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Abstract Book for

Raw materials and geomaterials: critical issues and industrial applications

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Abstract Book for 2° Workshop

Raw materials and geomaterials: critical issues and industrial applications

The second edition of the workshop "Raw materials and geomaterials: critical issues and industrial applications", organized by the National Group of Georesources, Environment, and Cultural Heritage (GABeC), took place at Sapienza University of Rome (Rome, Italy) on December 9th and 10th, 2024. The workshop attracted a diverse range of participants, including 100 researchers, PhD and master's students from over 20 national universities and research institutions. Additionally, representatives from the Italian Institute for Environmental Protection and Research (ISPRA) and the National Research Council (CNR), as well as more than 250 professional geologists, took part in the event. The primary objective of the workshop was to raise awareness among the public and Italian institutions about the importance of georesources, a critical issue in the current economic landscape. This topic has gained even more relevance following the recent European Critical Raw Materials Act (May 2024) and the urgent need to enhance the exploitation of European mines and strengthen the resilience of the European economy. During the workshop, Italian researchers had the opportunity to showcase the latest breakthroughs in their field, covering a wide range of topics—from the valorisation of geomaterial waste to the remediation and monitoring of abandoned mining sites, as well as the optimization of beneficiation processes.

Opening table of the workshop "Raw materials and geomaterials: critical issues and industrial applications", featuring introductory remarks and discussion on the challenges and industrial applications of raw materials and geomaterials

COVER PHOTOGRAPH: Micol Bussolesi, Giovanni Grieco | Panoramic view of the nichel mine of Kastoria, Vrysakia District, Greece.

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Recovery of quarry waste by production of pozzolanic mortars using Sardinian rhyolitic rocks

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The research presents a study on the use of pozzolans derived from rhyolitic rocks of local origin as hydraulic additives in experimental mortars, with the aim of reducing environmental impact and valorising quarry waste from the Monte Arci volcanic complex in Sardinia. Pozzolanic mortars, already used by the Romans for their strength and durability, are composed of a medium-high percentage of amorphous phase that gives them a significant chemical reactivity with lime. The experimentation included optical microscopic analysis, XRD and SEM-EDS analyses, as well as physical analyses and mechanical tests (He-pycnometry, compressive uniaxial strength, PLT) on the mortars formulated with main five rhyolitic samples with different petro-volcanological features: three perlitic rocks, a pumice-cineritic pyroclastite and a welded ignimbrite.

The experimental mortars were prepared with various mixes to understand the best aggregate/pozzolana ratio. One of the best performing mixes consists of 60% aggregate, 15% pozzolan and 25% binder (i.e., slaked lime and quicklime) by volume. The physical characteristics and mechanical strength were analysed at different curing stages (1 week, 1 and 2 months, 2 years) and showed an increase in compressive strength and reduction in porosity over time, especially in samples subjected to water immersion treatment at 25°C and 70°C to improve the reaction between the amorphous phase and the lime binder. The results highlight a good chemical reactivity between lime and pozzolans, evidenced by the early formation of hydraulic phases (CSH and CAH), detectable with SEM-EDS after two years of curing.

Thus, the use of pozzolan material makes it possible to produce environmentally friendly mortars, confirming it as a sustainable solution for applications in the construction sector and historical heritage restoration. The research highlights the potential of local Sardinian pozzolans as a resource for the production of mortars with high mechanical performance and long durability.

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Implementing Ophiolitic Chromite Concentrates from Metallurgical to Foundry Grade: The Case of Albanian Sands

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Chromite foundry sands are a particularly important feature of the stainless steel, foundry, and refractory industries. The foundry industry uses chromite sands, bound with resins, to form the mould in which molten metal is contained until it solidifies in the desired shape. Due to chromite physical and chemical properties, there is no substitute for this industrial use. Chromite foundry sands market is dominated by South Africa, the number one producer and the main provider of foundry-quality sands for the European market. Therefore, it is important for the EU to be able to diversify the sources of chromite foundry sands and reduce the supply risk. The present work aims to test metallurgical- grade sands from enrichment plant in Albania, implementing a new methodology to increase their quality parameters to fit the foundry use. To be used for casting, chromite sands must be as pure as possible as small amounts of low-T melting gangue minerals can damage the binding resins. Moreover, a very narrow sand grain size range is required to provide the correct permeability to the sand. These requirements are tested through three parameters: i. Acid Demand Test (ADT), a titration method, is used as a proxy of the sand-resin reaction potential; ii. Fineness Index (FI), to test the grain size of the sands; iii. SiO_2 content of the sands, a measure of silica impurities, should be as low as possible.

The Albanian sands were initially checked, together with two samples from commercial South African chromite foundry sand, for all the three quality parameters and compared with foundry industry thresholds. As expected, all Albanian sands did not meet the parameters. The worst results were obtained for the ADT value, always quite far from the thresholds. A selection of the Albanian sand closer to the quality thresholds were chosen for further depuration tests aimed to meet all three parameters. The main problem of the Albanian sands lies in the mineralogy of the silicate impurities. Albanian sand derives from metamorphosed ophiolite-hosted deposits, typically enriched in serpentine, while South African ones come from the major layered intrusion of Bushveld and their typical gangue minerals are olivine and orthopyroxene. The presence of serpentine negatively affects the ADT value as it is much more reactive than olivine or pyroxene (Bussolesi et al., 2020).

Two depuration tests were combined to lower the silicate impurities of the sands. Heating experiments conducted at 800°C for 1 hour were partially positive as the ADT value was reduced of about 30%, due to transformation of serpentine into a new phase as confirmed by XRD data. These were followed by a second depuration stage through magnetic separation. Preliminary results are positive, and it is possible that a combination of cooking and magnetic separation could lead to the production of Chromite Foundry Sands starting from Albanian chromite concentrates.

