree of REE homogenization.

The combined datasets support a genetic model in which continental weathering supplied Fe(III)-oxyhydroxides bearing adsorbed phosphate and REEs to the lagoon [24,39]. Microbial degradation of organic matter triggered Fe reduction, porewater phosphate release, and localized CFA precipitation on skeletal and microbial templates under sub-oxic conditions [27,28]. Fully anoxic conditions were restricted to microenvironments within skeletal cavities, where limited sulfate reduction facilitated pyrite formation [26]. Coeval precipitation of ferrous phyllosilicates (chlorite/chamosite) further records redox stratification within the sediment column [74].

These results refine current models of Early Cambrian phosphogenesis by demonstrating that phosphate concentration and REE fractionation were primarily porewater-controlled and strongly modulated by lithological context, depositional setting, and microbial redox processes. The Pedroche system contrasts with open-marine upwelling phosphorites dominated by direct seawater signatures [9] and instead highlights the importance of restricted lagoonal settings in regulating nutrient recycling, trace-element redistribution, and exceptional fossil preservation during a critical interval of early meta-zoan ecosystem expansion [7,111].

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16040405/s1>, Figure S1: Box plots of LA-ICP-MS elemental concentrations (Log_{10} ppm) for major, trace, and rare earth elements (REEs) measured across three compositional domains of the phosphoritic bioclastic limestone at 101.8 m depth. Figure S2: Hierarchical cluster analysis (HCA) heatmap of Log_{10} -transformed and z-score normalized LA-ICP-MS element concentrations for all analyzed spots in the 101.8 m phosphoritic limestone. Figure S3: Box plots of LA-ICP-MS elemental concentrations (Log_{10} ppm) for geochemically distinct groups identified in the siltstone at 102.6 m depth. Figure S4: Hierarchical cluster analysis (HCA) heatmap

of Log₁₀-transformed and z-score normalized LA-ICP-MS element concentrations for the 102.6 m siltstone. Figure S5: Negative ion mode ToF-SIMS imaging data and principal component analysis (PCA) of sample 101.8, showing ion distribution maps and PCA loadings for phosphorus-, sulfur-, carbonate-, silica-, and organic-related species. Figure S6: Conceptual flow diagram summarizing lithology-controlled biogeochemical pathways and resulting REE signatures in the Early Cambrian reef-lagoon system.

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Data Availability Statement: The complete LA-ICP-MS geochemical datasets for samples 101.8 m and 102.6 m are archived in the PANGAEA Data Publisher and are publicly available at <https://doi.pangaea.de/10.1594/PANGAEA.993263> (sample 101.8 m) and <https://doi.pangaea.de/10.1594/PANGAEA.993262> (sample 102.6 m). All summarized data supporting the findings of this study are available in the Supplementary Materials.

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

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Article

Characterization of Li-Ores from European Deposits for Mineral Processing

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Abstract

This study investigates the comminution behavior and beneficiation potential of lithium-bearing ores, zinnwaldite from Cínovec (Czech-Germany border) and lepidolite from Villarsrubias (Spain) by integrating mineralogical analysis and mechanical characterization. The research is driven by Europe's need for secure lithium supply chains. In particular, it focuses on the challenges associated with low-grade, fine-grained lithium micas found in hard-rock ores, which offer significant potential to supply in Europe but also pose substantial processing challenges. QMA (Quantitative Microstructural Analysis) revealed distinct differences in the textural and structural characteristics of the studied ores. Zinnwaldite-bearing rocks are coarser-grained with high interlocking and roughness, while lepidolite-bearing samples showed finer grains, lower roughness, and more disseminated mica distribution, indicated by their low clustering degree. In terms of mechanical characterization, zinnwaldite-rich ores have the lowest compressive strength, while lepidolite-rich samples showed the highest values, attributed to their finer grain size and more cohesive structure. This suggests that lepidolite may require higher energy input and finer crushing stages to achieve the target liberation size. These features influenced the breakage behavior observed during mechanical testing and comminution and are essential for enabling selective comminution, separating mica from gangue material. This study contributes to analyzing the potential of European hard-rock lithium resources from the perspective of upstream comminution, which is an essential step influencing downstream energy consumption, reagent use, and overall recovery efficiency. The results of this research emphasize that selective comminution should not rely solely on mineral hardness contrasts but must incorporate microstructural parameters such as clustering, grain size distribution, and orientation.

Keywords: lithium-bearing ores; zinnwaldite; Cínovec deposit; lepidolite; Villarsrubias deposit; quantitative microstructural analysis (QMA); comminution

1. Introduction

The accelerating global transition toward low-carbon energy systems has sharply increased the demand for electrification and battery technologies, positioning lithium as a critical raw material for producing lithium-ion batteries (LiBs). By 2030, global demand for lithium carbonate (Li_2CO_3) is projected to reach 4 million tons, representing a 700% increase relative to 2021 levels [1]. Over the same period, LiB demand is expected to grow

from 2.5 GWh in 2018 to 24.8 GWh, with lithium consumption alone rising by a factor of 9.3 due to its central role in all major battery chemistries [2].

Europe remains highly dependent on lithium imports from South American brines (Argentina, Bolivia, Chile) and hard-rock deposits in Australia and China. Accordingly, the European Critical Raw Materials Act designates lithium as both a strategic and critical raw material, reflecting its economic importance and high supply risk. To reduce this vulnerability, the EU has set ambitious 2030 targets: to domestically extract at least 10% of its annual lithium demand, refine or process 40% within the EU, and recover 25% through recycling [3,4].

Although Europe is not yet a significant lithium producer, it hosts substantial hard-rock lithium resources. Unlike South American brine-type deposits, European lithium occurrences are predominantly associated with hard-rock pegmatites and greisen systems. Several countries—including Portugal, Germany, the Czech Republic, Finland, Spain, Austria, and Serbia—are actively assessing their lithium potential [5]. The largest known European hard-rock resource is the Cinovec–Zinnwald deposit in the Erzgebirge region (Germany–Czech Republic border), where recent drilling by Geomet/European Metals and Zinnwald Lithium has yielded an updated total resource exceeding 1.9 Mt of lithium. This includes approximately 708.2 Mt of ore, averaging 0.2% Li, 0.05% Sn, and 0.02% W at the Czech Cinovec deposit, and 226.8 Mt at 0.22% Li at the German Zinnwald deposit [6]. Another prospective region is the Central Iberian Zone (CIZ) in western Spain, hosting multiple lithium-bearing pegmatite types enriched in spodumene, petalite, lepidolite, Li-muscovite, and zinnwaldite [7].

The main lithium minerals in European hard-rock deposits include spodumene ($\text{LiAlSi}_2\text{O}_6$), lepidolite ($\text{K}(\text{Li},\text{Al})_3(\text{Si},\text{Al})_4\text{O}_{10}(\text{F},\text{OH})_2$), petalite ($\text{LiAlSi}_4\text{O}_{10}$), and zinnwaldite ($\text{KLiFeAl}(\text{AlSi}_3)\text{O}_{10}(\text{F},\text{OH})_2$) [5]. Spodumene, the primary lithium mineral in Australian operations, contains the highest Li_2O grades (6.80–7.20%) and therefore remains the most commercially attractive option [8–10]. Lepidolite, extensively mined in China, typically contains 3.27–3.94% Li_2O and elevated K_2O and SiO_2 contents [11,12]. Zinnwaldite, characteristic of the Cinovec–Zinnwald district, exhibits 2.50–3.49% Li_2O , elevated Fe_2O_3 (up to 11.50%), and intermediate SiO_2 and Al_2O_3 contents [13–15]. It represents a group of trioctahedral Li-bearing micas within the siderophyllite polyolithionite solid-solution series [16]. Lithium-bearing muscovite, formed via hydrothermal or greisen-type alteration, incorporates Li mainly through substitution of Al^{3+} by Li^+ and Fe^{2+} in octahedral sites [17].

Despite its abundance, zinnwaldite is less attractive than spodumene or lepidolite due to its lower theoretical Li_2O content and high iron concentration. Elevated Fe_2O_3 complicates acidic digestion by forming iron–aluminum oxide hydrates that hinder solid–liquid separation and reduce lithium recovery [13]. Nevertheless, the same iron content provides a technological advantage in pre-concentration, as zinnwaldite responds strongly to magnetic separation [18,19]. Both zinnwaldite and lepidolite require high-temperature calcination (zinnwaldite: 950–1050 °C; lepidolite: 850–950 °C) to destabilize their crystalline structures [20]. Their fluorine contents pose additional processing challenges due to release of hazardous HF or SiF_4 during acid leaching [13]. Lepidolite processing is further complicated by fine intergrowths with quartz and albite, as well as surface properties similar to other silicates, which together hinder selective flotation [20].

While much research has focused on optimizing lithium extraction from these minerals, considerably less attention has been paid to upstream comminution, an essential step influencing downstream energy consumption, reagent use, and overall recovery efficiency. Layered Li-bearing micas such as zinnwaldite and lepidolite exhibit complex textures and anisotropic cleavage, necessitating tailored breakage strategies to achieve

optimal liberation while avoiding excessive fines generation. However, systematic studies linking mineral microstructure (grain size, texture, cleavage, intergrowths) to comminution machine selection remain limited, constraining Europe's ability to process these resources cost-effectively. This research, therefore, aims to strengthen Europe's lithium raw-material production potential by conducting a detailed quantitative mineralogical analysis (QMA) of two key hard-rock ore types—zinnwaldite- and lepidolite-bearing ores—and by using these insights to optimize the technological processing flowsheet, with particular emphasis on improving the comminution stage.

1.1. Brief Geological Overview

1.1.1. The Cínovec–Zinnwald Deposit

The Cínovec–Zinnwald deposit is located in the Erzgebirge region on the border between the Czech Republic and Germany and is situated in a geologically favorable area known for historic mining of tin and tungsten and other metals [5].

The Cínovec–Zinnwald deposit is hosted within a small, ovoid-shaped albite granite stock that intruded the overlying Teplice Rhyolite and has undergone extensive greisenization, particularly in its apical and marginal zones. This rock comprises fine- to medium-grained albite, quartz, and zinnwaldite, with accessory topaz, fluorite, and alteration minerals such as sericite, illite, and kaolinite [21,22]. Based on a recent study by [6], distinctions exist between the Zinnwald and Cínovec deposits despite their geological continuity within the same mineralized zone. These differences primarily arise from the more pervasive and voluminous greisen alteration observed at Cínovec, where the alteration forms dome- and lens-shaped bodies commonly associated with extensive stockwork veining [6]. The principal ore body of the Cínovec deposit is located at depths exceeding 100 m below the surface and is overlain by a sequence of rhyolitic volcanic rocks. Owing to the concealed nature of the mineralization, direct surface observation of the deposit is limited. Therefore, sampling activities were conducted within the former underground mining and processing areas at Cínovec, including adjacent brownfield sites.

The sampling campaign in 2024, as part of the joint Li4Life Project, focused on material derived from historical mining operations, particularly from dumps containing lithological fragments representative of the deposit. Collected material comprised granite, rhyolite boulders, greisenized granite, and fully developed greisen. These lithologies reflect the magmatic–hydrothermal evolution of the deposit and are genetically associated with lithium mineralization.

The sampling program was carried out in collaboration with Czech colleagues from MUNI (Masaryk University Faculty of Science) and Geomet LLC (Limited Liability Company), who were responsible for coordinating and supervising the sampling area. In total, approximately 2.1 tonnes of material were collected during the campaign to ensure representative bulk samples suitable for subsequent mineralogical, geochemical, and comminution analyses. This systematic sampling approach enabled the acquisition of statistically meaningful material from various alteration stages and lithological types associated with the Cínovec lithium deposit.

Based on the results of preliminary mineralogical analysis, two varieties were selected for further research: a sample of greisenized granite with a lower content of zinnwaldite (GCW-1) and a sample of greisen with a higher content of zinnwaldite (GCG-1) (Figure 1).



Figure 1. (a) Greisenized granite (zinnwaldite mica-poor GCW-1; (b) greisen (zinnwaldite mica-rich GCG-1).

1.1.2. The Villasrubias Lithium Deposit

The Villasrubias Lithium deposit is an early-stage exploration project located in the southwest of the Salamanca province, Castilla y León, Spain, near the Portuguese border and just 33 km from Ciudad Rodrigo [7]. It lies within the Central Iberian Zone (CIZ) of the Iberian Massif, one of the most geologically significant regions for lithium exploration in Europe, and hosts several other lithium- and tin-bearing deposits in Spain and Portugal. This project is associated with lepidolite-subtype granitic pegmatites of the lithium–cesium–tantalum (LCT) family. These pegmatites are genetically linked to the highly evolved, S-type Cadalso–Casillas de Flores granitic batholith and were emplaced into metamorphic rocks of the Schist–Greywacke Complex (CEG) [23]. Preliminary exploration conducted by SIEMCALSA, a government-backed entity in Castilla y León between 2017 and 2020, identified lithium-bearing minerals including lepidolite and lithium-muscovite, as well as cassiterite, tantalum, and niobium, with petrographic and geochemical analyses returning Li_2CO_3 grades of up to 0.88% and an average of 0.52% in lepidolite-rich apo-pegmatites [24]. The pegmatite group is also known under the name “La Canalita pegmatites” [23].

TME (Technology Metals Europe), a partner in the Li4Life project, provided approximately 5 tons of bulk material from promising areas of granite and granite pegmatite in Spain. After preliminary mineralogical analysis, two varieties were selected for further research and physical–mechanical tests: a sample of lepidolite-bearing aplite containing a small amount of lepidolite (LSA-1) and a sample of layered feldspar-lepidolite pegmatite as a sample of rich lepidolite ore (LSR-1) (Figure 2).



Figure 2. Lepidolite-bearing aplite (LSA-1, (a)) and feldspar-lepidolite pegmatite (LSR-1, (b)).

2. Materials and Methods

To evaluate the 3D-stereological properties of the ore, QMA is used. A correlation between microstructural characteristics, strength, and breakage behavior of the rocks has been established for a long time [25]. Hence, the parameters of microstructure, strength and

mineral hardness of the sample are to be established. The microstructural insights obtained form the basis for a targeted comminution strategy, tailored to selectively liberate lithium-bearing minerals. Both QMA and physical–mechanical tests were conducted as part of the EU Li4Life project and are being implemented at the Institute of Processing Machines and Systems Technology (IART) at the Technical University of Bergakademie Freiberg.

2.1. Quantitative Microstructural Analysis (QMA)

Rock names are not suitable as synonyms for rock properties in petrophysical modeling, as the petrographic description of a rock is based primarily on its genetic, mineralogical and chemical classification criteria, whereas aspects related to the rock fabric are only considered as a secondary factor. The influence of rock and ore properties on processing behavior is well established [26–28], making a detailed understanding of mineral behavior across all comminution stages essential, from selective coarse comminution to fine grinding. Such knowledge at the microscopic scale is critical for energy-efficient comminution and is highlighted by initiatives such as the Coalition for Energy Efficient Comminution (CEEC) [29,30]. It is also a prerequisite for reliable numerical modeling and simulation of comminution processes, including Discrete Element Method (DEM) approaches [31], where predictive calibration remains challenging without quantitative descriptors of ore fabric and structure [32].

In response, increasing attention has been directed toward quantitative microstructural analysis of ores. Advanced analytical techniques such as SEM-based Mineral Liberation Analysis (MLA) and QEMSCAN [33], as well as Computer Tomography (CT) [34], have significantly improved the quantitative characterization of mineral structure and texture. The application of QMA for structural and textural analysis represents a rapidly growing field, underlining the central role of QMA as a foundation for linking ore microstructure to comminution behavior and process modeling.

Based on the application of stereological methods, the rock is quantitatively described by means of its mode (content of the individual mineral phases in the rock fabric), characteristic values for the texture (e.g., grain size and shape, intergrowth) and characteristic values for the structure (e.g., direction, distribution and relative density), described in detail by [26–28]. After proper recovery of a defined number of rock samples from the deposit, three ground thin sections perpendicular to each other should be prepared from each rock specimen (Figure 3).

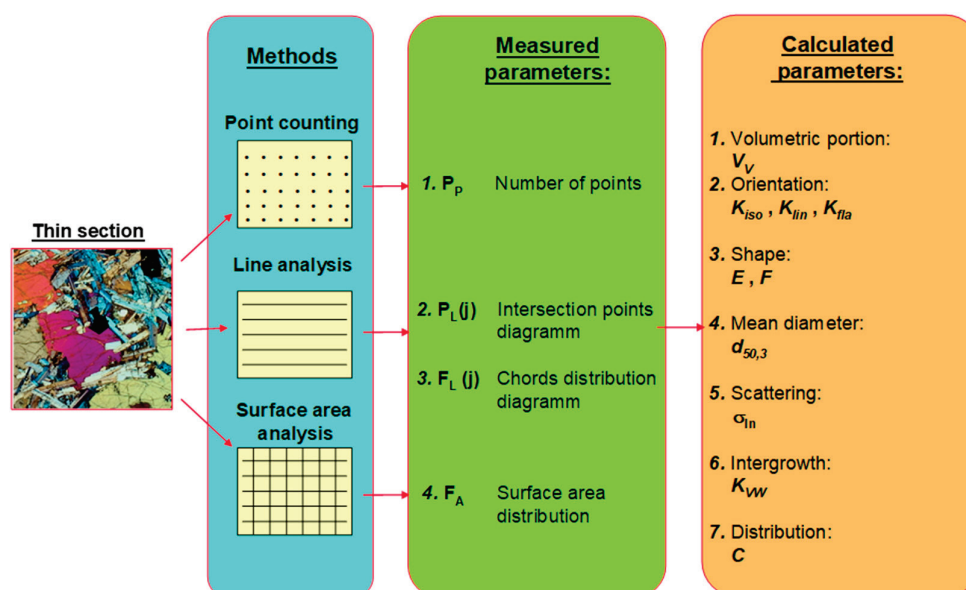


Figure 3. Process flow for QMA rock analysis.

2.2. Chemical Analyses

The lithium content in the studied samples was determined by ICP-OES (inductively coupled plasma optical emission spectroscopy) at the Institut für Technische Chemie, TUBAF, using the reference samples (lepidolite-ref OREAS 750b with a Li content of 2265.8 ppm). The samples were dissolved using microwave pressure digestion. The detection limit for lithium is 0.004 mg/L. For each measurement, 2–3 g per sample was required; all the samples must be representative and homogeneous. Each measurement was individually calibrated.

2.3. Determination of Point Load Strength Index of Rocks

The Point Load Test (PLT) is a simple, quick, and practical field method used to estimate the strength of rock materials. Testing was carried out using the portable point load tester from WILLE Geotechnik. A measurement range of 0 to 250 bar was used. The testing apparatus consists of a rigid steel frame, a manual hydraulic loading system, and a pressure gauge to record the peak load at failure. During testing, irregular rock samples are positioned between two conical steel plates, and the load is gradually applied using a hand-operated pump until the sample fractures. After failure, the dimensions of the fractured plane are determined. These measurements, together with the recorded failure load, are used to calculate the Point Load Strength Index $I_{s(50)}$ acc. [35,36]. For standardization to a reference diameter of 50 mm, a size correction factor f was applied:

$$I_{s(50)} = f \cdot \frac{P}{D_e^2} = \frac{P}{D_e^2} \cdot \left(\frac{D_e}{50}\right)^{2(1-m)} \quad (1)$$

where:

$I_{s(50)}$ is Point Load Strength Index (MPa or MN/m²)

P is failure load in Newton (N)

D_e is equivalent diameter (mm)

f is particle size correction factor

m is the slope constant of the regression curve

Since an empirical relationship exists between the corrected point load index $I_{s(50)}$ and the uniaxial compressive strength σ_D , the compressive strength can be approximated by multiplying $I_{s(50)}$ by a conversion factor c . According to ISRM guidelines [36,37], the typical range for the ratio $\sigma_D/I_{s(50)}$ lies between 20 and 25.

$$\sigma_D = c \cdot I_{s(50)} \quad (2)$$

The index $I_{s(50)}$ is used to classify rock strength and to estimate the Uniaxial Compressive Strength (UCS, σ_D) through empirical correlations. Both these mechanical strength values (σ_D and $I_{s(50)}$) provide insight into the breakage behavior and comminution response of different lithium ore types. For statistical reliability, 20 to 30 measurements were performed for each lithological category.

2.4. Determination of Vickers Microhardness of Minerals

The test was performed using a Shimadzu HVM-G21DT Micro Vickers Hardness Tester, equipped with a diamond Vickers pyramid indenter (a four-sided pyramid with a dihedral angle of 136°).

It is pressed into the material's surface under a small load to create a microscopic indent [38]. The Vickers Hardness Number (HV) is calculated in Equation (3). The in-

strument includes an integrated optical system, along with a specimen base to secure the prepared sample.

$$HV = \frac{1.854 \cdot F}{d^2} \quad (3)$$

where:

F is the applied load in N

d is the average diagonal length in millimeters

In addition to hardness, the Vickers indentation can also be used to determine microfracture toughness (K_{ic}), defined as the critical value of the stress intensity factor at which a crack starts to grow rapidly and uncontrollably. As load is applied to a material with an existing crack, the stress at the crack tip increases. Once this stress reaches a critical threshold, the crack extends suddenly, leading to failure [39]. The relationship between the applied load and the resulting crack geometry forms the basis for estimating fracture toughness of mineral grains [28].

$$K_{ic} = \frac{F}{(\pi \cdot c)^{\frac{3}{2}} \cdot \tan \alpha} \quad (4)$$

where:

c is the crack length measured from the center of the indentation to the crack tip (in m)

α is the half-angle of the Vickers pyramid, equal to 68°

Prior to testing, the specimen surfaces were required to be flat, polished, and free from surface irregularities. A controlled load, typically ranging from 0.098 to 1.961 N depending on the mineral tested, was applied to the indenter and held for 15 s. After unloading, the indentation was examined and measured under the microscope. In addition, crack patterns surrounding the indentation, particularly the crack lengths (c), were measured using the optical system to determine the microfracture toughness, particularly for brittle materials, since ductile minerals do not show such cracks in analysis. For statistical reliability, 15 to 20 measurements were collected for each mineral.

3. Results and Discussion

3.1. Quantitative Microstructural Analysis

3.1.1. The Cínovec–Zinnwald Deposit

Greisenized granite, GCW-1 (zinnwaldite ore)

The mineralogical composition of GCW-1 was dominated by quartz and feldspar, followed by a smaller proportion of mica, which was interpreted as lithium-bearing mica (zinnwaldite). The volumetric proportion of mica was determined to be approximately 10%. Feldspar showed advanced alteration, being partially replaced by clay minerals and carbonates (Figure 4). These alterations were considered to be a contributing factor to the overall reduced strength of the rock. “Non-differentiated (NDP)” (not analyzed by QMA) phases, such as topaz, fluorite, clay minerals, and carbonates, were also present in amounts up to 11%.

In terms of texture, the rock exhibited a disseminated crystalline fabric with a median grain size ($d_{50,3}$) of approximately 3.44 mm (Table 1). The median grain sizes of the main minerals varied notably: quartz grains reached about 2.3 mm, feldspar grains were ca. 4.7 mm, and mica grains were approximately 1.3 mm. The grain size distribution of quartz and mica (zinnwaldite) is relatively moderate, with a logarithmic standard deviation (σ_{ln}) of about 0.5, indicating relatively moderate variation in grain dimensions. In contrast, feldspar exhibited a broader size distribution, reflecting significant heterogeneity in grain sizes within these phases.

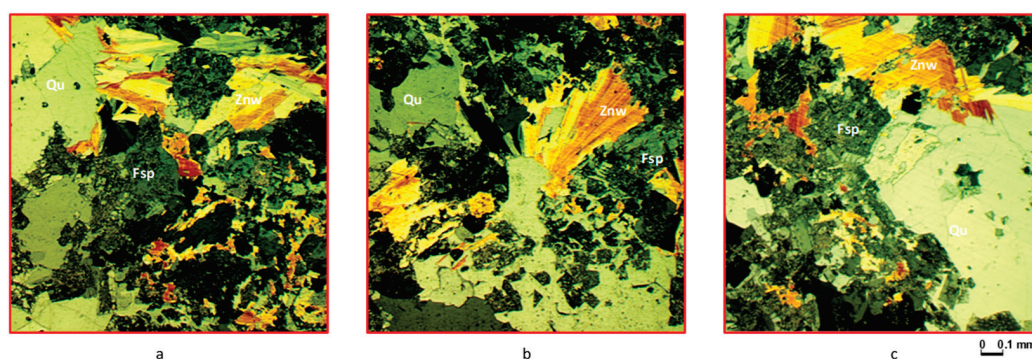


Figure 4. Selected digitized images of greisenized granite from Cínovec (Czech Republic); 16-x magnified, crossed polars. Thin sections (a–c): (GCW-1a–c).

Table 1. Rock characteristics. Greisenized granite from Cínovec (Czech Republic). Samples GCW-1a–c.

Raw Material	Rock Type: Greisenized Granite				Phase Related Features				Raw Material Features
	Deposit: Cínovec		Location: Czech Republic						
Mode	Properties		Symbol	Unit	Qu *	Fsp	Znw	NDP	Σ Microbodies
	Content	Volumetric Portion	E_V	%	32	47	10	11	100
Texture	Size	Mean diameter	$d_{50,3}$	mm	2.29	4.67	1.32	-	3.44
		Scatter parameter	σ_{ln}	-	0.57	0.72	0.55	-	0.65
	Grain surface	Specific surface	S_V	mm ² /mm ³	6.75	5.27	13.04	-	6.66
	Shape	Elongation	E	-	1.25	1.11	1.24	-	1.17
		Flatness	F	-	1.10	1.33	1.31	-	1.24
	Roughness	Roughness degree	K_R	%	63	56	71	-	60
	Structure	Orientation	Degree of linear orientation	K_{lin}	%	16	7	13	-
Degree of areal orientation			K_{fl}	%	5	14	14	-	11
Degree of isotropic orientation			K_{is}	%	79	79	73	-	88
Distribution		Degree of clustering	C	%	21	21	16	-	100

* Qu—Quartz, Fsp—Feldspar, Znw—Zinnwaldite, NDP—undifferentiated Phases (Topaz, Calcite, Clay minerals, Fluorite).

The shape of the mineral grains is described by their habit and expressed through elongation (E) and flatness (F) ratios. Feldspar grains show a distinct platy habit ($E = 1.11$, $F = 1.33$), while mica displays a mixed platy-needle morphology ($E = 1.24$, $F = 1.31$), reflecting the layered nature of phyllosilicates. Quartz appears nearly equant and slightly elongated ($E = 1.25$, $F = 1.10$). These shape parameters with elongated and platy grains are more likely to fracture along specific structural directions, which may influence breakage patterns during comminution.

A notable result of the stereological analysis was the high degree of mineral roughness within the sample. The overall roughness value (K_R) was approximately 60%, with mica reaching as high as 71%. This indicated a strong interlocking between mica and other mineral phases, particularly quartz and feldspar. This tight bonding makes it harder to separate mica along phase boundaries during crushing or grinding. In addition, the specific surface area (S_V) of the mineral phases was calculated to be around $6.7 \text{ mm}^2/\text{mm}^3$. Mica exhibited the highest specific surface among all phases, with a value of approximately $13 \text{ mm}^2/\text{mm}^3$, further underscoring its complex geometry and relevance for liberation efficiency. During grinding, once mica is partially liberated, its thin shape causes it to break further (overgrinding) and faster than more compact minerals.

Structurally, the rock structure was predominantly isotropic, with 88% of the mineral boundaries showing random orientation (K_{is}) and only 1% of the mineral boundaries exhibiting linear orientation (K_{lin}). This suggests a non-preferential internal grain arrangement, which could lead to unpredictable fracture behavior under mechanical stress. Furthermore, the clustering degree of quartz and feldspar is relatively low (both 21%), indicating that these grains are generally disseminated and not in direct contact with many grains of the same type. Mica shows the lowest clustering value (16%), meaning it is even more isolated in the rock. This dispersed distribution is beneficial for comminution, as it allows individual grains to break away more easily and may improve mineral liberation.

Greisen, GCG-1 (Zinnwaldite Ore)

The GCG-1 sample primarily consisted of quartz and mica (zinnwaldite), with a significantly reduced amount of feldspar compared to the greisenized granite (GCW-1). The zinnwaldite content was determined to be approximately 16%, and feldspar was reduced to 4%, indicating an increase in mica content as a result of progressive greisenization (Figure 5). Feldspar, in contrast, appeared in minor and less altered forms. Non-differentiated accessory minerals such as topaz, fluorite, carbonates, and clay minerals were present in minor quantities, not exceeding 10% of the total volume. The higher quartz content in GCG-1 contributed to the overall strength and resistance of the rock.

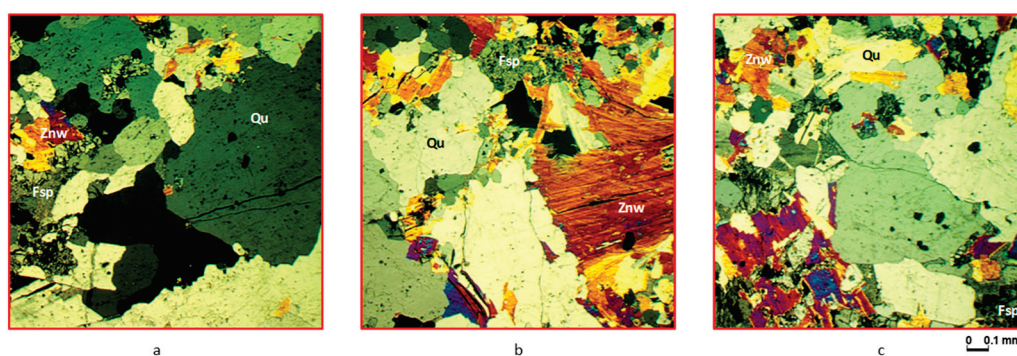


Figure 5. Selected digitized images of greisen from Cínovec (Czech Republic); 16-x magnified, crossed polars. Thin sections: 3196, 3197, 3198 (a–c) (GCG-1a–c).

Texturally, GCG-1 exhibited a coarsely crystalline structure with a median grain size ($d_{50,3}$) of approximately 2.23 mm, which was slightly finer than the grain size observed in the greisenized granite (Table 2). Quartz grains maintained porphyroblastic dimensions of around 2.6 mm, while feldspar grains were significantly finer, measuring approximately 1.0 mm. The grain size of zinnwaldite (mica) was approximately 0.7 mm, indicating a significant reduction in grain size compared to GCW-1. Compared to GCW-1, mica in GCG-1 showed a notable reduction in grain size. In terms of grain size distribution, quartz exhibited a relatively broad distribution, with a σ_{ln} of 0.640. Mica showed moderate variability $\sigma_{ln} = 0.574$, while feldspar, with a σ_{ln} of 0.348, displayed the most uniform

grain size among the primary phases. These textural characteristics suggest that GCG-1 underwent more advanced alteration and mineral replacement processes, typical features of progressive greisenization. The finer and more uniform mica in GCG-1 may enhance liberation but could also increase the risk of overgrinding.

Table 2. Rock characteristics. Greisen from Cínovec (Czech Republic). Samples GCG-1a-c.

Raw Material	Rock Type: Greisen				Phase Related Features				Raw Material Features
	Deposit: Cínovec		Location: Czech Republic						
Mode	Properties		Symbol	Unit	Qu *	Fsp	Znw	NDP	Σ Microbodies
	Content	Volumetric Portion	E_V	%	70	4	16	10	100
Texture	Size	Mean diameter	$d_{50,3}$	mm	2.65	0.95	0.75	-	2.23
		Scatter parameter	σ_{ln}	-	0.64	0.35	0.57	-	0.62
	Grain surface	Specific surface	S_V	mm ² /mm ³	5.08	8.63	10.75	-	6.25
	Shape	Elongation	E	-	1.34	1.31	1.63	-	1.39
		Flatness	F	-	1.06	1.22	1	-	1.06
	Roughness	Roughness degree	K_R	%	45	34	50	-	45
Structure	Orientation	Degree of linear orientation	K_{lin}	%	20	17	33	-	9
		Degree of areal orientation	K_{fl}	%	3	10	-	-	5
		Degree of isotropic orientation	K_{is}	%	76	72	67	-	86
	Distribution	Degree of clustering	C	%	62	13	20	-	52

* Qu—Quartz, Fsp—Feldspar, ZnW—Zinnwaldite, NDP—undifferentiated Phases (Topaz, Calcite, Fluorite).

The habit of the mineral grains, approximated by ellipsoidal models, reflected the geometric diversity of the constituent phases. Quartz grains in GCG-1 show a slightly elongated form ($E = 1.34$, $F = 1.06$), implying strong, compact grains that are more resistant to fracture. Feldspar, due to its limited presence, did not exhibit a dominant geometric trend, while zinnwaldite, with its distinctly elongated geometry ($E = 1.63$, $F = 1.00$), is prone to preferential breakage along its length due to its sheet-like crystal structure, potentially leading to thin flakes or fines and overgrinding risk.

The degree of roughness (K_R) between mineral grains is lower in GCG-1 than in the greisenized granite. Overall, the roughness reached approximately 45%, and for mica grains in particular, the value is lower than the 71% recorded in GCW-1. This reduction in interlocking among grains, particularly between mica and quartz, indicated potentially easier liberation of zinnwaldite during mechanical fragmentation. The specific surface area (S_V) of the mineral particles was measured at approximately 6.2 mm²/mm³, slightly lower than that of GCW-1. Among all mineral phases, mica again exhibited the highest specific

surface area at approximately $11 \text{ mm}^2/\text{mm}^3$, which remained an important parameter for its behavior during comminution.

Structurally, GCG-1 displayed predominantly isotropic mineral orientation, like GCW-1. Approximately 86% of the mineral boundaries exhibited isotropic orientation (K_{is}), while about 9% showed linear orientation (K_{lin}). The increased proportion of linearly oriented structures compared to GCW-1 (1%) indicated some degree of preferential alignment, although the rock remained largely random in texture.

A significant feature of GCG-1 was the high degree of cluster formation, particularly among quartz grains. Approximately 62% of quartz grains in the sample formed clusters, meaning they shared boundary surfaces with grains of the same mineral phase. This contrasted sharply with GCW-1, where only 21% of quartz grains exhibited clustering. The high clustering coefficient in GCG-1 suggested stronger mutual bonding and interlocking among quartz grains, which contributed to the higher mechanical integrity and higher comminution energy.

3.1.2. The Villasrubias Lithium Deposit

Lepidolite-bearing aplite, LSA-1 (Lepidolite Ore)

The LSA-1 sample, interpreted as a lepidolite-bearing aplite, is composed primarily of quartz (45%), followed by feldspar (31%) and mica (20%), with a minor portion (4%) consisting of non-differentiated phases such as topaz and fluorite (Figure 6).

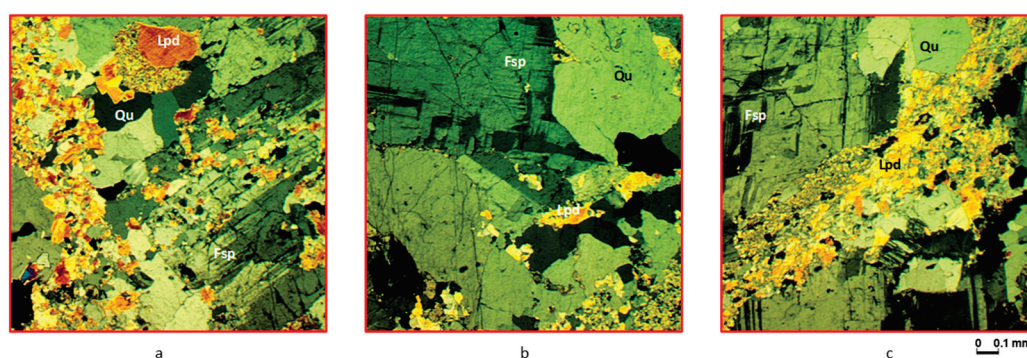


Figure 6. Selected digitized optical microscopy images of lepidolite-bearing aplite from the Villasrubias deposit (Spain). 16-x magnified, crossed polars (a–c). Samples LSA-1a–c.

The phase distribution reflects a moderately heterogeneous mineralogical fabric, with quartz as the dominant component and feldspar and mica in subordinate but significant proportions.

LSA-1 exhibits a fine-grained structure, with an overall median particle diameter ($d_{50.3}$) of 0.32 mm (Table 3). Among the major phases, feldspar has the largest grain size (0.50 mm), followed by quartz (0.29 mm), while mica (lepidolite) is the finest-grained phase, averaging only 0.10 mm. This large grain size contrast suggests that mica occurs as fine inclusions or small interstitial flakes within the coarser quartz and feldspar matrix. The particle size distribution, expressed by logarithmic standard deviation (σ), also highlights textural variability. Mica has the narrowest distribution ($\sigma = 0.30$), indicating a relatively uniform grain size. Quartz shows a broader spread ($\sigma = 0.41$), and feldspar displays the widest distribution ($\sigma = 0.45$), reflecting the greatest internal heterogeneity among the three phases.

Table 3. Rock characteristics. Lepidolite-bearing aplite from Villasrubias (Spanien). Samples LSA-1a-c.

Raw Material	Rock Type: Lepidolite-Bearing Aplite				Phase Related Features				Raw Material Features
	Deposit: Villasrubias		Location: Spain						
Mode	Properties		Symbol	Unit	Qu *	Fsp	Lpd	NDP	Σ Microbodies
	Content	Volumetric Portion	E_V	%	45	31	20	4	100
Texture	Size	Mean diameter	$d_{50,3}$	mm	0.29	0.50	0.10	-	0.32
		Scatter parameter	σ_{ln}	-	0.41	0.45	0.30	-	0.40
	Grain surface	Specific surface	S_V	mm ² /mm ³	19.95	9.02	27.29	-	17.91
	Shape	Elongation	E	-	4.01	2.42	1.51	-	2.98
		Flatness	F	-	1.68	1.24	1.05	-	1.41
	Roughness	Roughness degree	K_R	%	44	24	10	-	30
Structure	Orientation	Degree of linear orientation	K_{lin}	%	50	46	28	-	52
		Degree of areal orientation	K_{fl}	%	29	12	3	-	18
		Degree of isotropic orientation	K_{is}	%	21	42	69	-	31
	Distribution	Degree of clustering	C	%	45	20	18	-	31

* Qu—Quartz, Fsp—Feldspar, Lpd—Lepidolite, NDP—undifferentiated Phases (Topaz, Fluorite).

Grain shape analysis of the LSA-1 indicates that quartz shows a needle-like structure ($E = 4.01$, $F = 1.68$) and Feldspar also displays an elongated habit ($E = 2.42$, $F = 1.24$), though to a lesser extent. The needle-like and platy habit of quartz observed in LSA-1 is quite unusual for quartz; this morphology likely developed through post-magmatic processes such as hydrothermal alteration. Mica shows a more needle-shaped, slightly equant geometry, with an elongation of 1.51 and flatness of 1.05. The overall elongation value of 2.98 for the bulk sample indicates a general tendency toward elongated grain shapes.

The specific surface area of the particles varied significantly across the phases. Mica (lepidolite) exhibited the highest specific surface area at 27.29 mm²/mm³, followed by quartz (19.95 mm²/mm³) and feldspar (9.02 mm²/mm³). The overall specific surface area of the rock was estimated at 17.91 mm²/mm³. The high surface area of mica underscored its high liberation potential but also an increased risk of overgrinding during comminution [25–27]. The degree of roughness reflected how tightly mineral phases were bonded. Quartz showed a relatively high degree of roughness at 44%, feldspar at 24%, and mica (lepidolite) at 10%, resulting in an average degree of roughness of 30%. The low roughness degree of mica suggests it is weakly bonded to adjacent minerals, making it more favorable for mechanical separation with less energy input.

Structurally, the LSA-1 sample exhibits a quite moderate anisotropic orientation, with a total degree of isotropic orientation of 31%, with strong linear orientation in quartz ($K_{lin} = 50\%$) and feldspar (46%). Mica shows a lower linear alignment (28%) and high isotropy ($K_{is} = 69\%$), indicating a more random distribution. The areal orientation (K_{fl}) is

moderate for quartz at 29% but low for feldspar at 12% and mica (3%), confirming that mica grains are not directionally aligned. These patterns suggest that fracture propagation may be partially guided by mineral alignment in quartz and feldspar, whereas mica likely fractures independently of fabric orientation.

Clustering analysis reveals that quartz has the highest aggregation tendency ($C = 45\%$), forming phase-bound domains that may resist early disintegration. Feldspar and mica show lower clustering values (20% and 18%, respectively), with mica being the most spatially dispersed. This dispersed distribution supports easier mechanical liberation of mica and means it is less locked in with other minerals, although it may also make it more vulnerable to overgrinding, which could also be of interest for selective comminution.

Lepidolite-feldspar pegmatite, LSR-1 (Lepidolite Ore)

The modal composition of the sample and its mineralogical composition, considering the geological position, is consistent with layered lepidolite-feldspar pegmatite (apical parts of pegmatite veins). Modal analysis reveals a dominance of quartz (38%) and lithium-rich mica, likely lepidolite (34%), accompanied by subordinate feldspar (15%) and accessory phases such as topaz and fluorite within the undifferentiated mineral portion (13%). The textural analysis shows a fine- to medium-grained structure, with median grain sizes of 0.26 mm for quartz, 0.27 mm for feldspar, and 0.22 mm for mica, indicating a non-pegmatitic character (Table 4). The reduced feldspar content and enrichment in lithium mica and accessory minerals reflect intense hydrothermal alteration (Figure 7).

Table 4. Rock characteristics. Feldspar-lepidolite pegmatite from Villasrubias deposit. Thin section (LSR-1a-c).

Raw Material	Rock Type: Feldspar-Lepidolite Pegmatite				Phase Related Features				Raw Material Features
	Deposit: Villasrubias		Location: Spain						
Mode	Properties		Symbol	Unit	Qu *	Fsp	Lpd	NDP	Σ Microbodies
	Content	Volumetric Portion	E_V	%	38	15	34	13	100
Texture	Size	Mean diameter	$d_{50,3}$	mm	0.26	0.27	0.22	-	0.25
		Scatter parameter	σ_{ln}	-	0.38	0.33	0.36	-	0.36
	Grain surface	Specific surface	S_V	mm ² /mm ³	18.73	16.49	24.63	-	20.68
	Shape	Elongation	E	-	1.28	1.21	1.35	-	1.30
		Flatness	F	-	1.18	1.14	1.00	-	1.10
	Roughness	Roughness degree	K_R	%	31	16	14	-	22
Structure	Orientation	Degree of linear orientation	K_{lin}	%	17	13	22	-	14
		Degree of areal orientation	K_{fl}	%	9	7	-	-	5
		Degree of isotropic orientation	K_{is}	%	75	80	78	-	80
	Distribution	Degree of clustering	C	%	27	17	23	-	24

* Qu—Quartz, Fsp—Feldspar, Lpd—Lepidolite, NDP—undifferentiated Phases (Topaz, Fluorite).

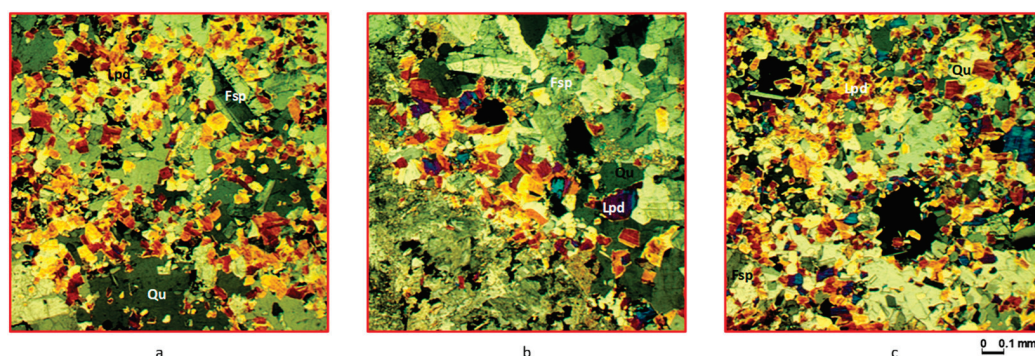


Figure 7. Selected digitized optical microscopy images of lepidolite-feldspar pegmatite from the Villasrubias (Spain). 16-x magnified, crossed polars (a–c). Samples LSR-1a–c.

The overall average grain shape ($E = 1.30$, $F = 1.10$) reflects a near-equant grain distribution with no extreme geometries. Mica (lepidolite) shows the highest elongation ($E = 1.35$) but a flatness of 1.00, suggesting a slightly elongated but compact form. Quartz and feldspar are similarly shaped, with elongation values of 1.28 and 1.21 and flatness values of 1.18 and 1.14, respectively. These moderate shape parameters imply that particle breakage during comminution is expected to be relatively uniform, though mica remains more susceptible to early fragmentation due to its structural cleavage.

The specific surface area (S_V) of LSR-1 varies notably among mineral phases. Mica (lepidolite) displays the highest S_V at $24.63 \text{ mm}^2/\text{mm}^3$, followed by quartz ($18.73 \text{ mm}^2/\text{mm}^3$) and feldspar ($16.49 \text{ mm}^2/\text{mm}^3$). The overall S_V of the sample is $20.68 \text{ mm}^2/\text{mm}^3$, indicating a high degree of surface interlocking. The elevated S_V of mica reflects its fine, platy morphology and suggests a high potential for liberation during grinding but also highlights its susceptibility to overgrinding due to increased exposure and structural weakness. The degree of roughness (K_R) further supports these observations. Quartz shows the highest interlocking at 31%, while feldspar and mica exhibit lower roughness values of 16% and 14%, respectively. The overall roughness degree is 22%, indicating moderate interparticle bonding. The relatively low roughness of mica suggests it is weakly interlocked in the matrix, offering favorable conditions for its selective liberation during mechanical fragmentation.

The clustering coefficient (C) in LSR-1 indicates that quartz grains have the highest tendency to form aggregates (27%), followed by mica (23%) and feldspar (17%), with an overall clustering degree of 24%. These values reflect a moderate level of mineral clustering, where individual phases are partially associated but not extensively interlocked. Structurally, the rock shows a highly isotropic orientation structure ($K_{is} = 80\%$), with low values for linear and areal orientation across all phases. This combination of moderate clustering and isotropic alignment suggests a texture favorable for disintegration during comminution, where grains are more likely to separate independently rather than breaking through strongly bonded aggregates.

QMA confirms that all samples represent quartz-dominant granitoid lithologies, with variable mica contents. The Cínovec samples (GCW-1 and GCG-1) show a coarser-grained texture of mica (0.75–1.3 mm) compared to the Villasrubias samples (LSA-1 and LSR-1), which are significantly finer grained (~0.25 mm).

The degree of roughness (K_R) of mica was higher in GCW-1 (71%) than in GCG-1 (50%). These tightly intergrown textures of GCW and GCG require higher breakage energy, careful control of grinding conditions, and may limit early-stage liberation. In contrast, lepidolite in the Villasrubias samples exhibits a much lower roughness (10–14%), suggesting weaker bonding to adjacent phases and easier detachment during mechanical comminution.

Although lepidolite-bearing ores show lower interlocking/degree of roughness, their finer grain size may also present higher comminution resistance. This is attributed to their compact and cohesive mineral textures, which enhance the mechanical integrity of the rock and hinder effective liberation of lithium mica during grinding. Structurally, both zinnwaldite and lepidolite samples exhibit a high degree of isotropy ($K_{is} = 80\text{--}88$), except in samples of lepidolite with low mica content. This predominantly random internal grain orientation supports more uniform stress distribution during breakage, potentially leading to more predictable fracture behavior under mechanical loading.

3.2. Chemical Analyses

As can be seen from Table 5, the division of rocks by ore-mineral content is obviously comparable with the lithium content. Thus, the minimum lithium content characterizes zinnwaldite-poor ores (1518.0 ppm), and the maximum lithium content is in lepidolite-rich ores (4462.8 ppm).

Table 5. Lithium content in the studied rocks according to ICP-OES results.

Location	Ore Name	Ore Type	Li, ppm
Cínovec (Czech Republic)	GCW-1 (greisenized granite)	Zinnwaldite-poor	1518.0
	GCG-1 (greisen)	Zinnwaldite-rich	4301.1
Villasrubias Lithium deposit (Spain)	LSR-1 (feldspar-lepidolite pegmatite)	Lepidolite-rich	4462.8
	LSA-1 (lepidolite-bearing aplite)	Lepidolite-poor	3409.2

Thus, it can be said that the studied zinnwaldite and lepidolite ores (GCG-1 and LSR-1 samples) correspond to the minimum lithium content prospects of the European Commission for rare and strategic metals [40].

3.3. Determination of Point Load Strength Index of Rocks

The zinnwaldite-rich greisen (GCG-1) exhibited the lowest strength, with an average PLT Strength Index $I_{S(50)}$ of about 2 MPa and a uniaxial compressive strength (UCS) value of 53.8 MPa (Table 6, Figure 8). The zinnwaldite-poor (GCW-1) samples followed with $I_{S(50)}$ values of 4.10 MPa and UCS values of 102.5 MPa, respectively (Figure 8, Table 6). According to the International Society for Rock Mechanics and Rock Engineering (ISRM) classification [41], GCG falls within the “moderate strength” range, while the GCW-1 sample is classified as “high strength” rock.

Table 6. PLT results for zinnwaldite and lepidolite ores, with conversion factor $c = 25$.

Rock Type	$I_{S(50)}$, MPa	Standard Deviation	σ_D , MPa	Standard Deviation
Zinnwaldite-rich (GCG-1)	2.15	0.80	53.8	12.8
Zinnwaldite-poor (GCW-1)	4.10	1.46	102.5	23.3
Lepidolite-rich (LSR-1)	5.13	1.32	128.2	21.21
Lepidolite-poor (LSA-1)	4.59	1.65	114.7	26.41

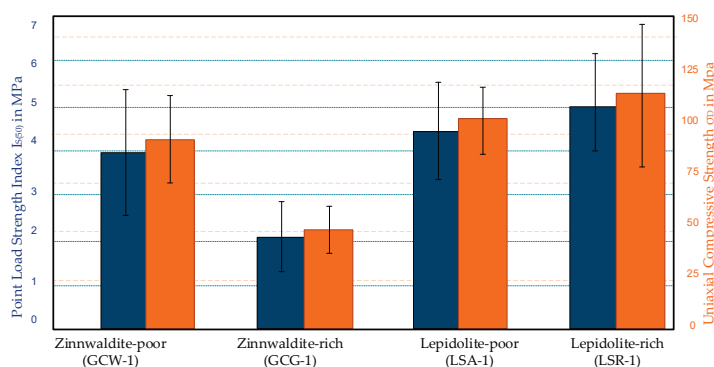


Figure 8. Point load test and uniaxial compressive strength results for zinnwaldite and lepidolite ores.

In contrast, both lepidolite ores showed consistently higher mechanical strength. The lepidolite-rich pegmatite (LSR-1 sample) recorded the highest UCS at 128.2 MPa, with an $I_{S(50)}$ of 5.13 MPa, followed closely by lepidolite-poor ore (LSA-1 sample), which showed UCS values of 114.7 MPa and $I_{S(50)}$ values of 4.59 MPa, respectively. The low variation (16.1%) in lepidolite-rich ore reflects a more homogeneous structure, suggesting consistent grain bonding. Both rocks are all classified as “high strength” by ISRM and “very strong” by the Geological Society classification [41].

The zinnwaldite-rich greisen (GCG-1 sample) showed a significantly lower Point Load Strength Index compared to the zinnwaldite-poor greisenized granite (GCW-1 sample), even though the quartz content in the GCG sample is nearly twice as high (Tables 1 and 2). This counterintuitive result can be attributed to differences in microstructural features, particularly surface roughness and textural bonding, as identified through QMA analysis. The overall degree of roughness in the zinnwaldite-rich ore was measured at approximately 45%, whereas the zinnwaldite-poor sample exhibited a higher roughness value of around 60%, indicating stronger interlocking between mineral phases. The low strength of zinnwaldite-rich greisen indicates that it is more susceptible to early breakage under mechanical stress.

Specifically, quartz crystals in the zinnwaldite-poor ore displayed a roughness of up to 63%, compared to 45% in the zinnwaldite-rich sample. As shown in Figure 9, the zinnwaldite-poor sample is characterized by abundant microcrystalline quartz, which likely formed through recrystallization during greisenization or hydrothermal alteration. This recrystallization enhanced the bonding between microcrystalline quartz and surrounding minerals, contributing to greater internal cohesion and mechanical strength. In contrast, the GCG sample is dominated by larger quartz crystals embedded in a relatively less altered matrix, resulting in reduced intergrowth and lower textural resistance to fracturing under point loading (Figure 9a).

The comparative results indicate that zinnwaldite ores, particularly zinnwaldite-rich greisens, are mechanically weaker and more susceptible to breakage, making them more favorable for coarse mineral liberation during comminution compared to lepidolite ores. However, their high quartz content also contributes to higher abrasivity [42,43], which can lead to increased equipment wear. In contrast, lepidolite ores are more competent, requiring higher comminution energy to achieve sufficient size reduction and liberation [44]. This increased resistance poses a higher risk of overgrinding, particularly given their finer grain size and more cohesive mineral textures, as observed in prior QMA analysis.