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Assessment of Critical Raw Materials in the Northern Apennines (Parma and Piacenza provinces) using bibliographic data and subsurface geological models

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The energy transition is an issue of fundamental importance in the current global context as an increasing number of countries commit to a sustainable, energy-efficient future. This also leads to the search for minerals and elements essential for the storage, distribution and supply of energy obtained from new sources. An increase in demand is expected for elements such as boron, barium, lithium, magnesium, and strontium that are essential to advancing the energy transition (EU, 2023). As these elements are only readily available in a limited number of countries outside Europe, the European Union has designated them as Critical Raw Materials (CRMs) (EU, 2024). Over the past decade, research has increasingly focused on the extraction from unconventional deposits, including geothermal waters, basinal/formation brines, and marine waters (Dini et al., 2021).

Despite the identification of possible extraction area of CRMs in the Italian territory, their extraction is hampered by various gaps: i) lack of regional and detailed maps of distribution of CRMs (e.g., along the N Apennine front and associated Po basin foredeep); ii) limited analysis of the lithological units influencing the composition of the waters with CRMs; iii) limited knowledge of tectonic structures influencing the migration of fluid containing CRMs; iv) inconsistency between older and more recent chemical analyses.

In the provinces of Parma and Piacenza, where the occurrence of salty waters has been known since Roman and medieval times and contain CRMs (Dini et al., 2021), we address and attempt to solve the above gaps and limitations.

To understand the origin, distribution and migration paths of these waters, a range of geological data types (such as maps, cross-sections, seismic reflection profiles, and well data) have been integrated with available geochemical analyses of spring and well samples. The data were first inserted in a GIS-based (QGis) database, then used to create new distribution maps for most significant CRMs above mentioned, and finally enclosed in a new 3D geological model built with Leapfrog Geo (Seequent TM) to have a faster and simplified view of the geological setting (Fig. 1).

Preliminary results indicate that the waters richest in CRMs are mainly contained in and sourced from the Middle Miocene sandstone-rich turbiditic unit. In this framework, the presence of tectonic structures (mainly fault-related folds), stratigraphic discontinuities in the post-Middle Miocene succession, and the absence of impermeable units that act as seals favor the ascent and exit of these waters towards the overlying and more recent geological units where the springs develop (e.g., the case of Contignaco). On the contrary, if there are impermeable units above, these waters containing CRMs remain below ground level (e.g., in the case of Sant'Andrea Bagni, Salsomaggiore Terme and Monticelli Terme). However, there are also intermediate situations where the water partly remains in the deep aquifers and partly reaches the surface (e.g., in Tabiano).

Our results show that the waters having higher availability for the extraction of CRMs are the Br-I-rich brine waters (Salsomaggiore Terme and Monticelli Terme).

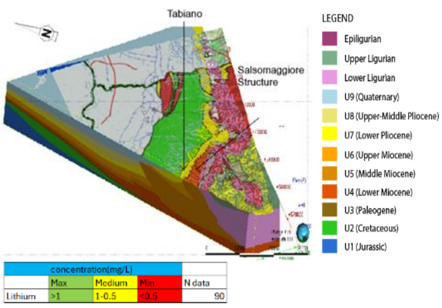

Figure 1 *3D model section passing through Tabiano and lithium data.*

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Recycling of fly-ash as hydraulic additive in eco-friendly mortars and concretes

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Waste fly-ashes from thermal power stations is the solid particulate matter collected by the dedusting systems of coal combustion flue gas for electricity production. It consists of amorphous, micrometre-sized, spheroidal particles, resulting from the melting in the boiler and subsequent recondensation along the flue gas path of the inert silico-aluminous fraction present in the coal dust used for steam generation. Coal combustion ashes, whose production in Italy has been in recent years even about 1 Mt/y and in Europe about 40 Mt/y, represent today an important resource for their possible use in construction materials. According to modalities specified by precise technical standards and in compliance with the regulations on the re-use of non-hazardous waste, they can be used for the production of cement-based premixes, mortars and concretes, where they play the role of an additional hydraulic additive/aggregate-filler, improving the resistance and durability to atmospheric agents of final products.

In this research a series of ashes produced by thermal power station over a period of about 10 years were tested as pozzolanic filler in the production of eco-friendly mortars, using raw materials with low environmental impact as a silicate sand aggregate and natural slaked lime (NL) / hydraulic lime (NHL) as binders. The ashes, as well as the number of experimentally produced mortars in the laboratory, were studied from a chemical and mineral-petrographic point of view by means of optical microscope, X-ray diffractometric analysis (XRD), scanning electron microscopy (SEM-EDS).

The results of the mechanical tests (according to UNI-EN 1926 and ISRM recommendations) and physical analysis (He-porosity, real and bulk densities, according to UNI-EN 1936) showed that the addition of ashes as pozzolanic filler in the hydrated lime mortars resulted in a considerable improvement of the physical-mechanical properties, with a clear increase in the uniaxial compressive strength and in the resistance to punching (i.e. Point Load Test index). The same behavior was also highlighted in the case of mortars based on natural hydraulic lime.

Thus, the analysed and studied ashes deriving from the waste products of coal combustion can be used as addictive pozzolanic material in the mortars and concretes used in the building industry, either as bedding mortars in the case of NHL-binder, or as plastering mortars in the case of the NL-binder. Furthermore, the use of fly-ash in the production of cement-based mortars and concretes reduces the use of mixing water (because increases the pumpability), as well the CO_2 emissions in cement production and volume of material to be disposed of in landfills.

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Identification and characterisation of mining residues through field surveys at a decommissioned Cu-Sb(-Ag) mine site (Monte Avanza, Carnic Alps, NE Italy)

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Decommissioned mining sites are frequently characterised by the occurrence of waste materials and tailings piles as a result of past mineral extraction and processing. Although these materials potentially still contain high amounts of minerals, they are still usually poorly characterised, resulting in a lack of information about their spatial distribution and content of several elements, which may include also potentially toxic elements and critical raw materials. Field investigations through portable devices integrating both geochemical and geophysical techniques represent a powerful tool for detecting mine residues occurrence and for their preliminary characterisation. The data obtained through this approach can indeed be useful to support the management of these materials, helping to assess the need for the implementation of monitoring or remediation plans or, conversely, the opportunity of their reprocessing for secondary recovery plans (Barago et al., 2021).