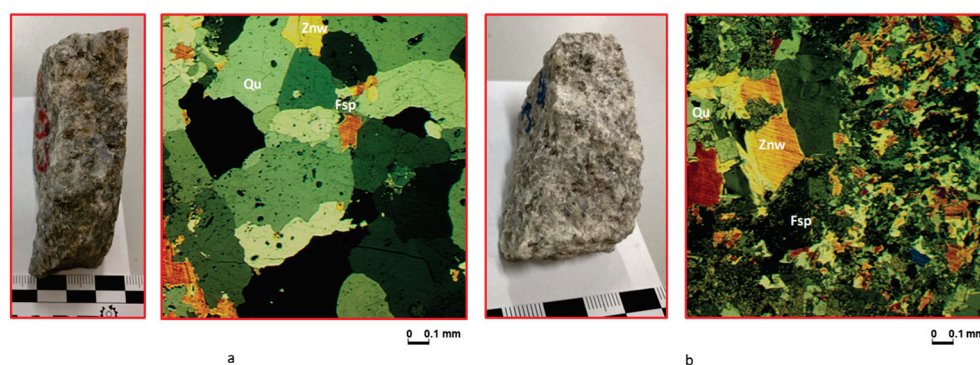


Figure 9. (a) Zinnwaldite-rich (GCG-1) sample shows larger quartz crystal and less altered matrix. (b) Zinnwaldite-poor (GCW) sample shows microcrystalline quartz as predominant mineral in the altered matrix. Thin section images with 16x-magnification, crossed polars.

3.4. Determination of Vickers Microhardness of Minerals

In the Vickers microhardness tests, mica consistently shows the lowest hardness ($154\text{--}195\text{ N/mm}^2$), compared to quartz and feldspar, which present significantly higher values. Quartz shows the highest Vickers hardness ($1234\text{--}1302\text{ N/mm}^2$) and fracture toughness ($2.11\text{--}2.49\text{ MN}\cdot\text{m}^{-3/2}$), indicating strong resistance to deformation and crack propagation [45,46] and causing the high abrasivity of the material [42,43] (Table 7, Figures 10 and 11).

Table 7. Vickers microhardness and fracture toughness for zinnwaldite and lepidolite ores.

Lithium Ore	Mineral	Content, %	Vickers Hardness Number, N/mm^2	Fracture Toughness, $\text{MN/m}^{3/2}$
Zinnwaldite-poor (GCW-1)	Quartz	32	1234.36 ± 94.72	2.11 ± 0.5
	Feldspar	47	903.0 ± 111.85	1.48 ± 0.51
	Mica	10	154.51 ± 48.63	-
Zinnwaldite-rich (GCG-1)	Quartz	70	1290.9 ± 66.87	2.39 ± 0.34
	Feldspar	4	740.369 ± 118.4	1.47 ± 0.63
	Mica	16	194.9 ± 49.06	-
Lepidolite-poor (LSA-1)	Quartz	45	1149.73 ± 103.2	2.24 ± 0.59
	Feldspar	31	838.72 ± 84.96	1.55 ± 0.42
	Mica	20	167.11 ± 40.36	-
Lepidolite-rich (LSR-1)	Quartz	38	1302.70 ± 132.92	2.49 ± 0.66
	Feldspar	15	879.17 ± 105.60	2.06 ± 0.75
	Mica	34	179.05 ± 42.70	-

Feldspar, while slightly softer ($740\text{--}903\text{ N/mm}^2$) and less tough ($1.47\text{--}2.06\text{ MN}\cdot\text{m}^{-3/2}$), still exhibits high values relative to mica, which corresponds with reference data [47,48].

Mica is a soft and flexible mineral with perfect cleavage, meaning it easily splits along certain planes. Because of its crystal structure, mica can deform plastically, changing shape without forming cracks (see Figure 12a). During testing, it was not possible to apply enough force to create measurable cracks without completely breaking the grain. As a result, its fracture toughness could not be determined.

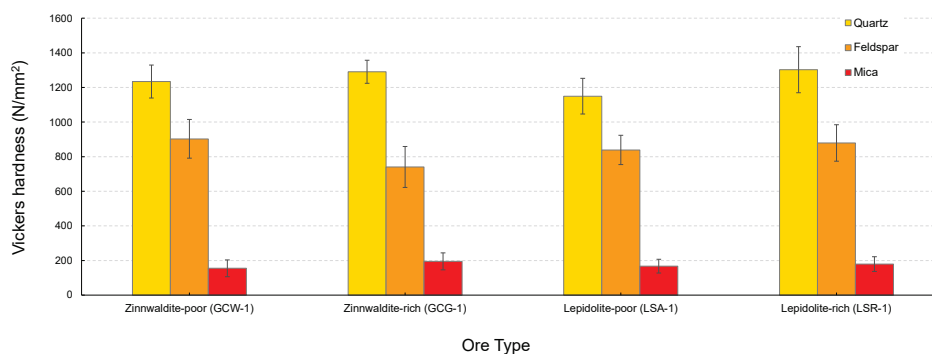


Figure 10. Vickers hardness of minerals across different types of lithium ores.

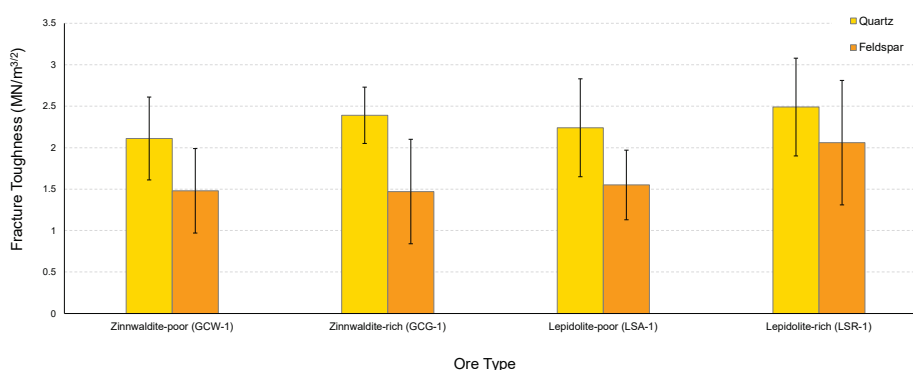


Figure 11. Fracture toughness of mineral across different types of lithium ores.

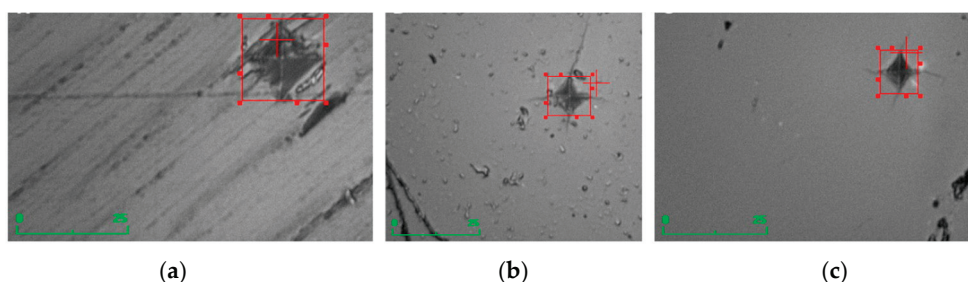


Figure 12. Vickers Hardness microindentation investigation. (a) Mica showed perfect cleavage. (b) Primary radial crack on quartz. (c) Primary radial crack on feldspar.

These findings indicate that both lithium-bearing ores show a pronounced mechanical contrast between the lithium micas and their associated gangue minerals [49]. A similar observation was made by [50]. It was noted that minerals with significantly lower hardness are often indicative of favorable conditions for selective mineral liberation. In the case of zinnwaldite, its relatively high grain boundary roughness, based on QMA, suggests that breakage can be more likely to occur preferentially across the mineral rather than along the grain boundaries. Conversely, for lepidolite, the relatively low roughness contrast between lepidolite and its surrounding gangue minerals, as identified through QMA, may facilitate grain boundary breakage and thus promote more efficient mineral liberation.

This noticeable difference establishes mica as the mechanically weakest phase in the mineralogical assemblage, making it highly susceptible to preferential fragmentation under moderate energy input. Such characteristics are advantageous for selective comminution strategies, where energy can be optimized to preferentially fracture the softer lithium-bearing phases while minimizing breakage of the harder gangue components.

4. Discussion

The present study integrates quantitative microstructural analysis (QMA), chemical characterization, and mechanical testing to analyze the comminution behavior of European lithium-bearing hard-rock ores. By comparing zinnwaldite-bearing ores from Cínovec and lepidolite-bearing ores from Villarsrubias, a clear link emerges between mineralogical fabric, mechanical competence, and selective breakage potential.

The QMA results demonstrate that textural parameters, particularly grain size, roughness (KR), clustering (C), and specific surface area (SV), play a decisive role in controlling mechanical strength and breakage response.

The zinnwaldite-rich greisen (GCG-1) exhibits lower roughness and higher quartz clustering compared to the zinnwaldite-poor greisenized granite. Despite its higher quartz content (70%), GCG-1 shows the lowest compressive strength. This result highlights that bulk strength is not solely controlled by modal mineral content but rather by the quality of grain boundary interlocking and microstructural bonding. In GCW-1, microcrystalline quartz recrystallization appears to enhance internal cohesion, resulting in significantly higher UCS values.

In contrast, the lepidolite-bearing ores from Villarsrubias (LSA-1 and LSR-1) are markedly finer-grained and exhibit lower mica roughness. Although the lower interlocking of mica suggests easier detachment along grain boundaries, both lepidolite ores display high compressive strength. This indicates that fine-grained, compact fabrics enhance bulk mechanical competence, increasing resistance to initial breakage. Thus, two different strength-controlling mechanisms can be distinguished in Cínovec ores, where strength is primarily governed by intergranular bonding and recrystallized quartz networks, and in Villarsrubias ores, where strength is controlled by fine grain size and compact, cohesive textures.

These findings confirm that microstructural descriptors obtained by QMA can provide a more reliable predictor of comminution behavior than modal composition alone.

A pronounced mechanical contrast exists between lithium-bearing micas and their associated gangue minerals. Vickers microhardness results show quartz and feldspar to be significantly harder and tougher than mica. This mechanical contrast is favorable for selective comminution strategies. However, the liberation mechanism differs between the two ore types:

Zinnwaldite ores (Cínovec):

Coarser mica grains (0.7–1.3 mm) combined with high roughness (up to 71%) suggest that breakage may occur transgranularly through mica rather than cleanly along grain boundaries. Although zinnwaldite-rich greisen is mechanically weaker overall, strong quartz intergrowth and high abrasivity may increase energy consumption and equipment wear during grinding, which should be the target of future research.

Lepidolite ores (Villarsrubias):

Finer mica grains (0.1–0.2 mm) and low roughness (10–14%) favor intergranular breakage and grain-boundary liberation. However, their high compressive strength and compact structure require higher energy input to initiate fracture. Once breakage begins, the low mica hardness may increase the risk of overgrinding and excessive fines generation.

Consequently, according to investigations conducted, process design must be deposit-specific: Zinnwaldite ores may benefit from controlled coarse comminution stages to exploit their lower UCS while minimizing quartz overgrinding. Lepidolite ores may require staged or energy-efficient fine grinding approaches to achieve liberation without excessive mica degradation.

5. Conclusions

This study examined the breakage behavior and beneficiation potential of lithium-bearing mica ores through an integrated mineralogical and mechanical approach, motivated by Europe's strategic need to strengthen domestic lithium supply chains. The results demonstrate that significant variations in grain size, mica distribution, interlocking, and surface roughness may strongly influence the mechanical response of the ores and their comminution behavior.

The study reveals an important theoretical trade-off between mechanical strength and interlocking: Zinnwaldite-rich greisen is weaker and therefore can be easier to fragment, but its higher quartz content and interlocking can increase abrasivity and potential wear, which could be the target of future studies within the current project. Lepidolite ores are mechanically stronger and more energy-intensive to crush, yet their lower mica roughness may enable more efficient liberation once the appropriate particle size is reached.

The findings, therefore, emphasize that selective comminution should not rely solely on mineral hardness contrasts but must incorporate microstructural parameters such as clustering, grain size distribution, and orientation. Otherwise, further study is needed to understand mineral liberation during grinding and the structural effect on the downstream processing to extract lithium from the samples, including studies of abrasiveness and material wear, evaluation of the energy efficiency of the milling process, and the yield of the useful component.

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Abbreviations

The following abbreviations are used in this manuscript:

LiB	lithium-ion batteries
QMA	quantitative mineralogical analysis
SIZ	Central Iberian Zone
LCT	lithium–cesium–tantalum
CEG	Schist–Greywacke Complex
GTMZ	Galicia–Trás-Os Montes Zone

IART	Institute of Processing Machines and Systems Technology
CEEC	Coalition for Energy Efficient Comminution
CT	Computer Tomography
TUBAF	Technical University Bergacademie Freiberg
PLT	Point Load Test
HV	Vickers Hardness Number
NDP	Non-differentiated phases
UCS	Uniaxial Compressive Strength
ISRM	International Society for Rock Mechanics and Rock Engineering
CINEA	European Climate, Infrastructure and Environment Executive Agency

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Article

New Contributions to Mineralogical and Geochemical Knowledge of Old Preguiça Mine, Beja, Portugal

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Abstract

Abandoned mining areas provide valuable opportunities to investigate ore-forming processes, supergene mineral transformations, and the geochemical behaviour of metals. In this sense, the old Preguiça mine (Beja, Portugal), exploited for Fe–Zn–Pb, was studied providing new mineralogical and geochemical data aimed at improving the understanding of the secondary mineral assemblages of this deposit. A total of 70 samples collected from three accessible underground levels (first, second and third) and mine waste, complemented by 16 samples from a deeper level (fourth) previously collected, were analysed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and a portable X-ray fluorescence (pXRF) equipment. Mineralogical phases are dominated by a wide range of secondary oxides, carbonates, arsenates, vanadates, silicates, phosphates and sulphates, but remnants of primary sulphides were also found. The following minerals can be emphasised: goethite, hematite, calcite, dolomite, descloizite, willemite, mimetite, cerussite, smithsonite and fraipontite. The presence of massicot in the Preguiça mine, is described for the first time. Bulk geochemical analyses show high concentrations of Fe, Ca, Zn and Pb, consistent with the observed mineralogy. The presence of vanadium- and arsenic-bearing minerals highlights the occurrence of critical raw materials, supporting the importance of reassessing other abandoned mining areas in the context of sustainable resource management and strategic raw-material planning.

Keywords: Preguiça mine; mineral phases; pXRF; historical Fe–Zn–Pb deposit; abandoned mine; Portugal

1. Introduction

Within the European Union, historical mining districts are increasingly recognised as potential contributors to resource security strategies, aligning geological research with circular economy and resource efficiency policies.

Additionally, abandoned mining areas provide valuable natural laboratories for investigating ore-forming processes, mineral transformations, and the geochemical behaviour of metals in supergene environments. The weathering of primary ore minerals and subsequent supergene processes can generate complex assemblages of secondary phases that evidence important information about fluid–rock interaction, element mobility, and post-depositional alteration [1]. Earlier exploration and analytical approaches—designed primarily to target the metals of interest at the time—now offer valuable opportunities for reassessment. By applying innovative methodologies and advanced analytical techniques, these areas can be re-examined for additional elements of interest. Advances in mineralogical characterisation techniques, have facilitated the identification of trace-element hosts and previously overlooked mineral species, thereby providing new insights into metal distribution and enrichment processes. The re-examination of abandoned mining areas represents an important approach for assessing secondary resources that may contribute to the future supply of critical and strategic raw materials (CRM and SRM) [2,3].

The old Preguiça mine (Moura, Beja, Portugal), located in the Ossa Morena Zone (OMZ), is an emblematic site within the context of Portugal’s extensive mining heritage and holds a significant place in the region’s mining history [4]. Preguiça constitutes a representative example of an abandoned Fe–Zn–Pb mineralisation. Currently, primary sulphide minerals, pyrite, marcasite, chalcopyrite, sphalerite, and galena, are locally preserved and occur only sporadically within the mineralized zones. Subsequent weathering has significantly modified the primary mineralisation, producing a diverse suite of secondary minerals including oxides, carbonates, arsenates, vanadates, silicates, and sulphates. These transformations provide important clues on the geochemical mobility of metals such as Zn, Pb, Fe, V and As in oxidising environments, e.g., [5]. Understanding these processes is essential not only for reconstructing the post-mineralization evolution of the deposit but also for evaluating potential environmental risks and resource opportunities associated with secondary mineral phases.

The present work aims to provide new mineralogical and geochemical contributions to the understanding of the Preguiça mine’s geological evolution. Through the study of samples collected from four underground levels and mine waste areas, this research seeks to identify the mineral phases present and evaluate the distribution of elements associated with the deposit. By combining X-ray diffraction (XRD), portable X-ray fluorescence (pXRF), and scanning electron microscopy (SEM) techniques, the study contributes to enriching the knowledge of the mineralogical diversity, describing the phase morphology and evaluating the geochemical characteristics of the Preguiça deposit. Furthermore, the results help clarify the role of supergene processes in the formation of secondary mineral assemblages and highlight the potential occurrence of elements of strategic importance within this historical mining environment.

1.1. Geological Setting

The old Preguiça mine is located in southern Portugal, approximately 20 km southeast of the town of Moura. Geologically, the area is located within the Ossa Morena Zone (OMZ), a heterogeneous and complex tectonostratigraphic zone, characterised by distinctive stratigraphic, magmatic and tectono-metamorphic features. These reflect the influence of two successive Wilson Cycles, namely, the Cadomian and Variscan Cycles [6,7], and part of the Magnetitic–Zinciferous Belt or Montemor-o-Novo—Ficalho Belt, where there are known mineralisations of (1) massive magnetite ores; (2) massive and stratiform sulphides ores; (3) iron skarns; (4) Au–As veins and (5) hydrothermal veins containing Cu [8]. The combination of volcanic influences, supergene alteration, Cambrian carbonate host rocks,

two major tectonic overprints, and the resulting mineral–textural transformations make Preguiça a notable geological case.

Geologically, the mine area is dominated by rocks of the Dolomitic Formation with probable Lower Cambrian age (Figure 1), composed at its base of intermediate to basic volcanic rocks and, more rarely with felsic volcanism overlain by dolomitic limestones with approximately 400 m thickness [9–12]. The dolomitic limestones are composed mainly of carbonate assemblages (calcite, dolomite, and ankerite) and accessorially by quartz, muscovite, chlorite, epidote and actinolite–tremolite [13].

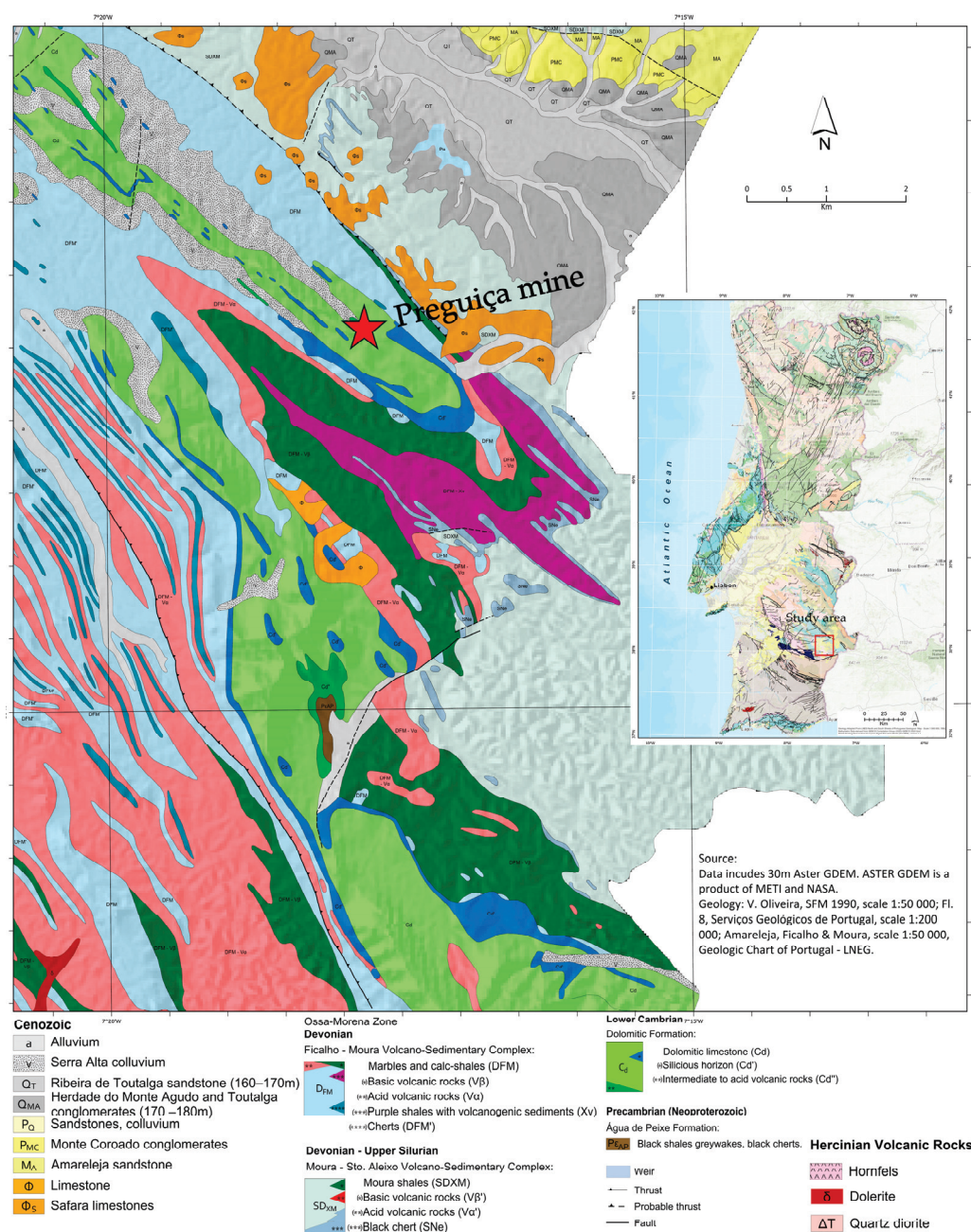


Figure 1. Geological map of the Ossa Morena Zone with the location of the Preguiça mine (adapted from [6,14]).

Two ore bodies are recognised from the surface down to the water table (100 m deep), where the primary sulphide mineralisation is found [10,15]. The sulphides' oxidation in the surface produced a gossan zone with 40 m thickness, very enriched in zinc, which was the

major target of exploration in the past (Figures 2 and 3A). In the NE flank of the structure, exploration boreholes crossed the mineralised horizon with 20.4% Zn, 5.2% Pb and 107 ppm of Ag [9,16]. The mineral potential of this area led to further detailed exploration by the former SFM Government Agency (Serviço de Fomento Mineiro, currently LNEG) in the 1980s, as well as several private exploration companies. These surveys generated a large knowledge database containing geologic, soil geochemistry (Cu, Zn, Pb), gravity (Bouguer 2.65) and magnetic (vertical field) data (200 × 200 m grid surveys) [14]. General aspects of the old Preguiça mine can be seen in Figure 3.

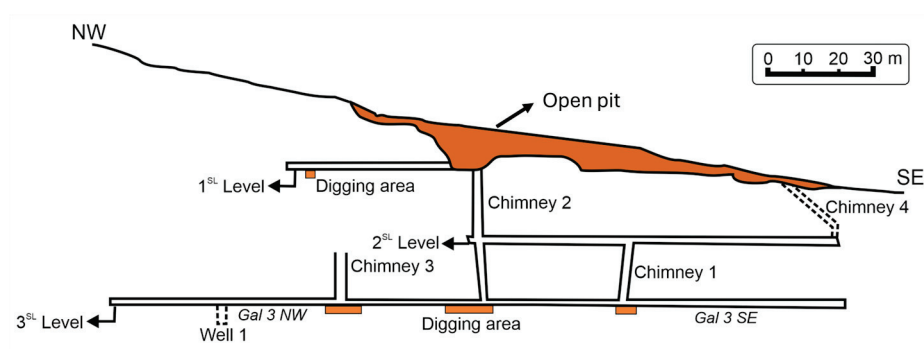


Figure 2. General map of the galleries of the old Preguiça mine aligned NW-SE (adapted from [17]).

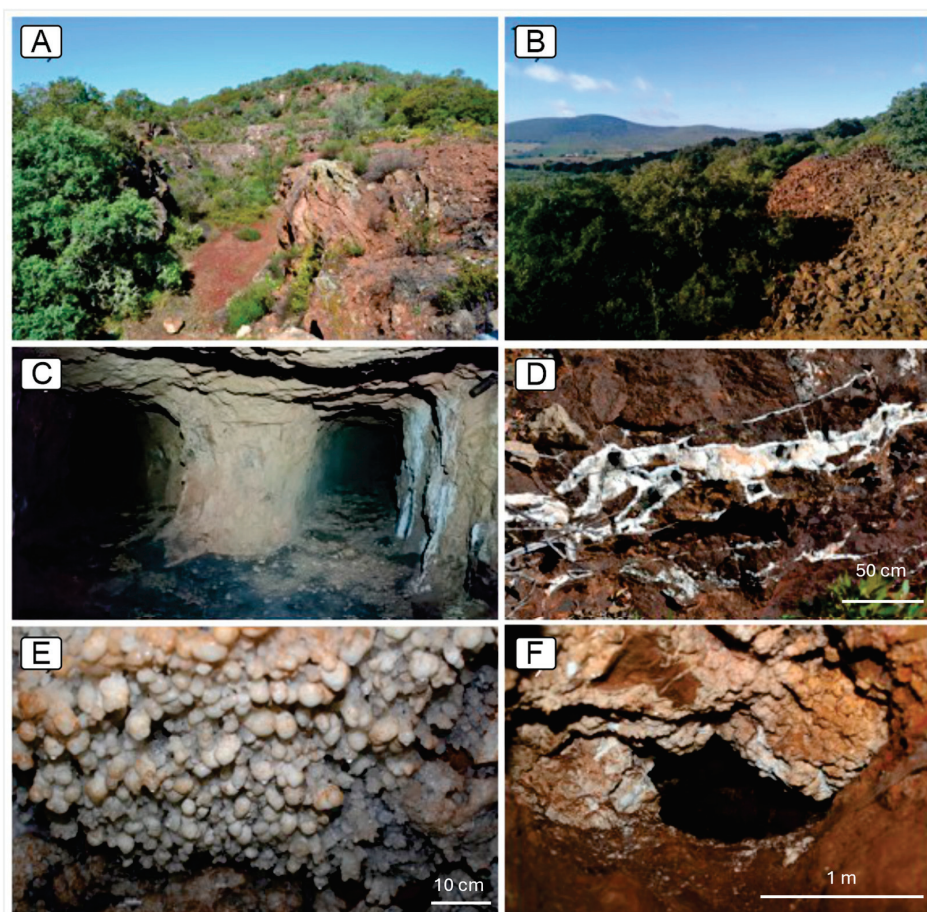


Figure 3. General aspects of the old Preguiça mine. (A) Open pit area of the gossan zone. (B) Mine waste area. (C) Ore access galleries on the third level. (D) Dolomites of the Dolomitic Formation (Lower Cambrian age) with secondary carbonate veins. (E,F) Natural cavity with carbonate concretions.

The ore genesis model remains controversial and has been described as comparable to Irish-type sedimentary exhalative (SEDEX) deposits [8,9]. Other authors attribute the primary genesis of the deposits to volcanic-hosted massive sulphide (VHMS) mineralisation, consisting of stratiform massive sulphides hosted in metacarbonate and metavolcanic horizons and affected by intense, albeit heterogeneous, hydrothermal alteration [18].

1.2. Historical Mine Overview

The Moura region has had a long history of mining, possibly from pre-Bronze Age times to the twentieth century [19]. Documented mining concessions in the Preguiça area date back to the late nineteenth century, notably Umbria da Preguiça (Fe–Pb, 1899) and Preguiça No. 6 (Fe–Mn, 1914; originally registered in 1872) [20,21]. Between 1911 and 1915, Preguiça No. 2 was actively exploited, producing approximately 2342 t of ore with grades up to 25% Zn.

Mining ceased due to World War I events and was definitively abandoned in 1929. In the 1950s, the Serviço de Fomento Mineiro (SFM) reassessed the deposits through underground development and sampling, recording Zn contents of up to 31% at the third level of Preguiça No. 2 [17]. This work led to renewed exploitation of the mine by the Compagnie Royale Asturienne des Mines, which acquired the mines in 1960 and resumed mining operations at Preguiça No. 2 under a pilot exploitation regime. New surveys enabled the identification of three mineralized bodies, with total reserves estimated at 600,000 t to 1 Mt, containing 8% Zn and 2% Pb. Mining activity was abandoned in 1966 [9,10]. More recent exploration campaigns were carried out by mining companies APAC (Asia–Pacific) Resources Company (1998), Northern Lion Gold (2007–2009), and Green Arrow/WalZinc (2016–2021), resulting in updated geological mapping and a 3D deposit model. The concession expired in March 2022, and the mine is currently inactive under environmental protection.

2. Materials and Methods

2.1. Sampling

A total of 70 samples were collected on the 1st, 2nd and 3rd levels of the mine and at the mine waste open pit, near the 2nd level. Due to the difficulty of accessing the 4th level, 16 samples previously collected by one of the authors (I.R.) were used for this study. Considering the safety conditions, only the 3rd level was adequate for careful sampling around almost all the galleries. Table 1 lists the provenience of each sample.

Table 1. Collected samples and their reference positions.

	1st Level	2nd Level	3rd Level	4th Level	Open Pit
Sample Reference	From PR68 to PR70	PR65	From PR1 to PR63	From P4–1 to P4–16	PR66

2.2. Methodology

Small fragments were selected (almost 300) for X-ray diffraction (XRD), using the stereomicroscope (Stemi SV-11, Zeiss, Oberkochen, Baden-Württemberg, Germany), with several images collected using a digital Zeiss camera (Axio-Cam Mrc, Oberkochen, Baden-Württemberg, Germany). To obtain high-quality images of the small crystals, several photographs were taken of the same fragment at different focus planes and then photo-stacked using the programme *Photopea* (<https://www.photopea.com/>, accessed on 23 March 2026).

Powder X-ray diffraction (XRD) data were collected using a D8 Advance Bruker AXS diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with Cu K α radiation, operating at 40 kV and 40 mA. The powder diffractograms (5–70° 2 θ) were obtained using a step size

of 0.015° and a step time of 0.3 s with a LYNXEYE XE-T detector. XRD data treatment was performed using DIFFRAC.EVA v5.1 software and the Crystallography Open Database (COD) or the Powder Diffraction File database (PDF-2) for phase identification.

Chemical analysis was necessary in some fragments to help phase identification, due to the overlap of some peaks in the XRD spectra and to the solid solution between end members of some mineral groups. For that, a portable X-ray fluorescence (pXRF) equipment, X-MET8000 Expert Geo from HITACHI (Tokyo, Japan), was used in the laboratory using a benchtop stand and the analytical programme “Mining” (60 s per sample), to analyse powder fragments. This apparatus was equipped with a Rh tube (4 W; 50 kV maximum, 200 μ A maximum) and a high-resolution silicon drift detector (SDD); the measurement spot size was 10.7 mm $\times$ 9.4 mm. pXRF equipment was also used for a bulk chemical analysis, allowing a rapid evaluation of the contents of a wide range of elements. For that purpose, samples were analysed as collected, using the programme “Mining” (for elements with an atomic number higher than Mg) and “REE” (for the rare-earth elements: La, Ce, Pr and Nd, during 180 s). The measurements were acquired by using the internal calibration set up in the equipment as provided by the manufacturer, based on the Fundamental Parameters (FP) method [22,23]. The general details of the equipment’s operating mode are described in, e.g., [24].

Some samples were also morphologically and chemically studied through scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) in backscattering mode (BSE), providing elemental distribution maps, using a Hitachi™ S-3700N variable pressure SEM (Hitachi, Tokyo, Japan), equipped with a Bruker™ XFlash 5010 silicon drift EDS detector (Bruker Corporation, Berlin, BE, Germany) (resolution: 126 eV at FWHM/Mn K α). Analyses were conducted at an accelerating voltage of 20 kV, beam current of 120 μ A, 10 mm working distance, and a variable pressure mode at 40 Pa, without preparation or carbon coating. Data acquisition and interpretation were carried out using Esprit 1.9 software (Bruker, Berlin, BE, Germany).

3. Results and Discussion

3.1. Identification of Mineral Species

The mineralogical phases identified in the Preguiça mine fragments are listed in Table 2. They are in accordance with the findings of other authors in this mine [25–29] or in similar geologic environments [30,31]. The number of occurrences of each phase at each level gives an approximation of their abundance in the total number of fragments analysed (n). Remaining primary sulphides (pyrite, marcasite, chalcopyrite, sphalerite, and galena), as referred by Gomes et al. [17], were sporadically observed on the third level (Figure 4A,B). Only at this level a magnesium sulphate hydrate (epsomite) was also found, which occurs as a whitish efflorescence (Figure 4C,D) over dolomite. Other secondary minerals, formed in a strongly oxidising environment [25,29], were observed: oxides (Mn, Fe and Pb) and carbonates (Mg, Ca, Fe, Zn and Pb) are spread along the mine, but goethite and quartz are frequent on the fourth level and in the mine waste open pit, while on the third level calcite, goethite and quartz are very frequent, followed by hematite, dolomite and descloizite (vanadate of lead and zinc). The zinc silicate willemite is very frequent on the first level, followed by goethite, quartz and mimetite (lead arsenate), while willemite, hematite and cerussite (lead carbonate) are also frequent in the mine waste open pit. The main mineral species identified are described below through their mineral groups (including illustrative images). Figure 5 displays some examples of the XRD spectra obtained, showing usually a mixture of phases, labelled in the legend of each spectrum.

Table 2. Minerals identified on the four levels of the Preguiça mine and in the mine waste open pit. The number of fragments where each mineral was found is displayed (in a total of n fragments analysed); the chlorites and micas formulas are not given (-) for simplicity, as they represent two groups of related mineral species displaying a similar XRD pattern inside each group.

Mineral Name	Formula	First Level (n = 19)	Second Level (n = 1)	Third Level (n = 216)	Fourth Level (n = 24)	Open Pit (n = 19)
Ankerite	$\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2$			2		
Aragonite	CaCO_3		1	2		1
Arsendesclouite	$\text{PbZn}(\text{AsO}_4)(\text{OH})$			1		
Beaverite (Zn)	$\text{Pb}(\text{Fe}^{3+}_2\text{Zn})(\text{SO}_4)_2(\text{OH})_6$				1	
Beudantite	$\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$				2	
Calcite	CaCO_3	2	1	114	4	2
Cerussite	PbCO_3	1		5		8
Chabazite-Ca	$(\text{Ca}, \text{K}_2, \text{Na}_2)_2[\text{Al}_2\text{Si}_4\text{O}_{12}]_2 \cdot 12\text{H}_2\text{O}$			1		
Chalcopyrite	CuFeS_2			1		
Chlorites	-	1	1	9	1	
Coronadite	$\text{Pb}(\text{Mn}^{4+}_6\text{Mn}^{3+}_2)\text{O}_{16}$	1				
Descloizite	$\text{PbZn}(\text{VO}_4)(\text{OH})$			52	1	
Dolomite	$\text{CaMg}(\text{CO}_3)_2$		1	64	4	1
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$			4		
Fraipontite	$(\text{Zn}, \text{Al})_3((\text{Si}, \text{Al})_2\text{O}_5)(\text{OH})_4$			8		2
Galena	PbS			1		
Goethite	$\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$	7		106	20	13
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$			8	6	
Hedyphane	$\text{Ca}_2\text{Pb}_3(\text{AsO}_4)_3\text{Cl}$			4	1	
Hematite	Fe_2O_3	1		53	5	7
Jarosite	$\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$			2	2	
Magnetite	$\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$			2		1
Marcasite	FeS_2			1		
Massicot	PbO			3		
Micas	-			23	2	
Mimetite	$\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$	9		17	1	
Minrecordite	$\text{CaZn}(\text{CO}_3)_2$			5		
Montmorillonite	$(\text{Na}, \text{Ca})_{0.33}(\text{Al}, \text{Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$			2		
Mottramite	$\text{PbCu}(\text{VO}_4)(\text{OH})$			1		
Phosphohedyphane	$\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}$	1		2	1	
Plattnerite	PbO_2			4		4
Plumbojarosite	$\text{Pb}_{0.5}\text{Fe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$			1		
Pyrite	FeS_2			1		
Quartz	SiO_2	9	1	122	19	13
Richterite	$\text{Na}(\text{NaCa})\text{Mg}_5(\text{Si}_8\text{O}_{22})(\text{OH})_2$				1	
Siderite	FeCO_3			2		
Smithsonite	ZnCO_3			7	4	1
Sphalerite	ZnS			3		
Talc	$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$			5		
Vanadinite	$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$	1		1		
Vermiculite	$\text{Mg}_{0.7}(\text{Mg}, \text{Fe}, \text{Al})_6(\text{Si}, \text{Al})_8\text{O}_{20}(\text{OH})_4 \cdot 8\text{H}_2\text{O}$			3		
Willemite	Zn_2SiO_4	18		16		12

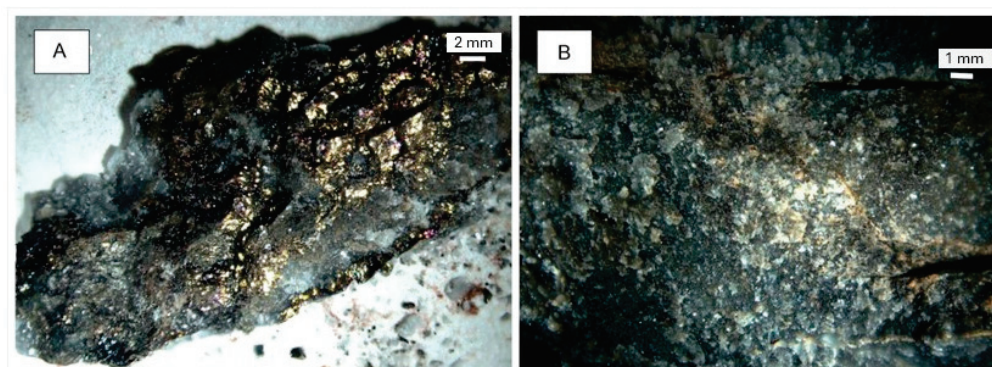


Figure 4. Cont.

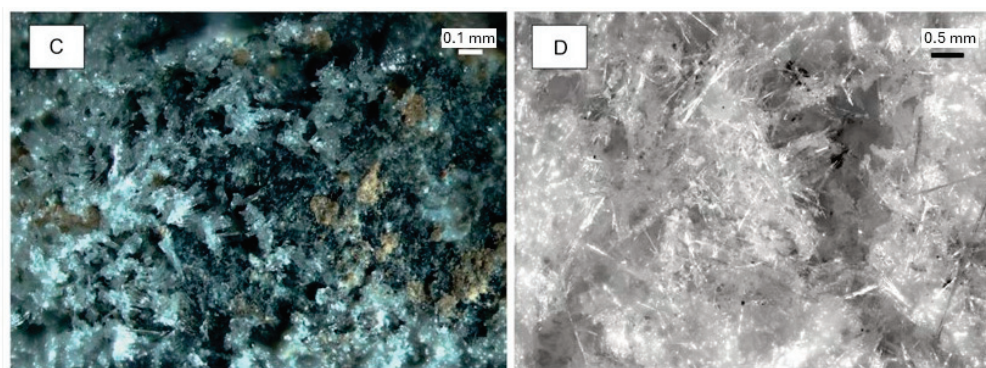


Figure 4. Stereomicroscope images of samples collected on the third level of the Preguiça mine. (A) Chalcopyrite+sphalerite+marcasite over dolomite (sample PR30). (B) Dolomite+pyrite (PR54); (C) Epsomite over dolomite (PR29). (D) Detail of epsomite crystals.

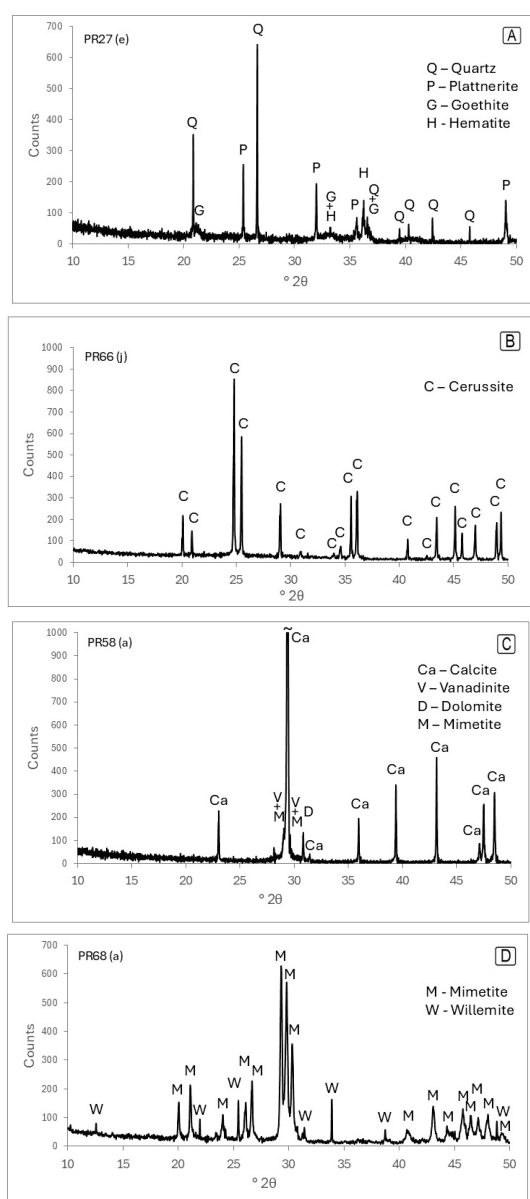


Figure 5. Illustrative examples of XRD spectra; the identified phases are shown in the legend: (A) sample PR27 (e); (B) PR66 (j); (C) PR58 (a); (D) PR68 (a). The mineral phases are simplified using the first letter/s of their name. COD card numbers: Q—1011172; P—9014175; G—1008766; H—9000139; C—9013803; Ca—9000095; V—9004057; D—9004933; M—1010997; W—9014832.

3.1.1. Plattnerite and Massicot

Plattnerite (PbO_2), whose XRD pattern is represented in Figure 5A, belongs to the rutile group and has a tetragonal structure. The acicular black crystals were observed on the third level (Figure 6A,B) and mine waste open pit. A BSE image of plattnerite and an example of the EDS spectrum obtained are shown in Figure 6C,D. Overlap between Pb M lines and S K lines can occur, and therefore the presence of galena cannot be ruled out. Occurrences of plattnerite have been described, e.g., in the Goodsprings mining district of Nevada [32], in Poland [33] and in Leadhills, Scotland [34]. Massicot (PbO), a mineral with orthorhombic structure, whose presence has not yet been described in the Preguiça mine, was sporadically found in traces.

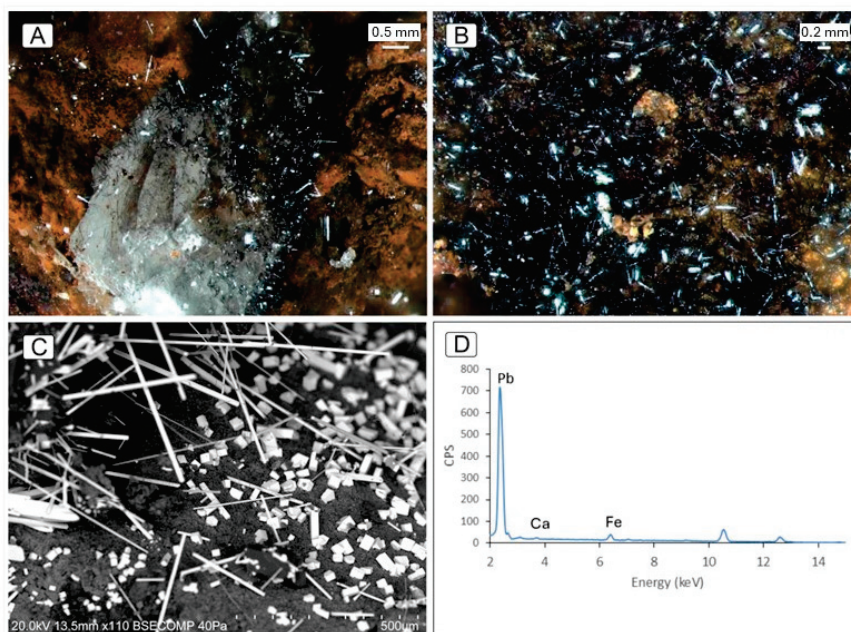


Figure 6. Stereomicroscope images of (A) black acicular crystals of plattnerite over calcite (sample PR27). (B) Detail of plattnerite crystals (PR33). BSE image of plattnerite (C). EDS spectra collected in acicular crystals or in parallelepipedal forms are similar (D).

3.1.2. Goethite, Hematite and Magnetite

Among the Fe-oxy-hydroxides, goethite [$\alpha\text{-Fe}^{3+}\text{O}(\text{OH})$] was the most common mineral found (Table 2), followed by hematite (Fe_2O_3). Black magnetite ($\text{Fe}^{2+}\text{Fe}^{3+}_2\text{O}_4$) crystals were only observed sporadically (Figure 7A).

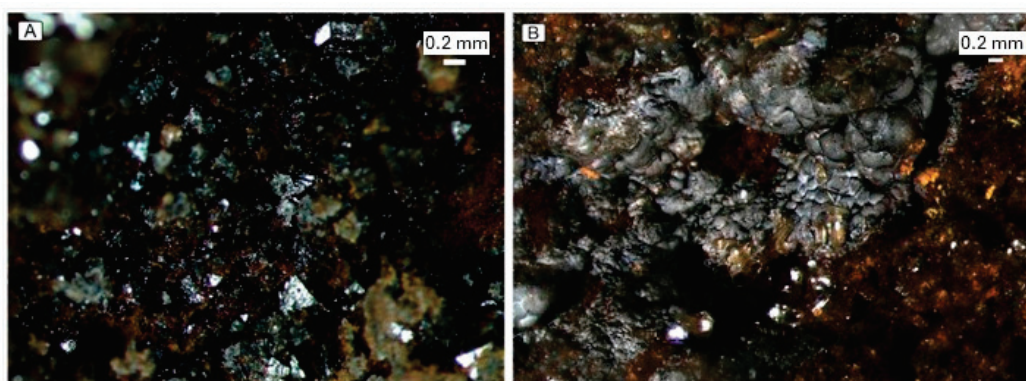


Figure 7. Stereomicroscope images of (A) magnetite crystals (PR66); (B) coronadite (PR70).

3.1.3. Coronadite

Botryoidal aggregates of dark grey coronadite $[\text{Pb}(\text{Mn}^{4+}_6\text{Mn}^{3+}_2)\text{O}_{16}]$, the unique manganese mineral observed and already described in the Preguiça mine [25,26], was only detected on the first level (Figure 7B).

3.1.4. Calcite, Smithsonite and Siderite

These carbonate minerals belong to the calcite group, being characterised by their rhombic, prismatic or scalenohedral crystalline structure. Calcite (CaCO_3) is very common in the mine and in the mine wastes, presenting variable forms and colours. Some examples can be seen in Figure 8A–D. Although the orange/salmon colour of calcite is usually attributed to the presence of Fe, its content is not very high (about 1%). Pearl-coloured smithsonite (ZnCO_3) botryoidal crystals are much less frequent (Figure 8E,F), and the occurrence of Fe^{2+} carbonate siderite (FeCO_3) on the analysed fragments is rare.

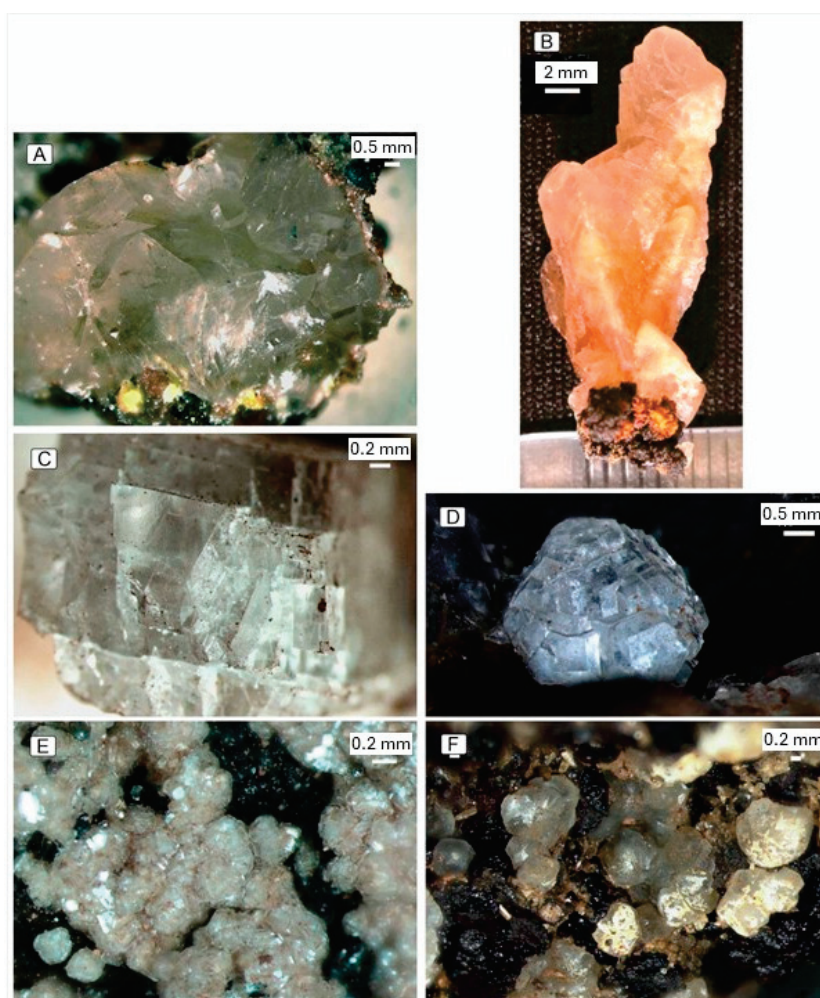


Figure 8. Stereomicroscope images and photo of calcite (A) from first level (sample PR70); (B) orange crystal from third level (PR19); (C) third level (PR42); (D) fourth level (P4-4); and smithsonite (E) from fourth level (P4-1); (F) mine waste open pit (PR66).

Hydrozincite, another zinc carbonate $[\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6]$ whose presence was previously described in the Preguiça mine, e.g., [25], was not found.

3.1.5. Aragonite and Cerussite

Aragonite (CaCO_3), a calcite polymorph (Figure 9A,B), and cerussite (PbCO_3) both belong to the aragonite group. The presence of tabular cerussite (Figures 5B and 9C,D) was more frequent than aragonite, particularly in the mine waste open pit.

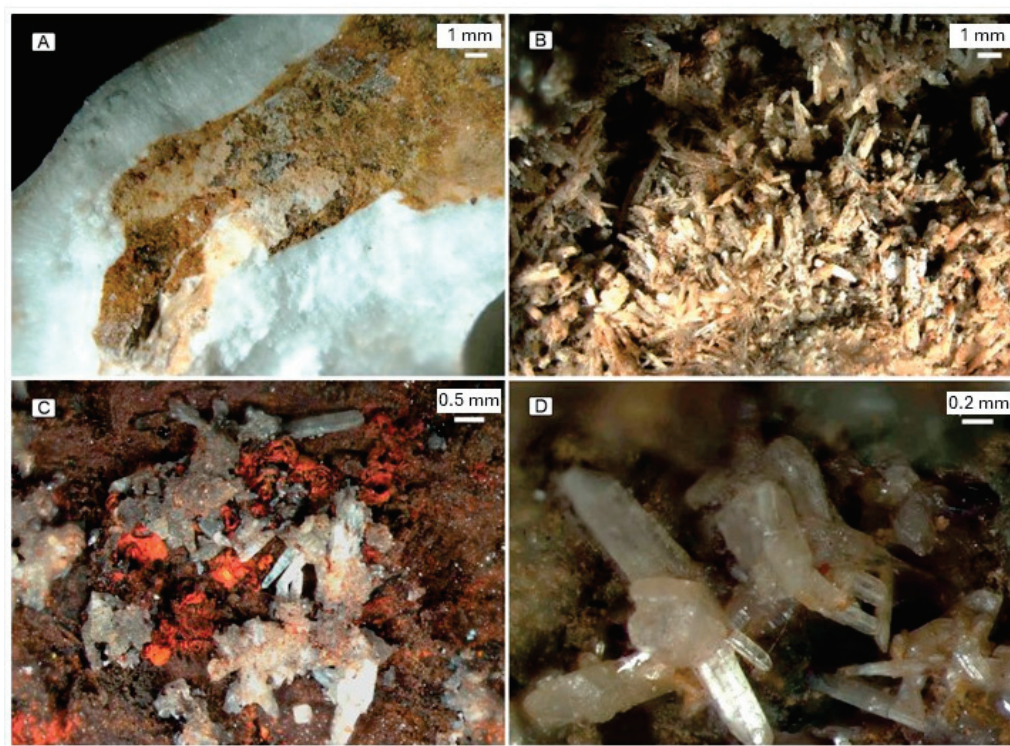


Figure 9. Stereomicroscope images of aragonite (A) from third level (sample PR53); (B) mine waste open pit (PR66–fragment 12); and cerussite from mine waste open pit: (C) sample PR66–fragment 3; (D) detail of sample PR66–fragment 6.

3.1.6. Dolomite, Ankerite and Minrecordite

The minerals dolomite [$\text{CaMg}(\text{CO}_3)_2$], ankerite [$\text{Ca}(\text{Fe}^{2+}, \text{Mg})(\text{CO}_3)_2$] and minrecordite [$\text{CaZn}(\text{CO}_3)_2$] belong to the dolomite group, being difficult to distinguish by XRD. Therefore, the zinc content obtained through pXRF gives a clue for their identification. Figure 10A shows an example of a dolomite sample with a high zinc content (20%), being probably minrecordite, while Figure 10B shows a brownish sample of calcite plus possibly ankerite.

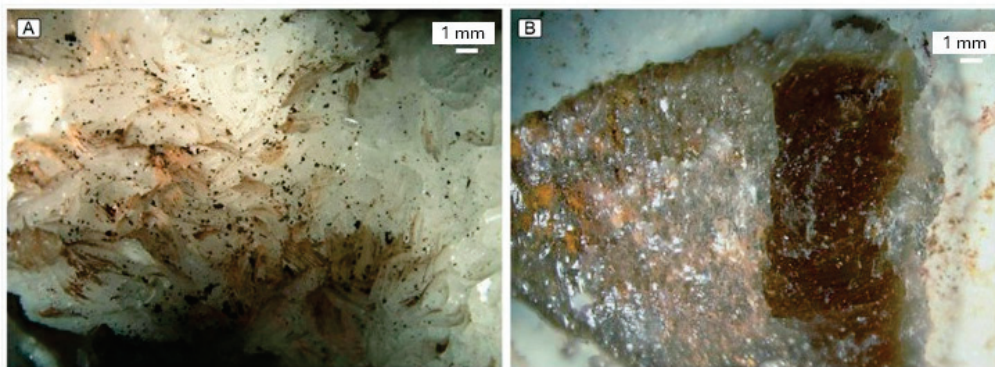


Figure 10. Stereomicroscope images of: (A) dolomite+minrecordite from third level (sample PR9); (B) calcite+ankerite (PR27).

3.1.7. Descloizite, Mottramite and Arsendedcloizite

Descloizite, $\text{PbZn}(\text{VO}_4)(\text{OH})$, mottramite, $\text{PbCu}(\text{VO}_4)(\text{OH})$, and arsendedcloizite, $\text{PbZn}(\text{AsO}_4)(\text{OH})$, are part of the adelite–descloizite group. The general formula of these orthorhombic minerals is $M1^{1+,2+}M2^{2+,3+}[X^{4+,5+,6+}(\text{O}_4,\text{O}_3\text{OH})](\text{OH},\text{O})$ where $M1 = \text{Na}^+, \text{Ca}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{Pb}^{2+}$; $M2 = \text{Mg}^{2+}, \text{Al}^{3+}, \text{Mn}^{2+,3+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$; $X = \text{Si}^{4+}, \text{P}^{5+}, \text{V}^{5+}, \text{As}^{5+}, \text{Mo}^{6+}$ and solid solutions are very common [35]. Descloizite (zinc-rich) is an end member of a series composed of the mineral mottramite (copper-rich) [36]. Both minerals usually contain significant percentages of both elements: $\text{Pb}(\text{Zn}, \text{Cu})(\text{VO}_4)(\text{OH})$; the ZnO content establishes the classification of the mineral: descloizite (if $\text{ZnO} > 18\%$), cuprian descloizite ($18\% > \text{ZnO} > 10\%$), zincian mottramite ($10\% > \text{ZnO} > 2\%$) and mottramite ($\text{ZnO} < 2\%$). The replacement of V by As is possible, with arsendedcloizite being the arsenate analogue of descloizite; Ga and Ge may also be present through incorporation into the crystal structure [37,38].

The first reference to the presence of descloizite in the Preguiça mine and even in Portugal is due to Bensaúde [39]. In that work, a chemical analysis was also published. Several fragments (grey/black, greenish) were identified on the third level (Figure 11A–D); although the XRD spectra usually showed a mixture of minerals, the chemical analysis allowed for a rough estimation of the descloizite composition (disregarding the iron or silica content) in selected fragments. Our results are in accordance with what was published by other authors [38–42] and point out that the majority could be considered descloizite and occasionally cuprian descloizite. Arsendedcloizite is also a possibility, as As_2O_5 content obtained with pXRF is higher than V_2O_5 in some fragments. BSE images of descloizite can be seen in Figure 11E–G, alongside an example of the EDS spectrum collected at various points of the descloizite crystals (Figure 11H).

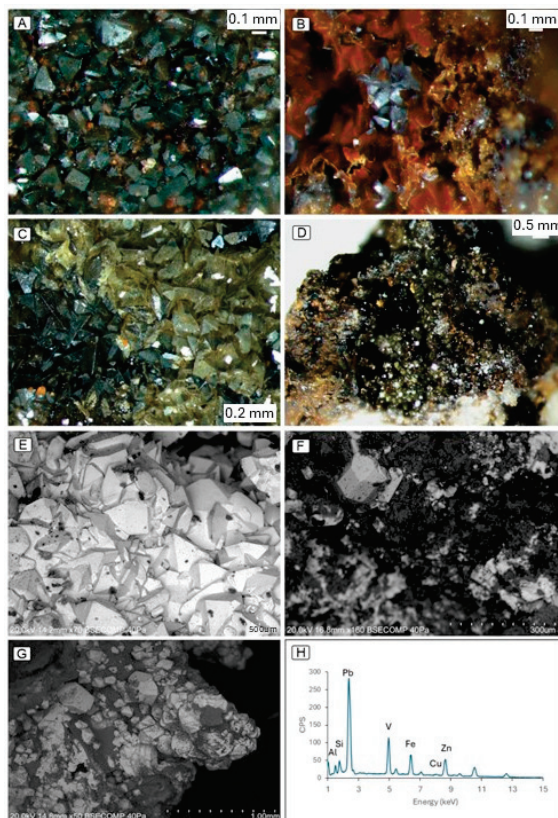


Figure 11. Stereomicroscope images of descloizite: (A) sample PR38–fragment 12; (B) PR59–fragment 2; (C) PR47–fragment 4; (D) PR46–fragment 3; BSE images of descloizite (E–G); example of EDS spectrum collected at various points of the descloizite crystals (H).

3.1.8. Vanadinite and Mimetite

Orange/red vanadinite $[\text{Pb}_5(\text{VO}_4)_3\text{Cl}]$, is another vanadium mineral found in the Preguiça mine (Figure 5C), although sporadically. It is a member of the apatite group (apatite supergroup) and forms a solid solution with mimetite $[\text{Pb}_5(\text{AsO}_4)_3\text{Cl}]$ (Figures 5D and 12A–D), a frequent yellow mineral (globular or in branching groups in sub-parallel position, tapering down to a point) on the first and third levels. Indeed, lead apatite has the general formula $\text{Pb}_5(\text{BO}_4)_3(\text{Cl})$, where $\text{B} = \text{P}^{5+}$ (pyromorphite), As^{5+} (mimetite) and V^{5+} (vanadinite); these three minerals with hexagonal symmetry are the end members of a ternary system and although observed in nature, substitutions of P–As–V are frequent [43–45]. The EDS spectra of the crystals showed the presence of both P and As, but also Ca (Figure 12E,F), leaving the doubt about the presence of mimetite/pyromorphite crystals, phosphohedyphane, or a member of the solid solution.

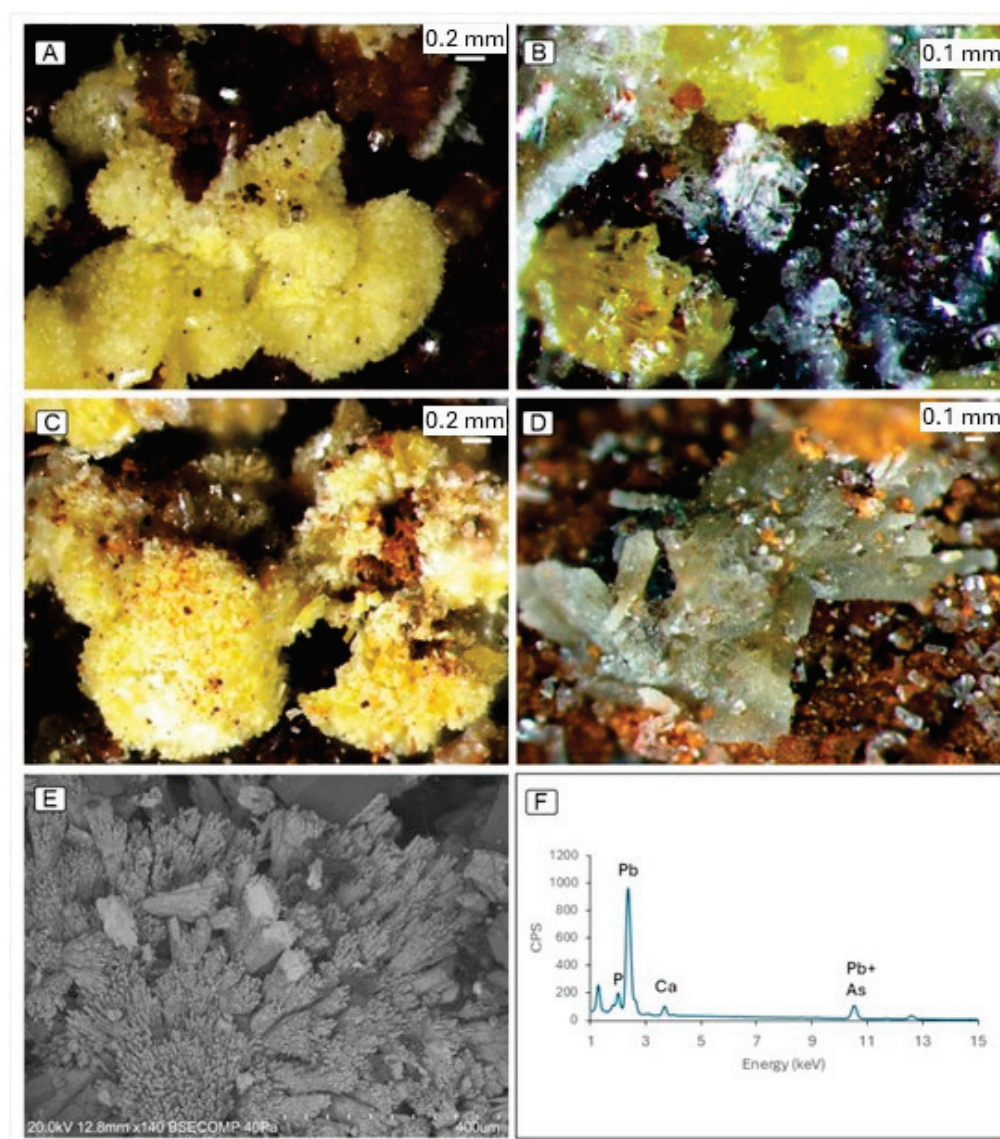


Figure 12. Stereomicroscope images of (A) yellow mimetite+orange vanadinite+ hyaline willemite (PR70–fragment 3); (B) mimetite+willemite (PR68–fragment 1); (C) globules of mimetite (PR68–fragment 2); (D) greenish crystals of mimetite (PR68–fragment 2); (E) BSE image of mimetite; (F) example of EDS spectrum collected at various points of the crystals.

3.1.9. Hedyphane and Phosphohedyphane

Hedyphane $[\text{Ca}_2\text{Pb}_3(\text{AsO}_4)_3\text{Cl}]$ and phosphohedyphane $[\text{Ca}_2\text{Pb}_3(\text{PO}_4)_3\text{Cl}]$ belong to the hedyphane group (apatite supergroup), with the general formula $\text{Ca}_2\text{Pb}_3\text{X}_3(\text{Cl,OH,F})$, where X is AsO_4^{3-} or PO_4^{3-} [46]. Isomorphic substitution of As for P in the phosphohedyphane structure was noticed [47], and solid solution series among the end members of the apatite and hedyphane groups have already been suggested, e.g., [48,49]: pyromorphite–phosphohedyphane and mimetite–hedyphane. Indeed, the yellow crystals found on the fourth level of the Preguiça mine (Figures 13A and 14) seem to be a mineral from mimetite–hedyphane solid solution, while white crystals (Figure 13B,C) look like hedyphane–phosphohedyphane. SEM images and EDS spectra point to phosphohedyphane crystals [50].

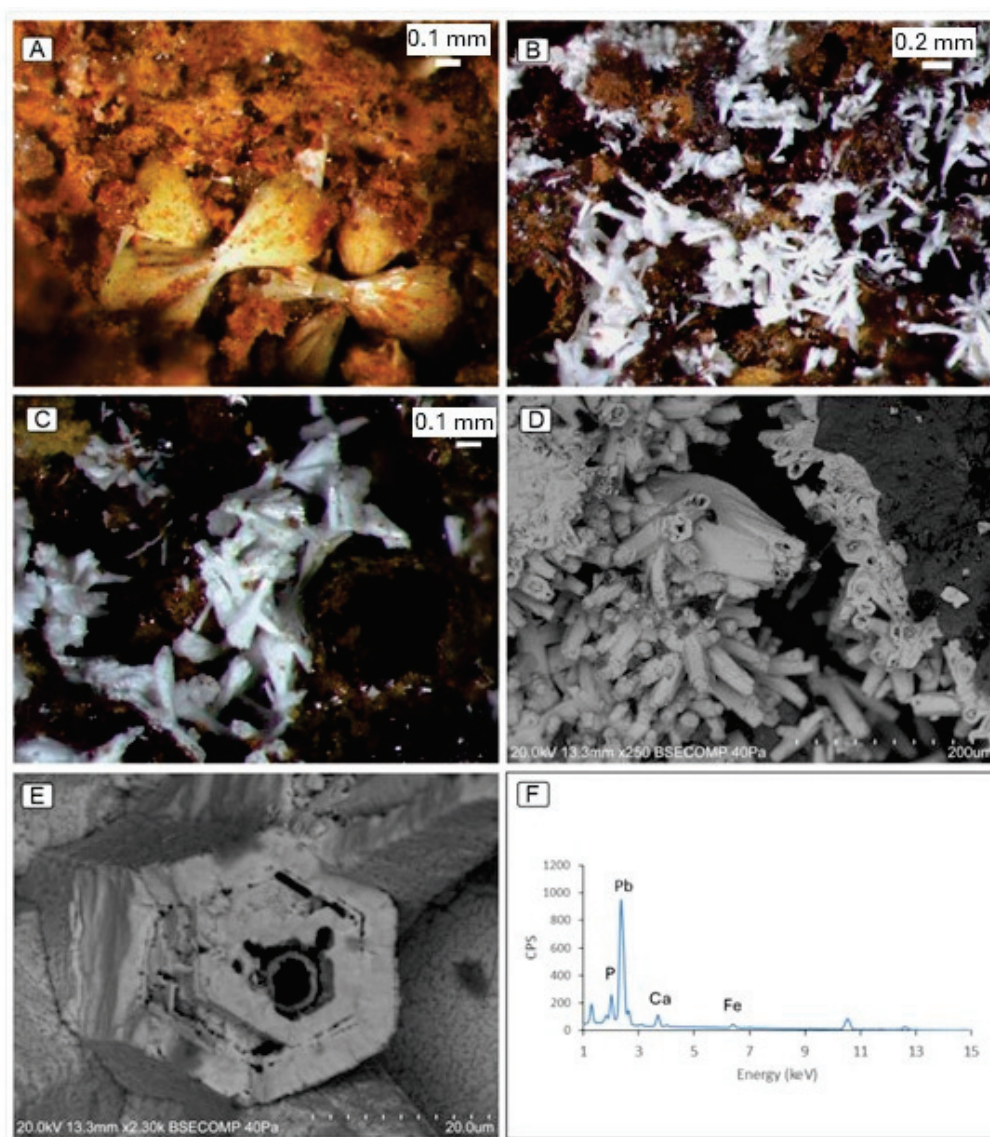


Figure 13. Stereomicroscope images of (A) branching groups in sub-parallel position of mimetite-hedyphane (P4-10-C); (B) phosphohedyphane from the fourth level (P4-10-A); (C) detail of the previous image. BSE images of phosphohedyphane (D,E); (F) example of EDS spectrum collected at various points of the crystals.

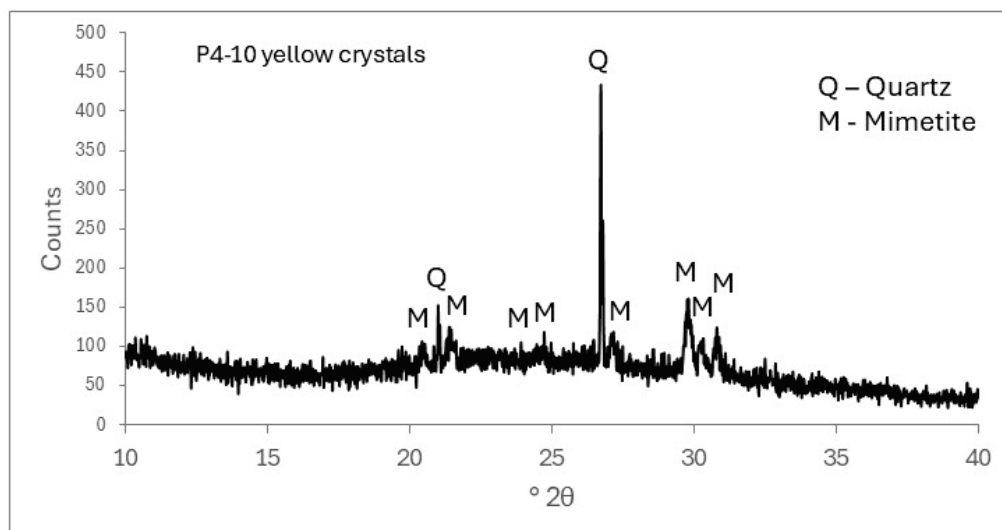


Figure 14. XRD spectrum of sample P4-10 with yellow crystals of mimetite-hedyphane. The mineral phases are simplified using the first letter of their name. COD card numbers: Q—1011172; M—1010997.

3.1.10. Beudantite

Beudantite ($\text{PbFe}_3(\text{AsO}_4)(\text{SO}_4)(\text{OH})_6$) group belongs to the alunite supergroup. The small brownish masses (Figure 15) were only observed on the fourth mine level. This mineral has been considered a stable host for As and Pb in the environment, e.g., [51].

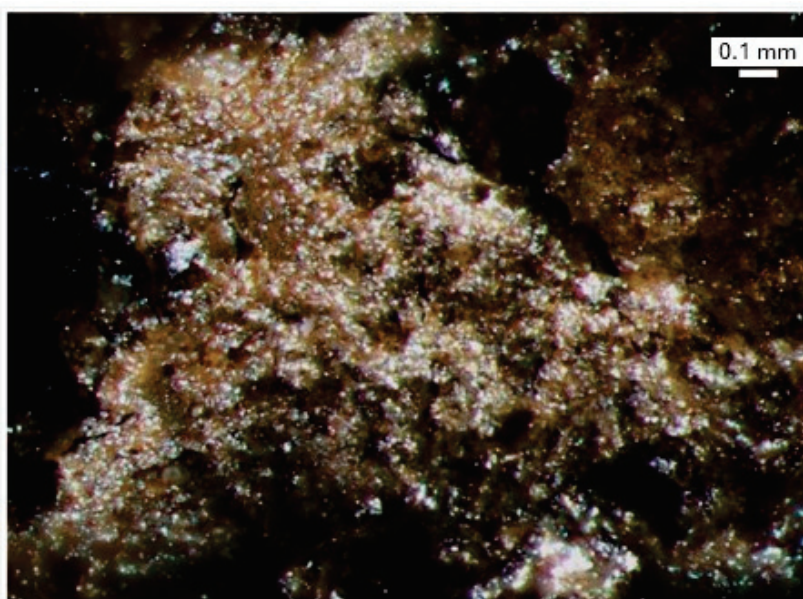


Figure 15. Stereomicroscope image of beudantite from fourth level (sample P4-5).

3.1.11. Willemite

Willemite (Zn_2SiO_4) belongs to the phenakite group and is the most frequent mineral observed on the first level of the mine, also appearing on the third level and in the mine waste open pit, mainly as hyaline, elongated, prismatic crystals (Figure 16A–F). A BSE image of prismatic crystals and the corresponding EDS spectrum are shown in Figure 16G,H. Willemite is a member of the $\text{ZnO-SiO}_2\text{-H}_2\text{O}$ system along with hemimorphite [$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$] and sauconite [$\text{Na}_{0.3}\text{Zn}_3((\text{Si},\text{Al})_4\text{O}_{10})(\text{OH})_2 \cdot 4\text{H}_2\text{O}$] [52]; although hemimorphite has already been described in the Preguiça mine, e.g., [25,29], its presence was not noticed in the present work.

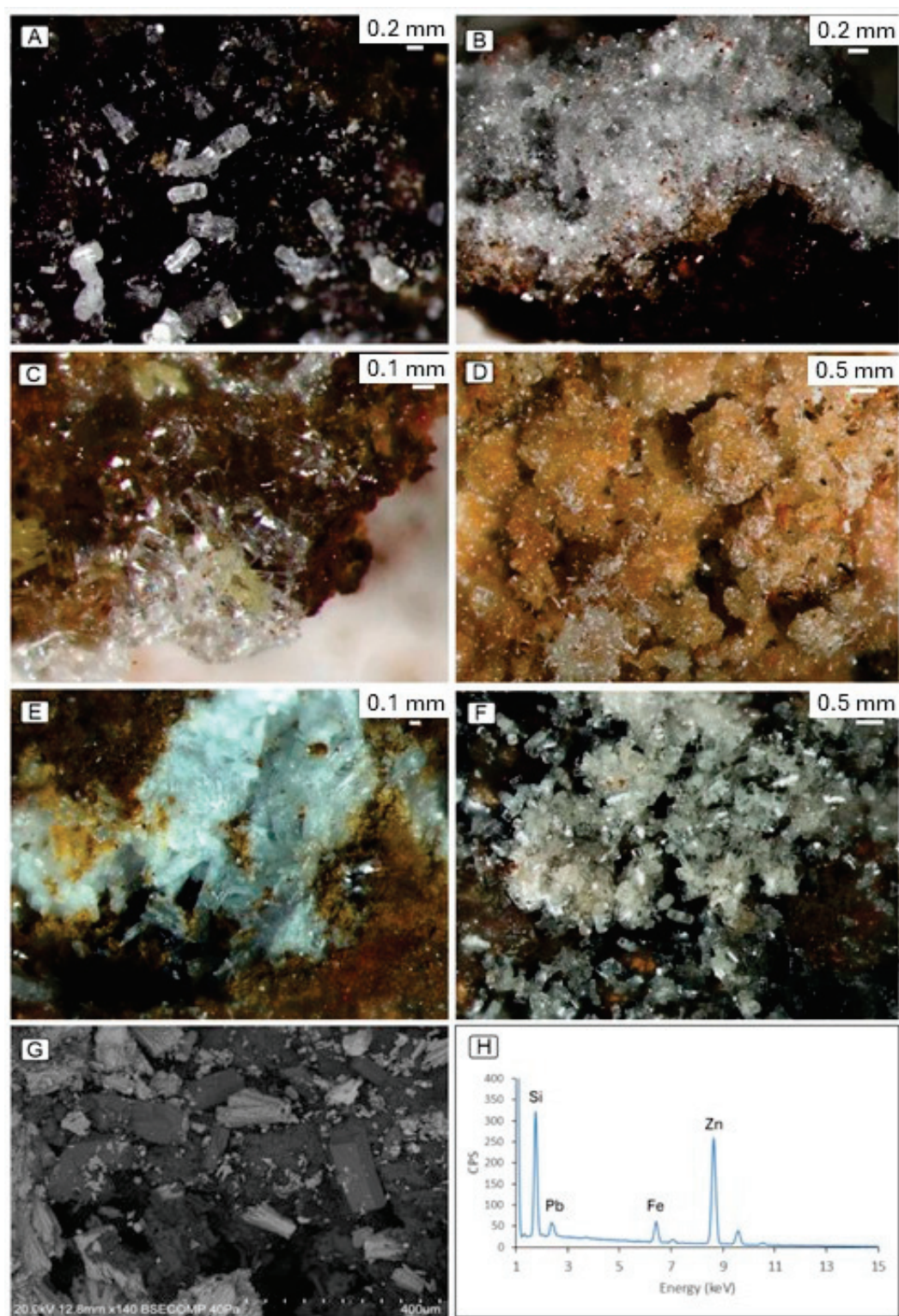


Figure 16. Stereomicroscope images of willemite from first level: (A) PR69–B; (B) PR70–fragment 6G; (C) PR70–fragment 6H; (D) PR69–A. (E) Willemite from third level (PR43–fragment 3A); (F) willemite from mine waste open pit (PR66–fragment 3B). BSE image of prismatic crystals of willemite (G); example of EDS spectrum (H).

3.1.12. Fraipontite

Fraipontite $[(\text{Zn}, \text{Al})_3(\text{Si}, \text{Al})_2\text{O}_5)(\text{OH})_4]$, a zinc berthierine $[(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Al})_3(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4]$, is a rare mineral [53], belonging to the kaolinite–serpentine group (serpentine subgroup). Fe, Cu, Mg, Ca and K may be present in traces. Massive silky whitish and greenish fraipontite

was identified (Figures 17 and 18) on the third level of the Preguiça mine. The approximate chemical compositions of the two samples, in which only fraipontite was identified by XRD, are presented in Table 3. The greenish colour observed could be due to a copper-bearing variety of fraipontite [54]. SEM data (Figure 17E–H) confirm this idea, as the spectrum of the greenish sample, in comparison with the whitish one, displays Cu and Fe peaks. It is also noteworthy that Zn level is higher in the greenish sample and Al is lower. The presence of vestigial Ca is noticed in both samples. These results are in accordance with data from other authors, e.g., [53,54]. Indeed, the presence of fraipontite/sauconite in the Preguiça mine has already been mentioned as a new interstratified clay mineral with fraipontite contents of about 70 to 90% [55].

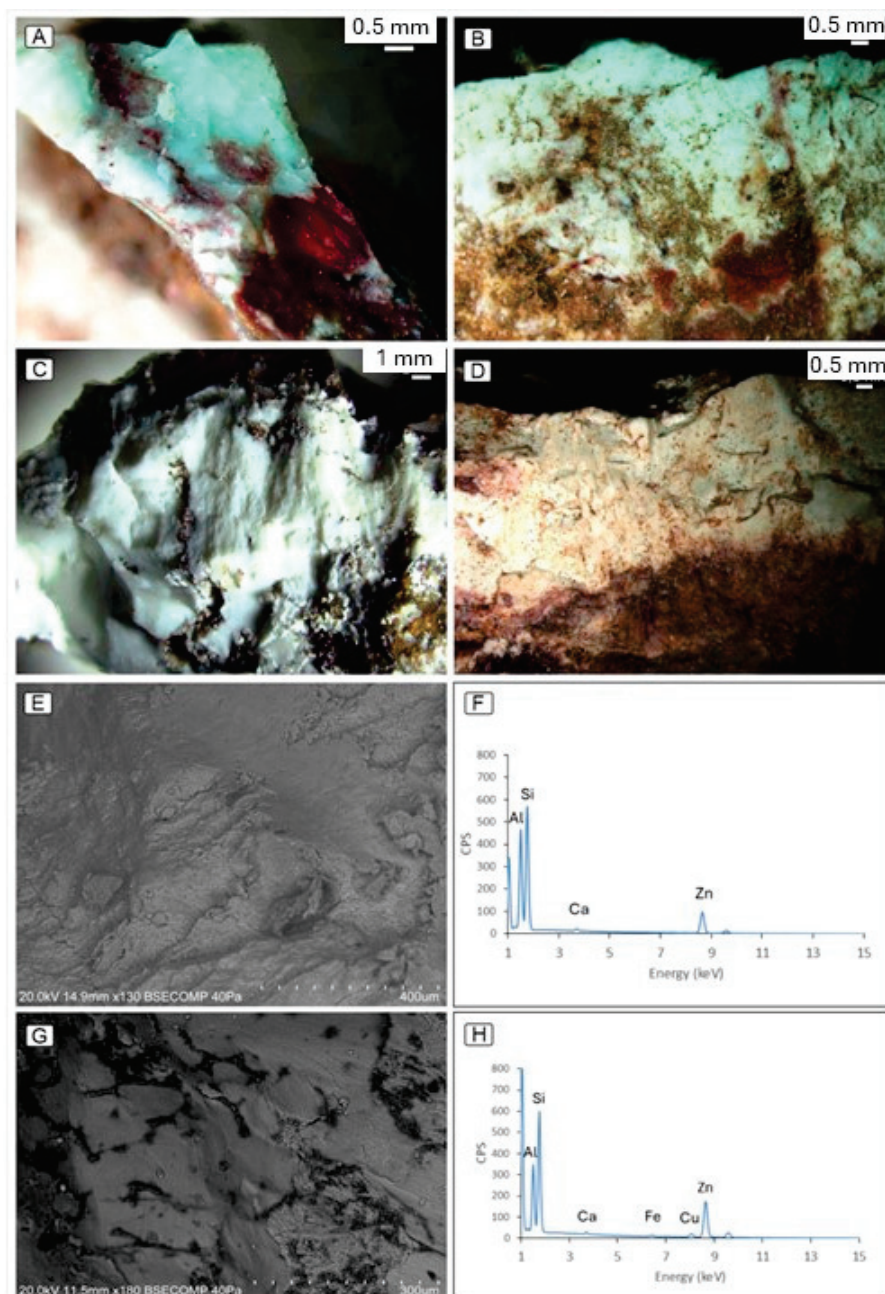


Figure 17. Stereomicroscope images of fraipontite from third level: (A) sample PR24A; (B) PR24B; (C) PR41A; (D) PR24C. BSE image and EDS spectrum of massive fraipontite: whitish (E,F); greenish (G,H).

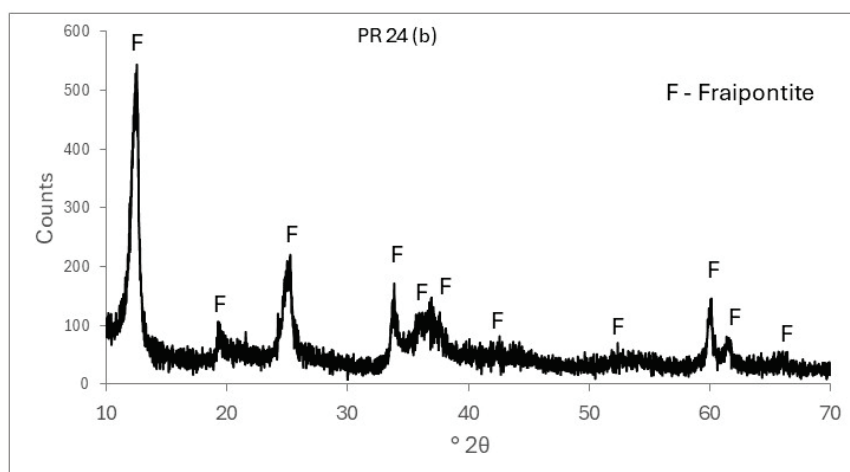


Figure 18. XRD spectrum of a greenish massive sample from the third level (PR24B). PDF card number: 00-034-0782.

Table 3. Approximate chemical composition (% major elements) obtained by pXRF; - means not detected.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	ZnO	CuO	Total
PR24B (greenish)	15	4	6	62	4	91
PR41A (whitish)	26	11	3	51	-	91

3.1.13. Gypsum

Gypsum crystals ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), one of the most common sulphate minerals, were observed on the third and fourth levels (Figure 19), associated with calcite, smithsonite, jarosite or epsomite.

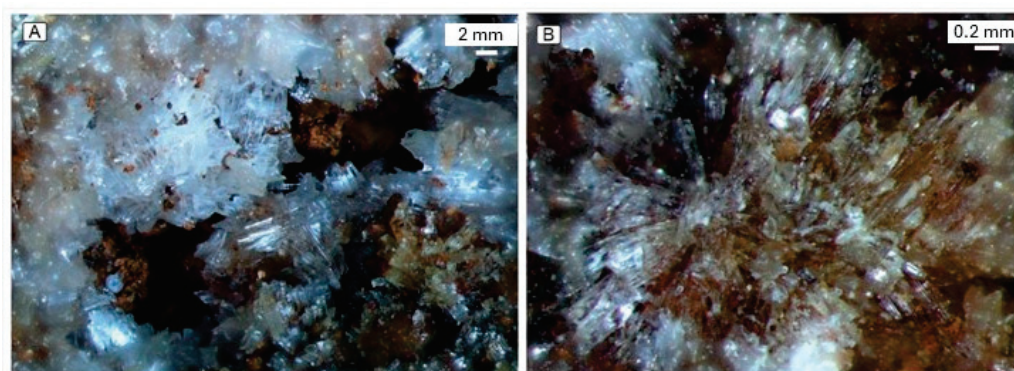


Figure 19. Stereomicroscope images of gypsum from fourth level: (A) sample P4-16A; (B) P4-16C.

3.2. Geochemical Characterisation

Chemical analyses were performed on the bulk samples as collected (see Supplementary Materials S1), allowing us to determine the major elemental concentrations and relate them to the observed mineralogy. Indeed, pXRF equipment is a useful tool for a quick and inexpensive overview of a wide range of elements, but a previous check of the precision and accuracy of the equipment must be done. The comparison between concentrations obtained using pXRF for various international reference standards and their published chemical contents allow us to evaluate analytical accuracy. Details of the applied methodology are presented in [56,57]. Additionally, the XRF spectra of some samples were visualised to really verify the presence of elements in minor or vestigial contents (examples in S1).

Considering that the obtained concentrations are only approximate, the major values obtained in decreasing order are Fe (63%), Ca (61%), Zn (59%), Pb (41%), Si (41%), S (36%),

Mg (16%), Cu (15%), Al (12%), V (8%), Mn (3%), As (3%), Sb (2%), K (1%), P (1%), Cr (0.9%), Cd (0.3%), Ba (0.3%), Ti (0.2%), Co (0.1%), Ta (0.1%), Sr (0.07%), Rb (0.06%), Zr (0.06%), W (0.06%), Ag (0.05%), Hg (0.05%), Bi (0.04%), Sn (0.03%), Ga (0.03%) and Au (0.03%). The very low values of Tl, Ni, Mo, Y, Nb, Se, Th, U and REE were not considered. From previous studies [56], some contents are obtained by excess, namely, Ca, Zn, Pb, S, Cu, Mn, As, Sb, K, Sr, Rb, W, Ni, Mo and Se, and others, namely, Fe, Mg, Al, Ba and Ga, by default; the Si and Ti values are real. The lowest reliability measurements will be for V, P, Cr, Cd, Co, Ta, Zr, Ag, Hg, Bi, Sn, Au, Tl, U and REE.

These results are, in general, in accordance with the mineral phases identified. The main Zn- and Pb-bearing mineral phases present in the samples included smithsonite (ZnCO_3), willemite (Zn_2SiO_4), fraipontite $[(\text{Zn},\text{Al})_3((\text{Si},\text{Al})_2\text{O}_5)(\text{OH})_4]$, minrecordite $[\text{CaZn}(\text{CO}_3)_2]$, descloizite $[\text{PbZn}(\text{VO}_4)(\text{OH})]$, plattnerite (PbO_2), cerussite (PbCO_3), mimetite $[\text{Pb}_5(\text{AsO}_4)_3\text{Cl}]$ and hedyphane $[\text{Ca}_2\text{Pb}_3(\text{AsO}_4)_3\text{Cl}]$, with the presence of descloizite, willemite and mimetite being more frequent among these supergene minerals [29]. The highest content obtained for Zn and Pb in the studied samples is related with the presence of smithsonite and descloizite respectively.

In the lead vanadate minerals, descloizite $[\text{PbZn}(\text{VO}_4)(\text{OH})]$, mottramite $[\text{PbCu}(\text{VO}_4)(\text{OH})]$ and vanadinite $[\text{Pb}_5(\text{VO}_4)_3\text{Cl}]$, V is in the oxidation state +5, forming (VO_4) tetrahedra [43,58,59], and according to the last authors, V may be critical for the transition to electric cars, as a component within Li-ion batteries $[\text{Li}_3\text{V}_2(\text{PO}_4)_3]$. These minerals have a high density, they are non-conductors and non-magnetic, and they have weak to negative magnetic susceptibility [60]. As reported, the Preguiça mine vanadate minerals precipitate from V-bearing solutions, e.g., [25], with their presence also assigned in southern Africa (Namibia, Zambia and Angola), associated with low-temperature, non-sulphide mineralisation [61]. Vanadium (V) is included in the most recent list of critical and strategic raw materials (CRM and SRM) [2]. Given the growing demand for these materials due to their wide range of industrial applications, the concentrations obtained for the Preguiça mine samples (S1), which have to be confirmed by other analytical methods, highlight the potential value of a more detailed future investigation. Vanadium (classified as a CRM) is used primarily in high-strength alloys for applications in aeronautics, space technology, and nuclear reactors, and it also serves as an important chemical catalyst. Fe-oxy-hydroxides (e.g., goethite or hematite) have the capability to host a wide range of elements, depending on the chemistry of the primary deposit and on the properties of the fluids [[62] and references herein]; these authors report that FeO/OH associated with supergene non-sulphide mineralisation is commonly enriched in Zn and Pb with traces of As, Cd, Co, Cu, Ga, Ge, Hg, In, Mo, Ni, Sb, Sc and V. Antimony, for example, is recognised as a valuable indicator in geochemical prospecting surveys [63,64]. It occurs in different oxidation states in nature (−3, 0, +3 and +5) and can substitute for Bi, Pb, As, Cu, Ag and S in various minerals [65]. Sb is considered a CRM and is commonly used as flame retardant, in defence applications, and in lead–acid batteries [2].

Mimetite, $[\text{Pb}_5(\text{AsO}_4)_3\text{Cl}]$, according to the results obtained in this work, is the main source for As, a CRM with applications in semiconductors and alloys. On the other hand, Sr seems to be more related with aragonite than calcite in substitution of Ca. However, dolomite is the main source of Mg, an SRM used, for example, in lightweight alloys for automotive, electronics, packaging or in construction and as a desulphurization agent in steelmaking.

4. Conclusions

This study provides new insights into the mineralogical and geochemical characterisation of samples from the old Preguiça mine (Beja, Portugal), highlighting the phase distribution associated with the historical Fe–Zn–Pb deposit. The various mineral phases identified on the different four mine levels and in waste materials demonstrate the miner-

alogical diversity generated by supergene alteration processes acting on primary sulphide mineralisation hosted in dolomitic limestones.

Although remnants of primary sulphides (i.e., pyrite, marcasite, chalcopyrite, sphalerite and galena) are scarce, the mine is dominated by a wide range of secondary oxides (Si, Mn, Fe and Pb), carbonates (Mg, Ca, Fe, Zn and Pb), arsenates (Ca, Fe, Zn, and Pb), vanadates (Cu, Zn, and Pb), silicates (Na, Mg, Al, K, Ca, Fe, and Zn), phosphates (Ca and Pb) and sulphates or hydroxysulphates (Mg, K, Ca, Fe, Zn and Pb). The following mineral phases can be emphasised: goethite, hematite, calcite, dolomite, descloizite (vanadate of lead and zinc), willemite (zinc silicate), mimetite (lead arsenate), cerussite (lead carbonate) and smithsonite (zinc carbonate); these denote the complexity of the processes involved in their formation and the capacity to carrier/concentrate possibly valuable elements. Two less commonly reported minerals, fraipontite (a Zn-rich clay mineral) and massicot (PbO), whose presence has not previously been described at the Preguiça mine, were also identified, contributing to a more comprehensive understanding of the mine's mineralogical diversity.

It is also worth noting that pXRF proved to be a reliable, cost-effective tool for a rapid evaluation of many elements of interest. Bulk geochemical analyses generally reflect the observed mineralogy, with high concentrations of Fe, Ca, Zn, and Pb corresponding to the presence of iron oxides (hematite and goethite), carbonates (calcite and dolomite), and Zn- and Pb-bearing supergene minerals, mainly descloizite, willemite, and mimetite.

The results also highlight the presence of several critical and strategic raw materials, particularly V and As, which are associated with vanadate and arsenate minerals such as descloizite and mimetite. The occurrence of Sb, Sr, and other potentially valuable elements within secondary minerals suggests that the supergene alteration zone of the Preguiça deposit may represent a promising target for further detailed geochemical and mineralogical investigations. The sustainable recovery of such elements also contributes to the mitigation of environmental risks associated with the presence and mobility of Pb-, Zn-, and As-bearing secondary minerals, highlighting the importance of future research to better understand contaminant dispersion and geochemical stability, particularly in the case of the waste pile. Indeed, this Preguiça mine study demonstrates the relevance of revisiting other abandoned mining areas within a sustainable and strategic raw material framework.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min16040348/s1>, S1: Chemical analysis and pXRF spectra.

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Article

Geology, Mineralogy, and Age of Li-Bearing Pegmatites: Case Study of Alday Area (Eastern Kazakhstan)

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Abstract

This study investigates the geological, mineralogical, and geochemical features of the Alday ore occurrence (Central Kalba, East Kazakhstan) and aims to identify indicators of rare-metal mineralization, with lithium considered to be one of its principal components. In this study, the structural–stratigraphic position of the occurrence is refined; three series of albite–spodumene pegmatites are identified; the compositions of the ore-bearing schists and the granitoids of the Kunush and Kalba complexes are compared; and the role of metasomatic alteration in the concentration of Li, Ta, Nb, Be, and Sn is established. The plagiogranites and dikes of the Kunush complex are characterized by Li anomalies (up to 306 g/t), Ta (up to 64 g/t), and a fractionated REE spectrum (La/Yb up to 108). In addition, the following predictive criteria are formulated: the presence of tectonically disrupted dikes in the Kunush complex with $\text{Na}_2\text{O}/\text{K}_2\text{O} > 4$, the presence of albite and muscovite alteration zones, and the presence of ladder-type spodumene-bearing pegmatites controlled by northwest-trending faults. The $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite age of the Alday pegmatites (~292 Ma) aligns with the age range of the Kalba granite complex. Based on the main principles of rare-metal pegmatite generation, it is determined that the Tochka pegmatites were formed during the fluid–magmatic fractionation of magma in large granitic reservoirs of the Kalba complex. The Karagoin–Saryozek zone—located between several large granite massifs of the Kalba complex, where host rocks function as a roof—may be promising for investigating rare-metal pegmatite mineralization.

Keywords: lithium-bearing pegmatites; rare metals; Karagoin–Saryozek zone; predictive criteria; East Kazakhstan

1. Introduction

The Central Asian Orogenic Belt (Altaids) contains extensive granitoid batholiths formed during the Phanerozoic [1–9]. The magmatism that produced these granites is associated with mineralization of various metals, such as Rb, Be, Mo, and W, as well as the more economically significant Li, Cs, Ta, Nb, and Sn [10–13]. Notably, rare-metal pegmatites—particularly those of the lithium–cesium–tantalum (LCT) family—are commonly found to have a spatial and genetic connection to large granitoid intrusions. These pegmatites typically form fields or swarms of veins located along the margins or in the roof zones of the parent plutons.

In addition to lithium and other rare metals *sensu stricto* (Li, Ta, Nb, Sn), the evolution of rare-metal pegmatite systems is commonly recorded by accessory mineral assemblages enriched in Ti, Th, and REE, such as monazite, xenotime, zircon, ilmenite, and rutile. Although these minerals are not ore phases themselves, they represent sensitive indicators of magmatic differentiation, fluid involvement, and redistribution of incompatible elements during the late stages of granitoid evolution. Therefore, the study of Ti–Th–REE-bearing accessory minerals provides important constraints on the petrogenetic type of magmatism and the conditions favorable for rare-metal mineralization.

East Kazakhstan, situated along a Late Paleozoic collisional suture between the Siberian and Kazakhstan cratons, hosts abundant mineralized rare-metal pegmatite of the LCT family, associated with granitic magmatism [14–17]. The most intensive magmatic activity occurred during the Early Permian, forming large batholiths such as those found in Kalba and Zharma. This large-scale magmatism took place in a post-collisional extensional setting, likely driven by heat from the Tarim plume. The region, characterized by multiple juxtaposed igneous complexes, contains vast amounts of base, noble, and rare metals [15,18–20]. Rare-metal deposits are primarily concentrated within the Kalba–Naryn belt, bounded by the West Kalba and Irtysh shear zones (Figure 1). Significant pegmatite, albitite–greisen, greisen–quartz–vein, and hydrothermal mineralization is found within the Early Permian granitoids of the Kalba batholith. This includes economic spodumene pegmatites in the Asubulak ore district, which contain Ta, Nb, Be, Li, Cs, and Sn and are located along the margins of the Kalba granite complex [13,21,22].

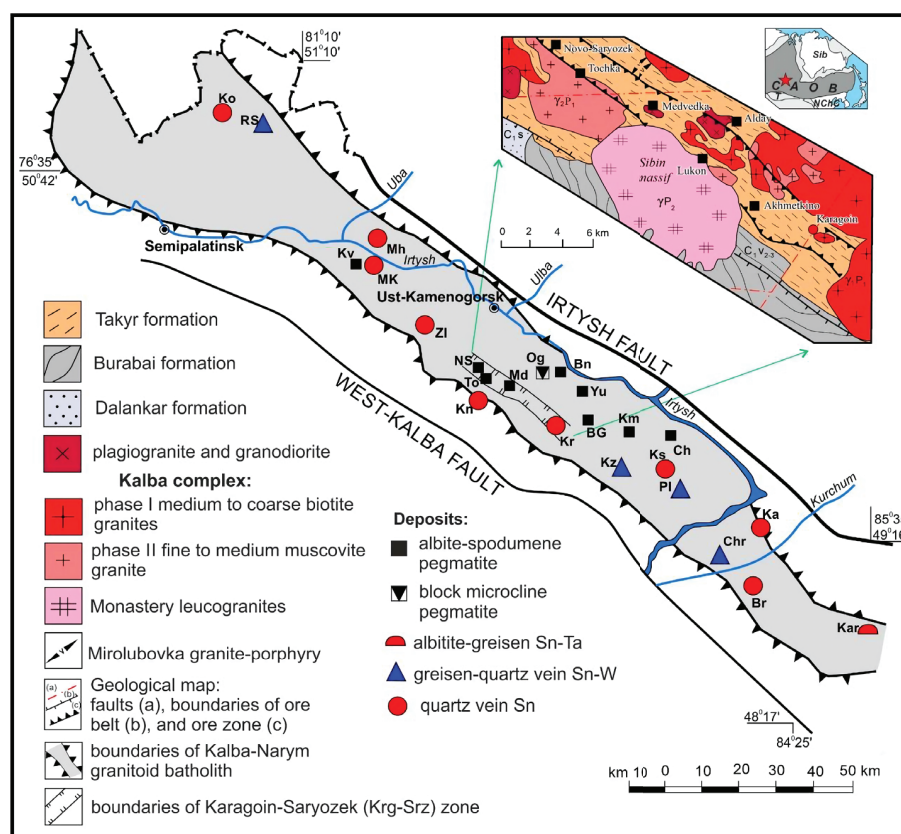


Figure 1. Location map of rare-metal deposits and occurrences in the Kalba–Naryn belt [14]. Abbreviations stand for names of mineral deposits: Ko—Korosteli; RS—Rzhavaya Sopka; Mh—Mokhnatukha; MK—Malaya Kaında; Kv—Kvartz; Zl—Zelenoye; Kn—Kanaika; NS—Novo-Saryozek; Md—Medvedka; To—Tochka; Kr—Karagoin; Og—Ognevka; Bn—Bakennoye; Yu—Yubileinoe; BG—Belaya Gora; Kz—Kozlovskoye; Km—Komarovskoye; Ks—Komsomolskoye; Ch—Chebuntay; Pl—Palatsy; Chr—Cherdoyak; Ka—Kasatka; Br—Burabay; Kar—Karasu. Sibiny pluton.

Within the Greater Altai structure, the Kalba–Narym zone is bounded by the Kalba–Narym and Terektinsky deep faults and is linearly elongated in the northwest direction for 500 km, with an average width of 35–40 km.

Several intrusive complexes have been identified in the structure of the Kalba–Narym granitoid belt.

The Kunush Complex (C_3) comprises small hypabyssal intrusions of plagiogranites and granodiorites, as well as dikes of granodiorite porphyries, plagiogranite porphyries, granite porphyries, and quartz porphyries [23]. They were formed during the Hercynian cycle in a collisional geodynamic setting, associated with strike-slip deformation and the suturing of the Kazakh and Siberian lithospheric plates, giving rise to fault-related intrusive-dike belts with a northwest orientation. Magmatic sources originated in the lower crust and possibly in the upper mantle [24,25].

In the Kalba–Narym zone, the small intrusions and dikes of the Kunush Complex (C_3) are truncated and metamorphosed by the Permian granites of the Kalba Complex, and in some cases undergo contact–metasomatic alterations (graphitization, greisenization, silicification, etc.) accompanied by the superimposed formation of ore components (Ta, Nb, Sn, W, etc.) [26]. Pegmatite and greisen–quartz-vein occurrences with superimposed rare-metal mineralization occur as dike- and vein-like bodies developed primarily within the contact zones of the Permian granites of the Kalba Complex (Medvedka, Tochka, Novo-Saryozek, Cherdoyak, etc.) [13,21,27–29].

The Kalba Complex (P_1) is represented by large granite massifs of the Kalba–Narym pluton (Priirtyshsky, Belogorsky, Mirolyubovsky, Kaındinsky, etc.) [23,30]. As a result of its formation conditions and material composition, it is subdivided into two intrusive phases of similar age, each accompanied by its own vein rocks, metasomatic formations, and rare-metal deposits [23,31].

In this study, for the first time for rare-metal objects of the Kalba–Narym belt, $^{40}\text{Ar}/^{39}\text{Ar}$ dating was performed on muscovite extracted from spodumene pegmatites of the Chudskaya vein at the Tochka deposit [13] and from the Alday area. The results (ages of 293–290 Ma) made it possible to refine the timing of spodumene pegmatite formation and to clarify the relationship of muscovite age with the granitoid complexes of the Kalba series [32–34]. These findings complement the geological–geochemical and mineralogical–petrographic criteria established in this study and provide a basis for constructing a geochronological model of the evolution of rare-metal systems in East Kazakhstan.

2. Geological Background

The Kalba–Narym structural–metallogenic zone represents a large metallogenic belt characterized by rare-metal-bearing granites of the Kalba Complex and a wide range of rare-metal, tin, and tungsten ore formations. Within this zone, several industrial and prospective ore districts and nodes have been identified, including rare-metal pegmatites of tantalum–niobium, beryllium, and lithium specialization, as well as quartz-vein and quartz–greisen formations of Sn–W affinity. The formation of rare-metal mineralization in the Kalba–Narym zone is closely related to granitoids of the Kalba Complex and is structurally controlled by systems of deep-seated and sublatitudinal faults that govern the distribution of ore nodes and pegmatite fields.

To date, studies on the Kalba–Narym zone have primarily focused on large and industrially significant deposits, such as Bakennoye, Belaya Gora, Yubileynoye, and Verkhne-Baimurzin, where pegmatite-body morphology, mineral composition, and ore specialization have been studied in detail. For these deposits, it has been established that albite and albite–spodumene pegmatites play a dominant role in the concentration of tantalum, niobium, beryllium, tin, and lithium, and structural control has proven important, includ-

ing that of sublatitudinal faults and dikes of the Kunush Complex. In addition, smaller occurrences confined to the Karagoin–Saryozek ore node, including the Alday occurrence, are comparatively under-studied, and available data on their geological structure, mineral composition, and rare-metal mineralization potential are fragmentary [21,23,29,35].

The Alday area is located in the Ulan District of East Kazakhstan Region, near the village of Besterek. It lies within the Central Kalba ore district, inside the Karagoin–Saryozek zone, and is represented by lithium-bearing albite–spodumene pegmatites. The Alday ore occurrence has been the subject of several previous geological investigations. In the present study, the authors investigate the geological structure and material composition of the ore-bearing rocks and rare-metal pegmatite veins to clarify whether the occurrence contains lithium raw materials.

The Alday area is situated on the northeastern flank of the Karagoin–Saryozek ore zone, which also includes deposits of lithium-bearing albite–spodumene pegmatites such as Novo-Saryozek, Tochka, Lukon, and Akhmetkino [35,36].

From a geological–structural perspective, the ore-controlling feature comprises a system of latitudinal (east–west-trending) faults along which the Tochka and Medvedka deposits and the Alday occurrence are sequentially arranged (Figure 2).

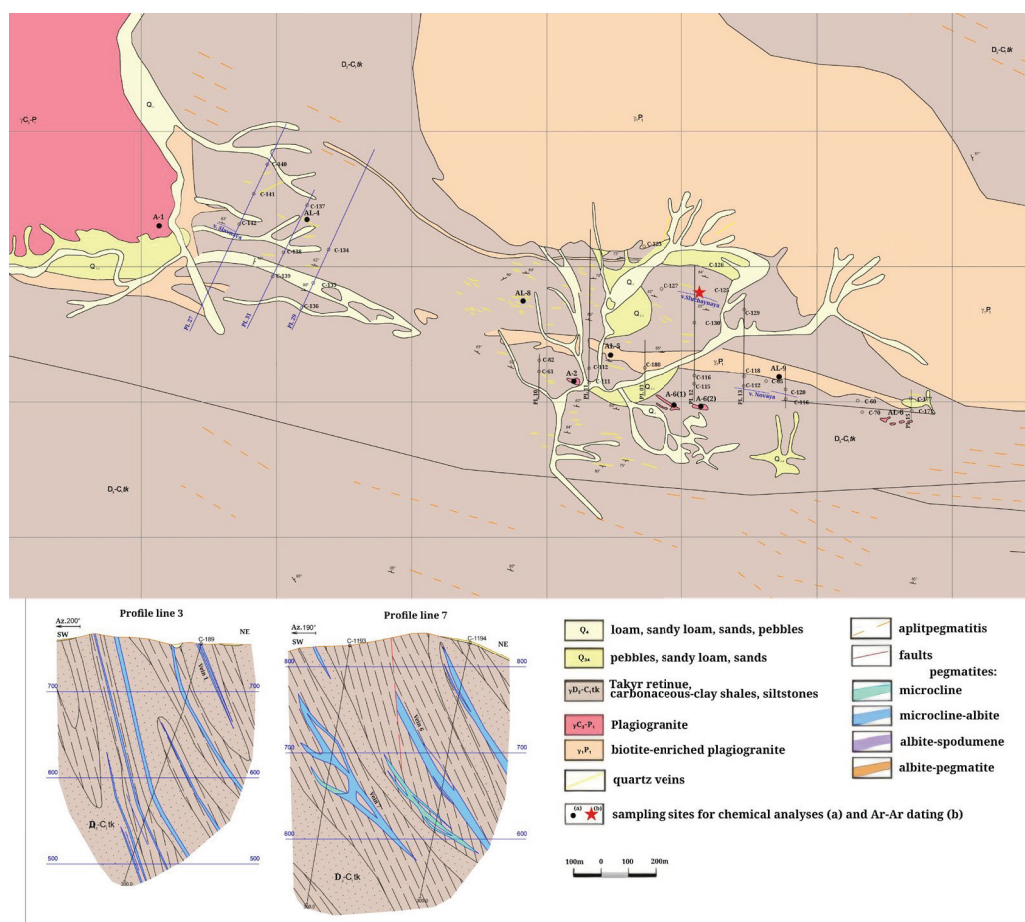


Figure 2. Geological map and cross-sections of the Alday area [35].