This multidisciplinary approach was used within the area nearby the former fahlore Cu-Sb(-Ag) mine at Mt. Avanza (Carnic Alps, NE Italy), intermittently exploited until 1952. The main exploited mineral is the tetrahedrite ($Cu_6[Cu_4(Fe,Zn)_2]Sb_4S_{13}$), which can host several other elements in its lattice structure. Among these elements, the ore at Mt. Avanza contains notable amounts of mercury (Hg) (Casali, 1996), which can easily volatilise to the atmosphere as gaseous elemental mercury (GEM) depending on its abundance in the substrate. A preliminary real-time survey of atmospheric GEM concentrations within the study area was thus performed using a portable analyser to detect the presence of GEM sources, which can represent a good proxy of the occurrence of mine residues thanks to the Hg enrichment of the ore. Moreover, samples of mine residues, soils, stream sediments, and water were collected for a first geochemical characterisation. Relatively high amounts of various elements (Cu, Sb, As, Pb, Zn, Hg) were observed, mostly in samples from waste rock piles (Barago et al., 2023).

For a more detailed analysis of mine residues dispersed within the area, a second field investigation was conducted. For each previously identified waste rock pile, sub-surface samples were collected both on a regular grid and in correspondence to peaks in atmospheric GEM concentrations. Trace element concentrations were preliminarly determined in the field using a portable X-ray Fluorescence (XRF) analyser and the results were used to select samples for further laboratory analysis. At the same locations, Electrical Resistivity Tomography (ERT) and Frequency Domain Electro-Magnetic (FDEM) geophysical surveys were performed to estimate the thickness of mine residues and evaluate potential correlations with the detected metal concentrations. Combined results provide useful information for a preliminary and rapid estimation of metal contents and distribution in mine residues, allowing optimisation of sampling for a subsequent more detailed characterisations.

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The potential reuse of Coal Combustion Wastes: The case study of the Angren Thermal Power Station (Uzbekistan)

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Coal plays a crucial role in global energy needs, but its extraction, combustion, and waste disposal have significant environmental and health impacts. Large amounts of coal combustion wastes (CCWs), accumulate near power plants, contain both toxic elements (e.g., Hg, As, Pb) and technology-critical elements (TCEs, e.g., REE). However, only a small fraction is recycled, mainly for brick production.

In this study, we provide a detailed overview of the mineralogy and geochemistry of the CCWs in the Angren Coal District (Tashkent Province, Uzbekistan), which hosts the largest lignite mine of Central Asia and two coal-fired power plants. The aim is to quantify the content of i) Fe and other associated metals (e.g., Mn and W) for Fe-alloy production and ii) the concentration of REE + Y (REY) for potential extraction.

Mineralogical and geochemical analyses were conducted on the bulk material and two distinct fractions: magnetic and non-magnetic. The main mineralogical components of CCWs are quartz, with minor amount of muscovite, mullite, hematite, and calcite. Chemically, the non-magnetic fraction consists mainly of SiO_2 and Al_2O_3 (up to 61 wt% and 16 wt%, respectively), whereas the magnetic fraction contains up to 87 wt% FeOt. Trace elements, including REY, are significantly enriched, with concentrations two orders of magnitude above the upper continental crust (UCC) levels.

The magnetic fraction, characterized by a hollow spherical morphology (Fig. 1a), is composed of nearly 95% iron. It also contains notable amounts of metals commonly used in steel production, such as Mn (up to 0.15 wt%) and W (up to 0.15 wt%).

Preliminary data suggest that if the magnetic fraction constitutes the 20% of the total CCWs and is composed of nearly 95% iron, along with other steel-enhancing metals (e.g., W and Mn), it holds promise for further exploration in steel manufacturing applications.

Regarding REY, the samples exhibit enrichment compared to reference values, with a Coutl value of 0.8 and 30% critical REY content. These parameters indicate potential interest for REY extraction (Fig. 1b). However, the ΣREY concentration (374 ppm) falls below the extraction threshold reported in the literature (REY > 1000 ppm).

As a result, extracting REY from these materials would require significant technological advancements. Comprehensive studies are needed to further characterize the deposit and assess its viability for reuse within a circular economy framework.

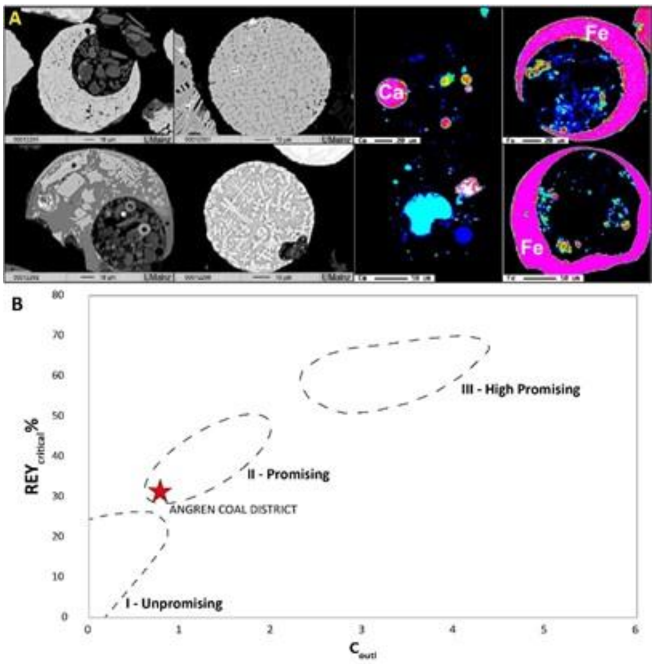

Figure 1 a) *SEM images and elemental composition of magnetic particles;* ***b)*** *$REY_{critical}$% vs C_{outl} Clusters of REE-rich coal ashes distinguished by outlook for REY composition: I - unpromising; II - promising; and III - highly promising (from Serendin & Dai, 2012).*

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The difference between a sceptic and a negationist. The CO_2 business and the role of geologists in a greener future

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The role of CO_2 in forcing the outgoing longwave radiation, which ultimately would cause global warming, grabs maximum attention. This is true in social media, as well as at all the economic levels, in all the industrial production strategies and in all the political choices, from local up to trans-national decisions. The mainstream is dictated by the IPCC reports, whose monolithic message points to the necessity of CO_2 decrease, assuring, without any realistic doubt, that human activities are responsible for >99% of the global warming. Following this approach, IPCC invite all the worldwide economies to ally to reduce CO_2 emissions as soon as possible, with the main target of reaching carbon neutrality by the end of 2050. The number of "green" technologies associated with renewable forms of energy and electrification of many aspects of the societies is skyrocketing, but the anthropogenic CO_2 emissions continue to increase. This is a failure of the entire strategy acted by IPCC, which, among the others, is blinded to anything but CO_2 content.