The occurrence is characterized by Takyr Formation sedimentary rocks, which are well developed in the area [23,36].

The Takyr Formation consists of packages of thin, rhythmically interbedded carbonaceous–argillaceous siltstones and fine-grained sandstones. In certain areas, small isoclinal folds of northwest strike are observed, with rocks dipping northeast at angles of 80–850°. Over large

areas, they are overlain by a cover of unconsolidated deposits. The intrusive bodies are represented by two complexes: (1) the Kunush Complex (C_3) and (2) the Kalba Complex (P_1).

The ore-bearing schists in fault zones are characterized by increased fracturing, with numerous pegmatite and quartz veins localized within them (Figure 3).

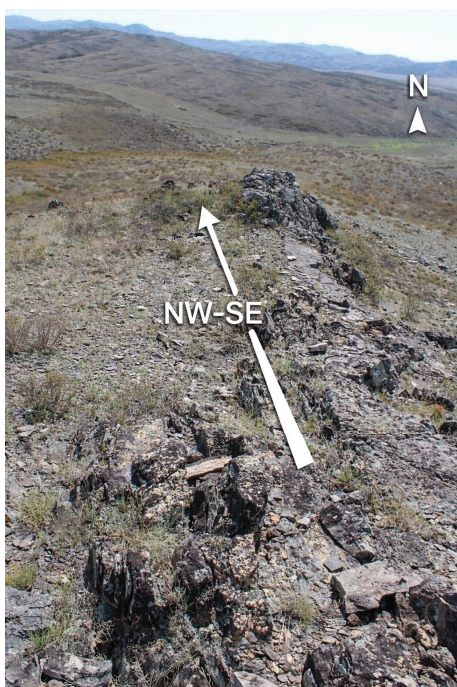


Figure 3. Exposure characteristics of the Alday area. Steeply dipping schists of the Takyr Formation that are exposed in the foreground host light-colored pegmatite veinlets striking NW-SE (north is indicated).

In the exocontact of the granite massif, the schists have undergone hornfelsing and silicification, with andalusite-bearing hornfels developed in the carbonaceous siltstones. At the contacts with pegmatite veins, greisenized and silicified varieties of hornfels are present. Externally, these are dark-gray-to-black rocks of quartz–feldspar–muscovite composition, sometimes containing andalusite and tourmaline (Figure 4).

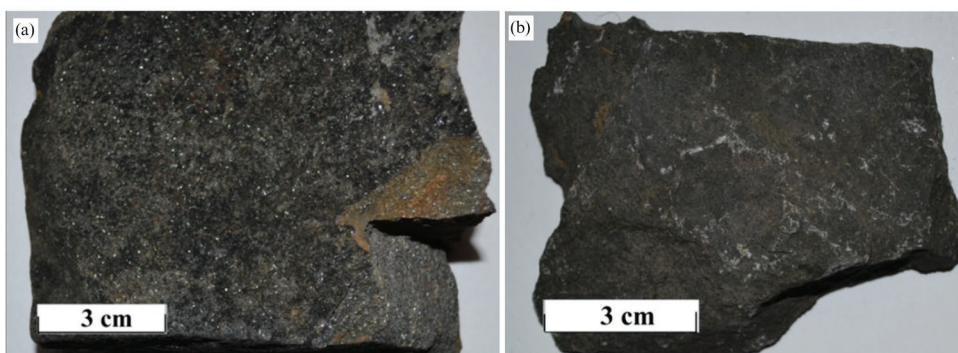


Figure 4. Typical hornfels samples from the Alday occurrence: (a) spotted hornfels with muscovite alteration along the grain boundaries and a protruding edge; (b) fine-grained hornfels with flaky muscovite aggregates and quartz veinlets crossing the surface.

3. Materials and Methods

This study included field observations and an analysis of published data. The author performed observations of the geological sections of the Alday area; three series of

pegmatite veins were documented (northern, southern, and western), and their thickness (0.3–6.2 m), length (up to 150 m), and dip angle (82° to the NE) were recorded.

In addition, samples of ore-bearing schists, granitoids of the Kunush and Kalba complexes, pegmatites, and metasomatic rocks were collected.

The research was carried out at the VERITAS Center of Excellence of D. Serikbayev East Kazakhstan Technical University (Ust-Kamenogorsk, Kazakhstan). Rock and mineral compositions were determined using inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500cx instrument (Agilent Technologies, Santa Clara, CA, USA), [37] and via electron probe microanalysis (EPMA) under standard conditions using a Cameca MS-46 system (Cameca, Gennevilliers, France), which enabled precise measurement of seventy-three elements, including Au, Ag, Pt, Cd, In, Ir, Y, REE, and U. To analyze micrometer-scale inclusions of metallic and vein minerals, scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM-EDS) were performed using a Jeol-100C microscope (JEOL, Tokyo, Japan) equipped with a Kevex-Ray detector (Kevex Corporation, Foster City, CA, USA) and a Jeol ISM-6390 LV microscope (JEOL, Tokyo, Japan) fitted with an Oxford INCA Energy system [38].

Isotope analysis was carried out at the Isotope-Analytical Geochemistry Laboratory of the Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences. The $^{40}\text{Ar}/^{39}\text{Ar}$ dating of muscovite was carried out using the stepwise heating technique [39,40]. The concentrations of petrogenic elements were determined by X-ray fluorescence analysis (XRF) using an SRM-25 spectrometer (Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia).

The accessory-mineral paragenesis of granites and pegmatites was studied using scanning electron microscopy on double-polished thin sections, and analyses were conducted in both high- and low-vacuum modes. Secondary and back-scattered electron images were obtained with a spatial resolution of 2–10 nm. Phase identification was performed using EDS on a MIRA 3 LMU (TESCAN ORSAY Holding, Brno, Czech Republic) scanning electron microscope equipped with INCA Energy 450+ / Aztec Energy XMax 50+ and INCA Wave 500 (Oxford Instruments Nanoanalysis) microanalysis systems.

Monomineralic fractions for isotope dating were separated using standard magnetic and density separation techniques from crushed material, with fraction purity monitored under a LEICA EZ4 binocular microscope (Leica Microsystems, Wetzlar, Germany).

4. Field Occurrence and Sample Description

The Kunush Complex is represented by a large tabular body of plagiogranites, developed in the central part of the occurrence (the Alday dike).

This dike is controlled by a system of northwest-trending faults, along the margins of which smaller vein-like dikes of plagiogranite porphyries, granodiorite porphyries, quartz porphyries, and quartz albite-porphyries, as well as quartz veins, are localized [21,23,35]. Their lengths range from tens to hundreds of meters, their thickness varies from 1 to 4 m, and their attitude is generally subparallel to the sedimentary strata. Of particular note is a large plagiogranite-porphyry dike measuring almost 4 km long, located in the southern exocontact of the Korzhimbay granite massif.

The Alday dike consists primarily of light-gray plagiogranites, in which white plagioclase grains and biotite flakes are clearly distinguished. Varieties with higher biotite content have a similar composition to plagiogranodiorites and granodiorites (Figure 5a,b). Small granodiorite-porphyry dikes are dark gray with a porphyritic texture containing plagioclase phenocrysts (Figure 5c). Plagiogranite porphyries are lighter in color, with fine-grained matrix containing porphyritic inclusions of plagioclase, quartz, and biotite flakes (Figure 5d).

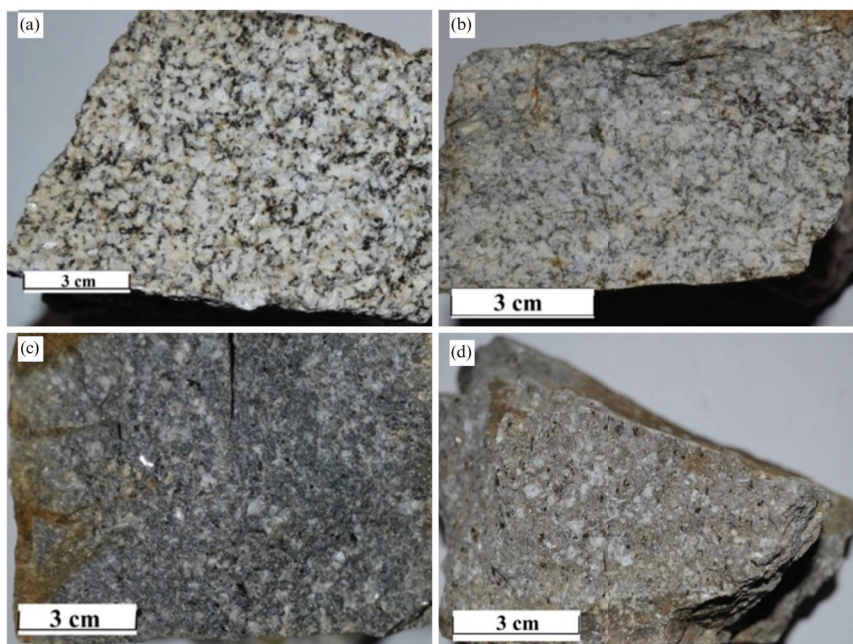


Figure 5. Examples of granitoid and dike samples from the Kunush Complex, Alday area. (a) medium-grained biotite granodiorite; (b) plagiogranite; (c) dikes of fine-grained granodiorite porphyries; (d) plagiogranite porphyries.

In the Alday area, the pegmatite veins are grouped into three series.

The Northern series is located at the southern exocontact of the Korzhimbay massif and includes microcline–albite and albite–spodumene veins (thicknesses of 0.3–4.9 m, lengths of 100–150 m, dip of 82° NE). The most prospective is the Sluchaynaya vein, with a Ta₂O₅ content of 0.0142%. The thickness of the pegmatite veins increases with depth.

The Southern series of rare-metal pegmatites, together with the Kunush dikes, frames the southern exocontact of the Alday dike and is characterized by thicker microcline–albite and albite–spodumene pegmatite veins (up to 6.2 m), including the Novaya vein, some of which are blind (buried).

The Western series is traced to the western part of the occurrence and is dominated by albite–spodumene veins up to 2 m thick, while stair-step-type veins are observed in the Kunush dikes.

Ore zoning is expressed in the transverse bundle distribution of pegmatite veins, with albite–spodumene pegmatites located on the hanging side of the bundle (cross-sections). In addition, the thickness of microcline–albite veins increases at depths of 200–300 m.

Thus, the geological characteristics of the Alday occurrence were determined by establishing a systematic description of albite–spodumene pegmatites and hornfels affected by contact alterations. The samples analyzed by ICP-MS (Figures 6 and 7) were collected specifically from these rock types, ensuring clear geological context and eliminating any impression of random selection.

In the Alday area, the ore bodies are predominantly represented by microcline–albite and albite–spodumene pegmatites. Microcline–albite pegmatites primarily occur within the shale sequence and are characterized by a tabular shape with sharp contacts with the host rocks (Figure 6a), while individual albite-altered pegmatite veins crosscut the Kunush dikes (Figure 6b). Pegmatites contain relics of sedimentary rocks in the form of shadow spots and streaks (Figure 6c) and are characterized by a coarse-grained texture (Figure 6d).

The pegmatites exhibit intense and uneven albitization, and compositionally, veins of quartz–microcline–albite–muscovite dominate (Figure 7a,b). According to exploration and

evaluation studies, the average contents of valuable components (in g/t) are as follows: Ta_2O_5 —87, Nb_2O_5 —120, Sn—113, BeO—206, Li_2O —140.

Albite–spodumene pegmatite veins also occur within the shale sequence, but a significant portion is localized in dike-like bodies of the Kunush complex, forming ladder-type structures. On the southeastern flank of the occurrence, large intensely deformed and fractured stock-like bodies of granodiorite porphyries host pegmatite veins with albite–spodumene mineralization (Figure 8a). In addition, there are steeply and gently dipping veins of irregular tabular shape that exhibit apophyses and sharp contacts with the host granodiorite porphyries (Figure 8b). The veins exhibit replacement structures, represented by zones of albitization and quartzification, and nests of spodumene crystals (Figure 8c,d).

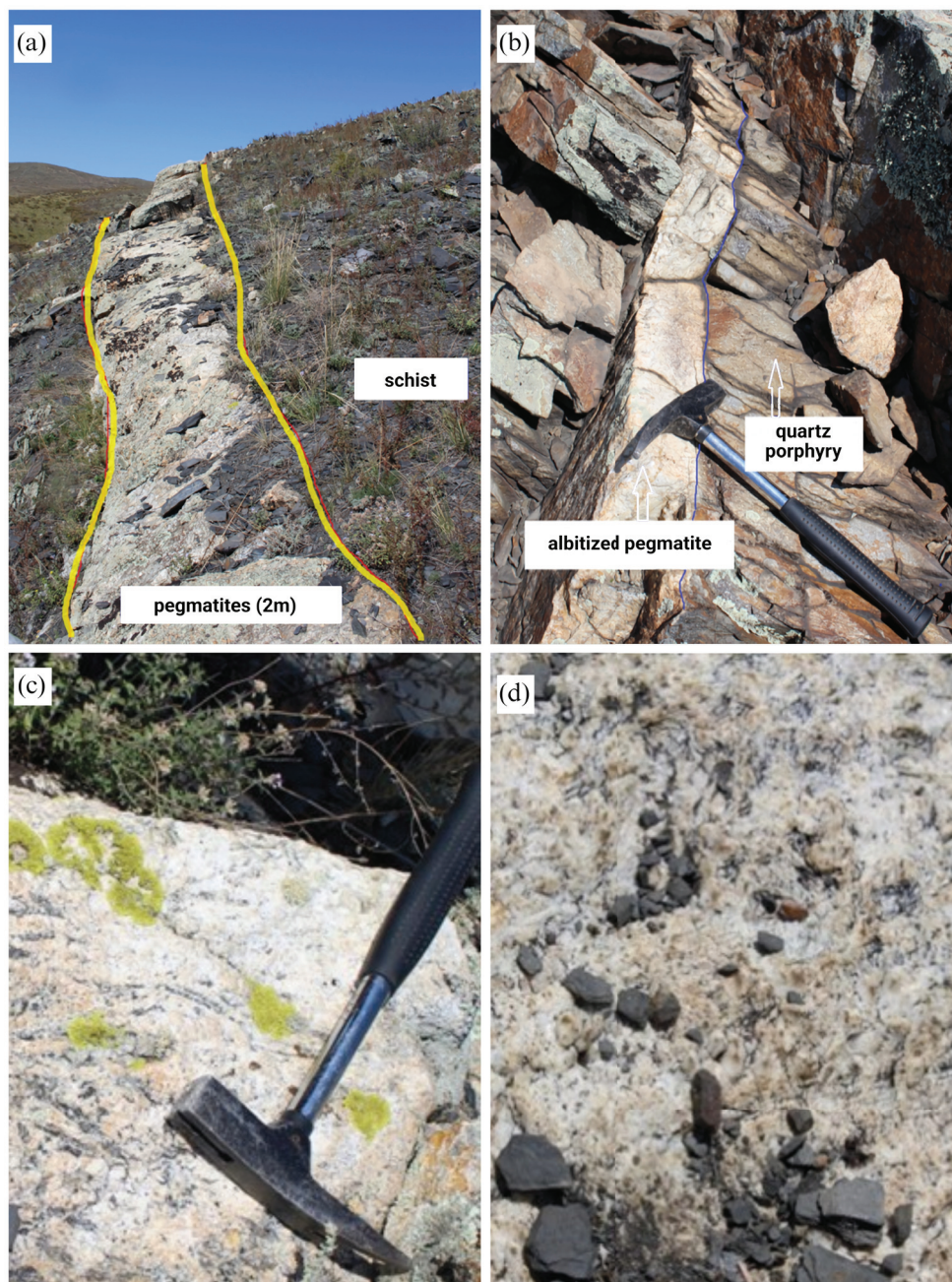


Figure 6. Morphology and internal structure of quartz–microcline–albite pegmatite veins: (a) tabular shape of a microcline–albite vein; (b) intersection of a Kunush complex quartz porphyry dike by a pegmatite vein; (c) pegmatite vein containing relics of sedimentary xenoliths; (d) internal coarse-grained structure of quartz–microcline–albite pegmatites.

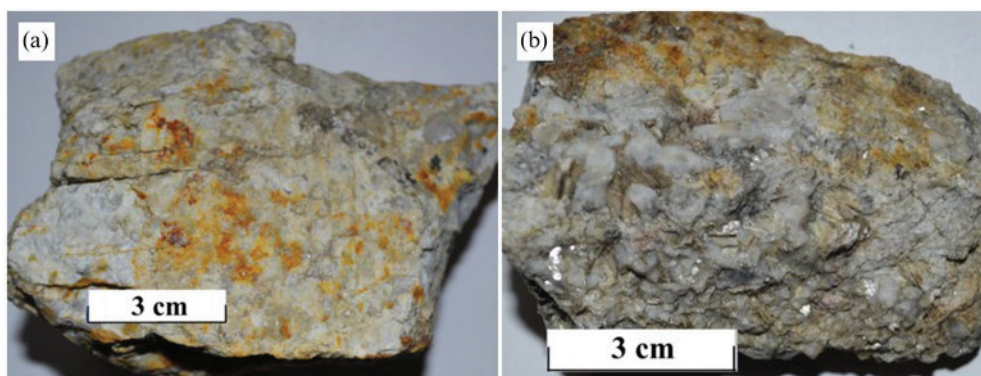


Figure 7. Examples of microcline-albite-type pegmatite samples: (a) medium-grained quartz-microcline-albite pegmatites; (b) coarse, inequigranular quartz-microcline-albite-muscovite pegmatites.

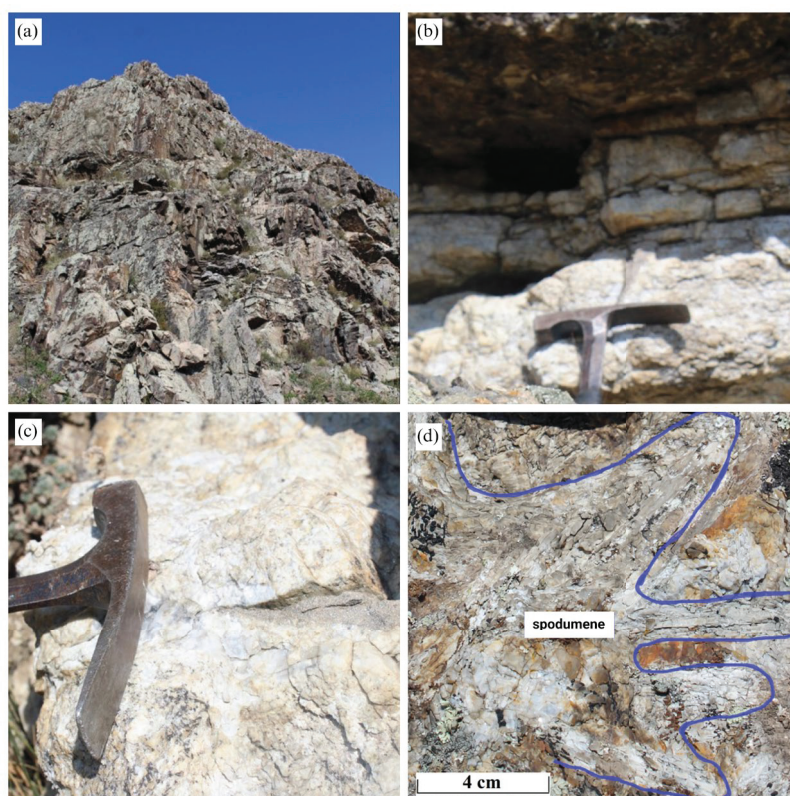


Figure 8. Morphology and internal structure of albite-spodumene pegmatite veins hosted in a granodiorite-porphyry dike of the Kunush complex: (a) a large intensely metamorphosed dike-shaped body of granodiorite porphyry with ladder-type albite-spodumene pegmatite veins; (b) a gently dipping albite-spodumene vein within a granodiorite-porphyry dike; (c) an internal replacement structure of complex composition within a quartz-albite-spodumene pegmatite vein; (d) a nest-shaped accumulation of spodumene folded into microfolds, showing replacement of spodumene by albite.

The oriented arrangement of spodumene crystals and microfolds may suggest that pegmatite formation processes were influenced by directed tectonic compression [18,41,42] (Figure 9a,b). Multistage albitization appears to play a major role in ore formation, as it is strongly manifested both in pegmatites and in associated dikes (Figure 9c,d).

Spodumene ($\text{LiAl}[\text{Si}_2\text{O}_6]$) is identified as the principal ore mineral of lithium-bearing pegmatites in the Alday area. Its crystal length reaches 10–15 cm, and it is replaced by the secondary minerals cymatolite and eucryptite.

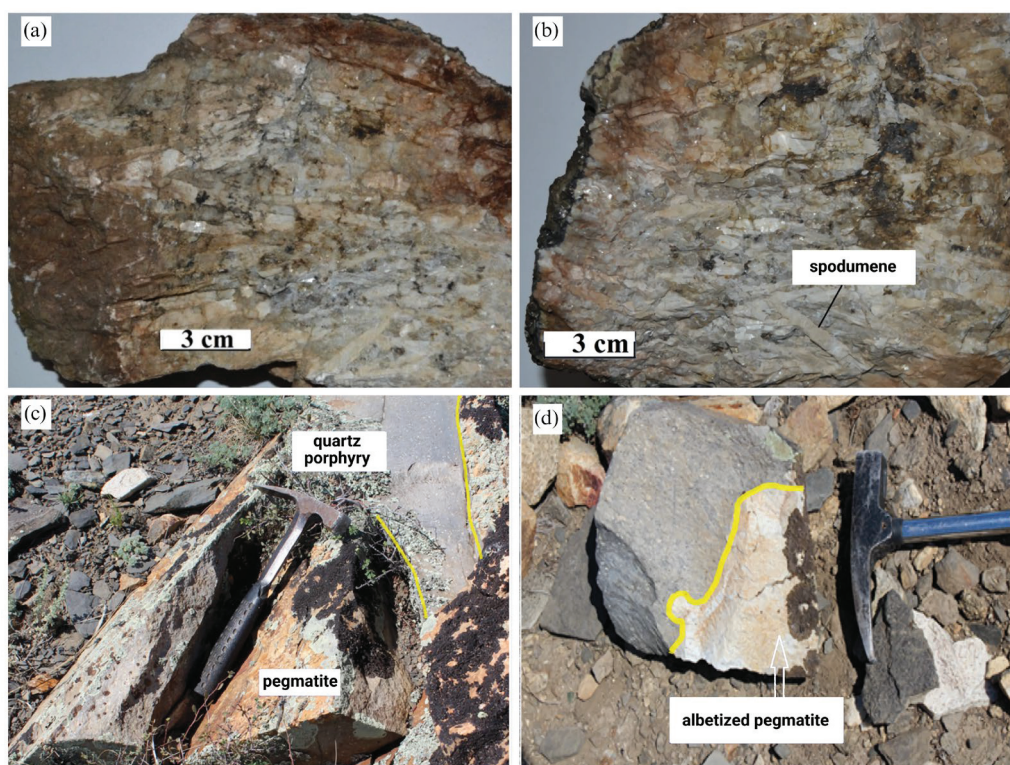


Figure 9. The nest-like distribution of spodumene in albite–spodumene pegmatites and the contacts of albite-bearing pegmatites with Kunush dikes: (a,b) albite–spodumene pegmatites with parallel-oriented distribution of spodumene crystals ($\text{LiAl}[\text{Si}_2\text{O}_6]$); (c,d)—metasomatic replacement of quartz porphyry dikes with albite-bearing pegmatites.

5. Results and Discussion

5.1. Mineralogy

Rare-earth minerals—including monazite, xenotime, zircon, ilmenite, rutile, and tourmaline—were identified at the microscale within the greisenized and silicified hornfels (Figure 10). Monazite forms nest-like xenomorphic aggregates with grain sizes ranging from a few micrometers to several tens of micrometers, and also occurs as submicroscopic, cloud-like inclusions composed of La, Ce, Nd, Th, and P (Figure 10a,b,e). Xenotime is represented by individual micrograins of nodular morphology (Y 19.48 wt.%, P 8.34 wt.%), as shown in Figure 10c, and crystalline micrograins of ilmenite are observed within quartz (Figure 10f).

On the SEM images, plagiogranites predominantly contain micrograins of monazite, zircon, fluorapatite, and ilmenite ranging in size from tens up to 200 μm (Figure 11). The largest grains are represented by high-relief monazite, containing the following (in wt.%): La (8.50), Ce (18.56), Nd (7.10), Th (1.53), P (8.73). In this study, for the first time at the micro-scale, Ce-rich rare-earth minerals were identified in plagiogranites, with Ce content up to 36.77 wt.% they also contained the following (in wt.%): Fe—3.54; P—3.17; Si—37.93; Al—1.85; Ca—1.30 (Figure 11c,d). Their composition is similar to that of the rare-earth mineral nagatelite, $(\text{Ca,Ce})_2(\text{Al,Fe})_3(\text{Si,P})_3\text{O}_{12}[\text{O,OH}]$. A rare Ti-bearing iridosomite mineral was also observed in biotite in the form of inclusions measuring a few micrometers (Figure 11e). Its composition (in wt.%) includes Ti—13.76, Fe—13.76, Y—4.92, Nd—3.24, Sm—2.37, Gd—2.60, Ca—0.59, and other elements. This mineral has compositional similarities to yttrio-titanite $(\text{Ca,Y,Ce})\text{Ti}[\text{SiO}_4]\text{O}$, though it differs from yttrio-titanite in terms of its rare-earth-element content.

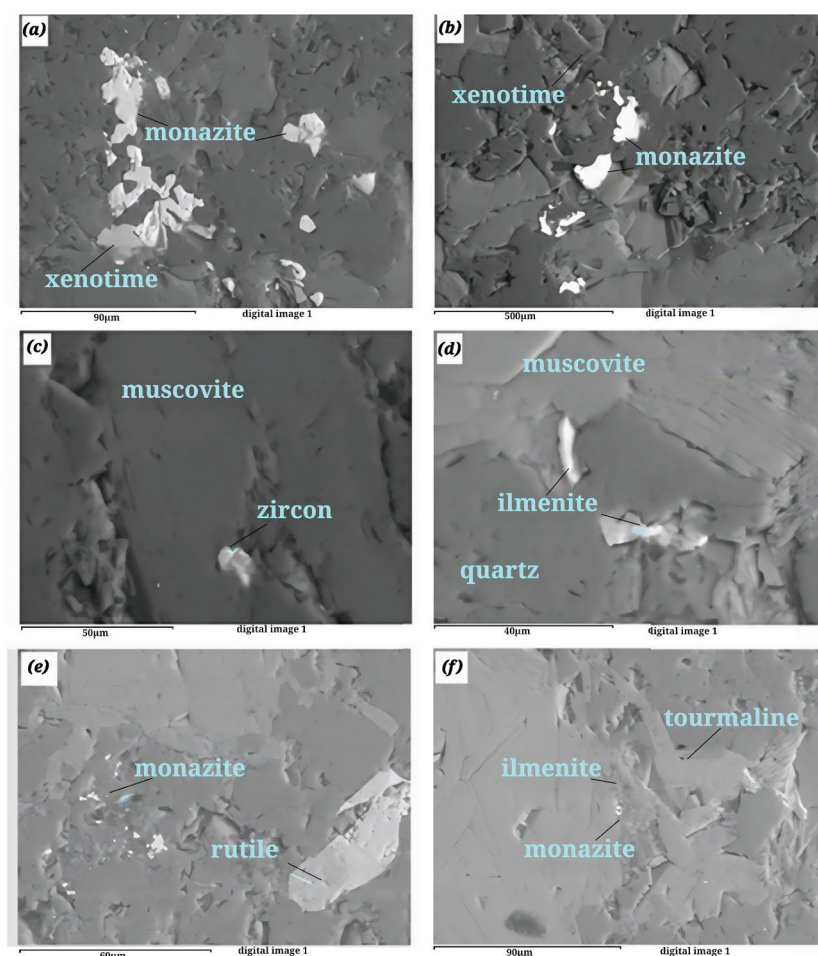


Figure 10. Fluid-related microinclusions of minerals in muscovitized and silicified hornfels of the Alday ore occurrence. (a,b) Aggregates of monazite and xenotime micrograins; (c) zircon grain in muscovite; (d) inclusions of ilmenite associated with quartz and muscovite; (e) minute clusters of monazite and prismatic rutile micrograins; (f) columnar tourmaline crystals, and micrograins of ilmenite and monazite in a quartz–feldspar matrix.

In the quartz albite-porphyry dikes, submicroscopic inclusions of Ti-bearing zircon with gray coloration and a zoned internal structure were identified, indicated by fine inclusions of white xenotime (P 6.53, Y 10.80, Si 21.64, O 55.27 wt.%) and submicroscopic monazite crystals (Figure 12).

In the biotitized plagiogranite-porphyry dike, inclusions of apatite and nest-like aggregates of low-relief ilmenite were observed (Figure 12a–c). In addition, zircon micrograins, likely of an early generation, were found to be fixed in the quartz of the main mass.

In metamorphosed quartz porphyries subjected to muscovitization, micrograins of manganese minerals that were compositionally close to jacobsonite (MnFe_2O_4) were identified (Mn—10.95, Fe—9.24, O—47.89 wt.%). These minerals occur as relatively large, complex-shaped grains (up to 400 μm) localized in quartz and in the surrounding matrix, containing zircon inclusions (Figure 13a,b). In addition, idiomorphic zircon micrograins are fixed in quartz (Figure 14c,d).

Thus, according to the SEM analysis, in the plagiogranites and dikes of the Kunush Complex, fluid inclusions are predominantly represented by zircon, monazite, xenotime, apatite, and ilmenite. These minerals are localized in the rock matrix and in rock-forming minerals (quartz, albite, biotite, and muscovite). Morphologically, primary idiomorphic crystals of monazite, zircon, and xenotime are distinguished, and zoned zircon crystals containing submicroscopic xenotime inclusions are found. For the first time in plagiogran-

ites, rare Ce-bearing REE minerals (nagatelite?) and Ti-iridosomite (yttrotitanite?) are identified, developed in rock defects and likely of secondary origin. A noteworthy feature is the occurrence of a manganese mineral (jacobsonite?) in the plagiogranite porphyries.

According to ICP-MS data, spodumene is characterized by high sodium-specific alkali content (in g/t) (Na—22,230, K—3243 (Na/K = 6.8)); elevated Al (54,100) and P (1983); and low Fe (90.32) and Mn (674), as well as lithium enrichment (1417 g/t) and relatively low Rb and Cs contents. Elevated concentrations (in g/t) of rare elements are also observed (Ta—15.27, Nb—108.92, Be—127.37, Sn—80). These data are corroborated by scanning electron microscopy results, which reveal microinclusions of rare-metal minerals (columbite–tantalite, columbite, and cassiterite) and associated apatite and zircon within the spodumene (Figure 15).

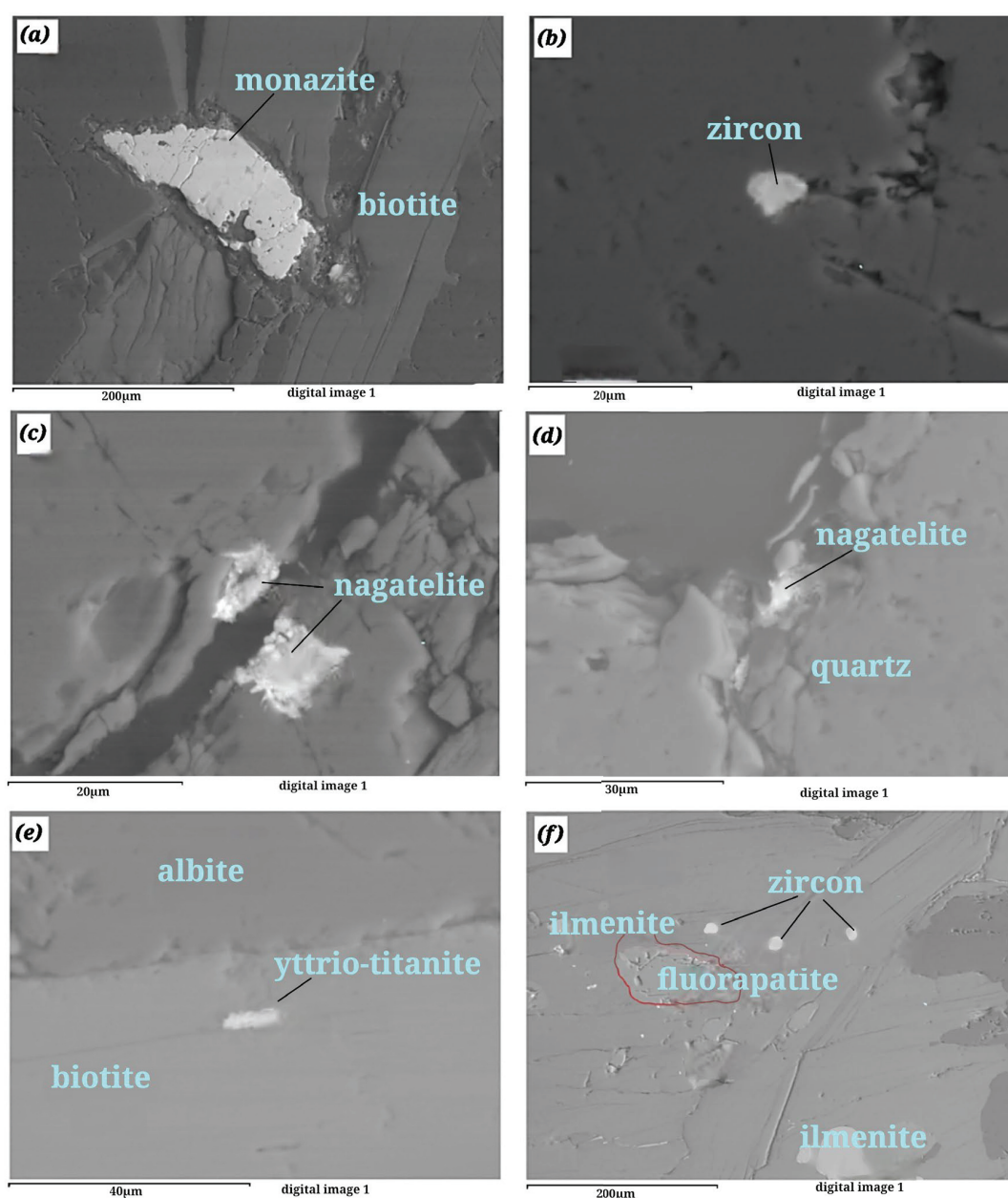


Figure 11. Fluid mineral inclusions in plagiogranites of the Kunush Complex at the Alday occurrence: (a) clump-shaped monazite micro-inclusion; (b) zircon micrograin; (c,d) Ce-rich rare-earth minerals (nagatelite? Ce 32.22–36.77 wt.%); (e) platy grain of Ti-iridosomite (yttro-titanite) in biotite; (f) micro-inclusion of fluorapatite, ilmenite, and zircon.

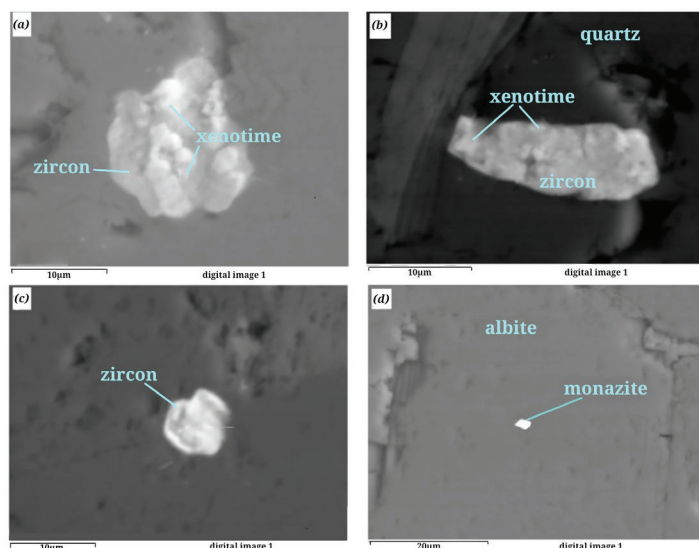


Figure 12. Fluid mineral inclusions in a quartz albite-porphyry dike: (a,b) zoned zircon micro-grains with xenotime inclusions; (c) submicroscopic rounded zircon grain; (d) idiomorphic monazite inclusion in albite.

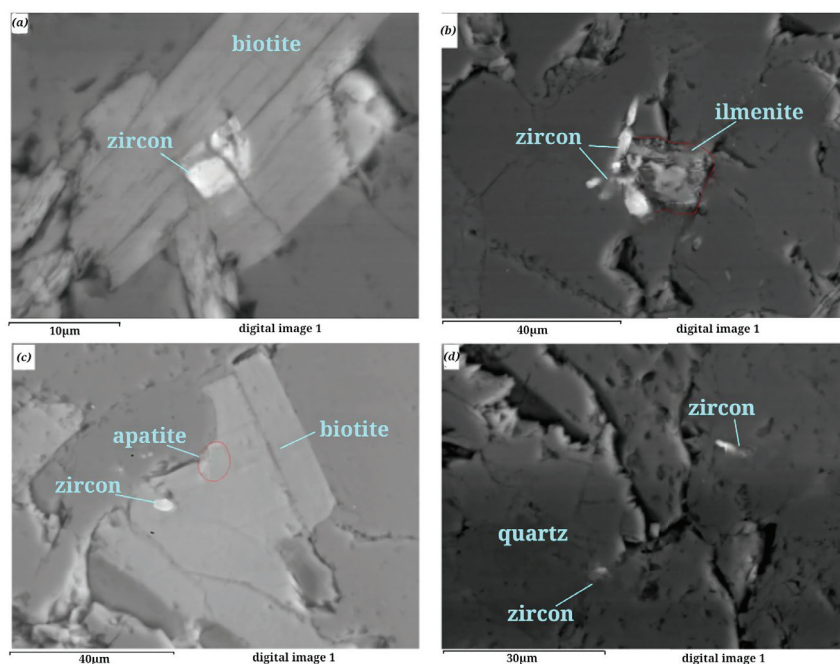


Figure 13. Fluid mineral inclusions in a plagiogranite-porphyry dike with porphyritic albite and biotite, Alday occurrence: (a) zircon inclusions in a biotite grain; (b) zircon micro-inclusions associated with ilmenite; (c) zircon and apatite grain inclusions in biotite; (d) submicroscopic zircon inclusions in quartz.

The widespread occurrence of Ti–Th–REE-bearing accessory minerals (monazite, xenotime, REE-rich zircon, ilmenite, rutile) in granitoids, dikes, and contact-metasomatic rocks of the Alday area reflects advanced magmatic differentiation and active fluid–magmatic interaction. Such mineral assemblages are typical of evolved granitoid systems approaching rare-metal specialization and record the enrichment of incompatible elements during late-stage melt and fluid evolution.

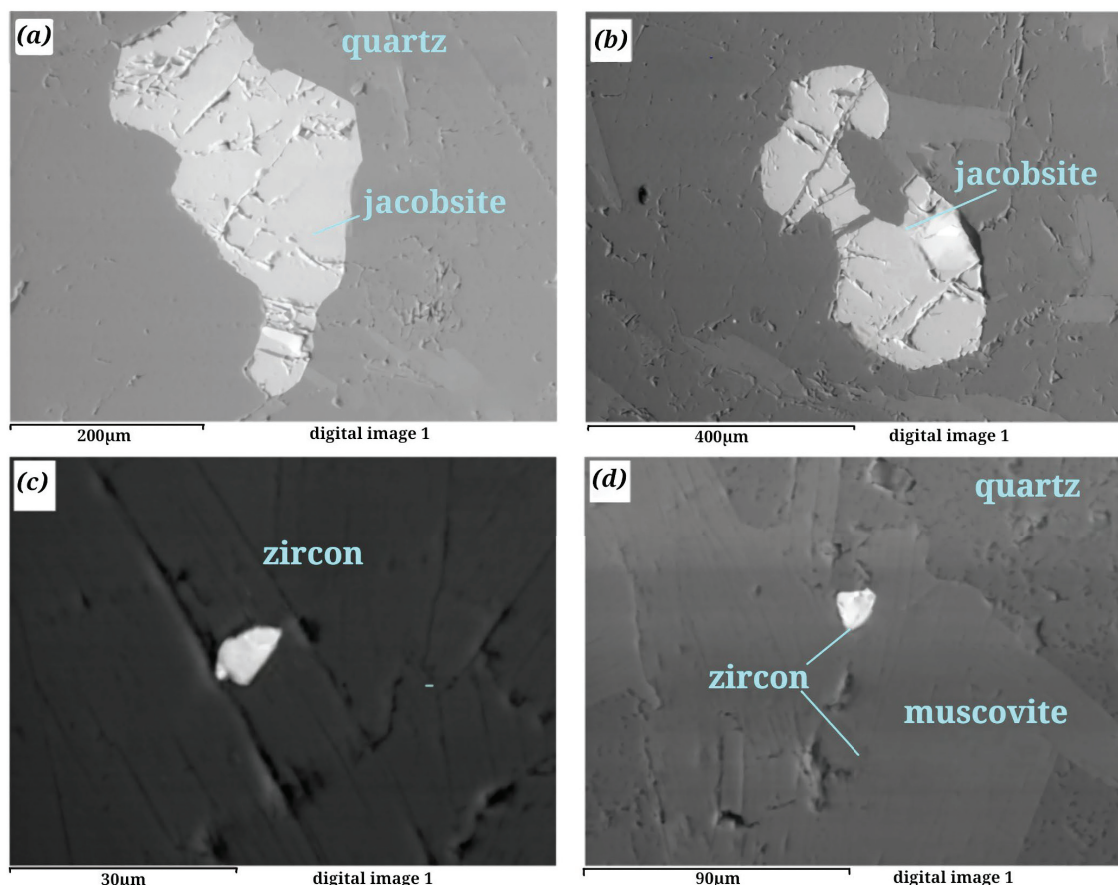


Figure 14. Fluid mineral inclusions in a quartz porphyry dike: (a) micrograin of a manganese mineral (jacobsite?) in the quartz–feldspar matrix; (b) complex-shaped jacobsite (?) micro-inclusion with zircon inclusions at the rim; (c) clump-shaped zircon inclusion; (d) crystallographic-shaped zircon in the quartz–muscovite matrix.

Although Ti–Th–REE minerals do not constitute economic mineralization in the Alday occurrence, their textural position and chemical composition indicate the same magmatic–hydrothermal system that ultimately generated lithium-bearing albite–spodumene pegmatites. The presence of monazite and xenotime, together with fractionated REE patterns and low Nb/Ta ratios, supports a genetic link between late granitoid differentiation, fluid activity, and the formation of Li–Ta–Nb–Sn mineralization. These accessory minerals therefore complement, rather than replace, the information provided by major rare-metal carriers such as cassiterite and columbite–tantalite.

5.2. Geochemistry

According to ICP-MS results, the elements with the highest concentrations (in g/t) in muscovitized hornfels are siderophile elements (Fe—26,780; Ti—5511) and petrogenic elements (Mg (13,356), Na (18,265), K (34,740), Ca (8225), P (1483), and Al (84,610)), primarily associated with muscovite. Chalcophile elements exhibit the following anomalous values: Cu—227.8, Pb—265.2, Zn—128.3. Among the rare-earth elements, the light REE group predominates (Ce—34.89, La—17.7, and Nd—13.16), which is consistent with the SEM data, which show monazite inclusions. The weighted concentrations of noble metals (in g/t) are as follows: Ag—1.24, Au—0.31, Pt—0.134, Pd—0.210. Hornfels are also characterized by elevated concentrations of alkali elements (Li—121.4–674.6; Rb—128.28; Cs—37.28) and rare metals (Ta—47.56, Sn—32.34, Nb—36.10), with measurable contents of Be, W, and Mo. This is likely due to the hornfels enrichment in muscovite, which acts as a concentrator of

lithium and rare elements. The concentrations of dispersed elements (Ba, Y) are equal to their Clarke values.

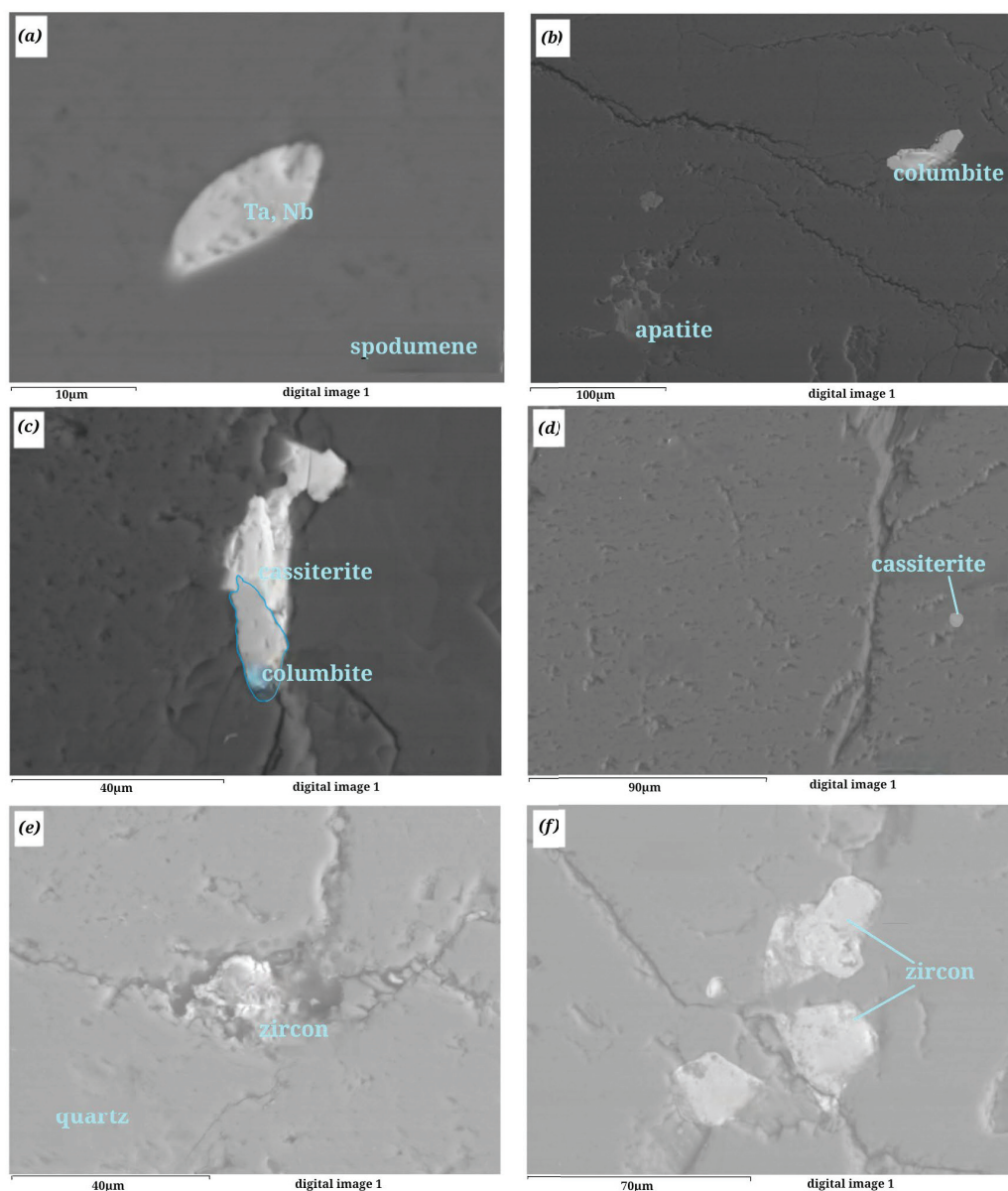


Figure 15. Photomicrographs of fluid inclusions within minerals. These are microscopic cavities of liquid and/or gas trapped during mineral crystallization, providing information about the composition and conditions of ore-forming fluids: (a) isometric grain of manganese-type columbite–tantalite; (b) microinclusions of columbite and apatite; (c) intergrowth of cassiterite and columbite; (d) submicroscopic inclusions of cassiterite; (e) inclusion of uraniferous zircon with Ir—5.99 and U—2.05 wt.%, localized in quartz microveins; (f) microinclusions of zircon of nodular shape (with Ir—8.70 and Hf—18.6 wt.%).

According to petrochemical data, the plagiogranites are characterized by low alkalinity, with a strong predominance of Na_2O over K_2O ($\text{Na}_2\text{O}/\text{K}_2\text{O} > 4$). In Figure 16, which presents a silica–alkalinity classification diagram, these rocks are plotted in the upper part of the granodiorite field. The nomenclature and general classification of igneous rocks follow widely accepted principles [43].

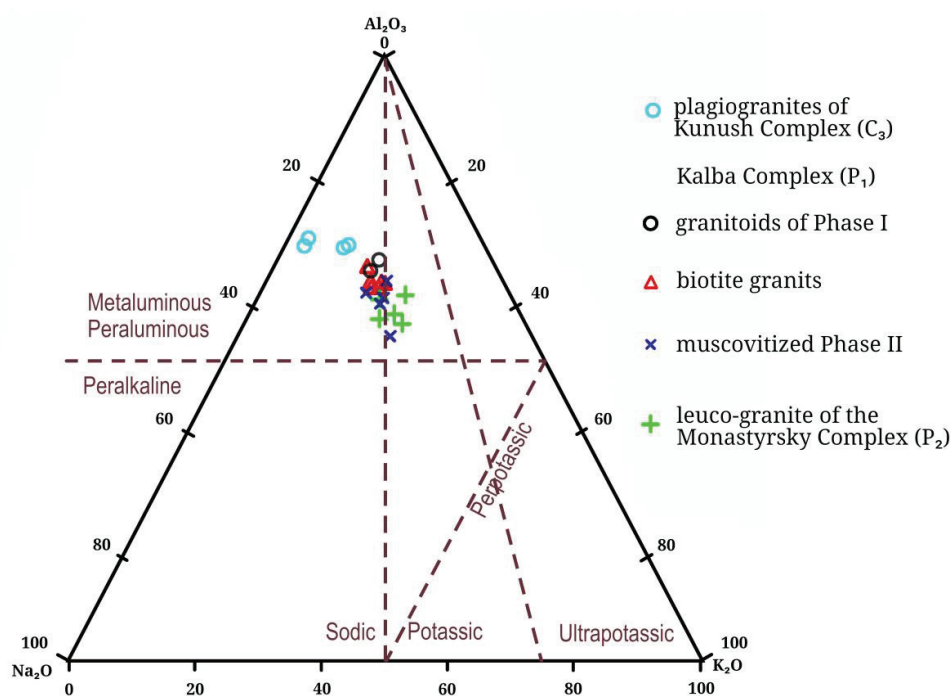


Figure 16. Petrochemical Na_2O – Al_2O_3 – K_2O diagram based on whole-rock analyses of granitoid samples from the Alday area (this study). Reference fields are shown according to widely used granitoid classification schemes proposed by Frost et al. (2001) and Maniar and Piccoli (1989) [44,45].

The diagram in Figure 17 presents the results of our whole-rock analyses of plagiogranites and related rocks, and the reference fields are taken from published classifications [46–48]. Identical SiO_2 values in several samples reflect analytical rounding and averaging, rather than data duplication.

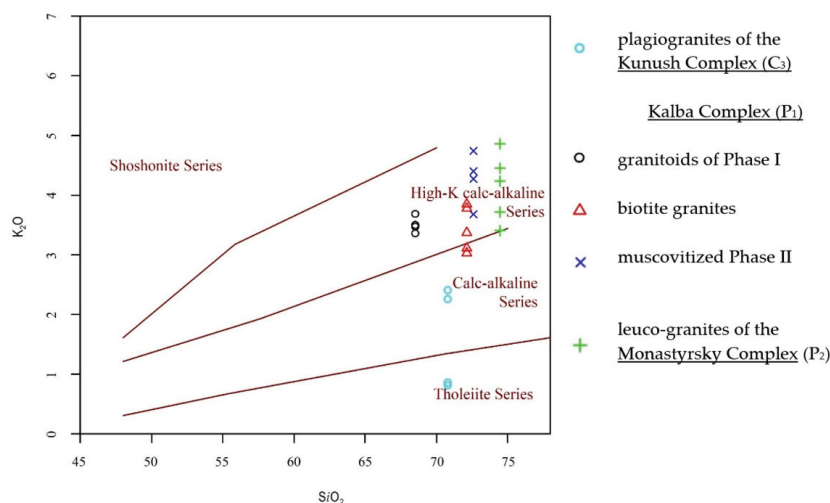


Figure 17. Petrochemical SiO_2 – K_2O diagram of granitoid samples from the Alday area (this study) [46].