The transition to a decarbonized society is certainly one of the priorities we have to deal with. It is certainly possible, but only if we accept a long-lasting and painful degradation of our life styles. None of the OECD politicians would have ever dare to clearly state this, because this would imply no election to the next call to the pools. Developing countries would significantly delay the transition to better living conditions, as instead envisaged by the United Nations' Sustainable Development Goals. We certainly could not ask them to make the sacrifices that OECD countries will have to face. Energy transition is extremely difficult, very expensive and certainly impossible to achieve except in a few decades of gradual adaptation. This could be done for economically advanced countries, but it is realistically impossible for most of the poorest countries. Discussions on the energy transition are unfortunately approached in a generally superficial way. When the reasoning is instead based on scientific argumentations, it is easy to see how it is based on unrealistic to easily refutable hypotheses. The arguments can be grouped in two main reasoning styles. One is of conspiracy-type, and considers the possibility of moving to a decarbonized world immediately as a real thing, hindered only by oil lobbies and old-style oil industrialists. The other view considers, with a greater dose of realism, that the energy transition is extremely difficult, very expensive and certainly impossible to achieve except in a few decades of gradual adaptation. To simply have doubts on the official message of IPCC or to consider CO_2 not as the most important problem to face would immediately used to indicate a thinker as a negationist. To doubt that tiny variations of CO_2 (which increased of a bit more than 0.01% in the last 250 years) would be sufficient to consider a person as a non-scientist, or a scientist on the payroll of fossil energy lobbies.

Is the role of a scientist incompatible with a sceptical approach on CO_2? Is CO_2 the real responsible of global warming, or are there other parameters we should take into account? Is global warming really an indisputable evidence? Is it possible to find an alternative explanation to the correlation between the variation of temperature and CO_2 concentration? What is the validity of the temperature proxies used to constrain the variation of the heat budget of the Earth surface? Up to what point heat islands should be taken into consideration to effectively evaluate temperature increase? How far a scientific temperature coverage can be extended, considering that the first (very limited and scattered) global measures started officialy in the occasion of the 1958 Geophysical International Year? Should we concentrate our activities to increase the penetration of green technologies or should we focus our efforts to other priorities? Renewable sources will never be able to satisfy lifestyles of rich countries because they are intermittent, inconstant, have poor energy density and cannot be stored in sufficient quantities. Indeed, the problem of modern societies is not the availability of energy, considering that solar radiation alone could satisfy all current energy requirements by many hundreds of times. The fundamental problems we will face are of two types: the availability of energy when we need it, not when it is most abundant, and the availability of matter, which will be transformed through renewable energy into the objects of our desires. The main target of modern societies should be not only to abandon fossil sources of energy, but simply to consume less. To consume less means to lower life standards and higher unemployment rate. It is not only a matter of low-carbon energy availability. Our worries would be to find sufficient matter (in particular metals) to be transformed into our desires. The role of geologists on this topic is and will remain fundamental.

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Decommissioned mining areas: an environmental issue or a source of critical raw materials? Insights from the Pb-Zn Raibl mining district (northeastern Italian Alps)

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The demand for natural mineral resources has been rising in recent decades due to changes in the energy, ecological and digital disciplines. This requires a greater demand for extraction and production of critical raw materials (CRMs). Among the CRMs, the occurrence of metal(loid)s including potentially toxic elements (PTEs) such as lead (Pb), zinc (Zn), thallium (Tl), arsenic (As), cadmium (Cd) and antimony (Sb) in the environment as the legacy of past mining activities is a well-known concern worldwide, posing a risk to water resources and human health (El Rasafi et al., 2017). However, the occurrence of metal(loid)s may also represent a resource since large amounts of mine wastes (such as tailings ponds), which normally are the major source of contamination for the surrounding environment, can host valuable amounts of elements of economic interest (Ceniceros-Gómez et al., 2018).

The extraction activity at the Raibl mining district (NE Italian Alps) has been documented since 1320 A.D. In its last years of operation, almost 350,000 tons of ore (sphalerite and galena) were mined annually. The Raibl mine was closed in 1991 as the deposits were no longer considered economically viable. The Zn-Pb ore deposit of Raibl includes sphalerite, galena, iron (Fe) sulphides (pyrite and marcasite), and baryte as primary minerals followed by Fe oxy-hydroxides, smithsonite, hydrozincite and cerussite with dolomite and calcite among gangue minerals.

Previous investigations on the area reported elevated concentrations of metal(loid)s near mine waste heaps (up to around or over 100 mg/kg for Tl, Sb, Cd, Ge; > 1,000 mg/kg for As; > 1% for Pb and > 10% for Zn and Fe), which are made up of flotation tailings and waste rocks scattered around the mining village and stored in the tailings ponds. Moreover, the weathered tailings showed a high potential as secondary source of Tl and other PTEs in surface and groundwater, especially during periods of high flow river conditions (Barago et al., 2023).

Current ongoing research aims to evaluate the occurrence of CRMs in the sludge accumulated in the tailings impoundments following mineral processing for the extraction of Pb and Zn during the mining activity. Some boreholes were performed in the tailings impoundments followed by in the field analyses using portable X-Ray Fluorescence Spectroscopy (pXRF), which is one of the main geochemical analytical techniques employed in multi-elemental screening for the management of contaminated sites.

Electrical Resistivity Tomography (ERT) profiles were executed to estimate the thickness of tailings and evaluate potential correlations with detected metal concentrations. This preliminary survey aided in the collection of representative subsamples for further geochemical characterisation by destructive standard laboratory techniques and extraction procedures thus allowing both to investigate the mobility of Tl and other PTEs in solution as well as to identify volumes of tailings that may represent a potential source of CRMs.

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Recovering lithium: from LIB to LAS and non-compliant Li-rich enamels. Literature insights and new perspective from the LyCicle Project

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Over the past decade, lithium has experienced a significant market transformation, driven largely by the rising demand for rechargeable batteries and electric vehicles. This surge has led to an increase in lithium consumption, with glass and ceramics now accounting for approximately 25-30% of global lithium use, marking them as the second-largest sector after batteries. This relationship highlights a critical intersection between lithium supply and various manufacturing industries.

In response, research is increasingly focused on alternative lithium sources and recycling methods. While lithium recycling efforts have predominantly targeted batteries, other lithium-containing materials have received limited attention. Recent studies underscore the economic benefits and essential processes for lithium recovery, suggesting that achieving a critical mass of lithium recycling will necessitate investments in advanced technologies (Balaram et al., 2024).

Despite extensive research on battery recycling, extracting lithium from industrial materials like lithium aluminosilicate (LAS) glass-ceramics and Li-rich enamels remains largely unexplored. In the last five years, only a few studies have proposed extraction protocols for lithium aluminosilicate (LAS) materials (Lee et al., 2021, 2022).

The Lithium Recovery from Non-Compliant Material (LiCycle) project, funded by the University of Florence, seeks to develop efficient recycling methods for lithium-containing industrial materials. The project's primary goal is to evaluate the feasibility of extracting lithium from various industrial wastes, including non-compliant Li-rich enamels and LAS provided by a Tuscany-based ceramics and glass company (Colorobbia Group, Empoli, Italy).

The project begins with a comprehensive characterization phase for the waste materials using techniques such as SEM-EDS, XRD, Raman spectroscopy, LIBS, and PIGE. Customized roasting-leaching procedures will be developed, focusing on salt roasting to convert LAS/enamels into water- and acid-soluble phases, allowing for effective lithium extraction. Additionally, the potential use of geothermal waters in the leaching process will be explored, leveraging the geothermal resources available in Tuscany to enhance sustainable lithium recovery.

Preliminary results will present materials characterization, while future perspectives and opportunities offered by the project will be discussed in light of existing literature.

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New perspectives on extracting and recycling lithium and REEs from mining and industrial wastes along with environmental safety and sustainability: the ARTU project

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Lithium and rare earth elements (REE) are classified as critical raw materials under the European Critical Materials Act. The increasing demand for these elements across diverse applications has prompted significant efforts to discover new resources, reassess existing deposits, and prioritize recycling initiatives (Amato et al., 2021; Dini et al., 2022; Garcia et al., 2023). In this context, the ARTU project—funded by the Tuscany Region FESR 2021-2027 program—focuses on evaluating the extraction potential of lithium and REEs from alternative mineral sources, as well as from mining and industrial waste along with environmental safety and sustainability of the extraction process.

Overall, the Artu Project promotes collaboration between research institutions (CNR-IGG-Pisa, University of Siena, University of Firenze) and Tuscan-based companies (Colorobbia, Eurit, Timme, Ergo, StudioLab) to establish and develop sustainable strategies aimed at enhancing separation techniques for wastes resulting from various industrial and mining activities, in the field of ceramics and special glasses production. The project specifically seeks to identify potential lithium and REE-enriched phases, thereby ensuring alternative sourcing of critical raw materials from waste and improving recycling strategies in line with circularity and end of waste and along with environmental safety and sustainability of processes. The project emphasizes the extraction of REEs from mining wastes while exploring innovative methodologies for lithium recovery from industrial wastes.

A significant aspect of the research is dedicated to evaluating the environmental impact of separation, enrichment, and extraction processes and the overall safety of it. This involves assessing the potential ecotoxicity of waste materials and enhancing the sustainability of extraction methodologies to mitigate potential negative ecological consequences. The separation and storage of potentially enriched phases are strategically planned to take place at designated mining sites provided by the partnering companies. This methodology aims to optimize the collection of critical masses, ensuring that these resources are available for subsequent industrial-scale recycling processes that are both economically viable and environmentally sustainable.

Overall, the project aims to promote circularity in the management of mining and industrial wastes by focusing on zero-emission enhanced separation processes, minimizing environmentally hazardous storage practices, and facilitating the extraction of rare earth elements (REEs) and lithium. This approach seeks to develop new perspectives for sourcing critical raw materials.

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The antimony (Sb) resource in south Tuscany: evaluation of a critical raw material potential and of the environmental impact of past exploitation

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Europe is completely dependent on foreign suppliers for Sb, as it no longer has active mining operations on its territory. Given the economic and strategic importance, Sb has been inserted in the Critical Raw Material (CRM) list of EU. To support the large demand for the green energy transition, new Sb deposits are to be explored and exploited within EU, together with the possibility of recovering Sb as e.g. by-product of other mining activities or from historical mining wastes. On the other hand, Sb is also an environmental pollutant and, therefore, a sustainable mining approach will be necessary to minimize the environmental impact.

In this scenario, Italy has recently adopted the EU CRMs Act, reviving a national exploration plan. Antimony has been extracted from Tuscany and Sardinia, leaving a heritage of geological data (e.g., drill logs, chemical data) as well as legacy of mineral wastes and tailings. The Sb districts of Tuscany and Sardinia are therefore exceptional case studies for the evaluation of potential resources of Sb and associated CRMs within the national borders, and to jointly evaluate the environmental impact of past mining activities, as well as the potential of remediation solutions to reduce Sb and associated potentially toxic elements (PTEs, e.g., As, Tl, Hg, W) in different environmental matrices.