In the SiO_2 – K_2O diagram presented in Figure 17, SiO_2 and K_2O correspond to the calc-alkaline and tholeiitic series. Plagiogranites also exhibit meta-aluminous characteristics and occupy a separate position in the diagram relative to the granitoids of the Kalba and Monastyrsky complexes [49,50].

In the SiO_2 – K_2O diagram presented in Figure 17, our samples correspond to the calc-alkaline and tholeiitic series, and the reference fields are plotted according to Peccerillo and Taylor (1976) [46].

According to ICP-MS data, rare-earth elements in plagiogranites and dike formations exhibit a fractionated distribution with a predominance of lanthanide-group elements ($\text{La/Yb} = 3.73\text{--}108.52$). The sum of rare-earth elements reaches a value of 137.83 g/t, and elevated contents of Ce and La are observed in plagiogranites, plagiogranite-porphyry dikes, and quartz albite-porphyries (samples 1–4, 8), and the rocks are characterized by sodium-dominated alkalis ($\text{Na} > \text{K}$ by 3–5 times) and elevated contents of petrogenic components (Ca, Al, Mg, P).

The distribution of rare metals and rare-earth elements is uneven. All rocks display anomalously high Li concentrations relative to the Clarke values in EC, reaching 208.30–306.00 g/t. In addition, elevated concentrations of Ta, Nb, and Sn are found in quartz porphyries and quartz albite-porphyries, which geochemically aligns them with the Ongonite dikes of Kalba [12,13], and the contents of Be, W, and Mo slightly exceed their Clarke values [12].

Table 1 presents the absolute concentrations of rare elements determined by ICP-MS in granitoid samples, which represent the baseline geochemical characteristics of different rock types. Table 2 summarizes indicative ratios and selected elements that are critical for tracing magmatic evolution. Unlike Table 1, which reports absolute concentrations, Table 2 emphasizes the geochemical parameters (K/Rb , Nb/Ta) used to classify granitoid groups into evolutionary stages (I–III).

Table 1. Absolute concentrations of rare elements (Ta, Nb, Be, Li, Rb, Cs, Sn, W, Mo; g/t) in granitoids of the Kunush Complex in the Alday area (this study).

No. 1	Sample	Ta	Nb	Be	Li	Rb	Cs	Sn	W	Mo
1	A-1	0.50	8.78	1.21	208.30	70.20	19.90	8.02	2.17	0.61
2	A-2	25.73	40.52	1.77	174.90	74.50	12.08	7.70	9.96	10.85
3	A-6 (1)	0.56	4.62	5.17	94.99	43.00	15.98	19.16	0.48	1.08
4	A-6 (2)	0.43	75.65	7.03	102.40	44.70	19.04	23.28	1.63	0.49
5	AL-6	7.00	12.26	3.14	306.00	100.38	22.79	65.88	1.32	2.46
6	AL-9	27.90	1.26	1.26	109.90	31.97	1.13	14.79	1.10	2.65
7	AL-5	9.41	13.01	13.20	74.90	54.44	22.79	18.62	1.32	3.17
8	AL-4	44.35	34.13	8.17	165.40	357.18	50.69	88.60	2.27	4.15
9	AL-8	64.13	41.58	0.63	23.50	30.66	0.06	47.72	0.72	3.50
Average value		20.00	25.76	4.62	140.03	89.67	18.27	32.64	2.33	3.22

1—plagiogranites; 2—plagiogranite porphyry; 3–5—plagiogranodiorites; 6—plagiogranite porphyry; 7—biotite-enriched plagiogranite porphyries; 8—quartz albite-porphyry; 9—quartz porphyry with muscovite flakes.

Table 2. Indicative geochemical ratios (K/Rb , Nb/Ta) and selected element concentrations (Li, Rb, Cs, Nb, Ta, Sn) in granitoid samples of the Kunush Complex in the Alday area (this study).

Type	Sample	Li	Rb	Cs	Nb	Ta	Sn	K	K/Rb	Nb/Ta
I	A-1	208.30	70.20	19.90	8.78	0.50	8.02	9200	131.05	17.56
	A-6 (1)	94.99	43.00	15.98	4.62	0.56	19.16	9500	220.93	8.25
	A-6 (2)	102.40	44.70	19.04	75.65	0.43	23.28	10,000	223.71	176.0
	AL-6	306.00	100.38	22.79	12.26	7.00	65.88	8200	81.67	1.75
II	A-2	174.90	74.50	12.08	40.52	25.73	7.70	8700	116.78	1.58
III	AL-9	109.90	31.97	1.13	1.26	27.90	14.79	9800	306.50	0.05
	AL-5	74.90	54.44	22.79	13.01	9.41	18.62	8500	156.15	1.38
	AL-4	165.40	357.18	50.69	34.13	44.35	88.60	9000	25.19	0.77
	AL-8	23.50	30.66	0.06	41.58	64.13	47.72	9400	306.65	0.65

I: Basic granitoid rocks, including plagiogranites and their dioritic variants. These are characteristic of the early stage. II: Porphyritic rocks of plagiogranite composition, including biotite-enriched varieties. These are a transitional group with a porphyritic texture. III: Quartz-enriched porphyries with muscovite and albite. These are an evolved group exhibiting hydrothermal features.

Based on the analysis of rocks from the Alday occurrence, the K/Rb–Li; K/Rb–Rb; K/Rb–Cs; and Nb/Ta–Li, Rb, and Cs diagrams show a clear evolutionary sequence from basic plagiogranites to quartz porphyries and albite-porphyries (Figure 18) [50].

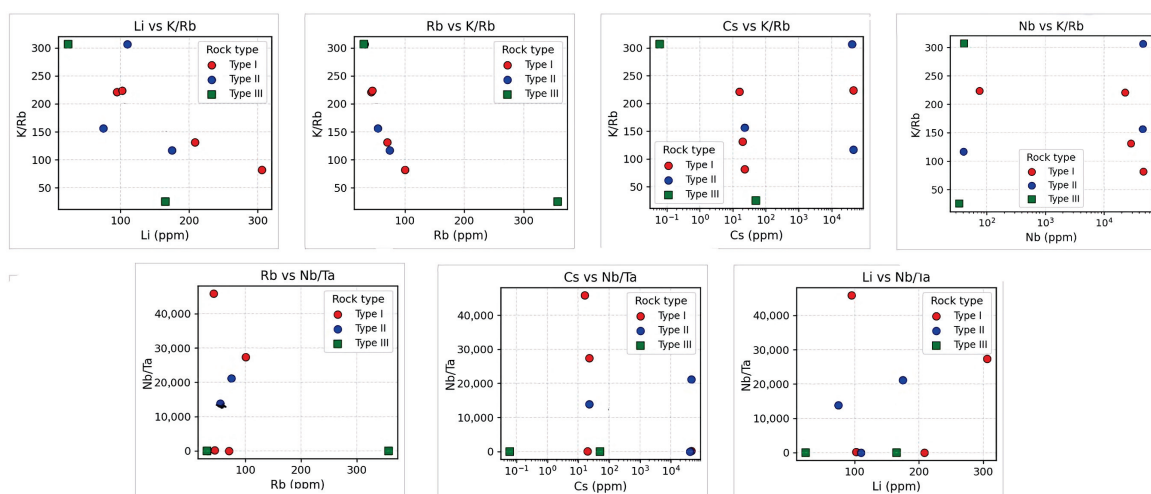


Figure 18. Correlation diagrams of K/Rb and Nb/Ta versus Li, Rb, and Cs for rocks of types I–III.

Group I (plagiogranites and plagiogranodiorites; samples 1, 3, 4, and 5) rocks are characterized by relatively high K/Rb values (81.7–223.7) and a wide Nb/Ta range (1.7–176), which reflects an early, weakly evolved stage of granitoid magmatism [47,50]. The lithium and rubidium contents are moderate, while the cesium content reaches 20 ppm. The presence of Nb-enriched samples (e.g., sample A-6 (2), Nb/Ta = 176) indicates cumulative niobium accumulation in the melt prior to the onset of crystallization.

Group II (plagiogranite porphyries, samples 2, 6, 7) is characterized by K/Rb values ranging from 116 to 306, accompanied by a sharp decrease in Nb/Ta (0.05–1.6). A distinct redistribution of tantalum relative to niobium is observed, indicating the transition to more evolved magmatic conditions. Elevated cesium contents (up to 22.8 ppm) and the presence of samples with anomalously low Nb/Ta (e.g., AL-9 = 0.05) reflect active fluid involvement and the onset of rare-metal specialization.

Group III (quartz porphyries and albitophyres, samples 8, 9) rocks are distinguished by minimal K/Rb values (down to 25), as well as a sharp increase in Rb (up to 357 ppm), Cs (up to 50.7 ppm), and Ta (up to 64 ppm). Nb/Ta remains low (0.65–0.77), reflecting active redistribution of niobium and tantalum during magmatic–hydrothermal evolution, while high tin contents (up to 88 ppm) confirm late hydrothermal overprinting. Collectively, these features make this group the most promising in terms of lithium–rare-metal mineralization [47,50].

The evolution of rocks at the Alday ore occurrence can be traced from plagiogranites with high K/Rb and Nb/Ta to porphyries with reduced Nb/Ta and elevated Cs to albitophyres and quartz porphyries, which exhibit maximum enrichment in Li, Rb, Cs, and Ta at minimal Nb/Ta values. This reflects the transition of the system to a magmatic–hydrothermal stage and the establishment of conditions favorable for rare-metal mineralization.

The rare-earth element (REE) contents of the granitoids of the Kunush Complex in the Alday area are shown in Table 3.

Table 3. Contents of rare-earth elements in granitoids of the Kunush Complex in the Alday area (g/t).

No. 1	Sample	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Cy _{MMA}	La/Yb
1	A-1	25.15	44.06	6.51	24.73	3.84	1.4	4.12	0.48	2.32	0.44	1.28	0.17	1.06	0.23	115.79	23.7
2	A-2	25.71	42.74	6.3	22.76	4.35	1.18	4.59	0.5	2.41	0.4	1.28	0.11	1.2	0.22	113.75	21.4
3	A-6 (1)	15.94	26.76	3.99	16.69	2.96	0.52	2.3	0.21	1.2	0.23	0.48	0.06	0.35	0.07	71.76	45.5
4	A-6 (2)	22.35	35.43	5.73	19.86	3.5	1	3.16	0.39	1.85	0.34	0.8	0.18	0.77	0.14	95.5	29
5	AL-6	4.73	10.35	1.39	4.93	1.93	0.55	1.8	0.4	1.06	0.24	0.43	0.127	0.51	0.18	28.627	9.27
6	AL-9	4.86	10.25	1.66	7.86	1.76	0.68	0.82	0.2	1.3	0.09	0.09	0.06	0.25	0.04	29.92	19.44
7	AL-5	20.5	40.37	5.33	25.32	4.3	0.87	4.27	0.34	2.25	0.36	0.95	0.19	0.51	0.18	105.74	40.20
8	AL-4	27.13	60.62	8.14	27.79	4.3	1.28	4.59	0.43	2.18	0.21	0.78	0.09	0.25	0.04	137.83	108.52
9	AL-8	4.25	11.46	1.79	6.25	2.54	0.32	1.8	0.6	0.83	0.42	1.04	0.13	1.14	0.08	32.65	3.73
Average value		16.74	31.34	4.54	17.35	3.28	0.87	3.05	0.39	1.71	0.30	0.79	0.12	0.67	0.13	81.29	33.42

ICP-MS analysis results. 1—plagiogranites; 2—plagiogranite porphyry; 3–5—plagiogranodiorites; 6—plagiogranite porphyry; 7—biotite-enriched plagiogranite porphyries; 8—quartz albite-porphyry; 9—quartz porphyry with muscovite flakes.

Among the chalcophile elements, elevated concentrations of Cu, Zn, and Pb are observed, exceeding their Clarke values by 2–4 times (Table 4). In plagiogranodiorites, the anomalous Pb concentration reaches 565.70 g/t, and in the noble-metal group, significant contents of Sb, Ag, Au, and Pd, as well as As (1.85–3.12 g/t) and Bi (up to 12.54 g/t), are detected, reflecting the geochemical specialization of plagiogranites of the Kunush Complex for gold mineralization. Another feature of these plagiogranites is their anomalously high strontium content (Sr up to 718.4 g/t, Sr/Y = 38.2–101.9 g/t), which is typical of rocks of the Kunush Complex and comparable to the strontium content of adakite-type granites.

Table 4. Contents of chalcophile and associated elements in granitoids of the Kunush Complex at the Alday area (g/t).

No.	Sample	Cu	Zn	Pb	Sb	Ag	Au	Pt	Bi	Pd	Cd	Ba	Sc
1	A-1	42.65	89.36	27.63	1.97	0.27	0.28	0.03	0.73	1.36	0.09	459.30	13.07
2	A-2	58.99	61.64	57.89	2.07	1.47	0.16	0.01	2.03	1.20	0.11	439.70	15.09
3	A-6 (1)	49.22	112.80	565.70	5.90	4.58	0.19	0.02	4.49	1.24	0.10	298.40	12.87
4	A-6 (2)	53.65	149.10	85.78	2.24	0.74	0.24	0.01	0.78	1.60	0.18	326.60	7.14
5	AL-6	126.03	102.60	65.98	0.70	1.39	0.36	0.03	2.21	0.16	1.71	502.40	8.28
6	AL-9	69.89	38.75	58.19	0.70	0.83	0.48	0.01	3.89	0.16	0.94	484.80	7.50
7	AL-5	45.53	55.20	79.44	2.45	1.98	0.28	0.03	12.54	0.32	0.80	499.20	9.96
8	AL-4	55.17	65.95	56.66	1.05	0.52	0.28	0.03	1.18	0.14	0.31	537.60	7.90
9	AL-8	81.33	81.00	58.19	0.70	1.71	0.48	0.01	3.89	0.047	1.06	484.80	8.20
Average value		64.72	84.04	117.27	1.98	1.50	0.31	0.02	3.53	0.69	0.59	448.09	10.00

The spodumene enrichment observed in lithium and rare elements (Ta, Nb, Be, Sn) is consistent with data from other pegmatite deposits in the Kalba region (Bakennoe, Yubileynoe, Tochka, etc.) as well as international occurrences, indicating that this mineral can serve as an indicator of the main productive stage of pegmatite mineralization and should be considered during exploration.

5.3. Geochronology

$^{40}\text{Ar}/^{39}\text{Ar}$ dating was performed on muscovite extracted from spodumene pegmatites of the Chudskaya vein of the Tochka deposit (3 samples) and the Alday area (Figure 19). All spectra show well-defined plateaus with concordant ages of 293 ± 4 , 293 ± 4 , 292 ± 4 , and 290 ± 4 Ma. These ages are consistent with geochronological data reported for rare-metal pegmatite systems in other regions [51].

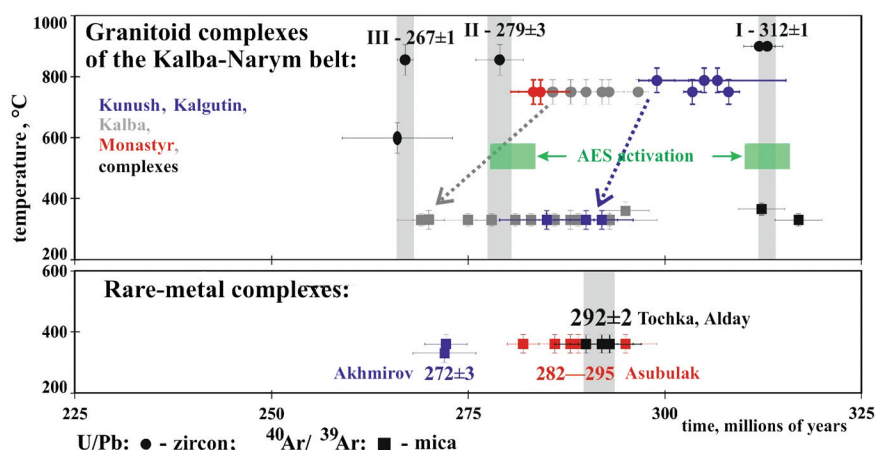


Figure 19. A thermochronological diagram summarizing the geochronological data for the Kalba granitoids and rare-metal deposits of the Kalba–Narym Belt (age vs. formation temperature, or closure of the isotopic system). In the upper diagram, black symbols indicate dating results for granitoid complexes of the Kalba–Narym Belt, compared with dating results for the following: I—gabbros of the Irtysh Complex; II–III—lamprophyre and dolerite dikes of the Mirolubov Complex. The lower diagram shows dating results for rare-metal deposits.

These results indicate that the spodumene pegmatites are significantly younger than the Kunush Complex plagiogranites (Figure 19). Assuming that the formation of spodumene pegmatites was associated with the Kunush Complex plagiogranites, and that emplacement of later intrusive complexes caused partial re-setting of the muscovite isotopic system (whose closure temperature is approximately 370 °C), one would expect the ages of spodumene pegmatites to correspond to the youngest of the nearby intrusions—the Sibinsky massif of the Monastyrsky Complex (284 Ma). Furthermore, it seems unlikely that, under superimposed thermal events, deposits located at different distances from intrusions would yield such similar ages.

Considering this, it is reasonable to assume that the ⁴⁰Ar/³⁹Ar dating results correspond to the actual formation age of the spodumene pegmatites. Thus, the rare-metal deposits of the Karagoin–Saryozek ore zone formed synchronously with the emplacement of granodiorites and granodiorite–granites of the first phase of the Kalba Complex.

In several Hercynian provinces, LCT-type pegmatites are temporally decoupled from the emplacement of the last peraluminous granites, with age gaps of up to 10–15 Ma—as documented, for example, in the French Massif Central [52]. In such settings, it has been proposed that pegmatite formation results from later partial melting of fertile crustal sources or from remobilization processes independent of nearby granitic intrusions. In contrast, geochronological data available for the Alday area indicate that spodumene-bearing pegmatites crystallized at ~292–293 Ma, contemporaneous with Late Paleozoic magmatism of the Kalba complex. This temporal coincidence suggests a closer genetic relationship between pegmatite formation and regional granitic magmatism in the Alday area than in some other Hercynian domains. Nevertheless, this comparison highlights that multiple genetic pathway of pegmatite formation may operate within Hercynian belts, depending on the local geodynamic and thermal conditions.

6. Conclusions

The Alday ore occurrence is characterized by the evolution of granitoid magmatism from plagiogranites to quartz porphyries and albite-porphyries.

The K/Rb and Nb/Ta indicator ratios clearly indicate a transition from early magmatic stages (high K/Rb and Nb/Ta) to late magmatic–hydrothermal stages (low K/Rb and Nb/Ta).

During the late stages, the rocks exhibit intensive Li, Rb, Cs, Sn, and Ta enrichment, reflecting fluid involvement and indicating favorable conditions for lithium–rare-metal mineralization [53–55].

The most prospective lithologies for mineralization are quartz porphyries and albite-porphyries, which display low Nb/Ta (<1) and high concentrations of rare metals.

The obtained data allow a set of predictive criteria to be established for Alday: the presence of rocks with low K/Rb and Nb/Ta; enriched in Li, Rb, Cs, and Sn; and associated with late phases of granitoid magmatic evolution.

Morphological criteria. At the Alday occurrence, the main indicators of the productive stage are albite–spodumene pegmatite veins, localized within dike-like bodies of the Kunush Complex and forming ladder-type structures. Their thickness increases with depth, indicating potential for further mineralization at deeper horizons.

Mineralogical criteria. The main ore mineral is spodumene, enriched in Li (up to 1417 g/t), which contains microinclusions of rare-metal minerals (tantalite–columbite, cassiterite, zircon). The presence of these inclusions suggests that rare-metal associations were formed specifically during the productive stage of pegmatite formation.

Geochemical criteria. Spodumene and pegmatites are characterized by high concentrations of Ta, Nb, Be, and Sn, as well as low Rb and Cs with elevated Li, indicating a sodium-specific system. The K/Rb and Nb/Ta ratios mark the transition from early granitoids to the magmatic–hydrothermal phase with rare-metal enrichment.

Structural–geological criteria. Zonation is expressed in the transverse, bundle-like distribution of pegmatite veins: albite–spodumene bodies are located in the hanging side of the bundle, whereas microcline–albite veins thicken with depth. This systematic vein distribution serves as a key guide for exploration.

Tectonic factor. The formation of ore bodies occurred under directed tectonic compression, as evidenced by parallel-oriented spodumene crystals and their micro-folds. This factor created conditions for multi-stage albitization, which acts as the principal ore-forming process.

The combination of morphological, mineralogical, geochemical, and structural features allows a comprehensive set of predictive criteria to be established for Alday that are fully consistent with data from other rare-metal pegmatites of the Kalba area (Bakennoe, Yubileinoe, etc.) and international analogs [21,23]

$^{40}\text{Ar}/^{39}\text{Ar}$ dating of muscovite from spodumene pegmatites of the Alday area yielded concordant ages of 293–290 Ma, indicating that these rare-metal objects formed synchronously with granodiorites and granodiorite–granites of the first phase of the Kalba Complex. These results refine the staging of rare-metal magmatism and confirm the genetic link of pegmatite mineralization with the late pulses of Kalba magmatism.

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Article

Assessment of Optical Light Microscopy for Classification of Real Coal Mine Dust Samples

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Abstract

Occupational exposure to respirable coal mine dust remains a significant health risk, especially for underground workers. Rapid dust monitoring methods are sought to support timely identification of hazards and corrective actions. Recent research has investigated how optical light microscopy (OLM) with automated image processing might meet this need. In laboratory studies, this approach has been demonstrated to classify particles into three primary classes—coal, silicates and carbonates. If the same is achievable in the field, results could support both hazard monitoring and dust source apportionment. The objective of the current study is to evaluate the performance of OLM with image processing to classify real coal mine dust particles, employing scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) as a reference method. The results highlight two possible challenges for field implementation. First, particle agglomeration can effectively yield mixed particles that are difficult to classify, so integration of a dispersion method into the dust collection or sample preparation should be considered. Second, optical differences can exist between dust particles used for classification model development (i.e., typically generated in the lab from high-purity materials) versus real mine dust, so our results demonstrate the necessity of site-specific model calibration.

Keywords: coal mine dust; Black Lung; dust monitoring; optical light microscopy

1. Introduction

Exposure to respirable coal mine dust can cause occupational lung diseases such as coal workers' pneumoconiosis (CWP) and silicosis. According to data from the Centers for Disease Control and Prevention (CDC), mortality from CWP declined by 69.6% and from silicosis by 53.0% between 1999 and 2018 [1]. Nevertheless, these diseases remain significant causes of impairment, disability, and premature death, especially among underground workers. Figure 1 illustrates the number of reported deaths attributed to CWP and silicosis in the United States from 2018 to 2024.

Rapid dust monitoring methods are sought to support timely identification of hazards and corrective actions. While a real-time instrument is now available for tracking the mass of respirable dust (i.e., the 'continuous personal dust monitor'), there are currently no tools enabling real-time, or even rapid, analysis of dust composition [2]. Some key limitations include cost, size, and permissibility in coal mine environments [2,3], accuracy and calibration challenges [4–6], timeliness of measurements [3,7], and mine-specific environmental factors [8].

A novel approach utilizing optical light microscopy (OLM) combined with image processing for dust monitoring has been proposed and explored by the authors of previous studies. An initial effort demonstrated the method's capability to distinguish between coal and mineral particle fractions [9]. Then, a follow-up study extended this approach by subclassifying the mineral fraction into highly birefringent carbonate particles and less birefringent silicates (i.e., including silica and other silicate minerals), which could allow for apportionment of the dust from three primary sources in underground coal mines (e.g., the target coal seam, the adjacent rock strata, and the carbonate-mineral based 'rock dust products' that are commonly applied in mines to mitigate explosibility hazards) [10]. However, an attempt to further subclassify silica, specifically, proved unsuccessful due to the similarity in optical features between silica and other silicate particles [11]. Nevertheless, the dust source apportionment capability may still be valuable for improving mine dust monitoring and exposure assessment—especially in mines where silicates are a reliable proxy for silica (i.e., where they consistently track together).

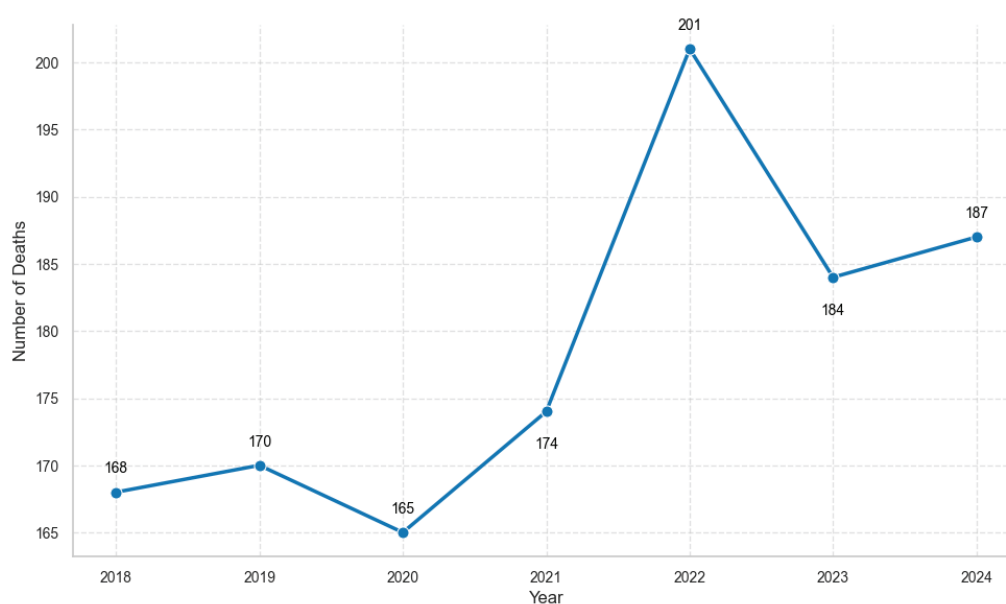


Figure 1. Number of reported deaths from coal workers' pneumoconiosis and silicosis in the United States since 2018. The figure was generated using data obtained from the [12].

Notably, the aforementioned studies have explored the capabilities and limitations of optical microscopy for classifying respirable coal mine dust in laboratory settings, using high-purity or well-characterized materials to generate dust particles. But applying the OLM classification technique to dust in (or collected from) real mine environments could present additional challenges. For example, particle loading density (PLD) (i.e., the number of particles per unit area on the dust collection substrate) is an important parameter for OLM since it can affect the ability to separate individual particles in images—and thereby the ability to assign optical signals to each particle. However, PLD is difficult to control during sampling because it is influenced by both the sampling duration and the concentration of airborne particles in the sampling environment—and the latter is difficult to know a priori. Moreover, the distribution of dust in the mine atmosphere is inherently dynamic and non-uniform, influenced by factors such as airflow geometry, ventilation patterns, and the nature of dust-generating activities [13–17]. This spatial variability introduces an additional layer of uncertainty, especially when compared to laboratory settings where experiments are conducted under more stable and controlled conditions.

Another potential challenge for applying OLM classification to real mine dust is the presence of agglomerated particles [18]. Agglomerates likely form due to high dust concentrations in the vicinity of dust generating activities [19] and might be influenced by particle surface properties [20], ambient humidity [21], and the use of surfactants in water sprays [22]. Additionally, energy distribution during advanced fracturing processes can affect particle size and morphology, which may in turn influence agglomeration behavior [23]. Given that agglomerates can have mixed compositions (e.g., coal and minerals clustered together), simple classification models built on individual particles may be confused [11,19]. In essence, an agglomerate may yield composited optical signals, but the model is forced to assign it to a single class. Finally, while a few broad mineralogy types (i.e., coal, silicates and carbonates) are expected to dominate airborne dust in many coal mines [24,25], there might be a wide distribution of optical signals associated with particles of each type. As mentioned, the prior research [10] on dust monitoring by OLM has used high-purity and well-characterized dust source materials to build classification models; but these may not be comprehensively representative of real mine dust particles. Further, in real mine dust samples, there could be minor fractions of other particle types including heavy minerals, metals or diesel particulates [24,26–30].

The objective of the current study is to evaluate the performance of OLM with image processing to classify real coal mine dust particles. Specifically, this work follows the approach of a recent study with lab-generated dust particles [10] in that (a) the same three mineralogy classes are targeted (i.e., coal, silicates, and carbonates) and (b) the same two-step classification process is used (i.e., categorizing particles as either coal or minerals, then categorizing minerals as either silicates or carbonates). Here, particle distributions predicted by the OLM method are evaluated against those determined by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) as a reference measurement.

2. Materials and Methods

2.1. Mine Dust Sampling

Coal mine dust samples for this study were collected from a room-and-pillar mine located in central Appalachia. Sampling was conducted in three distinct locations: downwind of a continuous miner (DCM), downwind of a roof bolter (DRB), and near a feeder breaker (FB). In each location, five pairs of duplicate samples were collected, each with varying sampling times; this yielded a total of 15 pairs. Since the sample PLD is a key parameter for OLM particle analysis, this approach was chosen to provide flexibility with respect to selection of samples for analysis.

Each pair of duplicate samples was collected using an ESCORT ELF® pump (Zefon International, Ocala, FL, USA), which pulled air through two 37 mm styrene filter cassettes (Zefon International, Ocala, FL, USA) using a Y-shaped tube splitter (see Figure 2A). The pumps were operated at a flow rate of 4 L/min, such that each cassette sampled at 2 L/min. In each location, five sampling apparatuses were mounted to a metal frame, which was suspended from the mine roof at approximately head height (i.e., 1.6 m from the floor). All pumps were started simultaneously, but the pumps were stopped on a staggered schedule to vary the total sampling times.

A detailed view of the filter cassette components is provided in Figure 2B. Each contained a polycarbonate (PC) filter (nominal pore size of 5 µm) placed on top of a cellulose support pad. A small circular glass slide with double-sided clear acrylic tape on top, was mounted off center on the PC surface using standard double-sided tape. This configuration enabled the simultaneous collection of particles on two substrates: the acrylic

tape and the PC filter. Dust particles collected on the acrylic tape were analyzed by OLM per [10], and particles on the PC filters were analyzed by SEM-EDX [31].

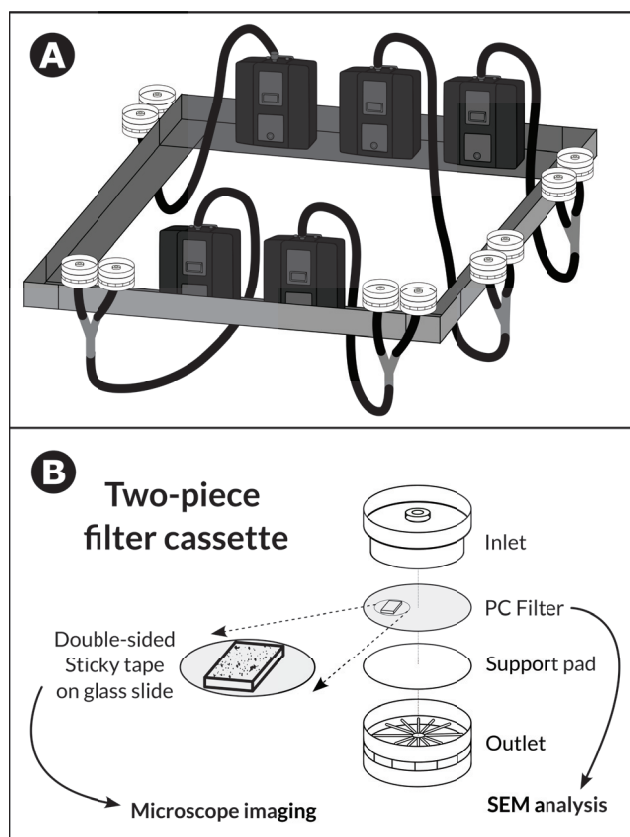


Figure 2. Mine dust sampling apparatus for each location (A), and detailed breakdown of the two-piece filter cassette components (B). The cassette includes a sticky acrylic tape mounted on a glass slide for OLM analysis and a PC filter for SEM-EDX analysis.

2.2. Selection of Samples for Analysis

Only a subset of the collected mine dust samples were selected for analysis based on assessment of tolerable PLD under the optical microscope (i.e., balancing sufficient loading to enable analysis of relatively many particles per field of view with minimal observance of physical interference between particles). Table 1 shows the selected samples (i.e., a total of three samples from each location), which were split into two separate groups for two stages of analysis.

The first group was used for preliminary analysis to evaluate the possible effect of agglomerates on OLM classification. This group included a single sample from each location, which was subjected to 'Direct-on-Substrate' (DOS) analysis—meaning the OLM and SEM-EDX analysis were performed directly on the acrylic tape and PC filter, respectively. The second group of samples was used for more in-depth evaluation of the OLM performance following a simple procedure intended to promote particle dispersion. As shown in Table 1, this group included six samples (i.e., one pair of duplicates from each location). Rather than analyzing DOS, these were used to generate 'Dispersed Dust' (DD) samples as described below.

Table 1. Summary of the mine dust samples used for direct-on-substrate (DOS) and dispersed dust (DD) analysis and the corresponding number of frames imaged by OLM and SEM-EDX. For each frame, images were captured under TPP and TCP lighting conditions.

Analysis Type	Field Sample Name	OLM Frames	SEM-EDX Frames
DOS	DCM_N321	256	5
	DRB_N321	256	5
	FB_N511	256	20
DD	DCM_N511	256	52
	DCM_N512	256	50
	DRB_N51	50	213
	DRB_N52	122	110
	FB_N411	256	340
	FB_N412	256	351

2.3. Preparation of Dispersed Dust Samples

Preparation of the DD samples was adapted from the procedure described by [19]. Briefly, approximately one-quarter of the PC filter (i.e., belonging to each of the six field samples shown in Table 1) was sectioned and submerged in a test tube containing isopropyl alcohol (IPA). The tube was placed in an ultrasonic bath for three minutes at 30 °C to recover dust from the filter surface and disperse particles. Following sonication, the filter section was carefully removed and the dust suspension was centrifuged at 2500 RPM for ten minutes. Finally, small aliquots (i.e., single drops) were carefully pipetted from the bottom of the test tube and alternately deposited onto a piece of double-sided acrylic tape (mounted on a glass slide) and a blank PC filter (see Figure 3), and each was allowed to dry completely in a clean hood. Thus, for each of the six field samples selected for DD analysis, this procedure yielded two new samples, one for OLM analysis and one for SEM-EDX analysis.

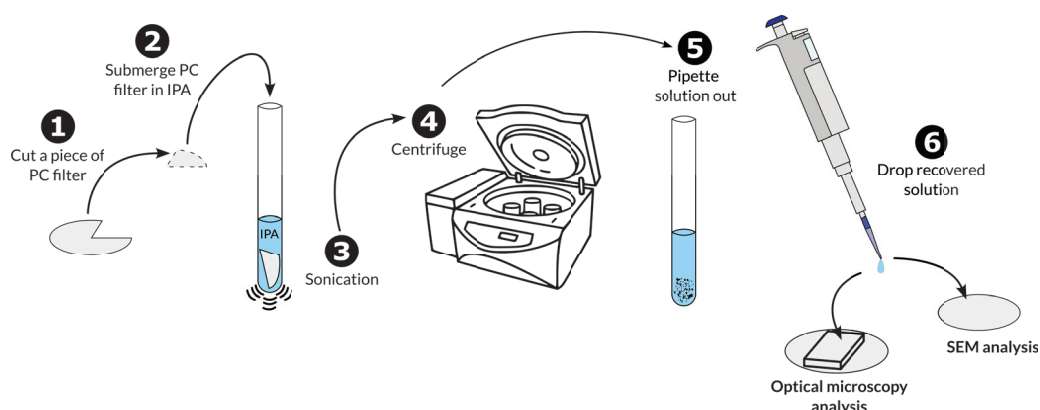


Figure 3. Sample recovery and redeposition procedure to create DD samples for OLM and SEM-EDX analysis.

Ultrasonic dispersion was selected based on prior studies [19,32], which demonstrated its effectiveness in reducing particle agglomeration without a substantial loss of particles from the sample. This method was therefore considered practical for improving agglomerate dissociation.

2.4. OLM Analysis

OLM analysis of both the DOS and DD samples was performed by analyzing particles on the acrylic-on-glass substrate. The OLM analysis followed the microscope settings, im-

age acquisition, processing, and feature extraction procedures described in [9,10]. Imaging was performed using an Olympus BX53M Polarizing Microscope with Stream Start 2.3 software. Transmitted plane-polarized (TPP) and transmitted cross-polarized (TCP) images were captured with exposure times of 30.51 ms and 815.06 ms, respectively, under 50% LED light intensity. The longer exposure for TCP was required to compensate for reduced light transmission under cross-polarized conditions, ensuring sufficient signal intensity for accurate particle feature extraction. Color balance was adjusted to 1.81 (red), 1.00 (green), and 1.28 (blue), with saturation and gamma both set to 1.00. A 40× objective and 0.63× camera magnification produced a total magnification of 25.008× and a spatial resolution of 87.971 nm/pixel. Images were saved in TIFF format at 2560 × 1920 pixel resolution. The image acquisition process was guided by an algorithm that analyzed each frame in real time, calculating particle sizes and maintaining a cumulative count. Once the algorithm determined that a sufficient number of particles had been captured—specifically, more than 500 particles within the 1–40 µm size range and at least 100 particles larger than 2.5 µm—it notified the user to stop imaging. This approach helped reduce the number of image frames required, streamlining the analysis process.

For particle classification, the current study used a relatively simple two-step model similar to that used by [9]. This is described in more detail below, but briefly, in Step-1, the mean intensity of particles under plane-polarized light (MITPP) was used to distinguish between coal and mineral particles, and in Step-2, the mean particle intensity under cross-polarized light (MITCP) was used to distinguish between silicates and carbonates. Particle class distributions were determined by calculating the proportion of particles in each class relative to the total number of particles analyzed on the sample (i.e., particle number percentage).

2.5. SEM-EDX Analysis

SEM-EDX analysis was performed by analyzing particles on the PC substrate as described by [31]. For the DOS analysis, a 9-mm subsection was carefully cut from each original PC filter belonging to the three samples shown in Table 1; for the DD analysis, the subsections were cut from the six PC filters prepared with dust recovered from the six samples shown in Table 1. Prior to analysis, each subsection was sputter-coated with a gold/palladium (Au/Pd) layer to render it electrically conductive. The analysis was conducted using a TESCAN FE-SEM system equipped with SE and BSE detectors, dual EDX detectors, and an Integrated Mineral Analyzer (called 'TIMA', Warrendale, PA). TIMA supports automated mineralogical analysis, enabling detailed, particle-by-particle characterization. For this study, the SEM-EDX was operated at 15 kV with a brightness setting between 16 and 18, a pixel size of 0.5 µm, a scan speed of 4, and standard segmentation settings. Multiple randomly selected frames were analyzed per sample following the same particle count thresholds described for the OLM analysis (i.e., at least 500 particles in the 1–40 µm range and at least 100 particles larger than 2.5 µm).

Using the EDX data, particles were categorized into the following classes: carbonaceous (likely coal), silicates (including silica), carbonates, or 'others'. Then, particle distributions were calculated using the same approach as in the OLM analysis (i.e., as the percentage of particles in each class relative to the total number of particles analyzed in the sample). Notably, results were normalized to exclude 'other' particles due to their minimal content (i.e., less than 4.6% of the total particle count in any given sample.) This enabled direct comparison of the SEM-EDX- and OLM-derived particle distributions.

3. Results and Discussion

3.1. Direct-on-Substrate OLM

The three mine dust samples selected for preliminary analysis (Table 1) were analyzed DOS by both OLM and SEM-EDX. The top plots in Figure 4 show the OLM MITPP and MITCP values (composited across all three samples) using a lower particle size threshold of either for 1 μm (left plot) or 2.5 μm (right plot). For comparison, the bottom row of the figure also shows MITPP and MITCP values observed for dust particles collected in the laboratory for a previous study [10]. For that study, the particles were sourced from high-purity materials (i.e., coal, quartz, kaolinite, limestone) and were collected onto the same acrylic-on-glass substrate and imaged under the same conditions used here.

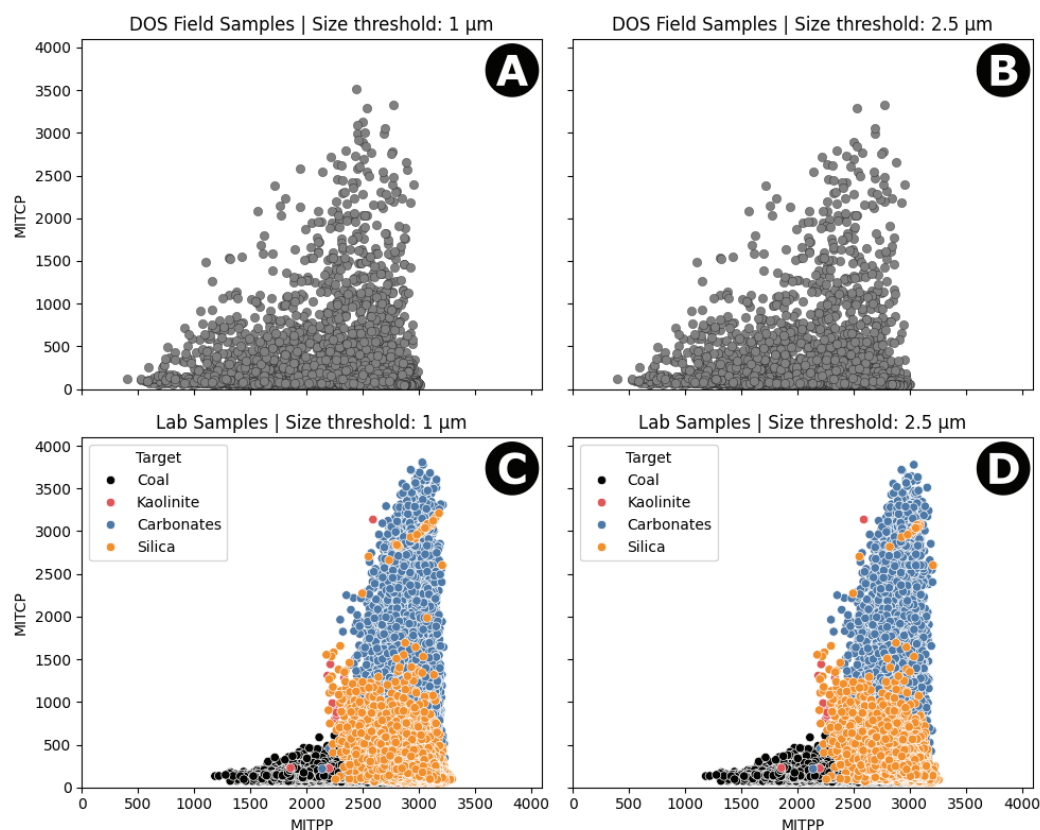


Figure 4. Comparison of MITCP and MITPP values observed for DD samples versus lab-generated dust samples using lower particle size thresholds of 1 μm and 2.5 μm . For the DOS samples (panels (A,B)), particle composition is unknown and all data points are shown in gray. For the lab-generated samples (panels (C,D)), particle sources are known and data points are color-coded by material: Coal (black), Kaolinite (red), Carbonates (blue), and Silica (orange).

Comparing the results for mine dust samples collected for the current work to those for the previously lab-generated samples, there are two main differences observable from Figure 4. First, the mine dust samples show much broader scatter toward the left side of the feature space. The data points observed in the region of low MITPP and high MITCP values in these samples represent particles that appear relatively darker under plane-polarized light but brighter under cross-polarized light. This might be related to the presence of agglomerated particles composed of mixed constituents, which can lead to complex interactions with optical signals. Compared to the lab samples, the mine dust samples might have been more susceptible to particle agglomeration—either due to the inherent nature of dust particles in the mine environment [19] or the fact that they were collected without the same cyclone size-selector used in the lab.

Second, overall, the field sample data appear to be shifted down and to the left (i.e., lower MITCP and MITPP values). The shift toward lower MITCP values might again be related, at least in part, to agglomeration of particles. For example, agglomerates containing both coal and minerals might illuminate less under TCP. However, the shift leftward toward lower MITPP values implies additional—and yet unexplained—differences between the field and lab-generated dust particles. One possible factor contributing to the presence of darker particles (low MITPP/MITCP) could be diesel particulate matter (DPM), as diesel equipment was operating in the study mine during sampling. While DPM particles are typically submicron in size, they may agglomerate with larger dust particles, potentially reducing brightness under both TPP and TCP conditions. However, we were unable to confirm the presence of DPM using the SEM-EDX method employed here, so this explanation remains speculative.

The optical signals observed in this study may also reflect differences in particle morphology, which is influenced by dust generation mechanisms. For example, fracture processes during cutting or blasting can produce angular particles with variable birefringence, while high-energy fracturing methods can yield finer, more irregular fragments [23,33]. Such morphological variability adds another layer of complexity to optical classification and warrants further investigation in future work.

Taken together, the above points indicate that an OLM model established with lab-generated samples is unlikely to yield accurate classification of particles for the mine dust samples. As an example, Figure 5 presents results for the three DOS mine dust samples using an OLM classification model that was developed with MITPP and MITCP thresholds derived from the lab-generated particles shown in Figure 4. (For this exercise, the model was developed and applied using a 2.5 μm lower particle size threshold). In essence, the model is attempting to use the MITPP threshold to differentiate coal from minerals (Step-1), and the MITCP threshold to differentiate silicates from carbonates (Step-2). In Figure 5, the top row of bar charts (Panels A-C) shows the results for Step-1 classification on each of the three DOS samples, with the SEM-derived results as reference, and the scatter plot (Panel D) summarizes the OLM prediction errors (i.e., versus SEM results); the bottom row (Panels E-H) shows the same for Step-2. It is immediately obvious the first classification step is unsuccessful, with the OLM substantially overpredicting the proportion of coal particles (and thereby underpredicting the proportion of mineral particles). This fits with the shift in MITPP values between the lab-generated particle data and mine dust particle data shown in Figure 4. While the OLM predictions are apparently improved for Step-2, it must be noted that the classification model is only considering a fraction of the true mineral particles in this case (i.e., since many particles were misclassified as coal in Step-1).

The unsuccessful outcome demonstrated by Figure 5 is not entirely surprising, as real coal mine dust particles are expected to be significantly more complex than high-purity particles collected in the lab. In the mine environment, optical signals can be influenced by numerous factors, including particle agglomeration, compositional heterogeneity, moisture content, and the presence of impurities. Because optical sensors detect a composite signal from such particles, accurate classification becomes challenging. This issue is particularly problematic when classification models are trained on high-purity, well-dispersed particles of single composition. Incorporating a particle deagglomeration step as a pretreatment could significantly enhance classification accuracy by ensuring more representative and separable particle features. Moreover, calibrating classification models using mine-specific data could offer a practical and efficient way to adapt optical methods. Therefore, the next section describes more in-depth work designed to (a) mitigate the presence and effect of agglomerated particles and (b) establish a mine-specific calibration model.

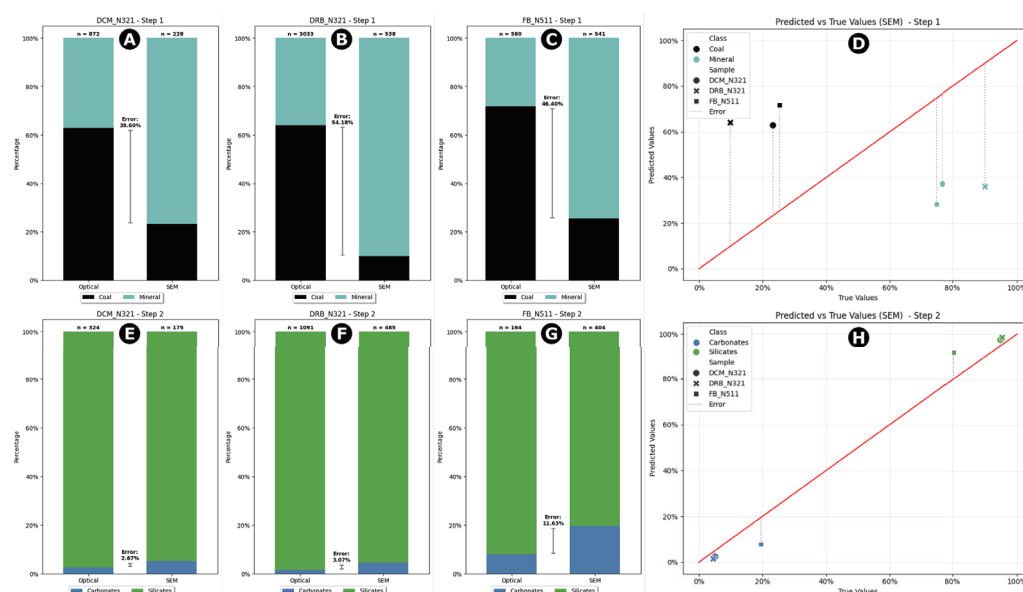


Figure 5. Preliminary results for DOS mine dust samples using a classification model based on the lab-generated dust results shown in Figure 4 with a 2.5 μm size threshold. Panels (A–C) show outputs from Step-1, which estimates coal and total mineral fractions. Panels (E–G) present results from Step-2, which further separates the mineral fraction into carbonates and silicates. Panels (D,H) display predicted vs. reference values for Step-1 and Step-2, respectively. The red diagonal line in panels (D,H) indicate perfect agreement, and vertical deviations from this line represent the error between OLM predictions and SEM-EDX-based validation.

3.2. Dispersed Dust OLM

To address the issue of agglomerated particles in the mine dust samples, the recovery and redeposition procedure described earlier was used to generate samples for DD analysis (i.e., using the six mine dust samples shown in Table 1).

To evaluate the effectiveness of ultrasonic dispersion, we compared the percentage of agglomerated particles (PAP) in untreated (DOS) and dispersed (DD) samples using SEM-EDX analysis. Table 2 summarizes PAP values by mine location and size threshold. On average, DOS samples exhibited a PAP of 39.28% and 62.01% for size thresholds of 1 μm and 2.5 μm , respectively. In comparison, DD samples showed a PAP of 29.04% and 43.66% for the same thresholds. For the 1 μm threshold, the PAP difference between ultrasonically dispersed samples and untreated samples was 10.24%, whereas for the 2.5 μm threshold, the difference increased to 18.35%. Although ultrasonic dispersion did not eliminate agglomerates entirely, the observed reductions indicate meaningful improvement in particle separability, which likely contributed to better OLM classification performance.

Figure 6 shows the DD sample results in terms of MITPP and MITCP values observed with OLM. (Again, the bottom row shows the values for lab-generated dust samples for comparison.) Clearly, the dispersion procedure facilitated at least some deagglomeration of particles, thereby reducing the scatter observed in the left region of the feature space with DOS analysis.

Although the DD data shown in Figure 6 exhibit improved alignment with the lab-generated dust data from the prior study [10], key differences remain. The DD results show a higher concentration of particles with relatively low values for both MITPP and MITCP, clustering in the lower-left region of the feature space. The differences in the MITPP values are most noticeable, and the maximum and mean MITPP values are shifted even lower for the DD results than for the DOS results. Respectively, the maximum MITPP values are 2971 versus 3005 (as compared to 3258 for the lab-generated dust particles), and mean values are 2281 versus 2386 (as compared to 2800 for the lab-generated particles). This suggests

that individual mine dust particles collected for this study are often darker than even the high-purity coal particles collected in the lab for the previous study [10]. This could be related to the abundance or quality of coal dust particles in the study mine, or the presence of constituents (e.g., DPM) which are not accounted for here. In any case, the results shown in Figure 6 clearly indicate that—even after dispersion—an OLM classification model based on lab-generated dust particles is not suitable for the mine dust samples.

Table 2. Percentage of agglomerated particles (PAP) for DOS and DD samples by mine location and size threshold.

Analysis Type	Field Sample Name	PAP 1 μm (%)	PAP 2.5 μm (%)
DOS	DCM_N321	38.78	51.91
	DRB_N321	36.68	62.16
	FB_N511	42.37	72.29
DD	DCM_N511	30.05	52.41
	DCM_N512	35.97	51.41
	DRB_N51	22.40	24.34
	DRB_N52	32.90	45.29
	FB_N411	27.27	46.19
	FB_N412	25.65	42.33

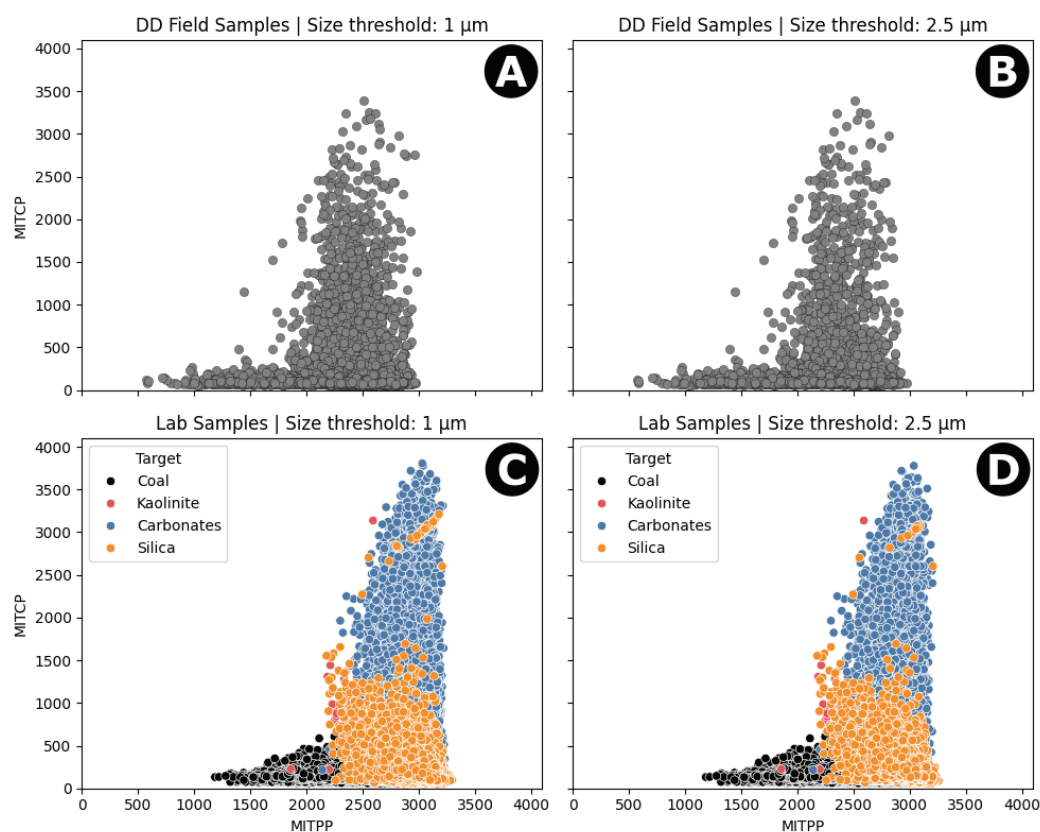


Figure 6. Comparison of MITCP and MITPP values observed for DD samples versus lab-generated dust samples using lower particle size thresholds of 1 μm and 2.5 μm . For the DD samples (panels (A,B)), particle composition is unknown and all data points are shown in gray. For the lab-generated samples (panels (C,D)), particle sources are known and data points are color-coded by material: Coal (black), Kaolinite (red), Carbonates (blue), and Silica (orange).