Herein, we present an overview of the MOLIERE project funded by PRIN 2022 PNRR, which combines different expertise to provide: i) a geological investigation of Sb resources in Tuscany with implications on ore genesis and exploration, ii) an updated picture of the long-term environmental impact of Sb ore exploitation, iii) solutions to limit Sb and PTEs mobility in the mining areas.

To define the characteristics of the primary Sb ores, a field, petrographic, mineralogical, and geochemical characterization of selected ore bodies of the Mancianese area (southern Tuscany) will be produced (Fig. 1). A specific effort will be devoted to a 3D reconstruction of the ore bodies (or potentially new unexploited ones) employing data from previous drilling programs in opensource Python-based software (Jüstel et al. 2023).

The long-term environmental impact of Sb ore exploitation will be assessed analysing Sb and associated PTEs in stream sediments, soils and waters from mining areas, and providing an assessment of the mass loads of Sb and PTEs transported by the surficial draining networks. As a final aim, the processes that might limit PTEs mobility, such as natural attenuation processes in the vegetation cover (hyperaccumulator plants) and possible cost-effective techniques for remediation at the plant-soil interface, will be investigated. Antimony sorption mechanisms of trap minerals such as LDHs as removal from freshwaters will also be studied.

Figure 1 *Stibnite embedded in a carbonatic host rock in the Mancianese area (Pozza del Lino site).*

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Characterization and valorization of fluvial sand fractions from the Emilia-Romagna region for the Recovery of Critical Raw Materials (CRMs)

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Fluvial sands, after undergoing a de-ferritization process, are found to contain significant concentrations of siderophile elements such as Ni, Co, Cr, V, Ti, and platinum group metals (PGEs). These elements are critical for advancing energy and digital transitions, yet their global availability is limited. The Emilia-Romagna region, with rich ophiolitic formations within the Po, Taro, and Trebbia river basins, offers a promising context for the sustainable development of these resources. These ophiolites, remnants of oceanic crust embedded within the continental crust, host mafic minerals (olivines, pyroxenes, amphiboles, serpentines, chlorites, spinels, iron oxides, and sulfides) that naturally contain CRMs, Kiss et al. (2023) in the Northern Apennines.

Sampling will target ophiolite–rich areas along the river basin of the Po, Taro and Trebbia rivers, to maximize the concentration of the desirable CRMs elements,

Advanced techniques will be implemented to isolate the mafic fraction, potentially rich in CRMs, from the bulk felsic mass. This process will involve determining particle size distribution to enhance separation. A Franz isodynamic separator will be deployed to determine the magnetic properties and separate the magnetic phases. Additionally, specific grains will be separated through careful hand–picking under a binocular microscope.

Analyses will include: X-ray Diffraction (XRD) and Electron Microprobe Analysis (EMPA) will be used to identify and characterize the mineral phases present, providing insights into the mineralogical composition of the sand fractions.

X-ray Fluorescence (XRF) and ICP-MS (including LA-ICP-MS) will be employed to quantify the CRM elements accurately and characterize the detailed geochemical composition of the sands. LA-ICP-MS will allow for micro-scale analysis, helping to pinpoint CRMs concentrations within individual mineral grains.

This research will assess the industrial feasibility and sustainability of large-scale CRMs extraction from fluvial sands, including cost-benefit analysis, environmental impact assessment, and potential scalability of recovery techniques.

This project will promote the EU's self-sufficiency in CRMs supply and encourage the sustainable reuse of local resources. By contributing to a circular economy model and supporting regional landscape conservation, it aligns with the 2030 Agenda. Ultimately, this initiative will foster a virtuous cycle for the regional economy, integrating environmental sustainability with industrial innovation.

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Cobalt removal from contaminated solutions through synthetic AMC carbonates

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Heavy metals (HMs, i.e., Pb, Cd, Ni, Co, Zn, Cu, etc.) represent the most hazardous pollutants in water and soils due to their high toxicity for human health and negative impact on biological systems (Nagajyoti et al., 2010). Cobalt pollution of water and soil is related to industrial activities such as electroplating and can be significantly intensified by mining activities, resulting in Co concentrations in the environment considerably higher than regional background levels (Leyssens et al., 2017; Mahey et al., 2020). Sustainability and waste management are keywords in remediation actions of HMs-wastes for EU policy. Moreover, low-cost and performant methods for waste treatment are prerequisites for sustainable development, environmental remediation, and human health. This study investigated the efficiency of Co removal from solutions using Mg-carbonates, previously synthesized through a mineralization process involving the interaction of gaseous CO_2 with $MgCl_2$ solutions. Amorphous Mg-carbonates (AMCs) are an optimal solution/sink for removing Co from solutions, as their open structure facilitates ion exchange between Mg and Co. Solutions with a concentration of Co 1000 mg/L were prepared using cobalt nitrate hexahydrate as the starting material. The removal experiments, performed at room temperature, were conducted by the interaction between these solutions and AMCs, considering 8 increasing interaction times. AMCs were characterized using SEM-EDS, XRPD, and FTIR analysis of solid materials. The residual solutions were analyzed using ICP-AES to assess the extent of Co removal and process efficiency; the removal capacity (q_e) and removal percentage (R%) were calculated from this data. SEM-EDS analysis showed the progressive changing of the morphological features of AMCs accompanied by the increase of Co content with the contact time. The XRPD results demonstrated that the AMCs lattice has been transformed in the structure of hydrated Co-carbonates, with the almost complete substitution of Mg by Co. R% was about 75% and q_e ranges between 373 and 378 mg/g. The study suggests that the proposed methodology could be an innovative and efficient solution for treating water contaminated by heavy metals and reducing CO_2 emissions.