To develop a mine-specific classification model, the available DD dataset (Table 1) was divided in half such that one sample from each duplicate pair was used for model

development and the other was used for testing. This decision is supported by the good agreement between duplicates with respect to the SEM-derived particle distributions shown in Table 3. The SEM-derived results were again taken as reference for the OLM results.

Table 3. SEM-derived distribution of coal, silicate and carbonate particles in each of the samples generated for DD analysis.

Sample	B	Silicates (%)	Carbonates (%)
DCM_N511	9.77	88.84	0.39
DCM_N512	7.67	91.51	0.83
DRB_N51	9.20	84.40	6.40
DRB_N52	12.16	81.96	5.88
FB_N411	35.97	56.95	7.08
FB_N412	31.15	55.52	11.33

To construct the model, an error minimization strategy was employed to iteratively determine optimal thresholds for MITPP and MITCP using observations from all three DD ‘development’ samples. In each iteration, a candidate MITPP value was applied in Step-1: Particles with MITPP values less than or equal to the threshold were labeled as ‘coal’, while those exceeding the threshold were labeled as ‘mineral’. Then, the resulting coal-to-mineral particle distribution was compared to the distribution determined by SEM-EDX analysis. The classification error was calculated based on the difference between the OLM-derived and SEM-derived distributions. Similarly, iterations were performed to find the optimal MITCP threshold to classify mineral particles in Step-2: Particles with MITCP was less than or equal to the candidate MITCP value were labeled as ‘silicate’, while those exceeding the threshold were labeled as ‘carbonate’. And, again, the OLM-derived and SEM-derived distributions were compared.

The calibration process was performed using two lower particle size thresholds: 2.5 μm and 1 μm . However, the optimal thresholds for MITPP (1893) and MITCP (1103) were identified based on the minimization of average classification error when applying the 2.5 μm threshold in Step-1 and Step-2, respectively (see Figure 7).

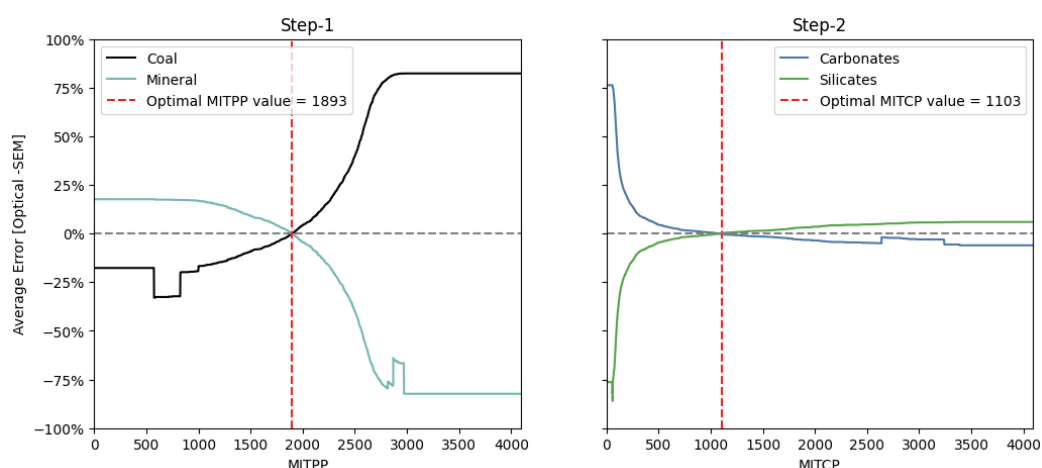


Figure 7. Average calibration error for Step-1 (left) and Step-2 (right) for the three DD samples used for model development with a 2.5 μm lower size threshold. The red dotted line indicates the optimal parameter value that minimizes the average error, as determined using SEM-EDX analysis as the validation reference.

Figure 8 presents the results when the mine-specific classification model (i.e., using the optimal MITPP and MITCP thresholds from Figure 7) was applied to the three DD

‘testing’ samples, using a 2.5 μm lower particle size threshold. Like the layout in Figure 5, in Figure 8 Panels A–C show the results for Step-1 classification on each sample, and Panel D summarizes the OLM prediction errors; and Panels E–H show the same for Step-2. This time, however, there is substantially better agreement between OLM predictions and SEM-derived reference measurements for classification of coal versus minerals (Step-1). Across all three samples, the root mean squared error (RMSE) is about 7% when using the mine-specific model, but was nearly 69% when using the model developed using lab-generated samples of high-purity materials. This demonstrates the potential for a mine-specific OLM model to classify coal versus mineral dust particles—even in the respirable size range.

For subclassification of minerals as silicates versus carbonates (Step-2), the results yielded by the mine-specific model are less compelling. In fact, the RMSE values derived from the data in Figures 8 and 5 are similar (i.e., about 9% versus 4%). This is at least partly attributed to the fact that all the field samples collected for this study had relatively low percentages of carbonates (i.e., less than 20% based on SEM-EDX analysis), which is an unfavorable condition for calibration exercises—if even representative of real mining environments. Nevertheless, the results also suggest that optical separation of major mineral classes is inherently challenging with real mine dust particles. This might be due to a relatively wide range of mineral types with overlapping optical features, impure particles (e.g., aggregates), or the persistence of some agglomerates in the DD samples generated in the current work [10].

Beyond the low abundance of carbonates and potential agglomeration effects, the sub-optimal performance in Step-2 likely reflects intrinsic similarities in optical properties among silicate minerals. Prior laboratory studies have shown that quartz and clay minerals (e.g., kaolinite) exhibit overlapping optical features under polarized light, making them difficult to distinguish [9,10]. The current work suggests that some overlap may also occur between silicates and carbonates in real mine dust, further complicating subclassification. These findings indicate that optical separation of major mineral classes is inherently challenging and may require more advanced feature extraction or complementary analytical techniques.

To observe the relative effect of particle size, a variation of the mine-specific model was also developed and tested with a lower particle size threshold of 1 μm . (Notably, this exercise used the same initial dataset considered for the model with a 2.5 μm threshold; the threshold was simply changed.) Table 4 compares the prediction errors for both 1 μm and 2.5 μm size thresholds. A slight improvement can be seen for the Step-1 results, which fits with the notion that finer particles are more prone to classification errors [9,10]. However, there is negligible difference for the Step-2 results, which may be related to any of the above factors challenging subclassification of mineral particles.

Table 4. Step-wise prediction error percentage for DD samples reserved for mine-specific classification model testing.

	Step	DCM_N511	DRB_N51	FB_N411	RMSE
1 μm	Step-1	17.49	2.14	4.78	10.54
	Step-2	12.14	2.03	6.33	7.99
2.5 μm	Step-1	8.28	3.81	8.59	7.23
	Step-2	14.06	0.36	5.33	8.68

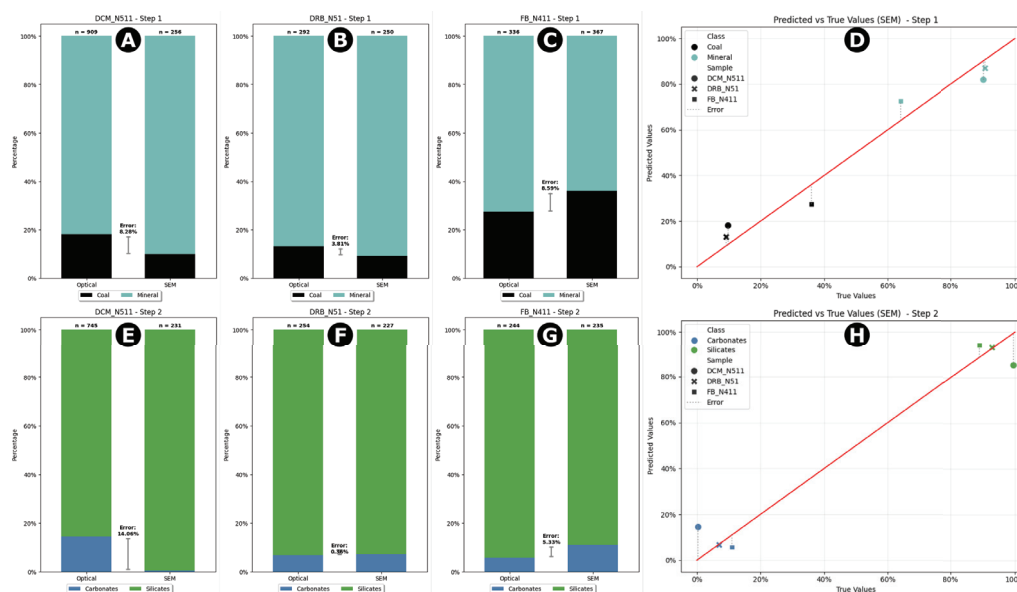


Figure 8. Results of calibrated mine-specific classification model on the three DD samples reserved for testing using a 2.5 μm size threshold. Panels (A–D) show outputs from the Step-1 model, which estimates coal and total mineral fractions. Panels (E–H) present results from the Step-2 model, which further resolves the mineral fraction into carbonates and silicates. Panels (D,H), indicate predicted vs. reference values for the Step-1 and Step-2 models, respectively. The red diagonal line in panels (D,H), indicate perfect agreement, and vertical deviations from this line represent the error between OLM predictions and SEM-EDX-based validation.

While the mine-specific calibration approach demonstrated promising results for classifying coal versus mineral fractions, the scope of this study was limited to samples collected from only three locations within a single mine. This narrow dataset constrains the generalizability of the findings and the developed model. Dust characteristics—including particle size distribution, mineralogy, and optical properties—can vary substantially across mines with different geological conditions, mining methods, and dust control practices. Therefore, the current model should be considered preliminary and site-specific. Future research should expand the dataset to include samples from multiple mines representing diverse geological settings and operational conditions. Such work will be critical to determine whether a robust, generalized OLM classification model is feasible or whether mine-specific calibration will remain necessary for practical implementation.

4. Conclusions

The findings of this study indicate that OLM-based classification of field samples is likely to be complicated by mixed or agglomerated particles that yield composite optical signals, suggesting that steps to promote dispersion during sampling or sample preparation could improve performance. Moreover, because the optical properties of real mine dust differ from those of the high-purity reference materials typically used in laboratory calibration, mine-specific OLM model calibration appears necessary.

In the current work, after taking steps to disperse field samples and build a mine-specific calibration, the results suggest that reliable classification of coal versus mineral fractions is achievable, even for respirable-sized particles. This capability could be quite valuable since, in many mining environments, the mineral fraction of respirable dust poses the greatest health hazard; thus, reliable classification of coal versus mineral particles could provide a practical means to track and manage exposure risks. However, subclassification of the mineral fraction was not possible here.

Several limitations of this study should be recognized. The dataset was small, with all samples collected from only three locations within a single mine. Consequently, the mine-specific model developed here cannot be assumed to generalize across different mines or geological conditions. Future work should prioritize expanding the dataset to include samples from multiple operations with varied dust sources and mining practices to determine whether a robust, generalized model is achievable. Further, all samples collected for this study exhibited relatively high silicate-to-carbonate ratios. This limits the insights that can be drawn from the attempt to subclassify the mineral fraction of the dust.

Author Contributions: Conceptualization, E.S. and N.S.; methodology, E.S. and N.S.; modeling, N.S.; validation, N.S. and L.J.; formal analysis, N.S.; data curation, N.S. and L.J.; writing—original draft preparation, N.S. and E.S.; writing—review and editing, N.S., E.S., and L.J.; visualization, N.S. and L.J.; supervision, E.S.; project administration, E.S.; funding acquisition, E.S. All authors have read and agreed to the published version of the manuscript.

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Article

A Raman Measurement and Pre-Processing Method for the Fast In Situ Identification of Minerals

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Abstract

Through this work, an experimental setup and pre-processing method for obtaining fluorescence and quasi-noise-free Raman spectra of minerals for in situ mineral identification in an underground environment is proposed. It uses a combination of methodologies like dual excitation wavelengths, Shifted Excitation Raman Difference Spectroscopy (SERDS), and deep learning-based U-Net model for background and noise correction. The dual excitation wavelengths technique employs a near-infrared SERDS laser for the fingerprint and a red laser for the large Raman shift region. The SERDS laser operates at two excitation wavelengths and is tuneable in the vicinity of 785 nm. The red laser uses 671 nm excitation wavelength. The obtained fingerprint and large Raman shift Raman spectra are then fed to a pre-processing method containing the trained U-Net model for obtaining a background-corrected and quasi-noise-free Raman spectrum. The proposed method addresses issues of existing handheld Raman systems in terms of spectrometer sensitivity, spectrum acquisition speed, pre-processing time, fluorescence effects, and other interferences due to surrounding light or vibration. The obtained final processed Raman spectrum is then deconstructed into pseudo-Voigt peaks. The identification of the minerals can be based on the number and the positions of the pseudo-Voigt peaks. Samples of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4) were used for evaluating the performance of the proposed method. The influence of measurement time on the reproducibility and precision of the peak identification and, thus, mineral identification is also analyzed.

Keywords: Raman spectroscopy; underground-in-situ mineral identification; U-Net; Shifted Excitation Raman Difference Spectroscopy (SERDS); dual excitation wavelength

1. Introduction

Deep geological formations are being investigated worldwide by many countries for the final disposal of radioactive waste. In Germany, the three types of host rock, salt, clay, and crystalline rock (granite), are being considered as sites for a future repository of high-level radioactive waste (HAW) [1,2]. After site selection, construction, and operation of the repository, the emplacement areas have to be sealed with suitable geotechnical barriers, i.e., with sealing elements to close shafts and drifts, after completion of the operating phase. The sealing elements, therefore, must be positioned in the intact rock to prevent or minimize possible flow paths. In the host rock salt, inhomogeneities can become preferred flow paths if they consist of easily soluble minor components (e.g., veins or nests of potash

salts) that are arranged unfavourably and are not recognized by the previous methods of geological exploration or investigation [3]. Up to now, the mineral phase composition has only been determined by point-by-point individual analyses of drill core material or material from the post-cut. An in situ mineral analysis using handheld Raman systems might be not targeted, as these systems usually feature low spectral resolution, making the identification of compounds having closer Raman peak positions difficult [4]; low spectrometer sensitivity and thereby need longer signal acquisition time [5]; fluorescence background obscure the Raman signal peaks in the measured spectrum, even with near-infrared excitation wavelengths [4]; and longer spectra pre-processing time [6]. This was also observed in our individual test measurements with loaner units. We have therefore started with our own developments.

As a result of these, we describe in this paper a Raman measurement method that is suitable for non-contact underground analysis of the wall, floor, or ceiling minerals in salt mines without sampling and demonstrate its performance. During the development of the measuring method, special attention was paid to the challenges that its upcoming underground use will bring. These challenges are (i) vibrations or (ii) extraneous light, both of which occur when machinery (e.g., trucks or wheel loaders) moves in the vicinity of the measuring device, (iii) short measuring times so that the material analysis can be carried out at as many measuring points as possible per time unit, and (iv) insensitivity to trace fluorescing substances like rare-earth elements that must not distort the evaluation of the material analysis.

The commonly used Raman measurement method for mineral analysis in the laboratory is Fourier-transformed (FT) Raman spectroscopy at a near-infrared excitation wavelength of usually 1064 nm [7]. The choice of the near-infrared excitation wavelength is intended to ensure that virtually no interfering fluorescence emissions are excited in addition to the Raman signal [8,9]. The red-shifted Raman spectrum with respect to the excitation wavelength is calculated from an interferogram by Fast Fourier transformation [7,10]. Because interferograms react sensitively to vibrations and extraneous light that is not constant during the measurement time, this measurement method is not suitable for the intended underground use. Another obstacle would be long measurement times of several seconds to minutes per spectrum [7,8,10–13]. In addition, the fluorescence might still be observed with 1064 nm excitation, either from the impurities existing in the sample or due to the crystal orientation within the sample [14,15].

In contrast to FT Raman spectrometers, dispersive (diffraction-based) Raman spectrometers are robust against vibrations. Although extraneous light influences have an effect on the detected spectra, they can be mathematically eliminated afterwards. The near-infrared dispersive Raman spectrometers (excitation wavelength 1064 nm) also largely avoid the laser-induced excitation of interfering fluorescence emissions. However, they suffer from considerable dark currents and the associated high thermal noise due to the small band gap of the detector array materials used [16,17]. If shorter excitation wavelengths are used, (thermally) lower-noise silicon-based standard detectors can be used [18]. A further significant advantage of shorter excitation wavelengths is that the Raman scattering cross-section increases by approximately the fourth power of the inverse excitation wavelength. So, for the same laser power, short-wavelength lasers generate a disproportionately higher signal than a long-wavelength laser. Unfortunately, the risk of interfering laser-induced fluorescence emissions increases as the excitation wavelength decreases [9,16,19,20]. In order to still be able to use the easy-to-handle and low-noise silicon-based detectors, excitation wavelengths in the red spectral range between 630 nm and 800 nm are often chosen, and the interfering fluorescence emissions that then occur are accepted, provided that these can be attenuated/eliminated by additional experimental precautions during the measurement or

subsequently by mathematical methods. Examples of experimental methods are the Shifted Excitation Raman Difference Spectroscopy (SERDS) technique [21–24] or the Sequentially shifted Excitation (SSE) technique [25,26]. Examples of the mathematical methods are U-Net deep learning model, Whittaker smoothing based algorithms or polynomial based algorithms [27–31]. Both SSE and SERDS are based on Kasha's rule [32] and are able to remove both narrow and broad fluorescence interference from the Raman spectrum, while the mathematical methods are only able to remove broad fluorescence interference present in the spectrum. Unlike SERDS, more than two excitation wavelengths are used in SSE. Since the processing time for the reconstruction algorithm in SSE depends on the number of excitation wavelengths used and also needs additional penalty time while switching between excitation wavelengths, the total acquisition time could be more in SSE in comparison with SERDS [6,25,26,33].

When analyzing minerals by Raman spectroscopy, their entire Raman spectrum should be taken into account, which includes both the so-called fingerprint region up to 2000 cm^{-1} and the so-called large Raman shift region between 2500 cm^{-1} and 4200 cm^{-1} . Both spectral regions contain information about the chemical composition of the mineral, the large Raman shift region in particular about water molecules incorporated into the crystal structure. Methods are known in which both spectral regions are excited one after the other using two different excitation wavelengths, and thus both spectral regions can be detected one after the other with the same spectrometer and high spectral resolution [16,34–36].

We here report a Raman method which

- Provides spectrally highly resolved Raman spectra that cover the fingerprint and the large Raman shift range from 380 cm^{-1} to 4200 cm^{-1} ;
- Eliminates spectrally broad fluorescence interferences;
- Eliminates spectrally narrow fluorescence interferences, which could easily be misinterpreted as Raman signals;
- Provides a quasi-noise-free spectrum, which is ideally qualified for the identification of all spectral peaks using peak finding algorithms.

All this has been achieved by the combination and further development of several experimental and mathematical methods. The performance of the proposed method is demonstrated by comparing the obtained spectra with the literature spectra of gypsum and anhydrite.

2. Materials and Methods

2.1. Materials

The inorganic minerals used in this work are the following:

1. Gypsum sample ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$): Merck KGaA, Darmstadt, Germany, (CAS number: 10101-41-4), p.a.-grade (Figure 1a).
2. Anhydrite sample 1 (CaSO_4): Synthetic anhydrite powder (technical by-product of hydrofluoric acid production provided by Fluorchemie Stulln GmbH, Stulln, Germany). This sample was chosen due to its significant fluorescence activity compared to other anhydrite sources. The raw material CaF_2 (due to its origin from natural deposits in China or South America) may contain traces of rare-earth elements (and therefore also the anhydrite), which are responsible for the observed fluorescence effects [37–39]. (Figure 1b).
3. Anhydrite sample 2 (CaSO_4): A drill core sample was taken from a depth of approx. 700 m below the surface of a rock salt horizon in the salt mine Sondershausen (Germany), drilled, and provided by the Institut für Gebirgsmechanik GmbH (IfG), Leipzig, Germany. The main body consists of halite (NaCl), with the white band of

anhydrite throughout the core (Figure 1c), analyzed in advance using non-destructive X-ray diffraction.

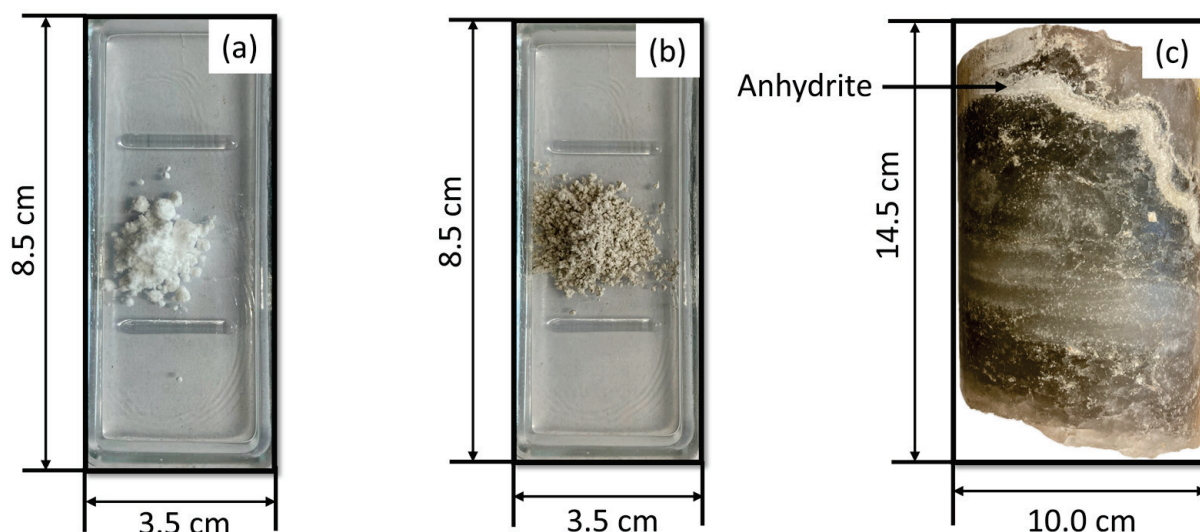


Figure 1. Materials used. (a) Gypsum sample, (b) anhydrite sample 1, and (c) anhydrite sample 2.

For gypsum and anhydrite, the Raman peak positions of both samples look similar in the fingerprint region, and only gypsum has Raman peaks in the large Raman shift region. A Raman spectrum free of background and noise is needed to clearly distinguish between anhydrite and gypsum in the fingerprint region. In addition, the existence of peaks in the large Raman shift region helps in identifying the presence of gypsum more easily. Hence, by using the mineral samples of gypsum and anhydrite, this work explains the ability of the proposed method in obtaining background and quasi-noise-free Raman spectra of minerals, and thereby its suitability for identification. The proposed method, however, could also be applied to other mineral samples.

2.2. Experimental Setup

As shown in Figure 2, the laser radiations from the “Red laser” (MLL-FN-671-800 mW laser, PhotonTec Berlin GmbH, Berlin, Germany; emission wavelength 671 nm) and the “SERDS laser” (dual wavelength-Y-DBR-RW-Diode laser, Ferdinand-Braun-Institut gGmbH, Berlin, Germany; emission wavelengths tuneable and switchable between two wavelengths in the vicinity of 785 nm) are focussed into the glass fibres of 50 μm core diameter (b) using focussing lenses (a) and are brought to the laser coupler. The laser coupler enables the alignment of the red and the SERDS laser radiations into a single Raman probe. Using the collimating lenses (c) and a beam splitter (e), another collimator (a) launches the radiation into the so-called excitation glass fibre of 200 μm core diameter (f), which carries the excitation radiation into the Raman probe. Electrically driven laser shutters (d) are installed between the beam splitter (e) and collimating lens (c) for the alternate turning OFF/ON of the radiation coming from the red or the SERDS laser. They assure that the radiation of the red and the SERDS laser is transferred to the Raman probe one after the other.

In the Raman probe, a reflective collimator (g) collimates the radiation leaving the excitation fibre. The collimated beam then passes through a short pass filter (h), with a cut-off wavelength at 800 nm onto the beam splitter (i). The short pass filter eliminates any radiation that might have emerged from light–matter interactions in the previous fibres and that would result in undesired interferences, if detected along with the Raman signal. The beam splitter (i) reflects the incoming laser radiation onto the achromatic lens (j) of 35 mm focal length, which in turn focusses the laser radiation onto the mineral sample. Hence, the working distance of the sample surface from the Raman probe is 35 mm. The

diameter of the laser focussing spot on the mineral sample is 0.12 mm. We refer to the laser focal spot on the mineral sample as the measurement spot.

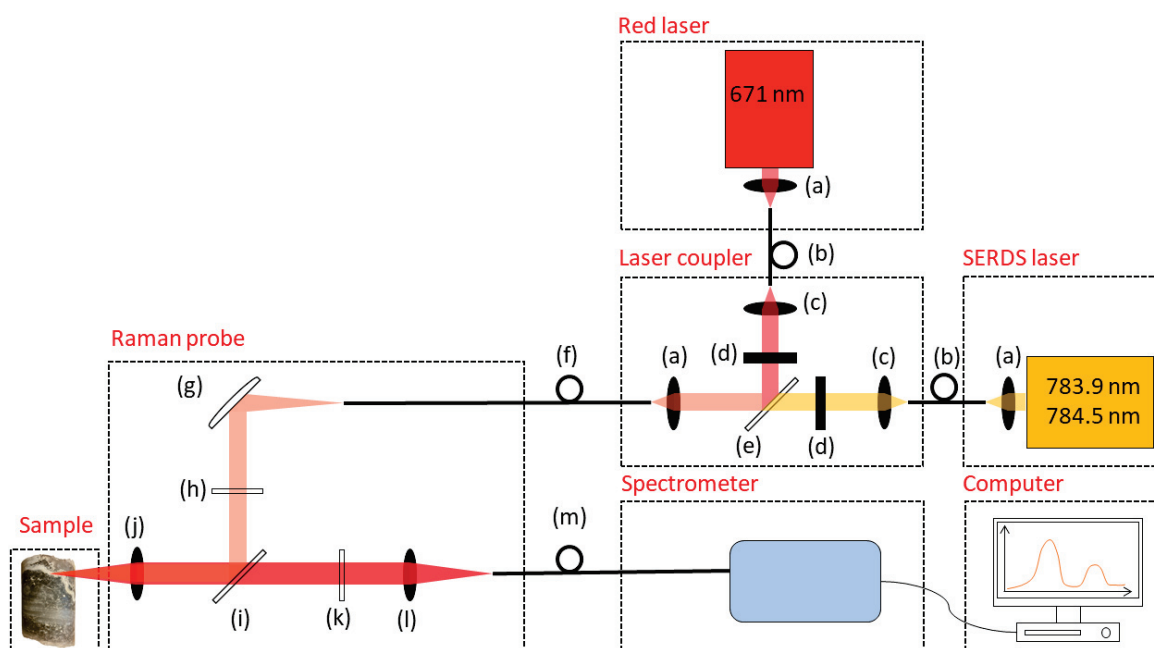


Figure 2. Sketch of the experimental Raman setup. (a) Focussing lenses (PAF2S-5B, PAF-SMA-11-A, PAF2S-A7B; Thorlabs GmbH, Bergkirchen, Germany), (b) glass fibre, (c) collimating lenses (PAF2S-5B, Thorlabs GmbH), (d) laser shutter, (e) beam splitter (Laser-Beamsplitter HC R685 1 lambda PV flat, AHF analysentechnik AG, Tübingen, Germany), (f) excitation glass fibre, (g) reflective collimator (RC12SMA-P01, Thorlabs GmbH), (h) short pass filter (FESH0800, Thorlabs GmbH), (i) beam splitter (Laser-Beamsplitter HC R785 1 lambda PV flat, AHF analysentechnik AG), (j) focussing and collimating lens (AC254-035-B-ML, Thorlabs GmbH), (k) long pass filter (FELH0800, Thorlabs GmbH), (l) focussing lens (AC254-060-B-ML, Thorlabs GmbH), and (m) detection glass fibre.

The radiation (signal) emerging due to the light–matter interaction in the measurement spot is detected in back-scattering direction and collimated by the same achromatic lens (j). The collimated signal beam passes through the beam splitter (i) and a long pass filter (k) with a cut-off wavelength at 800 nm onto another achromatic lens (l) with a focal length of 60 mm. The long pass filter (k) and the beam splitter (i) separate the undesired elastically scattered signals from the signal. The achromatic lens (l) focusses the Raman signals into the glass fibre of 600 μm core diameter (m). This glass fibre (m) is also called detection fibre, since it carries the detected signals into the standard spectral range (802 nm to 934 nm) spectrometer (WP-785-C-SR-IC, Wasatch Photonics, Morrisville, NC, USA), with a back-thinned CCD detector array for obtaining the signal spectrum of the sample. The average full-width half-maximum (FWHM) spectral resolution of the spectrometer is 10 cm^{-1} .

2.3. Measurement Method

Raman measurements of the vertically positioned drill core (Figure 1c) were made with a horizontally oriented Raman probe, as shown in Figure 2. The synthetic powder samples (Figure 1a,b) were presented in open glass containments. They were measured with a vertically oriented Raman probe in order to optically access the powders from the top. This measure avoids the excitation of the powdered sample through the walls of the glass containment, which would result in glass-born interferences.

In any case, at first, an averaged spectrum of 16 Raman spectra of the sample with an excitation wavelength of 783.9 nm was acquired using the SERDS laser. Then, the excitation wavelength of the SERDS laser was shifted to 784.5 nm, and another averaged spectrum

of 16 Raman spectra of the sample was acquired. The two laser excitation wavelengths are obtained by switching between two laser diodes available within the laser [33]. The two excitation wavelengths provide a wavelength difference of 0.6 nm. This wavelength difference was chosen because the spectrometer's spectral resolution of 10 cm^{-1} (FWHM of a Raman peak) is approximately 0.6 nm at 802 nm. Thus, the wavelength difference of 0.6 nm is desirable for both an efficient experimental fluorescence rejection and a successful reconstruction of meaningful refined Raman spectra using the SERDS technique [24]. The wavelengths were chosen in the vicinity of 785 nm because a quickly switchable laser is available in this spectral range, undesired fluorescence interferences can be reduced to an acceptable degree, and Si-based CCD detectors can detect the fingerprint spectral range of the Raman spectrum with an acceptable quantum efficiency between 46 and 66%. In this case, the spectrometer used covers solely the spectral region up to 2000 cm^{-1} , which contains the fingerprint range. Finally, another averaged Raman spectrum of 16 Raman spectra was acquired with an excitation wavelength of 671 nm using the red laser. The choice of the 671 nm excitation wavelength implied that now the same spectrometer covers the large Raman shift range of the Raman spectrum from 2500 cm^{-1} to 4200 cm^{-1} with the same quantum efficiency as the fingerprint spectral range. Thus, one spectrometer is sufficient for the spectrally highly resolved detection of the entire Raman spectrum, not simultaneously, but one after the other, with first the fingerprint and then the large Raman shift range. The excitation power in the measurement spot was around 67 mW for the red laser and 59 mW for the SERDS laser. Each spectrum used in calculating the averaged spectrum was obtained with a signal integration time of 50 ms. The averaged spectrum, therefore, corresponds to approximately 800 ms.

3. Results and Discussion

3.1. Pre-Processing

The pre-processing method of the raw Raman spectra is shown in Figure 3. In order to underline its general applicability, a simulated spectrum is utilized as raw Raman spectrum in this subsection. In the fingerprint region, two Raman spectra of any mineral sample are acquired, one excited with 783.9 nm and the other one with 784.5 nm. They are labelled as (p) and (q) in Figure 3. After z-score normalization, the difference spectrum (r) is calculated by subtracting spectrum (q) from spectrum (p) [24]. The difference spectrum (r) is baseline corrected using the baseline (s) determined with a third-order asymmetric least squares (AsLS) fitting [27,30,31]. The baseline correction compensates effects due to fluorescence quenching, excitation-dependent fluorescence quantum yields, or noise [23,40]. The baseline-corrected difference spectrum (t) is normalized between -1 and 1 in order to enhance the features that are represented by small peaks. The difference spectrum (t) is then given as input to a deep learning based trained U-Net model developed in our working group to predict the background and noise-corrected Raman spectrum (u) [28]. The enormous noise reduction capability of the U-Net model is not visible in Figure 3, as the considered raw spectrum features a high signal-to-noise (SNR) ratio. But the noise reduction capability can be seen in [28] or in the figures that follow. The U-Net model was trained using TensorFlow API in the Python programming language on a dataset containing 300,000 simulated difference spectra obtained by subtracting a shifted version from the unshifted version of raw simulated Raman spectra. Each simulated raw Raman spectrum is created using a random sum of the Voigt, Gaussian, and Lorentzian profiles. The maximum number of profiles in the simulated raw Raman spectrum for model training is less than 50 [28]. The trained U-Net model was tested using Raman spectra of liquid solvents and biological samples. The model was able to successfully remove the noise and background from the testing Raman spectra [28]. Since the model was trained on

a simulated dataset, the model could also be used for SERDS reconstruction as well as fluorescence removal in the fingerprint and large Raman shift region of Raman spectra of minerals. Further details of the U-Net architecture and the data used for creating the model are explained in [41] and [28], respectively.

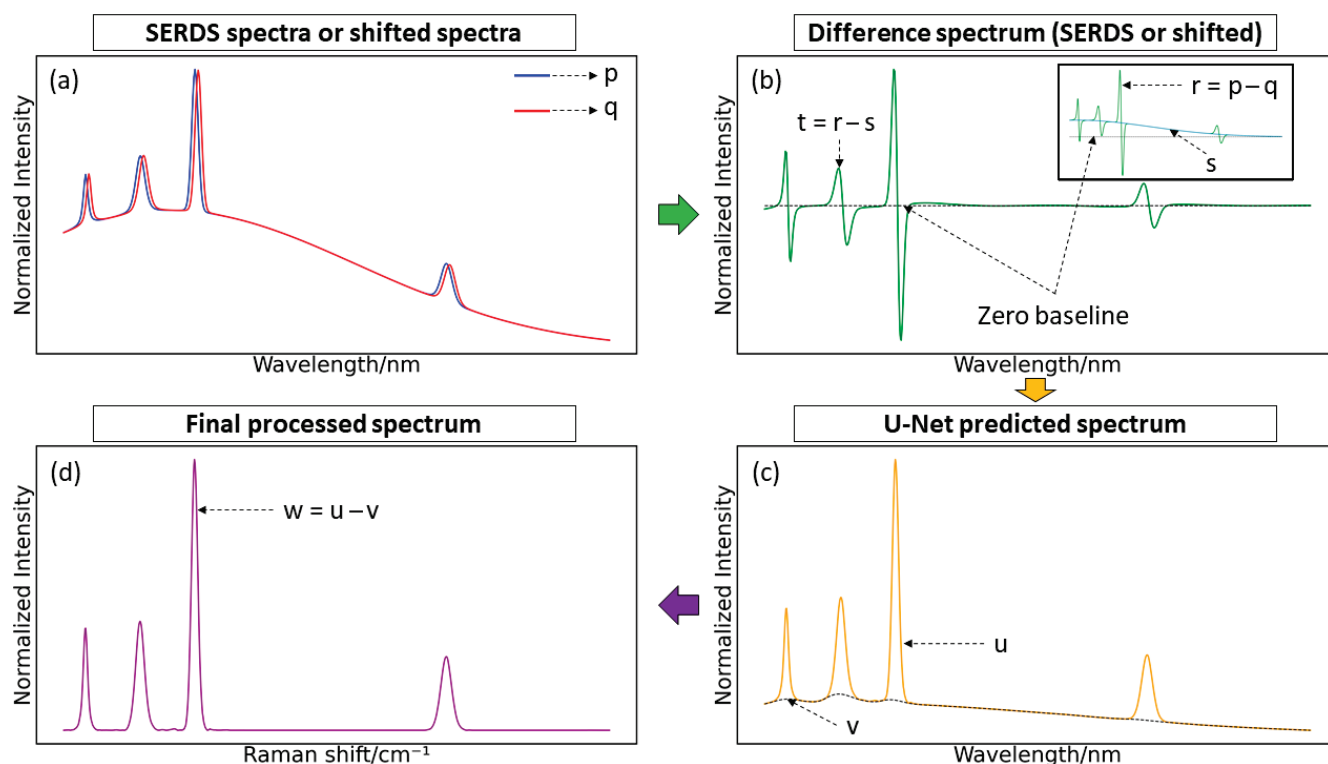


Figure 3. Pre-processing method. (a) z-score-normalized SERDS spectra or shifted spectra, (b) difference spectra determined by subtraction and a baseline correction, (c) predicting the Raman spectrum from difference spectrum using U-Net, and (d) final processed Raman spectrum obtained by subtracting baseline from U-Net predicted Raman spectrum.

The next step is solely required if the U-Net predicted spectrum (u) should be represented by a sequence of pseudo-Voigt peaks [42,43], whose number and position can be used later for mineral identification. This next step involves subtracting a third-order asymmetrically reweighted penalized least squares (arPLS) baseline (v) [29]. Finally, the so obtained spectrum (w) is deconstructed into pseudo-Voigt peaks.

For the large Raman shift region of the Raman spectra, the pre-processing method is almost the same as that of the fingerprint region. Since only one excitation wavelength of 671 nm is available (p), a second spectrum (q) for calculating the difference spectrum (r) is mathematically synthesized by shifting the spectrum obtained with 671 nm by 0.15 nm. As we did not shift the excitation wavelength in this case but the spectrum, we refer to the resulting difference spectrum in the large Raman shift region as difference spectrum, while we refer to the resulting difference spectrum in the fingerprint region as SERDS spectrum. A shift of 0.15 nm corresponds to the minimum wavelength difference between two pixels. The minimum value is chosen to have minimum noise in the non-peak regions when the difference spectrum is calculated. The U-Net model was trained on full-range Raman spectra (0 cm⁻¹ to 4200 cm⁻¹) with 1024 pixels [28]. In our current study, only the large Raman shift range is detected on 1024 pixels. As a result, the broader peaks in the large Raman shift region Raman spectra could be mistaken for broadband fluorescence. Therefore, in order to avoid this, the large Raman shift region Raman spectra were first compressed in order to adjust the width (in the form of the number of pixels) of the OH band to the training data. Some pixels had to be added at the beginning of the spectrum by extrapolation after

the compression in order to also meet the total number of pixels of the training spectra. A normalization between -1 and 1 for the difference spectrum is not performed in the large Raman shift region difference spectra, as anhydrous salts, like anhydrite, do not have peaks in large Raman shift regions; so, a normalization between -1 and 1 would just amplify the noise. Also, the large Raman shift region Raman spectra have larger peaks in comparison with fingerprint region Raman spectra. Hence, large Raman shift region peaks are well represented in the difference spectra without the normalization between -1 and 1 .

The pre-processing method is implemented in the Python 3.9 programming language. The pre-processing method took around 100 milliseconds for processing both the fingerprint and large Raman shift region Raman spectra of a single mineral (Windows 11 PC with 32 GB RAM and AMD Ryzen 7 Pro processor).

3.2. Gypsum Raman Spectrum

Figure 4a,b are the z-score-normalized fingerprint and large Raman shift region Raman spectra of the gypsum sample. The fingerprint spectra are quasi-fluorescence-free, and the broad fluorescence background is only seen in the large Raman shift region. The obtained final processed spectra of the fingerprint and large Raman shift region (by the method described in 3.1) are concatenated to obtain the full Raman spectrum of the synthetic gypsum shown in Figure 4c. The proposed method was able to completely remove the broad fluorescence background existing in the large Raman shift region. The root mean square (RMS) noise (same as the standard deviation) calculated using the signal-free region between 800 cm^{-1} to 900 cm^{-1} is around 10^{-5} . Thus, the method provides a quasi-noise-free spectrum.

For the pseudo-Voigt profile peaks shown in Figure 4c, the absolute differences between the obtained spectrum and the modelled spectrum were the least. The Raman shifts in the peaks given in Figure 4c are the central peak positions of the pseudo-Voigt profiles. The peaks in fingerprint regions are due to bending and stretching vibration modes of sulphate ions, and the peaks in the large Raman shift regions are due to OH stretching vibrations. Table 1 shows a comparison of the Raman peak positions of the final processed spectrum with the literature values. The determined peak positions are in similar ranges to those of the literature Raman shift values. The Raman shift values of the peaks are susceptible to small changes depending upon the measuring instrument resolution and the measurement conditions.

Table 1. Raman bands for gypsum (in cm^{-1}).

References	$\vartheta_2\text{ SO}_4$ Bending		$\vartheta_4\text{ SO}_4$ Bending		$\vartheta_1\text{ SO}_4$ Stretching	$\vartheta_3\text{ SO}_4$ Stretching	OH Stretching	
[44]	415	495	620	673	1008	1134	3401	3491
[45]	416	495	623	674	1010	1143	-	-
[46]	416	494	622	672	1010	1138	3410	3498
[47]	415	493	619	670	1008	1135	3404	3493
[48]	415	494	620	671	1008	1136	3406	3494
[49]	-	-	-	-	1011	1134	3397	3493
This work (Gypsum sample after pre-processing)	414	493	619	671	1006	1135	3395	3484

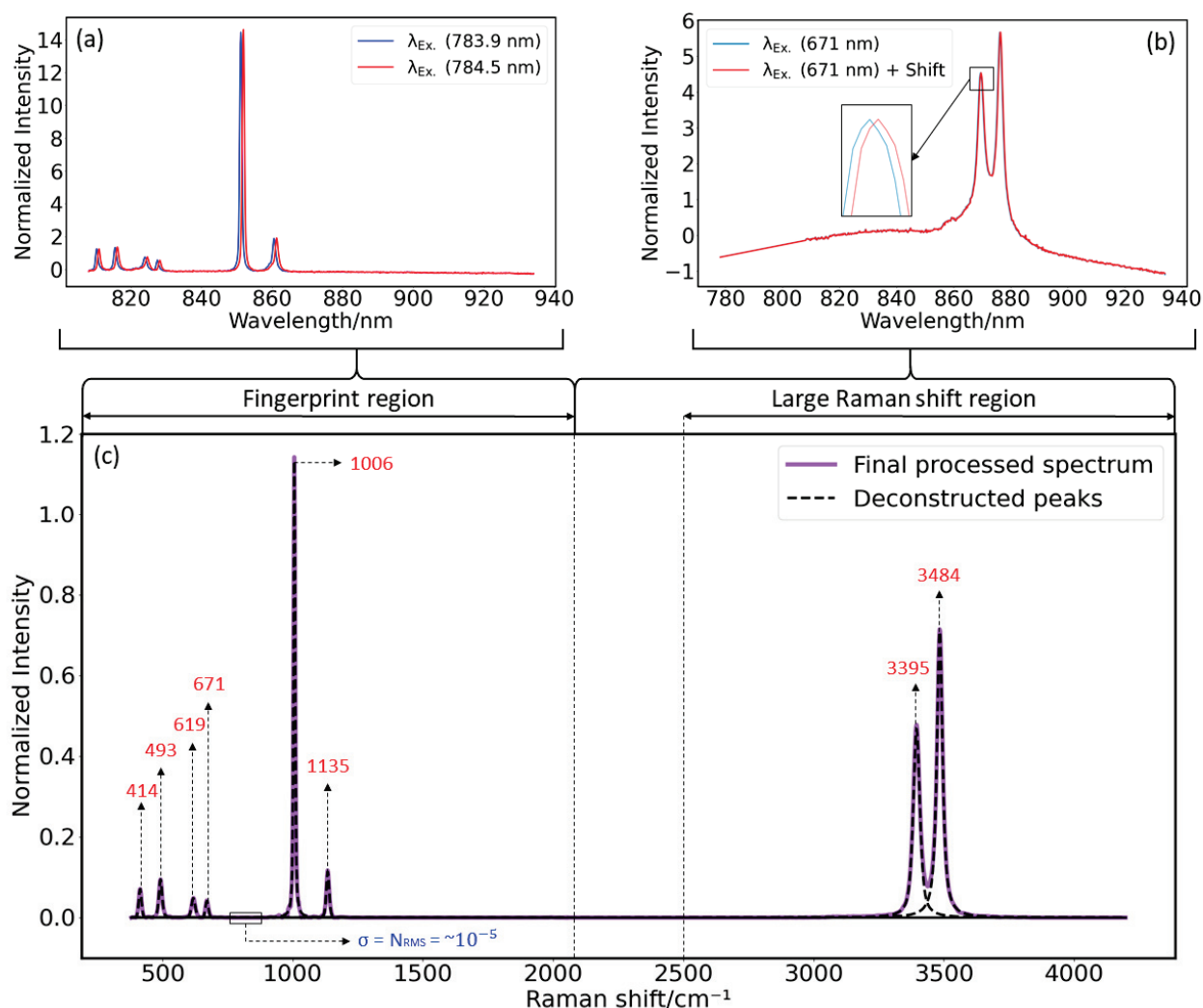


Figure 4. Raman spectrum of gypsum sample. (a) z-score-normalized fingerprint region of Raman spectrum with 783.9 nm and 784.5 nm excitation, (b) z-score-normalized large Raman shift region of Raman spectrum with 671 nm excitation and the same spectrum shifted by 0.15 nm, and (c) final processed and concatenated Raman spectrum.

3.3. Anhydrite Raman Spectrum

Figure 5 shows the z-score-normalized and finally processed spectra of anhydrite sample 1. It is shown that the large narrow peaks in Figure 5a, which—due to their shape—could easily be taken as Raman peaks, do not shift with the excitation wavelength. They thus can be clearly identified as interfering fluorescence emissions. Spectrally rather narrow fluorescence emissions could be due to the rare-earth elements (lanthanide group elements) associated with the mineral's particular phase or structure [14,15,26]. The proposed method provides in Figure 5c a fluorescence-cleared fingerprint Raman spectrum. It has been shown in [50,51] that the wavelength of the fluorescence emissions of rare earths is not a function of the excitation wavelength, and the probability of absorption at 785 nm is more than at 671 nm. Therefore, one can identify either the same interfering fluorescence emissions appearing at the same wavelength when the material is excited with 671 nm as well as with 785 nm, as shown in Figure 5a,b, or interfering fluorescence emissions will only be seen in the Raman spectrum obtained with 785 nm excitation wavelength. Thus, as indicated in Figure 5b, the intensities corresponding to the fluorescence interference in the large Raman shift regions are replaced with a baseline of this region calculated using a second-order arPLS algorithm [27,29]. The corrected large Raman shift Raman spectrum

is then shifted in order to obtain the difference spectrum, from which the final processed Raman spectrum is obtained, according to the method described above in the context of Figure 3.

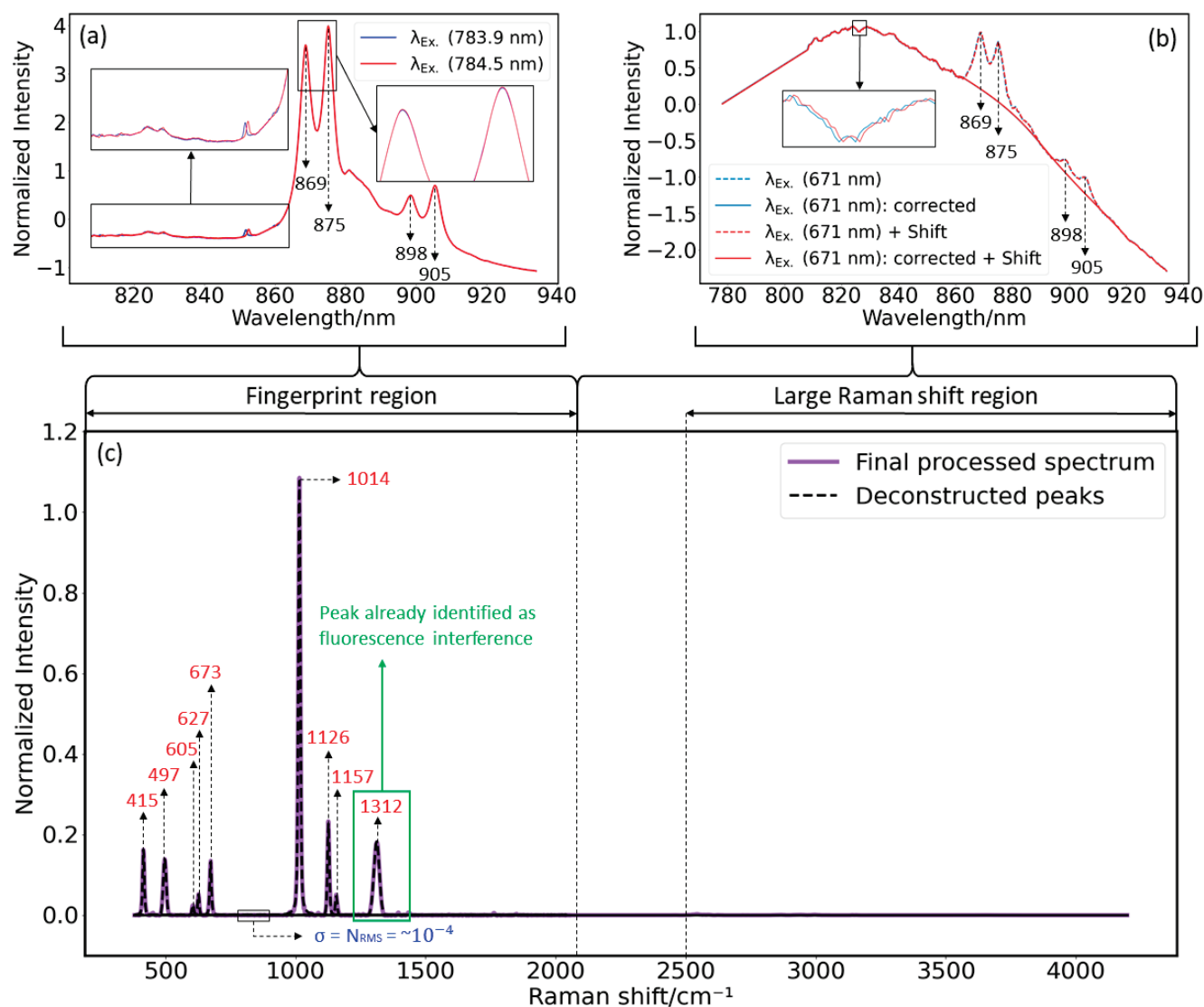


Figure 5. Raman spectrum of anhydrite sample 1. (a) z-score-normalized fingerprint region of Raman spectrum with 783.9 nm and 784.5 nm excitation, (b) z-score-normalized large Raman shift region of Raman spectrum with 671 nm excitation and the same spectrum shifted by 0.15 nm, and (c) final processed and concatenated Raman spectrum.

The pre-processing method in combination with the additional correction procedure was able to clear both, the narrow and broad fluorescence interference from the fingerprint and large Raman shift region, as shown in Figure 5c. The final processed spectrum is then deconstructed into pseudo-Voigt peaks for peak position determination. The peaks are listed in Table 2 for comparison with the literature values. The baseline correction on the U-Net predicted spectrum, as explained in the context of 3.1, is able to remove most of the remaining fluorescence interference due to excitation power sensitivity of the fluorescence. However, because of the strong fluorescence interference at 869 nm and 875 nm, fluorescence interference is not completely removed, and a corresponding peak is observed in Figure 5c at 1312 cm^{-1} . But as observed in Figure 5a, the fluorescence interference does not change its position; hence, any remaining fluorescence interference that appears close to strong fluorescence interference in the final processed spectrum could

be identified as part of the fluorescence interference, and the corresponding pseudo-Voigt peak can be easily discarded.

Table 2. Raman bands for anhydrite (in cm^{-1}).

References	$\nu_2 \text{ SO}_4$ Bending		$\nu_4 \text{ SO}_4$ Bending		$\nu_1 \text{ SO}_4$ Stretching		$\nu_3 \text{ SO}_4$ Stretching	
[44]	417	499	609	628	675	1017	1128	1160
[45]	420	503	-	630	678	1018	1129	1160
[46]	410	492	602	620	668	1010	1122	1154
[47]	417	499	609	628	675	1017	1129	1160
[48]	417	499	-	628	675	1017	1128	1160
[52]	471	500	609	627	675	1017	1130	1160
This work (Anhydrite sample 1 after pre-processing)	415	497	605	627	673	1014	1126	1157
This work (Anhydrite sample 2 after pre-processing)	414	496	604	625	673	1015	1127	1158

For analyzing the performance of the pre-processing procedure on a Raman spectrum with a broad fluorescence interference in the fingerprint and large Raman shift regions, the proposed method is also applied to the Raman spectrum of anhydrite sample 2 shown in Figure 6. No narrow fluorescence interference due to rare-earth ions was observed in the Raman spectrum of analyzed anhydrite sample 2. Hence, unlike anhydrite sample 1, the additional correction procedure in the large Raman shift region was not needed. The deconstructed pseudo-Voigt peak positions shown in Figure 6c are also listed in Table 2 for comparison with the literature values.