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Advancing Sardinia's Mineral Resource Database: Updates from the Geosciences IR Project

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The 2024 Critical Raw Materials Act outlines the increasing demand for Critical and Strategic Raw Materials (CRMs and SRMs) and calls for an innovative approach to mineral exploration that aligns with the EU's economic and environmental ambitions. The ISPRA-UniCa project (GeoScience IR) is set to reassess resource exploration in Sardinia by developing an updated Metallogenic Map and comprehensive database, paving the way for informed resource management. Focusing on mining areas rich in fluorine (F), barium (Ba), light rare earth elements (LREE), lead-zinc (Pb-Zn), and iron-skarn (Fe-skarn) deposits (Fig. 1), this project aims to transform the previous Metallogenic Map of Sardinia (2008) (Tocco et al., 2008) into a digital, multi-layered format. This updated map will showcase known CRM and SRM occurrences and incorporate new data crucial for exploring previously untouched ore bodies. A groundbreaking aspect of this project is mapping Sardinia's historical mining waste, estimated to include 70 million cubic meters of tailings primarily located in the Sulcis-Iglesiente and Fluminèse-Arburèse areas (Regione Autonoma Sardegna, 2003). These wastes may still contain relevant amounts of Pb-Zn sulfides and oxides, barite and fluorite. Initial analyses of 70 samples from key sites, such as Montevecchio-Ingurtosu, have revealed the presence of CRMs like LREE (Sedda et al., 2024), fluorite, and barite. By digital mapping these tailing deposits, the project will provide essential insights into their composition, promoting sustainable exploitation that offers economic advantages while aiding environmental recovery. In this way, the project positions Sardinia as a possible future example of sustainable mining, contributing to establishing a National Mining Map and reinforcing Italy's know-how in responsible resource management.

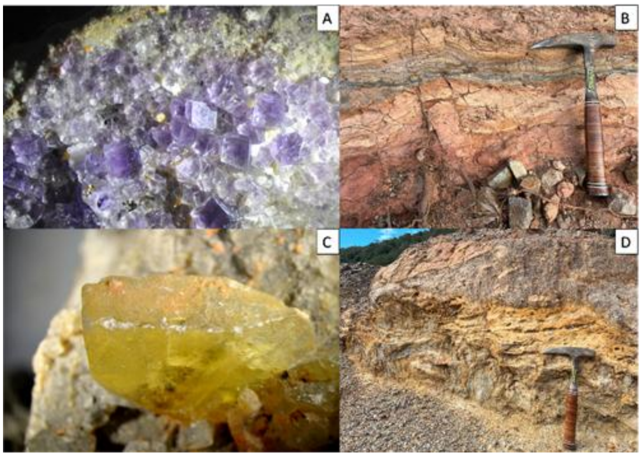

Figure 1 a) *Fluorite sample collected from the Santa Lucia mine (Fluminimaggiore – SW Sardinia);* ***b)*** *Barite sample collected from the Santa Lucia mine (Fluminimaggiore – SW Sardinia);* ***c)*** *Flotation tailings from the Perda Lai mine (Sardara – SW Sardinia).*

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Crystal and Glass Distribution in a Thermally Treated Bottom Ash: An Experimental Approach

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The chemistry and texture of crystal and glass phases formed from heat treatments of municipal solid waste bottom ashes (BA) are considered. The starting BA composition presents CaO, FeO_{tot}, Al_2O_3, SiO_2, and (Na_2O+K_2O) contents of 17.20, 16.31, 9.31, 46.05 and 6.44 wt.%, respectively (Stabile et al., 2019) and falls within the overall CaO-Al_2O_3–SiO_2 system (Fig. 1; Stabile et al., 2023). This starting material was heated up to an initial *T* of 900°C at room-*P* and -fO_2, reproducing the same conditions used in the municipal solid waste plant. Then, the sample was further heated to following final conditions 2, 4, 8 and 16 hours at 1000, 1100, 1200 and 1300°C; the experiments were ended by rapidly quenching the run-products in a water bath from high-*T* to room conditions (estimated quenching rates of 10°C/s).

The run-products obtained at 1300°C and quenched after 8-16 h contain only glass, whereas those experiencing 1000, 1100 and 1200 °C (2, 4, 8 and 16h) and 1300 °C (2 and 4 h) are crystal-rich samples. Back-Scattered Electron (BSE) images and X-ray powder diffraction (XRPD) spectra evidence that crystals are quartz, pyroxene (mainly augite), wollastonite, spinel (Cr-spinel and magnetite). Low-*T* runs at 1000°C (4 h) show crystallization of small diopside needles on the surface of larger wollastonite crystals. Here, the textural evolution of the main solid phase has also been studied; for example, a shift from elongated, anhedral crystals to the needle-shaped texture of wollastonite was observed in the low-*T* runs across the different experimental durations. By contrast, the samples at 1200°C (2 and 4 h) resulted enriched in spinel, with Cr substituting for Al in some of the identified crystals; in the same runs, the residual melts are more enriched in CaO, Al_2O_3, and FeO compared with lower *T*-runs.

The low-*T* runs present chemical heterogeneities in the residual glass, specifically marked variations in CaO, Al_2O_3 and Fe_2O_3 contents (ranging from 4.51 to 8.88, 1.06 to 9.80, and 0.20 to 9.51 wt. %, respectively).

Finally, Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) spectroscopy has been employed on the highest-*T* run products (final *T* of 1200 and 1300°C) with a focus mainly on the Si-vibrational modes. These ATR spectra are similar to basaltic silicate natural analogs glasses. In detail, treated BA results close to basalt or trachy-basalt volcanic glasses differing mainly in higher CaO and lower Al_2O_3 contents. Thus, the BA vitrification glasses can likely be good raw-material alternatives for applications where their natural analogs are usually contemplated (e.g., rock wool or high-temperature glass fibers for insulation, road base or pavement aggregates).