It could be observed from the results shown in Figures 5c and 6c that, for both anhydrite samples 1 and 2, the proposed method was able to provide fluorescence and quasi-noise-free final processed spectra, with a root mean square (RMS) noise value of around 10^{-4} at the silent region of Raman spectrum.

From the comparison listed in Table 2, the final processed Raman spectra of anhydrite samples 1 and 2 have the central peak positions of the pseudo-Voigt peaks in similar ranges to each other and to the literature values. In Figures 5c and 6c, no peaks are seen in the large Raman shift region Raman spectrum due to the absence of water molecules in anhydrite.

To further demonstrate the effectiveness of the proposed method, a comparison as shown in Figure 7 is performed between raw and final processed Raman spectra of anhydrite samples 1 and 2. The raw Raman spectra used in this comparison are the same as the spectra used in Figures 5a and 6a obtained with 783.9 nm excitation wavelength. Both the raw spectra and the final processed spectra are normalized between 0 and 1 for comparison. As one can observe, the raw fingerprint region Raman spectra (dashed curves) of both anhydrite samples differ largely from each other. Without the pre-processing method, the raw Raman spectrum of anhydrite sample 1 can easily be mistaken for other minerals due to the narrow fluorescence interference at Raman shift values of 1249 cm^{-1} (869 nm), 1328 cm^{-1} (875 nm), 1621 cm^{-1} (898 nm), and 1707 cm^{-1} (905 nm). But through the proposed method, the Raman peaks of anhydrite sample 1, which were otherwise not clearly distinguishable, were recovered after pre-processing. The remaining fluorescence interference at 1312 cm^{-1} is removed from the final processed spectrum of anhydrite sample 1. As a result, the final processed Raman spectrum (solid curves) of both samples looks similar.

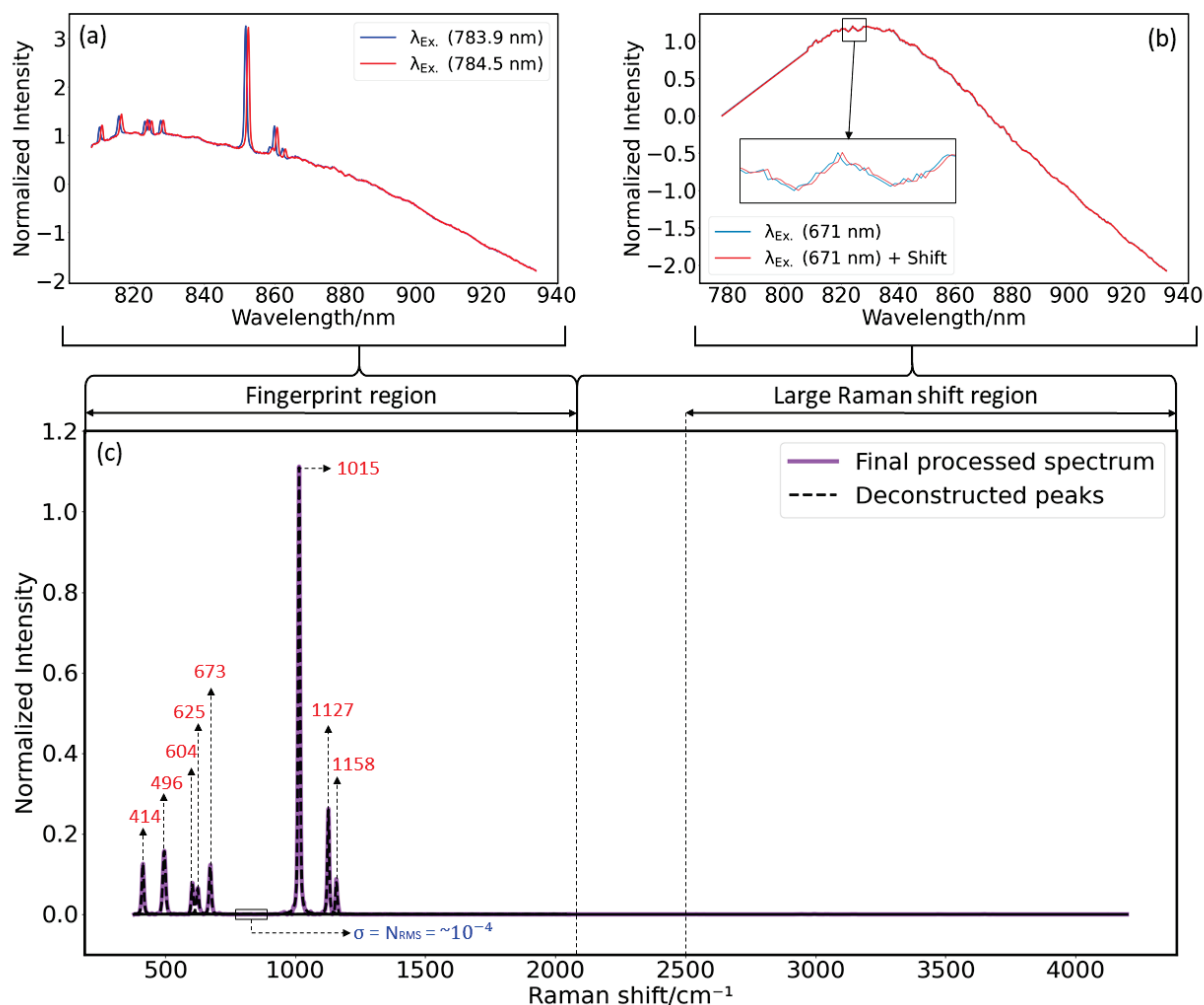


Figure 6. Raman spectrum of anhydrite sample 2. (a) z-score-normalized fingerprint region of Raman spectrum with 783.9 nm and 784.5 nm excitation, (b) z-score-normalized large Raman shift region of Raman spectrum with 671 nm excitation and the same spectrum shifted by 0.15 nm, and (c) final processed and concatenated Raman spectrum.

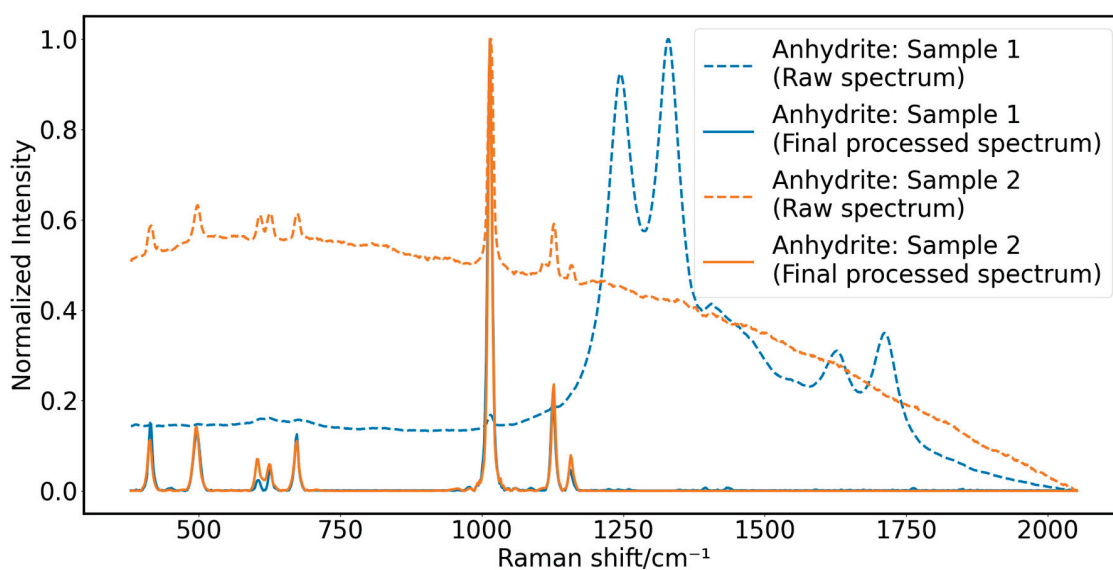


Figure 7. Comparison of the raw and final processed spectra of anhydrite samples 1 and 2 based on the fingerprint region.

Normally, a background and noise-free fingerprint Raman spectrum of a mineral sample is sufficient for the identification of minerals. Hence, the final processed large Raman shift Raman spectrum is needed only when the sample is a mixture of similar minerals like gypsum and anhydrite. In order to simulate such a mixture, the final processed spectra of the gypsum sample and anhydrite sample 2 are added together to create a simulated mixture spectrum, as shown in Figure 8. From the simulated mixture spectrum, it can be observed that most of the gypsum Raman peaks overlap with Raman peaks of anhydrite. As a result, the fingerprint region Raman spectra of the mixture spectrum can easily be mistaken for an anhydrite spectrum. The presence of gypsum is indicated only by small features, which are highlighted in Figure 8 by the green boundary. Hence, the presence of the OH stretching vibration peaks (regions marked with red boundary in the large Raman shift region) in gypsum and the absence of these peaks in anhydrite help in identifying clearly the presence of gypsum in the mixture.

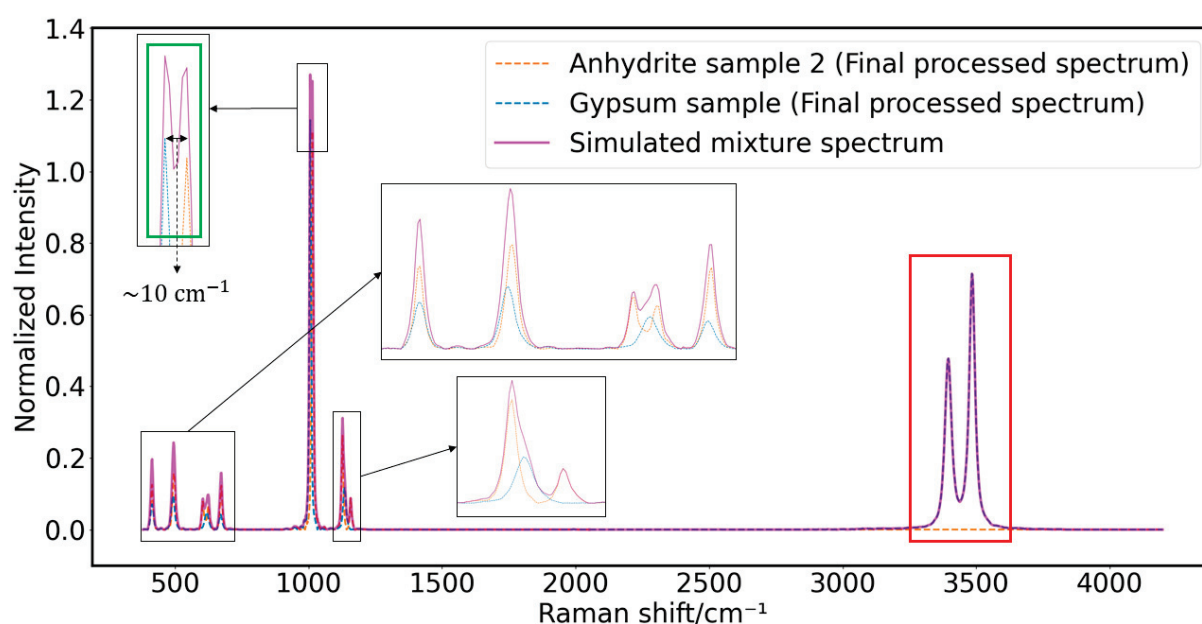


Figure 8. Simulated mixture spectrum obtained by summation of the final processed spectra of gypsum sample and anhydrite sample 2 (regions with green and red borders indicate clearly distinguishable peak positions).

3.4. Effect of Spectral Averaging in Peak Finding

The single spectrum integration time of the anhydrite sample 1 was limited by the fluorescence interference to 50 ms. Longer integration times saturated the detector. Unfortunately, the Raman peaks are much weaker than the fluorescence interference; thus, at such short signal integration times, the signal might be hidden within the noise of the spectrum. Then, averaging is the method of choice in order to improve the signal-to-noise ratio and to make hardly recognizable Raman signals more clearly recognizable. But averaging is time demanding, and we motivated our work in the introduction by the need for a fast measurement method for the identification of minerals. Therefore, we analyzed the impact of the number of single spectra we utilized for averaging on the outcome of the pre-processing method we proposed.

In total, 16 batches, with each batch containing 16 SERDS spectra, are obtained. In the first batch, each SERDS spectrum was computed from one non-averaged Raman spectrum excited with 783.9 nm and one non-averaged Raman spectrum excited with 784.5 nm. In the second batch, each SERDS spectrum was computed from one averaged Raman spectrum excited with 783.9 nm and one averaged Raman spectrum excited with 784.5 nm, where

the number of spectra in averaging was two. In batch 4, each of the 16 SERDS spectra was computed from one averaged Raman spectrum excited with 783.9 nm and one averaged Raman spectrum excited with 784.5 nm, where the number of spectra in averaging was four. This acquisition process is repeated for 16 batches. When neglecting the time required for reading out the spectra, in batch 7, for example, each averaged spectrum corresponds to a measurement time of 350 ms (seven times 50 ms/single spectrum). As the SERDS spectrum is computed from two averaged spectra, the measurement time of one SERDS spectrum in batch 7 would correspond to 700 ms. One SERDS spectrum in batch 2 would correspond, for example, to 200 ms. For each batch, 16 final processed spectra are determined using the proposed method explained in the context of 3.1 for the fingerprint region Raman spectrum. After that, each of the 16 final processed spectra in each batch is deconstructed into pseudo-Voigt peaks. As we neither dictate the number of pseudo-Voigt profile peaks nor their peak position, the number and position of identified peaks depend on whether weak Raman signals are recognizable as peaks in the final processed spectrum before pseudo-Voigt profile deconstruction. Figure 9, therefore, shows which of the eight anhydrite peaks were found, with what probability, and at which central peak position, depending on the number of spectra in averaging. The number of spectra in averaging, which corresponds to the batch number, is given from left to right. The eight peaks of anhydrite are shown from the bottom to the top. The data point highlighted by a greenish square in Figure 9 corresponds, for example, to batch number 5 and peak number 8. The greenish background colour implies that this peak was represented by a pseudo-Voigt profile in approximately 50% of the 16 final processed spectra of this batch. Thus, in 8 of these 16 final processed spectra, this peak was not recognized. The data point and the error bars represent the mean central position of this peak, which was averaged from the eight identified peaks, and their deviation between maximum and minimum peak positions among these eight identified peaks, respectively.

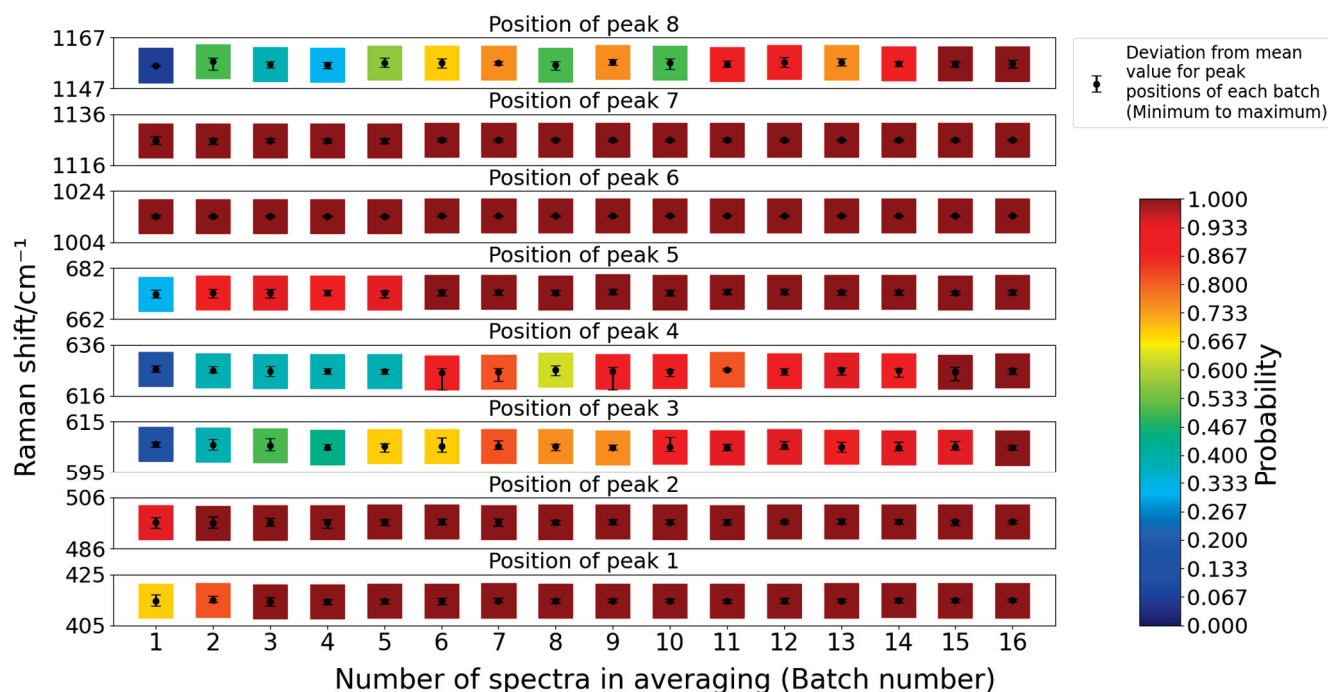


Figure 9. Peak position existence probability with number of spectra in averaging.

It can be observed from Figure 9 that the probability of existence of the strong peaks 1, 2, 6, and 7 in the final processed spectra is high (>0.5), irrespective of the number of spectra used in averaging. But the probability of existence of the weaker peaks 3, 4, 5 and 8 is low

(<0.5), when the number of spectra in averaging is less. This is because, when the number of spectra used in averaging is less, the existence of noise in a Raman spectrum causes the Raman peaks with small intensity to be less prominent in the difference spectrum. This, in turn, causes the corresponding peaks to be absent in the final processed spectrum. With an increasing number of spectra in spectra averaging, the noise reduces and the peaks become more prominent in difference spectrum; as a result, corresponding Raman peaks appear in the final processed spectrum.

It should also be noted that in batch one, four of the eight peaks having a probability greater than 0.5 were determined without averaging during spectra acquisition and with a measurement time of 100 ms, which is faster in comparison with the existing methods of SSE and FT Raman spectroscopy. In batch two, already six out of eight peaks are identified with a probability exceeding 0.5. This corresponds to a measurement time per measurement spot of only 200 ms. For such short measurement times, not the signal acquisition time itself, but the time required to move the Raman measurement device from measurement spot to measurement spot would define the rate at which measurements can be made.

3.5. The Challenges and Considerations of In Situ Implementation

The experimental setup and pre-processing method were designed considering practical challenges in transferring the proposed method to an underground mine. As the proposed method can remove both narrow as well as broad fluorescence interference in Raman spectra of mineral samples, the method can be transferred to real in situ measurements in underground environments containing fluorescing substances. The underground environment is subjected to vibrations and light from either moving vehicles or operating machinery in the measurement surroundings. These can cause the Raman probe to move or the surrounding light to enter the Raman probe. These factors could affect the SERDS measurement by either a variation in the measurement spot position or a difference in the background interference during the two subsequent spectra acquisitions for SERDS measurement. To overcome the effect of vibration, the Raman probe will be securely mounted. To prevent interference from surrounding light, an opaque and flexible light protection cover will be attached to the end of the Raman probe to cover the region between the measurement spot and the Raman probe end. In addition, the quick spectra acquisition of the proposed method also helps in reducing interferences from vibration and surrounding light.

4. Conclusions

In this work, a method is proposed for obtaining the Raman spectrum of minerals using a combination of SERDS, deep learning-based U-Net model for noise and background removal, and dual excitation wavelengths. Since the proposed method uses the combination of both experimental and mathematical methods, it successfully removes narrow as well as broad fluorescence interference from the fingerprint and large Raman shift regions of Raman spectra and provides a background-free spectrum with significantly reduced noise. The method was also able to recover all the Raman peaks from the raw Raman spectra of minerals that were acquired using a comparatively shorter spectra acquisition time, even in the presence of a strong and narrow fluorescence background. The dual excitation wavelength technique with SERDS laser and 671 nm laser ensures that the fingerprint and large Raman shift regions of the Raman spectrum are obtained with good as well as similar quantum efficiency. The large Raman shift region Raman spectrum obtained with a 671 nm laser helps in clearly distinguishing the existence of minerals in a mixture of minerals like gypsum and anhydrite, having similar fingerprint region Raman spectra.

The background and quasi-noise-free spectrum can then be subjected to peak finding algorithms, from which the number and positions of pseudo-Voigt peaks within the spectrum can be extracted. This information is valuable input for the computation of the modelled spectrum, which is the summation of pseudo-Voigt peaks. The mineral identification can in the future then be based on the number and positions of the pseudo-Voigt peaks.

The future application of the proposed method is in underground salt rock, where various constituent minerals are identified in situ using the fluorescence and quasi-noise-free Raman spectrum obtained with this method. Since the measurement spot has a diameter of 0.12 mm, and the area for analysis in a salt mine is large, quick spectral acquisition and short pre-processing time of the proposed method is beneficial over other standard methods. In addition, unlike other existing mathematical methods of background and noise removal, the proposed pre-processing method eliminates the need for human intervention. While using the proposed method in an underground environment, measures will also be implemented to prevent the interferences from vibration and surrounding light on the measurement.

With the proposed experimental setup, the fluorescence interference in minerals that appear either in both fingerprint and large Raman shift regions or only in the fingerprint region could be removed. But in future work with samples having fluorescence interference only in the large Raman shift region, the shifting of the Raman spectrum adopted in the current work for calculating the difference spectrum in the large Raman shift region could be replaced with another SERDS laser having excitation wavelengths tuneable in the vicinity of 671 nm.

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Data Availability Statement: The data will be made available on request.

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Conflicts of 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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Article

Petrophysical Characterisation and Suitability of Serpentinites from the Monteferrato Area (Tuscany, Italy) for Architectural Restoration

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Abstract

This study investigates the mineralogical and physical properties of serpentinite from the Monteferrato area (Tuscany, Italy) to evaluate its potential use in Tuscany architectural restoration. The research addresses the need to identify replacement materials compatible with historic stones while preserving their original features. Representative specimens from the Bagnolo quarry were analysed through physical testing and a wide range of mineralogical and geochemical techniques, including polarised light microscopy, X-ray diffraction, electron probe micro-analysis, whole-rock chemistry, and fibre quantification. The results show a mineralogical composition dominated by serpentine-group minerals and magnetite, with physical properties generally consistent across samples. Measured capillary water absorption ranges from 3.27 to 5.27 g/m²·s^{0.5}, open porosity from 5.25% to 8.93%, apparent densities range from 2.49 to 2.56 g/cm³, and imbibition coefficient from 2.16% to 3.71%. Comparative analysis with serpentinite from historic sources (Figline di Prato quarry, Tuscany) and from monuments (Baptistery of San Giovanni, Florence) demonstrates close compositional and textural affinities, supporting the suitability of the rock from the studied quarry for restoration purposes in Tuscany monuments. However, chrysotile concentrations up to 14,153 mg/kg, exceeding Italian regulatory thresholds, represent a critical limitation. This not only requires the implementation of strict safety measures but also raises serious concerns regarding the practical feasibility of using this stone in conservation projects. More broadly, the presence of asbestiform minerals in serpentinites highlights a significant and often underestimated health risk associated with their extraction, processing, and use. Despite its importance, detailed fibre count data are rarely published or made publicly accessible, hindering both transparent risk assessment and informed decision-making. By integrating petrographic, mineralogical, and physical–mechanical characterisation with fibre quantification, this study not only assesses the technical suitability of Monteferrato serpentinites for restoration of Tuscan monuments but also contributes to a more responsible and evidence-based approach to their use, emphasising the urgent need for transparency and health protection in conservation practices.

Keywords: serpentinite; Bagnolo quarry; Tuscany historical building materials; physical and chemical characterisation; chrysotile content; restoration materials

1. Introduction

Natural stone has played a fundamental role in architectural heritage since antiquity, valued for its mechanical strength, durability, and aesthetic appeal. From the earliest

civilisations, stone has been used to construct enduring monuments, temples, and infrastructure, establishing a legacy of resilience and permanence. Historically, builders relied on locally sourced stone due to the high cost and difficulty of transport, resulting in towns constructed primarily with a single material. This gave rise to distinctive cultural landscapes defined by regional geology. Today, these traditions are being revalued, as natural stone is increasingly recognised for its role in expressing local identity and supporting both community heritage and tourism [1,2]. Despite the widespread belief in the inherent durability of stone, all stones are ultimately subject to weathering and deterioration [2]. Once quarried and fashioned into building elements, natural stone becomes vulnerable to environmental conditions, construction techniques, and maintenance practices. Over time, the degradation of stone-built structures has become a critical concern in conservation and heritage management. Finding suitable replacement materials often requires searching for new quarries. Quarry landscapes are dynamic, often transitioning from active exploitation to abandonment. The cessation of quarrying activities may result from various factors: depletion of extractable material, hazardous properties of the stone, or its environmental impact. This is particularly relevant for older quarries located near built-up areas and, in some cases, even close to historic centres. These conditions have influenced territorial planning, leading to the cessation of ancient quarry exploitation and the redevelopment of abandoned quarry landscapes. Consequently, fostering a technological culture in the quarry industry that embraces ecological principles has become essential [3–5]. In addition, stricter environmental regulations in industrialised nations have led to the closure of many traditional quarries, limiting access to historically used materials. This shift has disrupted traditional restoration practices, contributed to the loss of regional architectural identity, and created a reliance on imported stones, often sourced from less regulated countries. While these materials are often more affordable, they rarely match the geological and aesthetic qualities of native stones, complicating conservation efforts. Understanding the long-term performance of stone in built environments requires an interdisciplinary approach. Contributions from geologists, materials scientists, architects, and conservation specialists are crucial in assessing stone durability and developing effective preservation strategies. The use of ornamental stones, such as serpentinite, granite, and marble, reflects both historical and cultural preferences, while also demanding scientific evaluation of their physical and mechanical properties. Non-destructive techniques have become vital in heritage conservation, enabling assessments that respect the integrity of historic structures. Within this broader context, this paper focuses on serpentinite sourced from the Bagnolo quarry (Monteferrato area, Tuscany), evaluating its intrinsic properties and its interaction with environmental factors. The search for serpentinite materials is driven by the need to find suitable replacements for deteriorated original stones. This is a widespread issue in many historic cities, for example Florence, where serpentinite was widely used in the cladding and decorative elements of numerous monuments (e.g., Cathedral of Santa Maria del Fiore and churches of Santa Croce, Santa Maria Novella, and San Miniato). This study analyses serpentinite from the Monteferrato area to evaluate its suitability for architectural restoration, with particular attention to its mineralogical features and chrysotile content. Despite its significant implications for public health, there is a notable lack of studies reporting detailed data on chrysotile in ornamental stones. Addressing this knowledge gap is crucial for both heritage conservation and the protection of public health.

2. Overview of Serpentinite

Petrologically, serpentinite is a fine-grained, dark green to black, metamorphic rock predominantly composed of serpentine-group minerals. It forms through low-temperature hydration of olivine-rich ultramafic rocks, resulting in the transformation of olivine, or-

thopyroxene, and clinopyroxene into hydrated magnesium silicates, magnetite, and occasionally brucite. This process reduces the density of the rock relative to its peridotitic protolith. Three main serpentine minerals, lizardite, chrysotile, and antigorite, are commonly present. Lizardite has platy crystals and frequently dominates the mesh textures, replacing olivine. Chrysotile is characterized by a cylindrical fiber morphology, which can reach lengths of several centimetres. These fibres, which may possess hollow or amorphous-filled cores, commonly fill secondary microfractures crosscutting the host serpentinite. While valued industrially for its insulating properties, chrysotile is also a recognised health hazard due to the inhalation risks associated with its fine, airborne fibres [6–10]. Antigorite, in contrast, forms at higher temperatures and is structurally distinct, with curved, modulated layers bonded by strong Si–O linkages. This gives it greater hardness, higher seismic velocities, and reduced cleavage, making it common in recrystallised and metamorphosed serpentinites [11,12].

Serpentinite has been used since ancient times, notably by the Egyptians, as both a building material and an ornamental stone [13,14]. Today, prominent commercial sources include Rajasthan Green and Emerald Green from India, often heavily altered to carbonates. In contrast, serpentinites from other regions, including Vermont Verde Antique (USA) and Verde Pirineo (Spain), preserve more of their primary mineralogy [15,16]. In Italy, serpentinite outcrops are widespread across both the Alps and the Apennines, with Tuscany representing a particularly important region. Occurrences are also found in the southern Apennines, especially in Calabria, although they were not traditionally employed as building stones.

In Tuscany, serpentinites associated with the Northern Apennine Ophiolitic Complex occur near Florence (Impruneta), Prato, Pistoia, Siena, and Volterra. The serpentinite examined in this study was sourced from a quarry (Bagnolo), located in the Monteferrato district, historically regarded as the primary source of the serpentinite employed in the Baptistery of San Giovanni, Florence [17].

3. Geological Overview of the Bagnolo Quarry

The Bagnolo quarry, located within the Monteferrato geological complex, near Montemurlo (Tuscany), forms part of the Northern Apennine orogenic system. This area is dominated by ultramafic and metamorphic rocks, with serpentinite as the prevailing lithology. These rocks originated through the hydration of peridotite within an ancient oceanic lithosphere and are associated with ophiolitic sequences emplaced during the Jurassic period [18,19]. Subsequent Alpine tectonic processes led to their deformation and uplift [20–22]. The Monteferrato serpentinites display massive to foliated textures. Their distinctive greenish color results from extensive serpentinization. The region represents a significant tectonic window, exposing fragments of the former Tethyan oceanic crust and offering valuable insights into the structure and evolution of ophiolite complexes in the Apennines.

Several historic quarries were exploited across the region, where serpentinite was locally known by names such as Verde di Prato, Nero di Prato, Marmo Nero, and Paragone [23–29]. This rock was widely used during the Romanesque and Renaissance periods in the construction of religious and civic buildings [17,29]. Among the earliest known extraction sites are the quarries at Piano di Gello, on the eastern slope of Monte Piccioli in the Monteferrato area. Active since at least the 11th century, these quarries are now abandoned but remain significant for understanding historic stoneworking practices.

The Bagnolo quarry (Figure 1), also known as Cava Guarino after its owner, is a historic serpentinite quarry of significant geological and cultural interest. The site is part of a broader area known for the presence of serpentinite, commonly referred to as

“Prato green marble”, a metamorphic rock with distinctive green to dark bluish tones. The quarry has been exploited since the Middle Ages, supplying serpentinite blocks for use in notable architectural works throughout Tuscany. Today, the quarry is no longer active for industrial extraction, but it remains an important heritage site. Its surroundings, now partially reclaimed by vegetation, bear traces of historical quarrying activity and offer insight into traditional stoneworking techniques.

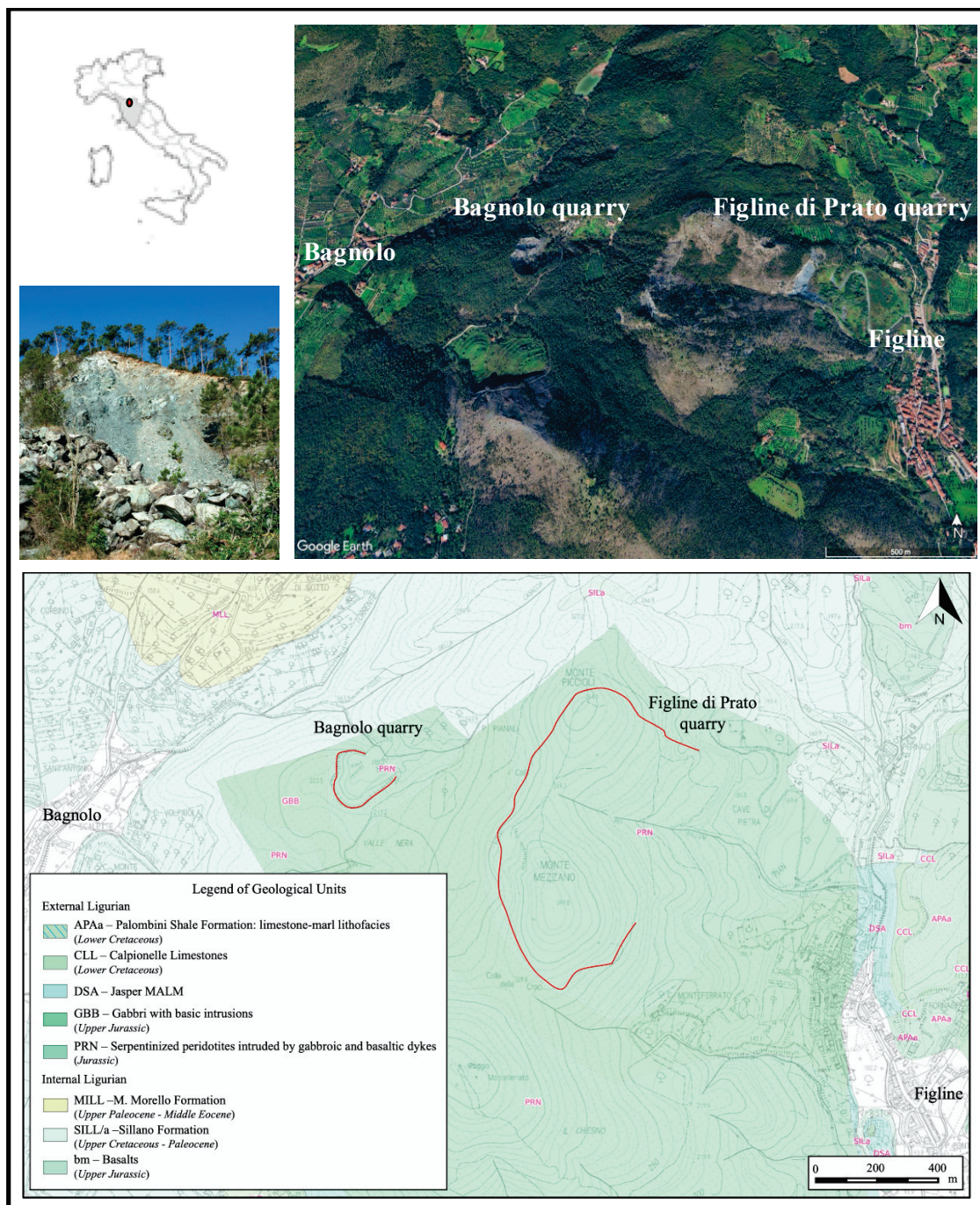


Figure 1. (Top right): Google Earth view of the Monteferrato area showing the location of the Bagnolo and Figline di Prato quarries. (Top left): location of the Monteferrato area (red dot) within Tuscany, Italy (Tuscany region highlighted in grey). (Middle left): outcrop view of the Bagnolo quarry. (Bottom): geological map of the study area.

Sampling and Sample Preparation

The studied area is integrated into local trekking routes, such as the “Cave di Bagnolo trail”, which guides visitors through former extraction sites, natural amphitheatres, and panoramic viewpoints. These trails are part of a broader initiative to promote the sustainable use of geological heritage and to raise awareness of the region’s geo-cultural landscape. In addition to its geological relevance, Bagnolo quarry represents a valuable case study for the conservation and reuse of natural stone in architectural restoration, and serves as a living archive of Tuscany’s stone-working history. The stone material present in the quarry shows, when freshly cut, a general green colouration with varying textural characteristics, marked by the presence of granules and dark veins of various sizes. These features result in clear differences in macroscopic appearance. Therefore, the sampling was conducted in a way that would be representative of the different observed types. Five different rock portions were collected from different areas and were identified with the codes from CB1 to CB5. Before characterising the lithotypes, all rock samples were cleaned by removing degraded outer surfaces.

Two different sizes of test specimens (Figure 2) were prepared from each sample for physical testing. To assess reproducibility, two specimens per sample were tested. For mineralogical and geochemical characterisation, powder of each sample was obtained for X-ray diffraction (XRD) and whole rock analysis by inductively coupled plasma (ICP-MS). Selected samples were ground and sieved for fibre quantification. Polished thin sections of the rocks were also prepared for observation under a polarising microscope (PLM) and for mineral phase analysis using an electron probe micro-analyser (EPMA).

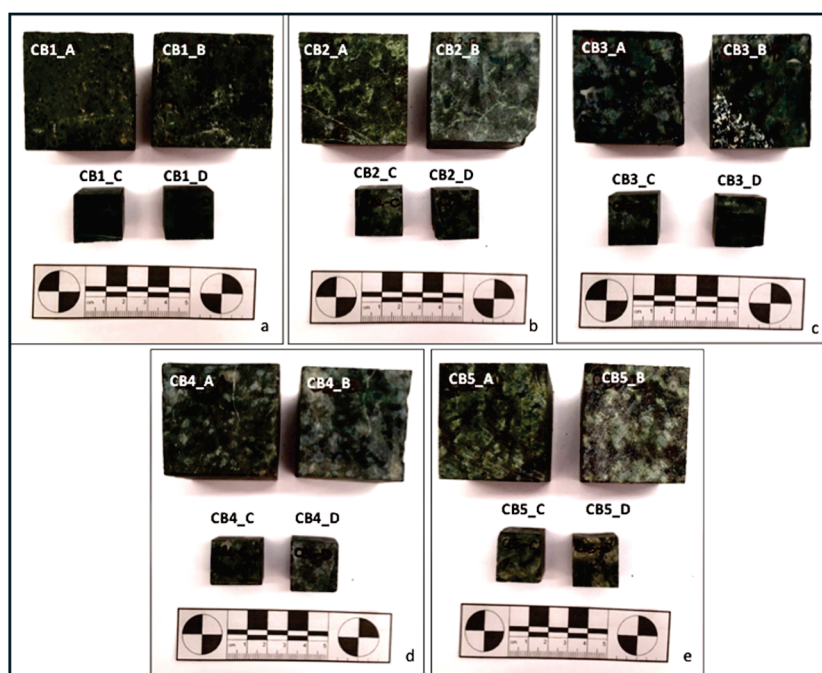


Figure 2. The test specimens from the Bagnolo quarry used to measure their physical properties. (a–e) show the five main samples (CB1–CB5) and their corresponding subsamples (A, B, C, D).

4. Analytical Methods

4.1. Physical Analyses

In studying the physical properties of stone materials used in cultural heritage, it is essential to understand how water moves within them. This requires determining open porosity, apparent density (also known as bulk density, calculated as the mass of the sample divided by its total volume, including both mineral grains and pore spaces),

imbibition coefficient, and capillarity water absorption. These parameters were measured on Bagnolo samples in accordance with the European Standards [30–32]. For the capillary water absorption tests, two prisms measuring 4 cm × 4 cm × 4 cm were cut from each rock sample, while for the analyses of open porosity, apparent density, and imbibition coefficient, two smaller prisms of 2 × 2 × 2 cm were prepared (Figure 2).

4.2. Polarising Microscope Observations

Petrographic observations in polarised light were carried out using a Zeiss Axioscope A.1 microscope (Carl Zeiss, Jena, Germany), equipped with a 5 Megapixel resolution video camera and Zen lite 3.1 image analysis software. This technique enabled the characterisation of the texture and mineralogical composition of the samples [33].

4.3. X-Ray Powder Diffraction Analysis

Qualitative mineralogical analyses were performed by X-ray powder diffraction on powdered samples, using a Philips PW 1050/37 diffractometer (Philips, Almelo, The Netherlands), coupled with a Panalytical X'Pert PRO system and HighScore software version 2021 for data acquisition and interpretation. The detection limit of the method is 4%. The operating conditions were set at 40 kV and 20 mA, with a Cu anode, graphite monochromator, and a goniometer speed of 2°/min, over a scanning range of 5–70° 2θ [34–36].

4.4. Electron Probe Micro-Analysis

The chemical composition of the main mineral phases was obtained using a JEOL JXA-8600 electron microprobe (Jeol Ltd., Tokyo, Japan) equipped with four wavelength-dispersive spectrometers (WDS), under the following operating conditions: accelerating voltage of 15 kV, beam current of 10 nA, and beam diameter of 3–5 µm. Counting times were 10 s for Na, 15 s for the other major elements, and 40 s for minor elements (e.g., Mn, Sr, and Ba). Matrix effects were corrected using the PAP algorithm following the method of Pouchou and Pichoir [37]. Primary standards included natural and synthetic phases (e.g., Albite for Si/Na, Olivine for Mg, Diopside for Ca, Apatite for P, Ilmenite for Ti/Fe). Secondary standards from Smithsonian, MAC, and Astimex were analysed to verify accuracy. Long-term replicate measurements on secondary standards show precision <1% for Si, ≤2% for other major elements, and ≤5% for minor elements. Accuracy is within 1% for major and most minor elements. Detection limits are typically 100–300 ppm for minor elements, depending on the element and counting conditions.

4.5. ICP-MS Whole Rock Analysis

Whole-rock major and trace element composition was obtained at the Actlabs (Ancaster, ON, Canada), where samples were prepared using a batch system. Each batch included a method reagent blank, a certified reference material, and 17% replicates. Samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The resulting melt was immediately poured into a 5% nitric acid solution containing an internal standard and continuously stirred until completely dissolved (~30 min). Analyses were performed using a Thermo Jarrell-Ash ENVIRO II ICP in simultaneous/sequential mode. Calibration was carried out with seven certified reference materials (USGS and CANMET). One of the seven standards was analysed with every group of ten samples. The detection limit ranges between 0.01% and 0.001%.

4.6. Fibre Quantification

The fibre quantification was carried out at the laboratory of ECOLStudio/lifeanalytics (Vicenza, Italy). According to the Italian Ministerial Decree DM 06.09.1994, which sets

regulatory limits and safety requirements for the use and handling of asbestos-containing materials, representative samples (0.5–1 g) were ground and sieved to <500 µm, then milled to 10–100 µm. An aliquot of the powdered material was suspended in a dispersant solution, filtered through a polycarbonate membrane (0.8 µm porosity, 25 mm diameter), and mounted on stubs for scanning electron microscopy (SEM) analysis. Fibres were counted only if they exhibited characteristic morphology and elemental composition (EDS) matching standard asbestos species (chrysotile, amosite, crocidolite, tremolite, actinolite, anthophyllite). The minimum count of 4 fibres defines the method detection limit ($LOD \approx 1.2 \times 10^4$ fibres/mg, ~120 ppm), and the limit of quantification (LOQ) is 100 ppm. Fibre dimensions were measured and concentrations calculated assuming a density of 2.6 g/cm³ for chrysotile. Expanded measurement uncertainty ($k = 2.95\%$ confidence) is ~50%, considering contributions from sample weight, dilution, SEM magnification, fibre sampling, and repeatability. Method robustness was verified by varying milling times and assessing particle size distributions (10–100 µm), while repeatability was confirmed on samples of known concentrations (300, 1000, 3000 mg/kg) with ten replicates each.

5. Analytical Results

5.1. Physical Analyses

Table 1 shows the results of the physical analyses obtained from replicate measurements for each block. The dataset highlights some differences in the physical behaviour of the Bagnolo serpentinite samples. Capillary water absorption varies from 3.27 g/m²·s^{0.5} (CB2) to 5.27 g/m²·s^{0.5} (CB5), with CB5 showing the fastest uptake, well above the mean (3.79 g/m²·s^{0.5}). Open porosity ranges between 5.25% (CB3) and 8.93% (CB5).

Table 1. Physical properties of serpentinite from Bagnolo (CB) and Figline di Prato (SF) quarries, and pavement of Florentine Baptistery (Bpt). SF and Bpt data are from Santo et al. [17].

Sample	Capillarity Water Absorption (g/m ² ·s ^{0.5})	Sample	Open Porosity (%)	Apparent Density (g/cm ³)	Imbibition Coefficient (%)
CB1_A	3.74	CB1_C	6.52	2.52	2.64
CB1_B	3.83	CB1_D	6.41	2.52	2.60
CB2_A	3.27	CB2_C	7.83	2.49	3.23
CB2_B	3.32	CB2_D	7.65	2.49	3.16
CB3_A	3.86	CB3_C	5.25	2.54	2.35
CB3_B	3.62	CB3_D	5.66	2.54	2.28
CB4_A	4.70	CB4_C	5.43	2.56	2.16
CB4_B	4.42	CB4_D	5.98	2.55	2.40
CB5_A	5.27	CB5_C	8.93	2.49	3.71
CB5_B	5.14	CB5_D	8.63	2.50	3.56
SF	3.46	SF	5.59	2.55	2.24
Bpt	3.18	Bpt	7.14	2.51	2.92

CB5 is the most porous variety, while CB3 displays lower open porosity, suggesting greater compactness. In general, these results indicate a relatively low to moderate capacity for water uptake, consistent with the petrophysical behaviour of this rock type. Apparent density is fairly uniform, oscillating between 2.49 and 2.56 g/cm³, reflecting a consistent mineralogical composition across the samples. Finally, the imbibition coefficient varies from 2.16% (CB4) to 3.71% (CB5). The lowest values (CB3 and CB4) are associated with the denser and less porous materials, while CB2 and especially CB5 show a greater capacity

for water uptake. Overall, CB3 and CB4 emerge as the most compact and potentially more durable samples, whereas CB5 and, to a lesser extent, CB2, exhibit higher porosity and water absorption, features that may negatively affect long-term resistance and durability. The data obtained from the Bagnolo rock samples are consistent with values reported in the literature for serpentinite from various regions [38–43]. Table 1 also reports, for comparison, the results obtained on a serpentinite specimen (SF) from another historic quarry in the Monteferrato area (Figline di Prato quarry; Figure 1), as well as on the serpentinite (Bpt) from the pavement of the Baptistery of San Giovanni in Florence [17,29]. The physical properties of the SF and Bpt samples are consistent with those of the CB quarry samples. In fact, their values lie within the variability range observed for the CB series or are close to their mean values. The Bpt sample shows relatively high porosity and water absorption, comparable to the more porous CB samples (e.g., CB2 and CB5). Conversely, the SF sample displays lower porosity and imbibition, similar to the more compact CB samples (e.g., CB3 and CB4). This indicates that both SF and Bpt materials fall within the natural variability of serpentinite from the Bagnolo and Figline di Prato quarries, suggesting that the lithotypes used in the Baptistery pavement and those from the quarry sources share broadly comparable physical characteristics.

5.2. *Minero-Petrographic Analyses*

5.2.1. Polarising Microscope Observations

Under the polarising microscope (Figure 3a,d), the samples from the Bagnolo quarry exhibit overall similar textures, characterised by a medium-grained serpentine matrix crosscut by a dense network of thin, chrysotile-rich veinlets. These veinlets are irregularly oriented and intersect at various angles, forming a pervasive mesh texture typical of highly serpentinized ultramafic rocks. The fibrous habit of chrysotile is clearly visible under crossed nicols, with intense interference colours and well-developed alignment along fracture planes. Veins are evenly distributed throughout the rock, producing a fairly homogeneous microstructure. Primary silicate minerals (olivine, clinopyroxene, and orthopyroxene) are completely or almost completely replaced by serpentine-group minerals, magnetite, and spinel, although some pyroxene remnants are still visible. Serpentine minerals occur as fibres (100–250 µm), forming mesh textures typically associated with the replacement of olivine, and as pseudomorphs after pyroxene (commonly referred to as bastite). Samples from the Figline quarry (Figure 3e,f) display mineralogical and textural features broadly comparable to those of Bagnolo, but with a denser and more regularly oriented vein network, resulting in a slightly more anisotropic texture. Chrysotile fibres show similarly intense interference colours and strong alignment, indicating a comparable degree of serpentinisation. Pyroxene relics are rarer and more scattered than in the Bagnolo samples. In contrast, the samples from the baptistery pavement (Figure 3g,h) are characterised by a less pervasive vein network, with veins that are fewer, thicker, and more irregularly spaced. This gives the rock a more massive and less fibrous appearance. Chrysotile fibres are still present and display clear interference colours, but their distribution is more localised. Pyroxene relics are more abundant compared to the other two quarries, suggesting a slightly lower degree of serpentinization. Overall, the three groups of samples share a common mineralogical assemblage dominated by serpentine-group minerals, magnetite, and spinel, and similar textural features (mesh textures and bastite pseudomorphs), but differ mainly in the density and orientation of chrysotile-rich veinlets and the abundance of primary mineral relics.

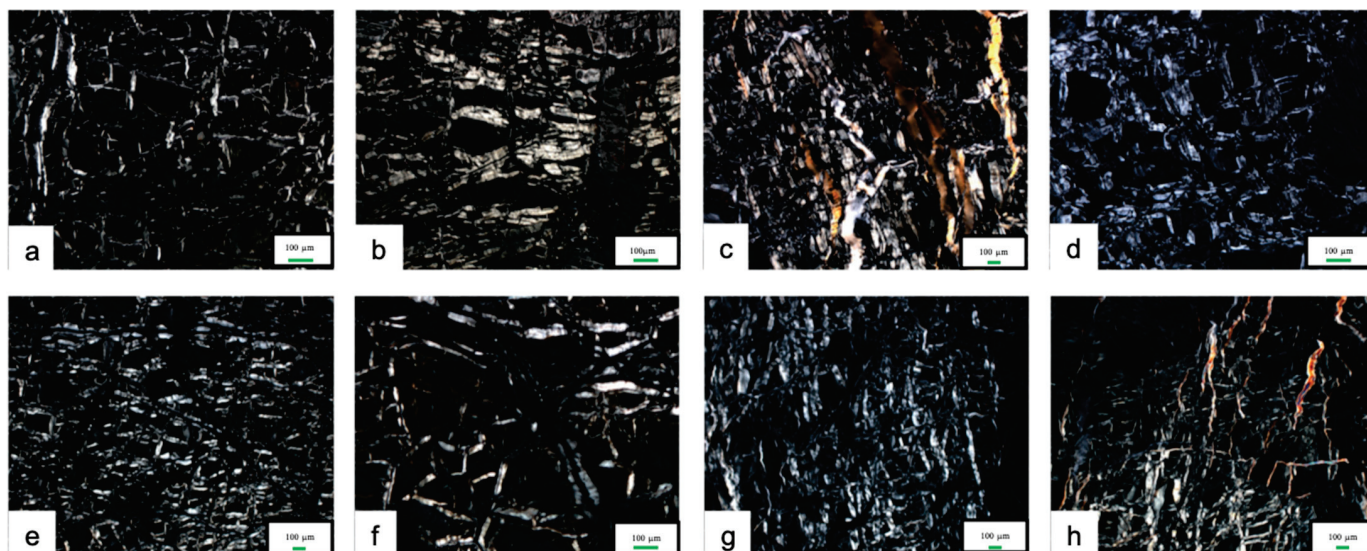


Figure 3. Thin-section photomicrographs of serpentinite samples observed under crossed nicols. All samples show a fine- to medium-grained serpentinite matrix crosscut by chrysotile-rich veinlets, forming a characteristic mesh texture. Samples (a–d) (Bagnolo quarry) display a dense network of thin, irregularly oriented chrysotile veinlets. Samples (e,f) (Figline quarry) exhibit more closely spaced, subparallel veins, giving the rock a slightly more anisotropic texture. Samples (g,h) (baptistry pavement) are characterised by a coarser and less pervasive vein system, with locally higher interference colours.

5.2.2. X-Ray Powder Diffraction Analysis

The XRD patterns of the Bagnolo samples show very similar profiles (Figure 4). The identified phases are chrysotile, lizardite, and magnetite. Peak broadening of the main phases indicates a predominance of lizardite (although it is not readily visible in the thin section images), with chrysotile also present in significant amounts, and magnetite occurring in substantially lower amounts. For comparison, Figure 4 reports the XRD patterns of the Figline di Prato quarry sample (SF) and the Baptistery pavement sample (Bpt), which closely match those of the Bagnolo quarry specimens.

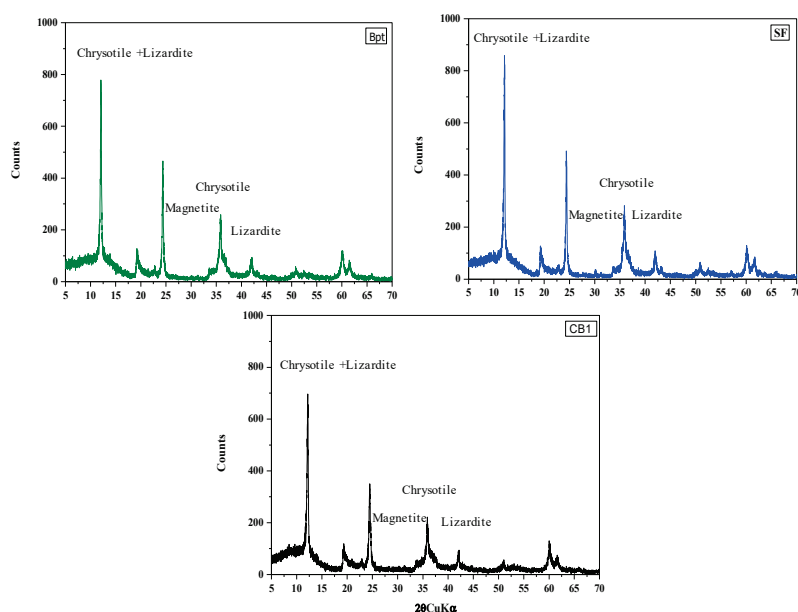


Figure 4. XRD patterns for serpentinites from Bagnolo (CB1), Figline di Prato (SF), and San Giovanni Baptistery pavement (Bpt).

5.2.3. Electron Probe Micro-Analysis

The analysed Bagnolo samples include both mesh textures (olivine-derived) and bastite (pyroxene-derived) pseudomorphs (Table 2). They exhibit wide ranges in FeO (1.8–11 wt.%) and Al₂O₃ (0.9–9.2 wt.%), including an anomalously Al-rich specimen (CB4-1), as well as locally elevated Ni contents, reflecting contributions from olivine and accessory phases such as plagioclase or spinel. When considering the mean compositions of the Bagnolo samples and comparing them with serpentinites from the Figline di Prato quarry and the Baptistery pavement, the three groups display broadly similar bulk composition, characterised by high MgO, moderate FeO, SiO₂ contents close to 40 wt.%, and very low concentrations of CaO, Na₂O and K₂O. All samples are strongly magnesian, with high Mg# values. Overall, the chemical compositions of serpentine phases are broadly comparable across CB, SF, and Bpt samples. The observed variations fall largely within analytical uncertainty and are interpreted to reflect minor fluctuations linked to precursor mineralogy and local alteration conditions rather than fundamental geochemical differences. All samples consistently plot within the compositional field of Mg-rich serpentines, highlighting a common serpentinization signature modified locally by texture and protolith variability.

Table 2. Representative microprobe analyses of serpentine-group minerals from Bagnolo (CB) and Figline di Prato (SF) quarries, and pavement of Florentine Baptistery (Bpt).

Sample	CB1-1	CB1-2	CB2-1	CB2-2	CB3-1	CB3-2	CB4-1	CB4-2	CB5-1	CB5-2	SF *	Bpt *
Texture	bastite	mesh	mesh	bastite	bastite	mesh	mesh	mesh	bastite	mesh	#10	#25
SiO ₂	38.3	40.7	40.9	39.2	40.2	41.3	36.4	41.9	40.5	38.8	39.7	39.1
TiO ₂	0.07	0.02	-	0.04	0.01	-	0.11	-	-	0.03	0.04	0.15
Al ₂ O ₃	5.09	0.90	1.62	3.56	4.07	1.22	9.18	2.16	2.41	1.86	1.96	3.11
FeO	5.98	10.7	5.71	6.57	3.71	2.86	4.92	1.78	4.49	10.2	5.61	5.47
Cr ₂ O ₃	1.36	bdl	0.03	0.96	1.63	0.04	0.44	0.23	0.92	bdl	0.70	1.00
MnO	0.15	0.14	0.08	0.11	0.07	0.05	0.10	0.01	0.09	0.15	0.11	0.13
MgO	28.8	30.9	34.5	35.6	38.2	37.9	34.4	31.7	27.2	35.8	37.5	36.2
CaO	0.10	0.05	0.05	bdl	bdl	0.08	0.08	0.14	0.06	bdl	0.07	0.06
Na ₂ O	bdl	0.09	0.07	bdl	0.02	0.01	0.13	0.06	bdl	bdl	0.03	0.06
K ₂ O	0.01	bdl	bdl	bdl	0.06	bdl	bdl	0.01	0.05	0.01	0.01	0.02
NiO	0.28	0.10	0.20	0.03	0.01	0.42	0.04	0.13	0.29	0.05	na	na
H ₂ O **	11.6	11.6	12.1	12.4	12.8	12.3	12.5	11.7	11.2	12.2	12.4	12.3
Mg#	0.83	0.74	0.86	0.84	0.91	0.93	0.87	0.95	0.86	0.78	0.87	0.87
Cations per 14 O												
Si	3.95	4.13	4.05	3.80	3.76	4.01	3.50	4.28	4.33	3.80	3.84	3.80
Ti	0.01	-	-	-	-	-	0.01	-	-	-	-	0.01
Al	0.62	0.11	0.19	0.41	0.45	0.14	1.04	0.26	0.30	0.21	0.22	0.36
Fe ²⁺	0.52	0.92	0.47	0.53	0.29	0.23	0.40	0.15	0.40	0.83	0.45	0.44
Mn	0.01	0.01	0.01	0.01	0.01	-	0.01	-	0.01	0.01	0.01	0.01
Mg	4.43	4.62	5.10	5.14	5.33	5.49	4.93	4.83	4.33	5.22	5.41	5.25
Ca	0.01	0.01	0.01	-	-	0.01	0.01	0.02	0.01	-	0.01	0.01
Na	-	0.02	0.01	-	-	-	0.02	0.01	-	-	0.01	0.01
K	-	-	-	-	0.01	-	-	-	0.01	-	-	-
Cr	0.11	-	-	0.07	0.12	-	0.03	0.02	0.08	-	0.05	0.08
Ni	0.02	0.01	0.02	-	-	0.03	-	0.01	0.02	-	-	-
sum	9.68	9.82	9.86	9.96	9.96	9.92	9.96	9.58	9.49	10.09	10.02	9.98

* = mean values; #10 = ten analyses; #25 = 25 analyses; ** = calculated from stoichiometry (4 H per formula unit); bdl = below detection limit; na = not analysed; Mg# = MgO/(MgO + FeO).

5.2.4. ICP-MS Whole Rock Analysis

Table 3 reports the average whole-rock composition of the serpentinite from Bagnolo quarry. The different samples analysed show very similar concentrations of both major and trace elements, and therefore only the average values are presented. For comparison, the table also includes the composition of serpentinite from Figline di Prato and that from the pavement of the Florentine Baptistery [17].

Table 3. Major (%) and trace (ppm) element composition of serpentinites.

Sample	CB	SF *	Bpt *
SiO ₂	38.9	37.7	37.8
TiO ₂	0.05	0.03	0.04
Al ₂ O ₃	1.70	0.85	1.60
Fe ₂ O ₃	8.14	8.30	7.60
MnO	0.13	0.07	0.12
MgO	37.5	39.1	38.6
CaO	0.06	0.02	0.03
Na ₂ O	0.01	<0.01	0.02
K ₂ O	<0.01	<0.01	<0.01
P ₂ O ₅	<0.01	<0.01	<0.01
LOI	13.7	13.6	13.9
Sc	11	7	11
V	43	32	51
Cr	2440	2480	2380
Co	92	106	97
Ni	2120	2230	1970
Rb	<1	<1	<1
Sr	2	2	<2
Y	1.1	<0.5	1.1
Zr	4	1	<1
Nb	0.3	<0.2	<0.2
Cs	<0.1	<0.1	<0.1
Ba	8	<2	<2
La	<0.05	<0.05	<0.05
Ce	<0.06	0.08	<0.05
Pr	<0.01	0.02	<0.01
Nd	<0.05	0.11	<0.05
Sm	0.09	0.03	0.04
Eu	0.070	0.018	0.014
Gd	0.19	0.06	0.09
Tb	0.03	0.01	0.02
Dy	0.28	0.06	0.18
Ho	0.04	0.02	0.04
Er	0.11	0.04	0.12
Tm	<0.005	0.006	0.020
Yb	0.09	0.04	0.14
Lu	0.018	0.005	0.022
Hf	<0.1	<0.1	<0.1
Ta	0.04	0.04	<0.01
Th	<0.05	<0.05	<0.05
U	0.01	<0.01	<0.01

* Major elements from Santo et al. [17]; CB= mean of Cava Bagnolo samples; SF = Figline di Prato; Bpt = baptistery pavement; LOI = loss on ignition.

The whole-rock composition of the CB sample corresponds to a typical ophiolitic serpentinite. Major elements are dominated by SiO₂ (38.9 wt.%) and MgO (37.5 wt.%), consistent with serpentine-group minerals. The relatively high Fe₂O₃ content (8.1 wt.%) re-

flects the presence of magnetite, while Al_2O_3 (1.7 wt.%) indicates a slightly more aluminous character compared to most serpentinites. Calcium, sodium, and potassium oxides are nearly absent, in line with the highly depleted nature of the protolith. The loss on ignition (13.7 wt.%) corresponds to structurally bound water in serpentine minerals. Trace elements are characterised by high concentrations of Cr (2440 ppm) and Ni (2120 ppm), as expected from ultramafic precursors, together with significant Co (92 ppm) and V (43 ppm). The abundance of incompatible elements such as Sr, Zr, and REE is very low, confirming the depleted geochemical signature. When compared to the other samples, CB exhibits values very close to Bpt, especially in terms of major oxides and Cr–Ni contents, highlighting strong compositional homogeneity across different serpentinite sources. SF, however, displays slightly higher MgO (39.1 wt.%) and Ni (2230 ppm) but lower Al_2O_3 (0.85 wt.%), suggesting a more depleted protolith. Despite these minor variations, all three serpentinites share a comparable chemical fingerprint, reinforcing their common ophiolitic affinity and supporting the close compositional match between the Bagnolo serpentinite and materials historically used in Florentine monuments.

5.2.5. Fibre Quantification

Quantitative analyses were conducted on three serpentinite samples collected from different blocks within the Bagnolo quarry to assess their chrysotile content. The results revealed the presence of chrysotile fibres with concentrations of 14,153 mg/kg, 15,881 mg/kg, and 18,461 mg/kg, found in the samples CB1, CB3, and CB5, respectively. These values represent the chrysotile content quantified and, therefore, should not be directly compared to the total serpentine mineral content of typical serpentinites. The values indicate the amount of fibrous chrysotile present under the adopted analytical protocol, rather than the bulk mineralogical composition of the rock. Figure 5 shows an SEM image of one of the analysed samples.

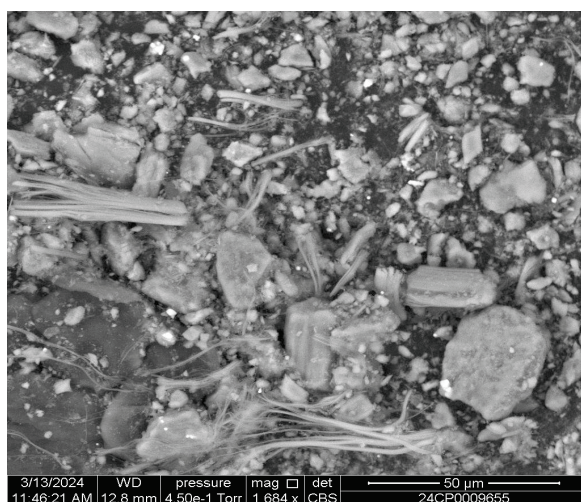


Figure 5. SEM image of a sample from the Bagnolo quarry, displaying the characteristic fibrous morphology of serpentine minerals. Elongated, acicular fibres are observed alongside irregularly shaped fragments of the ground material.

6. Discussion

The study conducted on serpentinite from the Bagnolo quarry enabled its characterisation. Historical sources (e.g., [17,44,45]) report that serpentinite, already in use by the 11th century in Florentine architecture, was quarried in the areas of Monteferrato (Prato) and Impruneta (Florence). Among the oldest known quarries were those located at Pian di Gello, on the eastern slope of Monte Piccioli (Monteferrato). A comparison with samples

from a historic quarry in Figline di Prato, considered the source of the so-called marmo verde used for the Baptistery of San Giovanni in Florence, and with a sample from the original flooring of the Baptistery itself [29], suggests that the boulders from Bagnolo quarry closely resemble the serpentinite historically employed in terms of appearance, texture, and mineralogical composition. This stone was locally known by various names, including Verde di Prato, Nero di Prato, Marmo Nero, and Paragone. The differences observed among samples from different boulders at the Bagnolo quarry are attributable to heterogeneities within the outcrop and to local variations in the agents and processes responsible for the serpentinization of peridotite. Despite these differences, the mineralogical composition of the samples is fairly homogeneous, with the same mineral phases present across all specimens. In terms of physical properties, samples CB2 and CB3 show the lowest capillary water absorption, while CB1, CB3, and CB4 exhibit the lowest water uptake imbibition coefficients. The variability of the capillary water absorption values is likely related to differences in microfracturing, degree of alteration, and textural heterogeneity within the serpentinite. Nevertheless, all values remain consistent with the range commonly reported for this rock type, indicating a generally low to moderate water uptake capacity. Overall, apparent density values are nearly identical across all boulders. Sample CB5, however, displays the highest chrysotile fibre content and the greatest capillary water absorption and imbibition values, making it the least suitable in terms of performance. The observable differences at the hand-sample scale already evident within the quarry, together with the characterisation of the various available lithotypes, make it possible to select appropriate boulders depending on specific needs. These criteria include block size, workability, and intended use location, whether indoor or outdoor. It should be noted that only five blocks (two specimens each) were analysed, which may not fully capture the intra-quarry variability. Therefore, the results should be interpreted with caution, and future studies should include a larger number of specimens to provide a more robust assessment. Our sampling strategy was designed to be representative of the different macroscopic types, rather than to provide a statistical characterisation of the entire deposit.

The serpentinite from the Bagnolo quarry exhibits properties that make it suitable as a replacement material for monument restoration in Tuscany, ensuring structural and chemical compatibility with the original stones. In particular, these rocks display physical properties in line with those of the baptistery pavement. Among them, CB3 and CB4 are the most suitable for restoration or substitution, as their apparent density, open porosity, and water absorption closely match the original material, ensuring greater compatibility and durability. Conversely, CB5, with higher open porosity and imbibition, appears less appropriate for direct substitution in exposed architectural contexts. However, attention must be given to their chrysotile content due to well-known health risks [7–10,46,47]. In this context, quantifying fibres in this type of serpentinite is a critical parameter, directly determining the safe feasibility of its use. The concentrations of chrysotile fibres in the serpentinite from Bagnolo quarry substantially exceed the regulatory threshold of 1000 mg/kg (0.1%) established by Italian and European legislation for classifying a material as asbestos-containing [48]. The obtained technical data confirm the high chrysotile content through detailed morphometric and gravimetric analyses of 26 individual fibres.

The calculated total asbestos mass in the analysed area corresponds to an estimated chrysotile concentration of at least 14,153 mg/kg, with an associated uncertainty of 7%, validating the consistency of the results across the three samples. Given these findings, the serpentinite from Bagnolo quarry must be considered non-compliant with current safety regulations for architectural, ornamental, or structural applications unless rigorous containment and abatement protocols are applied. It is worth noting that, in addition to the mass-based classification threshold, Italian legislation also sets an occupational

exposure limit of 0.1 fibres/cm³ [49], compared to the previous threshold of 0.6 fibres/cm³ established by Law No. 257/1992 [48]. The recently approved EU Directive 2023/2668 further reduces this limit to 0.01 fibres/cm³, to be adopted by December 2025 [50]. The elevated asbestos content also raises concerns regarding environmental and occupational safety during extraction, handling, and potential reuse.

In addition to considering the bulk concentration of fibrous minerals within the serpentinite, it is important to evaluate the potential for fibre release during quarrying and processing. The degree of fibre liberation largely depends on the texture and fabric of the rock, the morphology and orientation of the fibrous minerals (e.g., chrysotile or fibrous antigorite), and the mechanical actions involved in extraction, cutting, and polishing. Even serpentinites containing only minor amounts of fibrous phases may generate airborne fibres when subjected to intense mechanical stress, particularly if the minerals occur along cleavage planes or microfractures. Therefore, assessing fibre release potential provides a more realistic evaluation of occupational and environmental risks associated with the material's exploitation and use. In the studied samples, the compact structure and the massive, non-oriented distribution of fibrous phases suggest a low propensity for fibre release during standard quarrying and processing operations [51–53].

Our results highlight the need for careful material selection and pre-emptive characterisation in the context of the historical reuse or commercial exploitation of serpentinite outcrops, especially in geologically complex ophiolitic settings such as the Monteferrato complex. In this regard, fibre quantification in serpentinite becomes a critical parameter that cannot be overlooked, as it directly determines the safe feasibility of its use. Furthermore, potential exposure to airborne asbestos fibres should be considered during mining and polishing processes, as well as through the wear or handling of products such as floor tiles made from asbestos-bearing serpentinite. Proper risk assessment and mitigation measures are therefore essential to ensure safe use.

Several recent studies support the importance of assessing fibre release, not just bulk fibre concentration. For example, Marzini et al. [53] found that serpentinite with a massive, undeformed texture, even with chrysotile content up to approximately 20%–25%, released very few inhalable fibres in grinding tests, while foliated or cataclastic serpentinite with fibrous veins exhibited much higher release indices. Similarly, in Valmalenco quarries, Cattaneo et al. [51] and Cavallo and Rimoldi [52] reported that airborne chrysotile concentrations varied greatly depending on the presence of veins, surface exposures, and the extent of mechanical disturbance during quarrying or stone processing.

7. Concluding Remarks

The comparative study of serpentinite from Bagnolo quarry demonstrates a strong compositional and textural affinity with historic serpentinite used in Florentine monuments, particularly the Baptistery of San Giovanni. The physical and mechanical properties of the studied blocks indicate their potential suitability for restoration, with samples CB3 and CB4 exhibiting the highest compatibility and durability. However, chrysotile concentrations substantially exceed Italian and EU regulatory thresholds, posing serious health and environmental risks and limiting the material's practical application. To resolve the apparent contradiction between geological suitability and regulatory non-compliance, a structured decision framework is proposed, considering the following factors: Compatibility (matching mineralogical and textural characteristics with historic stones); Durability (long-term performance under restoration conditions); and Safety/Regulatory compliance (asbestos content and occupational exposure limits). Within this framework, Bagnolo serpentinite scores highly for compatibility and durability, but fails on the safety criterion. Therefore, despite its strong match with historic serpentinite, the practical use of this material in

conservation is constrained, and any application would require stringent containment and risk mitigation protocols.

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Article

Spatial Distribution of Uranium and Thorium in the Soils of North Macedonia

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Abstract

The aim of the study was to determine the spatial distribution and assess uranium and thorium contamination in the soils of North Macedonia. Topsoil samples (0–30 cm) were collected from 995 locations across the country on a 5 × 5 km grid. The soil samples were analysed by inductively coupled plasma–mass spectrometry (ICP-MS) using the total digestion method. The distribution of uranium and thorium in the soils is discussed according to the country's 8 statistical regions, 15 major geological formations and 13 pedological units. The average uranium content is 2.1 mg/kg, ranging from <0.1 to 13 mg/kg (median 2.0 mg/kg), while the average thorium content is 9.3 mg/kg, ranging from 0.20 to 92 mg/kg (median 9.5 mg/kg). The spatial distribution patterns of U and Th in the soils of North Macedonia are very similar and are determined by geology (parent material and mineralisation). High uranium (2.9–13 mg/kg) and thorium (42–92 mg/kg) contents were found mainly in soils in the areas of Neogene and Palaeozoic igneous rocks and Neogene clastites (Pelagonian, East Macedonian zone), as well as in the Kratovo-Zletovo Massif in the north-eastern part of the country and in the Kožuf Mountains in the central and southern parts, where Neogene igneous rocks predominate. According to the pedological units, the hydromorphic soils (mean content of 2.9 mg/kg U and 12 mg/kg Th) in the valleys of the country's main rivers, which predominate in the western part, were the richest for these elements.

Keywords: uranium; thorium; soil; statistical regions; geological formation; pedological units; North Macedonia

1. Introduction

The origin and near-surface distribution of about 250 known uranium and/or thorium minerals provide insight into the principles of mineral evolution. Uranium and thorium represent a unique pair in the periodic table and are of particular importance to geoscientists. Uranium and thorium are the two largest naturally occurring elements and the most abundant of the actinide series. The energy released by the radioactive decay of U and Th has driven the thermal evolution of the Earth, resulting in its layered internal structure and the continuous movement of plates at the Earth's surface [1]. The radioactive decay of ²³⁸U, ²³⁵U and ²³²Th also provides a rich array of radiogenic elements, such as radon, which are found in three naturally occurring radioactive decay chains.

²³⁸U and ²³²Th, which are at the top of the primordial radionuclide decay series, have been present in the Earth's crust throughout its history [2]. The distribution of radionuclide

concentrations reflects the migration of uranium and thorium under surface conditions, with the capacity for migration proceeding in the order $U > Ra > Th$. Uranium can remain in a soluble state over long periods of time and is translocated over long distances by the flow of streams or rivers. The horizontal transfer of uranium and thorium is determined by the alternation of sorption and desorption [3].

Rocks or minerals containing long-lived parent isotopes of the decay series (U and Th) are necessarily associated with other members of the decay series. Rocks that host U and Th include some crystalline rocks such as granites and quartz conglomerate metamorphic rocks, as well as certain sedimentary rocks, such as organic shales, sandstones, carbonates and phosphorites. The behaviour of radioelements found in the natural environment, therefore, depends on their geochemistry, their half-life and the nature of their environment [4].

Uranium (atomic number 92) is the 46th most abundant element in the Earth's upper continental crust with an estimated abundance of 2.7 mg/kg [5]. The average uranium content in European topsoil is 2.45 mg/kg [6], while the average content in arable and pasture soils in Europe is 0.77 mg/kg and 0.74 mg/kg, respectively [7]. It occurs in nature in three radioactive isotopes. Its main oxidation state is +6. The three typical uranium minerals are uraninite (UO_2), brannerite $[(U,Ca,Ce)(Ti,Fe)_2O_6]$ and carnotite $[K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O]$. Uranium is also found in phosphate rock, lignite, and monazite sand. In common rock types, uranium content is highest in granite (4 mg/kg), felsic gneiss, shale, and schist (3 mg/kg), and its content is the lowest in basalt (0.1–0.5 mg/kg) and ultramafic rocks (0.02 mg/kg). Uranium is used extensively in glass and ceramics as a pigment, while depleted uranium (^{238}U) is used in military shells and armour. Some apatite-based phosphate fertilisers can contain high levels of uranium. Uranium and its compounds are highly toxic, both chemically and radiologically [7].

Thorium (atomic number 90) is the 38th most abundant element in the Earth's upper continental crust with an estimated abundance of 10.5 mg/kg. The average thorium content in European topsoil is 8.2 mg/kg [8]. Thorium belongs to the actinide series and occurs naturally as the radioactive isotope ^{232}Th . Its predominant oxidation state is +4. Thorite ($ThSiO_4$) and thorianite (ThO_2) are two typical thorium minerals. Thorium is more widespread as an accessory element in rock-forming minerals such as zircon, epidote, sphene, apatite and allanite. In common rocks, Th concentrations are highest in granite (15 mg/kg), shale and schist (12 mg/kg) and lowest in basalt (0.3 mg/kg) and ultramafic rocks (0.05 mg/kg). Limestone contains traces of Th (2 mg/kg). When Th is released during weathering, it is strongly sorbed by clay minerals [7]. Thorium is an important alloying element in magnesium. It is used to coat tungsten wire for electronic devices. It is both chemotoxic and radiotoxic. All Th isotopes are sources of α -rays.

The occurrence of Th and U in surface soils and sediments is predominantly of geogenic origin [9]. However, some anthropogenic activities, such as electronics and mining, have contributed to their increased content [10–15]. The use of Th and U in newer technologies, the combustion of biomass and fossil fuels, the application of fertilisers, and electronic waste further increase their content in soil [15–17].

To date, very few results have been published on the U and thorium content of soils in North Macedonia, and these relate to a small number of measurements (around 200) that were not carried out as part of a systematic, standardised network [18]. Instead, the research has focused on the risk assessment of radionuclides in soils (including U and Th radioisotopes) at the national level [19,20] and for specific regions, such as Veles [21], Kavadarci [22] and Bitola [23,24] regions.

The aim of this work is to monitor and determine the distribution of uranium and thorium in soils from the entire area of North Macedonia using an evenly distributed

5 × 5 km sampling system, in which topsoil samples (0–30 cm) were taken at 995 locations. All statistically analysed data on U and Th contents, as well as the distribution maps of U and Th contents across the whole territory of North Macedonia, will allow for a detailed interpretation of the distribution of U and Th in soils by statistical regions, geological formations and pedological units.

2. Materials and Methods

2.1. Study Area

North Macedonia is a landlocked country in the central part of the Balkan Peninsula, located between 40°50' and 42°20' north latitude and between 20°28' and 23°05' east longitude (Figure 1). North Macedonia covers an area of 25,436 km² and has a total population of 1,837,000 inhabitants (2021 census). Geographically, North Macedonia is characterised by a central valley formed by the Vardar River and framed by mountain ranges. The country is rich in minerals, with significant deposits of chromium and other non-ferrous metals (Cu, Pb, Zn, Ni and Mn). The country also has gypsum, marble and granite mines, while lignite provides 80% of Macedonia's electricity [25]. North Macedonia is divided into eight statistical regions: Skopje, Pelagonia, Polog, Vardar, east, southeast, northeast and southwest.

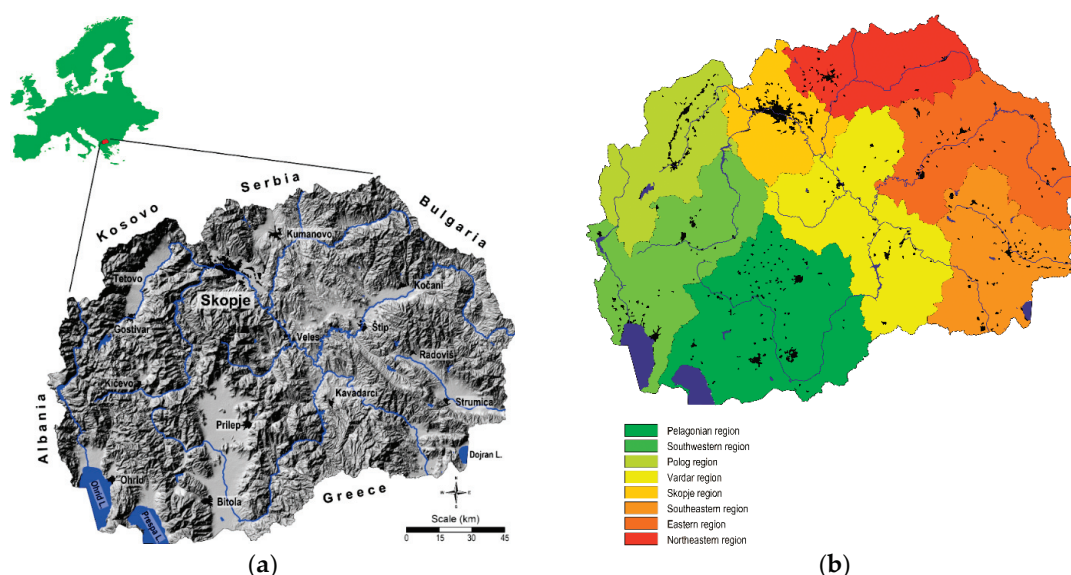


Figure 1. Topographic map (a) and map of the statistical regions (b) of North Macedonia.

Because of its characteristic natural and geographical features, there are two different climates in Macedonia: an altered Mediterranean climate and a temperate continental climate, with two distinct seasons—cold, wet winters and dry, hot summers—associated with the transitional seasons, spring and autumn. In mountainous regions, the climate is characterised by short, cool summers and significantly cold and moderately wet winters, with precipitation mostly as snow [25].

2.2. Geological Characteristics

The main geological and tectonic features of North Macedonia are described in detail by Stafilov & Šajn [25] and Petrušev et al. [26] based on earlier studies by Pendžerkovski [27], Hadži-Mitrova [28], Dumurdžanov et al. [29,30] and Arsovski [31]. From a tectonic point of view, Macedonia comprises six major tectonic units: the Vardar Zone (VZ) in the central region, the Pelagonian Massif (PM), the West-Macedonian Zone (WMZ) and a small part of

the Cukali-Krasta Zone (CKZ) in the west, and the Serbo-Macedonian Massif (SMM) and the Kraishtide Zone (KZ) in the east of the country (Figure 2).

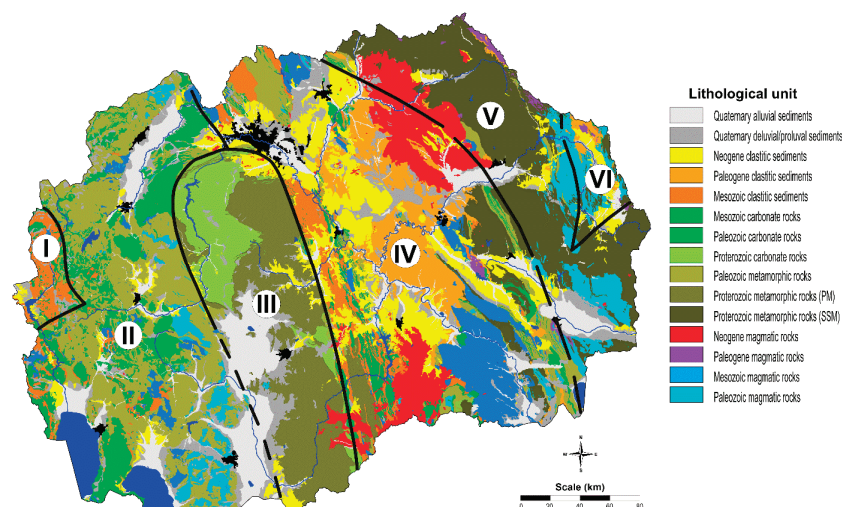


Figure 2. Simplified geological map of North Macedonia. Tectonic units: I—Cukali-Krasta zone (CKZ); II—West-Macedonian zone (WMZ); III—Pelagonian massif (PM); IV—Vardar zone (VZ); V—Serbo-Macedonian massif (SMM); VI—Kraishtide zone (KZ).

The Cukali-Krasta Zone consists of Upper Cretaceous conglomerates, including sandstones, claystones and limestones with olistostromes and rudist limestones. The West-Macedonian Zone consists of low-grade metamorphic rocks, anchi-metamorphic Palaeozoic rocks and magmatites, Triassic and Jurassic sediments and magmatites, as well as Tertiary sediments. The Pelagonian Massif consists of a Proterozoic crystalline mass, with pronounced domes, brachy and open folds. Lithologically, it is composed of highly metamorphic rocks and granitoids.

The Vardar zone is characterised by the presence of Paleozoic low-metamorphic rocks, Triassic continental sediments, Jurassic ophiolites and ultrabasites and Cretaceous sediments, which are divided into numerous shells intruding Eocene-Oligocene sediments and volcanites. The main mass of the Serbo-Macedonian massif (SMM) consists of Lower or overthrusting Proterozoic and Upper Riphean-Cambrian complexes as well as relicts of Lower Paleozoic schists and intrusions of Hercynian granitoids. The Kraishtide Zone (KZ) represents the increased occurrence of metagabbros, metadiabases and green metasandstones within Hercynian aplitic granitoids [25].

The territory of Macedonia is covered by the following 15 main geological units, which are given in Figure 2: Quaternary alluvium (10.1%), Quaternary deluvium/proluvium (8.3%), Neogene clastites (9.7%), Paleogene clastites (5.0%), Mesozoic clastites (4.1%), Mesozoic carbonates (5.2%), Paleozoic carbonates (3.0%), Proterozoic carbonates (3.6%), Paleozoic metamorphic rocks (14.1%), metamorphic rocks of the Pelagonian Massif (8.5%), metamorphic rocks of the Serbo-Macedonian massif (11.6%), Neogene magmatic rocks (5.6%), Paleogene magmatic rocks (0.4%), Mesozoic magmatic rocks (4.8%) and Paleozoic magmatic rocks (5.3%) [25].

2.3. Pedological Characteristics

The soils in North Macedonia are extremely heterogeneous and vary greatly over small distances [32]. The following soil types have been defined: lithosols, regosols, arenosols, colluvial soils, rendzinas on hard limestones and dolomites, rendzinas, rankers, vertisols, chernozems, chromic cambisols, red soils (terra rossa), brown soils on limestones and dolomites, brown forest soils, illimerised soils, brown podzolic soils, alluvial soils, fluvatile

meadow soils, hydromorphic black soils, gleyic soils, peat soils (histosols), pseudogleys, solonchaks and solonetz [33].

2.4. Soil Sampling and Analysis

This study involved determining the uranium and thorium contents in the topsoil (0–30 cm). Soil samples were collected between 2012 and 2014 from 995 sites within 5×5 km density grids (Figure 3). This grid is commonly used for the preparation of national soil atlases [34]. A denser grid was used for some smaller areas, as suggested by Golabkesh et al. [35], Vaziri et al. [36], or in some of our studies [37,38]. The soil samples were collected according to the relevant standards [39]. The soil samples were cleaned of plants and stones, then homogenised and dried at room temperature. They were then passed through a 2 mm sieve and ground in a porcelain mortar until they reached a final grain size of 125 μm .

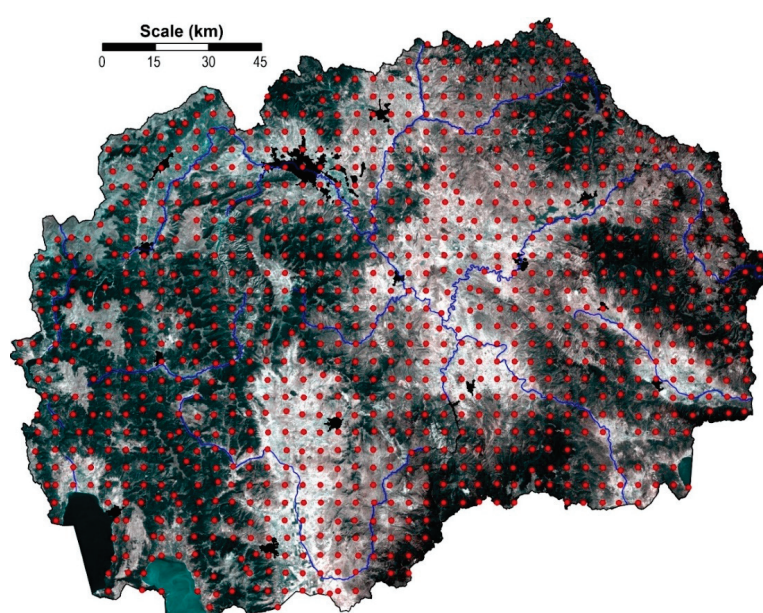


Figure 3. Soil sampling sites in the territory of North Macedonia.

All soil samples were sent for analysis to the accredited laboratory ACME Ltd. in Vancouver, Canada. After complete digestion of the samples (Multi Acid—ICP-ES/MS, Method MA200). The detection limit for uranium and thorium content of the method was 0.1 mg/kg. The precision was tested using the relative differences between pairs of analytical determinations of the same sample. Thirteen selected samples were replicated to achieve a precision of 4.68% for U and 8.05% for Th, respectively. The *t*-test [40] was used to estimate the accuracy and precision of the two analysed data sets. The value of 0.07 for U and 0.05 for Th at $p < 0.05$ means that the difference between the means of the two groups is not statistically significant. The estimation of trueness and precision of the two analysed data sets was also performed by calculating the precision and *t*-test, by analysing two certified reference materials of soil, OREAS 25a and OREAS 45A. From the results of precision (3.36% and 2.73% for U and 5.93% and 4.02% for Th) and *t*-test (0.40 and -0.82 for U and 0.99 and 0.25 for Th at $p < 0.05$), it could be concluded that there are no significant differences between the certified and received data.

All data processing and calculations, geostatistical data interpretations and visualisations (mapping) were performed using the following software programmes: Statistica (Stat Soft Inc., Tulsa, OK, USA), Autodesk MAP 3D (Autodesk Inc., San Francisco, CA, USA), QGIS (Open Source Geographic Information System, Chicago, USA) and Surfer

(Golden Software Inc., Golden, CO, USA). For the development of the distribution maps, the Kriging method with linear variogram interpolation was applied.

3. Results and Discussion

The basic statistical data on uranium and thorium contents in the topsoil of North Macedonia are presented in Table 1. The mean uranium and thorium contents are 2.5 mg/kg and 11 mg/kg, respectively, while the median U and Th contents are 2.0 mg/kg and 9.5 mg/kg, respectively. The low detection limit for uranium below 0.1 mg/kg was observed in fewer samples. The analysis showed that these cases are related to the nature of the area, which is mainly of lithogenic origin [41].

Table 1. Descriptive statistics of the analysis of uranium and thorium in the topsoil of North Macedonia.

Parameter	U (mg/kg)	Th (mg/kg)
Number of sampling locations	995	995
Detection limit	0.10	0.10
Arithmetic average (mean)	2.5	11
Geometrical mean	2.1	9.3
Box–Cox transformed average	2.1	9.6
Arithmetic standard deviation	1.6	6.1
Geometric standard deviation	0.050	0.19
Coefficient of variation	64	58
Minimum	<0.10	0.20
P ₁₀ —10th percentile	1.0	5.2
P ₂₅ —25th percentile	1.5	7.3
Median	2.0	9.5
P ₇₅ —75th percentile	3.1	13
P ₉₀ —90th percentile	4.4	17
Maximum	13	92
Skewness	2.07	3.95
Kurtosis	6.66	36.18
Box–Cox transformed skewness	0.02	0.11
Box–Cox transformed kurtosis	1.09	2.83

It was found that the mean and median values for U and Th are similar to those for the European topsoil (2.36 mg/kg and 2.0 mg/kg for U and 11 mg/kg and 9.5 mg/kg for Th) and in the upper continental crust (2.7 mg/kg U and 10.5 mg/kg Th) (Table 2). In some areas of the country, U and Th contents increase up to their maximum values of 13 mg/kg U and 92 mg/kg Th.

Table 2. Comparison of data on the U and Th content in the soils of North Macedonia, Europe and the world (in mg/kg).

Unit	North Macedonia, This Work		Europe, Topsoil [6]		World (Upper Continental Crust) [5]	
	U	Th	U	Th	U	Th
Average	2.5	11	2.36	8.24	2.7	10.5
Median	2.0	9.5	2.03	7.24		
Minimum	<0.10	0.20	0.21	0.30		
Maximum	13	92	53.2	75.9		

Data on national-level contents of U and Th in neighbouring countries are scarce. Only data on Th content in soils from Croatia are available, with a mean of 13 mg/kg and

a median of 12.5 mg/kg, which are similar to those for North Macedonia (Table 1). In preparing the study for Chemistry of European Soils [7], general data were provided for many European countries, but these were obtained by analysing soil samples using aqua regia dissolution, with a smaller grid and a significantly smaller number of samples. It was found that uranium content in soils from neighbouring countries is highest in Slovenia, followed by Croatia, North Macedonia, Greece, Serbia, and Bulgaria (ranging from 3 to 6 mg/kg). For thorium content, it is highest in soils from Bulgaria, followed by Slovenia, North Macedonia, Croatia, and Greece (ranging from 3 to 6 mg/kg).

The basic statistical data (mean, median, minimum and maximum) for U and Th content in soils according to country regions (Table 3, Figures 4 and 5) show higher median values in the Pelagonian region in the western part of the country, with contents of 3.0 mg/kg U and 12 mg/kg Th. In the other regions, the median content is below the national median (2.5 mg/kg U and 11 mg/kg Th).

Table 3. Mean, median, minimum and maximum Tl content by statistical regions in North Macedonia (in mg/kg).

Region	Number of Samples	Mean		Median		Minimum		Maximum	
		U	Th	U	Th	U	Th	U	Th
Pelagonian	192	3.0	12	3.0	12	0.3	0.20	12	32
Southwestern	135	2.0	9.7	2.1	10	0.4	2.2	8.5	20
Polog	96	1.4	7.2	1.3	6.9	0.4	2.0	4.1	20
Vardar	162	2.1	11	1.8	9.7	0.3	0.90	13	92
Skopje	72	1.6	8.2	1.5	8.1	0.6	2.4	7.5	28
Southeastern	105	1.9	8.4	2.1	9.1	0.1	0.70	9.1	36
Eastern	141	2.3	9.1	2.2	9.4	0.7	2.5	8.1	23
Northeastern	92	2.1	9.4	1.9	9.1	0.7	2.0	6.9	44

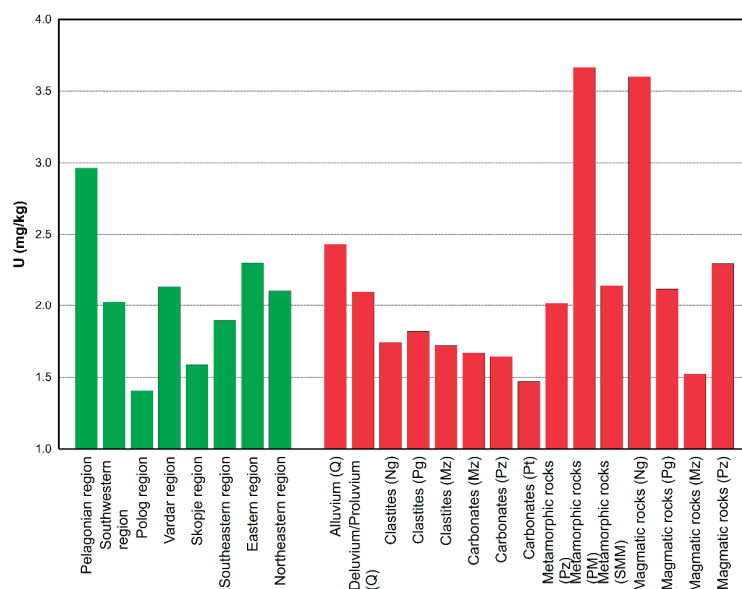


Figure 4. Mean values of uranium content by statistical regions and geological formations.

Depending on the geological formation, the elevated U and Th contents in this region are mainly due to the presence of Neogene magmatic rocks and Mesozoic carbonates, which have relatively high U and Th contents compared to other geological formations (Table 4, Figures 4 and 5). The highest mean uranium and thorium contents in soils were found in the area where metamorphic rocks of the Pelagonian Massif (3.7 mg/kg U and 12 mg/kg

Th) and Neogene magmatic rocks (3.6 mg/kg U and 16 mg/kg Th) predominate. The areas with Quaternary alluvium (2.4 mg/kg U and 11 mg/kg Th) and Paleozoic magmatic rocks (2.3 mg/kg U and 9.3 mg/kg Th) were found to have slightly higher mean uranium contents than the mean contents in soils across the entire national territory.

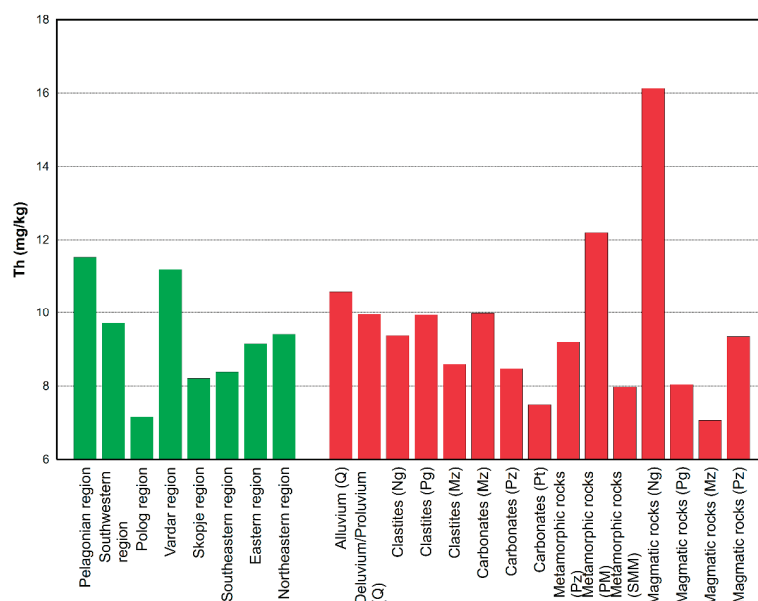


Figure 5. Mean values of thorium content according to statistical regions and geological formations.

Table 4. Mean, median, minimum and maximum uranium and thorium contents depending on the main geological formation (in mg/kg).

Geology	Number of Samples	Mean		Median		Minimum		Maximum	
		U	Th	U	Th	U	Th	U	Th
Alluvium (Q)	114	2.4	11	2.4	10	0.7	2.3	7.7	49
Deluvium (Q)	80	2.1	10	2.1	9.9	0.8	3.5	6.4	23
Clastites (Ng)	95	1.7	9.4	1.7	8.9	0.6	2.5	6.3	52
Clastites (Pg)	60	1.8	9.9	1.7	9.1	0.9	3.8	8.2	92
Clastites (Mz)	40	1.7	8.6	1.4	8.2	0.6	2.6	12	26
Carbonates (Mz)	120	1.7	10	1.7	10	0.5	2.3	4.0	19
Carbonates (Pz)	52	1.6	8.5	1.6	8.3	0.8	2.4	4.4	30
Carbonates (Pt)	32	1.5	7.5	1.6	9.1	0.3	0.20	4.8	21
Metamorphic rocks (Pz)	43	2.0	9.2	2.0	10	0.4	1.9	8.5	21
Metamorphic rocks (PM)	84	3.7	12	3.7	12	0.7	3.0	13	42
Metamorphic rocks (SMM)	115	2.1	8.0	2.2	8.4	0.7	2.0	8.1	26
Magmatic rocks (Ng)	50	3.6	16	3.8	16	0.3	0.90	9.7	44
Magmatic rocks (Pg)	7	2.1	8.0	2.2	8.8	1.0	2.8	4.2	20
Magmatic rocks (Mz)	51	1.5	7.1	1.5	8.0	<0.10	0.70	7.3	33
Magmatic rocks (Pz)	52	2.3	9.3	2.3	9.5	0.7	3.8	9.1	24

Q—Quaternary, Ng—Neogene, Pg—Paleogene, Mz—Mesozoic, Pt—Proterozoic, PM—Pelagonian massif, SMM—Serbo-Macedonian massif.

According to the pedological units (Table 5), the hydromorphic soils in the valleys of the country's main rivers, which predominate in the western part of the country, were the richest in these elements. It is known that geochemical processes such as reduction and oxidation are involved in these increased concentrations [42,43]. The mean uranium content is 2.9 mg/kg, ranging from 1.1 to 7.7 mg/kg, while the mean content of Th is 12 mg/kg, ranging from 7.8 to 17 mg/kg. The lowest contents were found in the anthroposols with 1.1 mg/kg U and 6.4 mg/kg Th. According to the pedological units (Table 5), the hydromorphic soils in the valleys of the country's main rivers, which predominate in the

western part of the country, were the richest in these elements. The mean U and Th contents were very similar in the other pedological units, regardless of land use, with the lowest content in the anthropogenic soils being 1.5 mg/kg U and 6.4 mg/kg Th.

Table 5. Mean, median, minimum and maximum values of uranium and thorium content according to the main pedological units in North Macedonia (in mg/kg).

Pedological Unit	Number of Samples	Mean		Median		Minimum		Maximum	
		U	Th	U	Th	U	Th	U	Th
Lithosol	57	2.0	10	2.1	9.8	0.80	5.6	4.2	20
Lithosol (C)	38	1.7	9.2	1.7	9.5	0.40	2.6	5.1	30
Regosol	69	2.3	11	2.1	9.9	<0.10	1.1	9.7	35
Colluvial soil	55	2.2	10	2.2	9.3	0.60	3.6	6.7	49
Rendzina	72	1.6	8.9	1.6	8.2	0.60	2.6	6.1	26
Ranker	72	2.3	8.7	2.0	8.5	0.30	0.90	11	33
Vertisol	319	2.1	11	1.8	10	0.90	3.8	6.9	44
Cambisol (H)	99	1.8	8.8	1.8	9.0	0.60	2.4	6.4	19
Cambisol (M)	80	2.4	9.7	2.4	9.7	0.20	0.20	13	52
Cambisol (C)	15	1.5	7.9	1.5	8.6	0.40	2.0	4.8	22
Fluvisol	93	2.4	11	2.4	11	0.70	2.3	6.6	92
Hydromorphic soil	21	2.9	12	2.7	11	1.3	7.8	7.7	17
Anthroposol	5	1.1	6.4	1.1	6.4	0.80	3.5	1.8	9.2

Lithosol (C)—lithosols on limestone-dolomite chernozems; Cambisol (H)—cambisols, mostly cinnamomic forest soil; Cambisol (M)—cambisols, mostly brown forest soil; Cambisol (C)—cambisols, mostly brown soils on limestone and dolomite.

The spatial distribution of uranium and thorium content in soil throughout the country is shown in Figures 6 and 7. In general, the spatial distribution patterns of U and Th in the soil samples are mainly determined by geology (parent material and mineralisation).

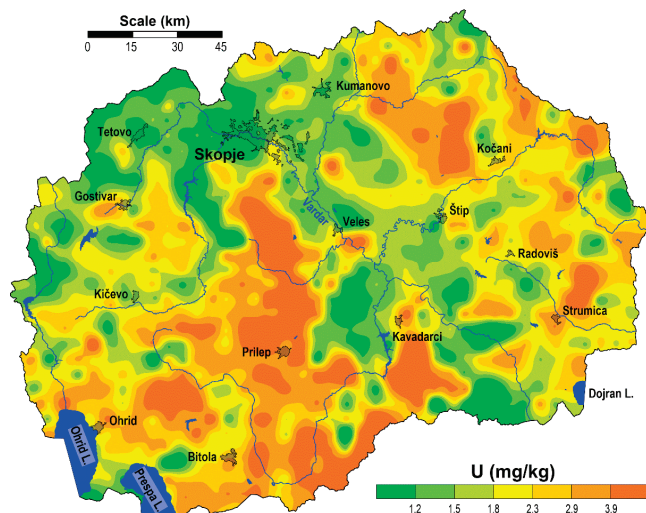


Figure 6. Spatial distribution of the uranium content.

High uranium contents (2.9–13 mg/kg) were found mainly in soils from the area where Neogene and Paleozoic igneous rocks and Neogene clastites occur in the Pelagonian, Eastern Macedonian zone, as well as in the Kratovo-Zletovo Masiff in the northeastern part and the Kožuf Mountains in the central-southern part of the country, where Neogene magmatic rocks predominate. High uranium contents (9.1–13.1 mg/kg) were also found in soils from the area with a dominant occurrence of metamorphic and magmatic rocks in the Vardar and Pelagonian regions. The highest uranium content, 13.1 mg/kg, was found in a soil sample taken in the Kavadarci area on Kožuf Mountain in the Vardar region,

located in the area of Proterozoic metamorphic rocks. In the same area, another soil sample on the Vitačevo plateau (near the village of Stragovo) had a high U content (9.7 mg/kg). A high U content (11.9 mg/kg) was also found in soil samples from the Mariovo area in the Pelagonian region: a sample near the village of Gugjakovo (11.9 mg/kg) and a sample on Mount Kajmakčalan (11.1 mg/kg), which are located in the area of Mesozoic clastites and metamorphic rocks, respectively. A similar value of U content (11.6 mg/kg) was found in soils from Mount Babuna in the Veles region (Vardar region), which lie in an area of Proterozoic metamorphic rocks. It should also be noted that a high uranium content (9.1 mg/kg) was found in a sample from Mount Ogražden in the north of the town of Strumica.

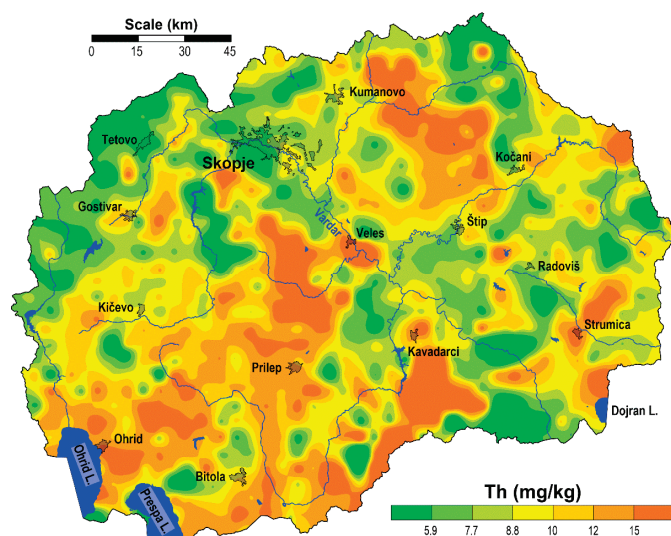


Figure 7. Spatial distribution of the thorium content.

The highest thorium content (92 mg/kg) was found in soils collected near the town of Veles, close to the confluence of the Babuna and Vardar rivers, in an area with a dominant occurrence of Paleogene clastites. Two other soil samples with the next highest thorium content were collected in the same area of the town of Veles (Vardar region). Both samples were located near the village of Omorani on Mount Babuba. The sample with a Th content of 52 mg/kg was located in the area of Neogene clastites, and the sample with a Th content of 49 mg/kg was in the other area of the Quaternary alluvium. High Th contents (44 mg/kg) were also found in soil samples from the area of Kumanovo in the Northeastern region, near the village of Dragomance, and in a sample from Kožuf Mountain (Vardar region, in the area of Proterozoic metamorphic rocks) with a content of 42 mg/kg.

4. Conclusions

The distribution of total uranium and thorium content in the surface soil (0–30 cm) at 995 sites on a 5×5 km grid in North Macedonia was investigated. The mean and median values of uranium (2.0 mg/kg and 2.5 mg/kg) and thorium (11 mg/kg and 9.5 mg/kg) in soil are very similar to their contents in European soils and the upper continental crust. In general, the spatial distribution patterns of U and Th in the collected soil samples are mainly determined by geology (parent material and mineralisation). Thus, uranium and thorium contents in soils by region showed higher median values in the Pelagonian region in the west of the country, with contents of 3.0 mg/kg U and 12 mg/kg Th, while in other regions, the median content was below the median value for the whole country. According to geological formations, the highest mean uranium content in soils was found in areas where metamorphic rocks of the Pelagonian Massif (3.7 mg/kg U and 12 mg/kg Th) and Neogene

magmatic rocks (3.6 mg/kg U and 16 mg/kg Th) predominate. The highest thorium content (92 mg/kg) was found in soils collected near the town of Veles, near the confluence of the Babuna River with the Vardar River, and in an area dominated by Paleogene clastites. In the same area of the town of Veles (Vardar region), two soil samples with high thorium content were collected near the village of Omorani on Mount Babuna (52 mg/kg, where Neogene clastites predominate, and 49 mg/kg, where Quaternary alluvium predominates).

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