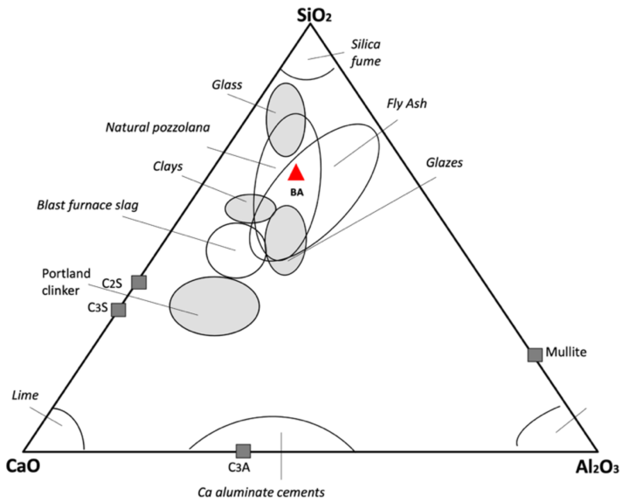

Figure 1 *CaO- Al_2O_3– SiO_2 diagram showing the Bottom Ash (red triangle) composition along with some approximate waste and industrial materials (modified by Stabile et al., 2023).*

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Critical Raw Materials (CRMs) petro-geochemical investigation in historically dismissed ophiolite-related Volcanogenic Massive Sulfide (VMS) deposits from the Emilia-Romagna region

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Critical Raw Materials (CRMs) are essential elements, minerals, or materials for technology and the green transition, whose supply is insufficient to satisfy the global demand (Kiss et al., 2023). This caused several European countries to focus on locally dismissed mine sites. Italy has more than 100, just in the North, and, among them, the diffused Volcanogenic Massive Sulfide (VMS) deposits of the Emilia-Romagna region are now under investigation for potential exploitation of critical metals (i.e. Cu, Zn, PGE, Kiss et al., 2023). They are stratiform accumulations of sulfide minerals that result from underwater volcanic eruptions, associated with hydrothermal events, and classified according to several parameters, i.e. the ore composition (Cu, Cu-Zn, Cu-Zn-Pb groups), formation environment (Cyprus, Kuroko, Besshi), and the host-rock association (mafic, bimodal mafic, siliciclastic-mafic, bimodal felsic, bimodal-siliciclastic, as observed by Kiss et al.. 2023 and references therein).

In the Emilia-Romagna region, they occur as pods within small bodies of ophiolitic basalts cropping out as olistoliths in the Northern Apennine External Ligurian units and owe their origin to the metal-rich hydrothermal circulation which developed quartz-sulfide veins when mixed with seawater through a fissures network (Saccani, 2015; Dini et al., 2024). These ophiolites represent Jurassic Alpine Tethys oceanic crust fragments obducted in the continental crust (Saccani, 2015). Sequences of pillow lavas associated with serpentine and gabbro breccias, radiolarian cherts, limestones, and abundant serpentinized subcontinental mantle peridotites define the area (Saccani, 2015). Basalts, there, show Ocean Continent Transition Zone (OCTZ) chemical features with transitional-MORB affinity and a garnet signature (Dy_n/Yb_n: 1.2-1.4, Saccani, 2015), in agreement with Cyprus-type VMS deposits related to ophiolites (Kiss et al., 2023, Dini et al., 2024).

Whole-rock major and trace elements analyses were conducted on a group of basalts from the Toggiano and the Montecreto mine districts (Modena Province) and compared to the few data available for the area (e.g., Kiss et al., 2023 and references therein). Based on the chemical composition, the VMS deposits of the area belong to the Cu and the Cu-Zn types, with Cu up to 6000 ppm (up to 200 time Upper Continental Crust, UCC), and Zn 3000 ppm, i.e. 118 times UCC, with almost no Pb contents (up to 3 ppm, 0.42 times UCC). These results are comparable to Italy's most productive Cu-Zn VMS ophiolites deposits (i.e., those in Tuscany, as seen by Dini et al., 2024).

Mineralogic analyses on selected samples revealed a sulfide association of pyrite, chalcopyrite, sphalerite, kesterite, and pyrrhotite. *In situ* analyses are planned to better constrain the VMS ore potential.

These preliminary results provide the first relevant geochemical information to map trace metal enrichment distribution in the main rocks of the area. Radiogenic (Sr-Nd-Pb) and stable (S-C) isotopic analyses, as well as mineralogical and in-situ analyses, will provide further information on the enrichment and distribution of VMS deposits in the region. These results are fundamental for creating an updated ore deposits-themed national map.

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Monitoring the quality of a kaolin mine over time: Piloni di Torniella (Tuscany, Italy)

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The outbreak of war in Ukraine and the resulting disruption in the supply of high-plasticity ball clays has made clear the risks for ceramic tile industry of relying on raw materials from countries outside the EU. This awareness has led to a renewed interest in national raw materials, both for the plastic and the flux components (Altimari et al., 2023; Fantini et al., 2024). The Piloni di Torniella mine (Tuscany, Italy) could play a significant role in this context, being one of the most important kaolin mine in Italy. In this site, the pre-existing Roccastrada rhyolites underwent a multi-stage hydrothermal weathering, which led to the development of an economically exploitable kaolin deposit (Viti et al., 2007). However, due to their own nature, the hydrothermal processes are spatially very discontinuous, resulting in marked spatial heterogeneity of the material extracted from the mine. Consequently, temporal variations in the chemical and mineralogical composition may be significant in such a heterogeneous context, potentially imparting different technological properties when the material is added to porcelain stoneware batches.

The present study addresses this issue by performing a quality monitoring of the material extracted over a seven-year period, from 2018 to 2024. The adopted multi-technique protocol involved X-Rays Fluorescence (XRF), Loss on Ignition (LOI) determination, Fourier Transform InfraRed Spectroscopy (FTIR), polarising-light optical microscopy, X-Rays Powder Diffraction (XRPD) and Scanning Electron Microscopy with Energy-Dispersive Spectrometry (SEM-EDS). The methodology presented has enabled the characterisation of raw materials quality and the identification of temporal variations therein. In particular, the quality of raw materials extracted from a mine depends not only on the heterogeneity of petrogenetic processes, but also on the constraints imposed by the mining license. Finally, an indicator based on LOI and chemical composition was also proposed for a rapid and approximate assessment of raw material quality. This could be implemented at the mine exit as well as at the ceramic factory entrance. The results of this study, although at a preliminary stage, could support the planning of mining activities, not only for the Piloni site but also for all the other deposits characterized by similar spatial heterogeneity of the extracted material.

References

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