Introducing the Sardinian mine waste spectral library

Marco Casu[1,2,] Ilaria Nobile[1], Lorenzo Sedda[1], Claudia Collu[1,2] , Stefano Naitza[1], Massimo Musacchio[3], Francesco Dessì[1], Salvatore Noli[1], Maria Teresa Melis[1]

[1] Dept. of Chemical and Geological Sciences, University of Cagliari, Monserrato, Italy. Marco.casu4@unica.it, ilaria.nobile@unica.it, lorenzo.sedda96@unica.it, snaitza@unica.it, colluclaudia92@gmail.com, fdessi@unica.it, noli.salvatore@unica.it, titimelis@unica.it.

[2] Dept. of Civil, Constructional and Environmental Engineering, Sapienza University of Rome, Rome, Italy. Marco.casu@uniroma1.it, Claudia.collu@uniroma1.it.

[3] Istituto Nazionale di Geofisica e Vulcanologia, Osservatorio Nazionale Terremoti, Via di Vigna Murata 605, 00143 Roma, Italy; massimo.musacchio@ingv.it.

Abstract

In recent years, hyperspectral imaging has become an increasingly utilised technique across geological and environmental applications, involving a large number of airborne, spaceborne, and ground-based hyperspectral sensors. The creation of spectral libraries of multiple types of materials is a widespread procedure that supports the interpretation and analysis of remote sensed hyperspectral data, enabling the precise identification and mapping of different rock, minerals and natural objects, significantly enhancing the utility and effectiveness of this data in numerous fields and applications. In a continually evolving hyperspectral data framework, spectral libraries will become increasingly essential for calibrating and validating satellite-acquired data, as well as for geological mapping, mineral exploration, and environmental monitoring. Considering the growing interest in reliable ground-truth data and the search for new potential sources of Rare Earth Elements (REEs), this study aims to build a spectral library containing detailed spectral signatures of rocks and minerals from various sites in Sardinia. The goal is to support spaceborne hyperspectral missions in mineral mapping and identification while detecting indicator minerals associated with the presence of LREEs (Light Rare Earth Elements) in samples collected from both active and abandoned mining sites, including tailings. Mapping LREE in these areas holds significant potential for the reclamation of abandoned mining sites, transforming them into economically viable resources through rare earth extraction while contributing to environmental remediation (Fig. 1). Integrating this information will not only enhance the accuracy of hyperspectral missions in studying Sardinia's minerals but also promote sustainable development and site rehabilitation strategies, offering both economic and environmental benefits. The spectral library will be enhanced with spectral signatures obtained from both in-situ and laboratory-based reflectance measurements, complemented by mineralogical and chemical analyses using XRD (X-ray Diffraction), portable-XRF (X-ray Fluorescence). We strongly believe that this study could provide new insights and benefits for both the community and the advancement of scientific research by integrating the detection of new potential economic resources with mine site rehabilitation.

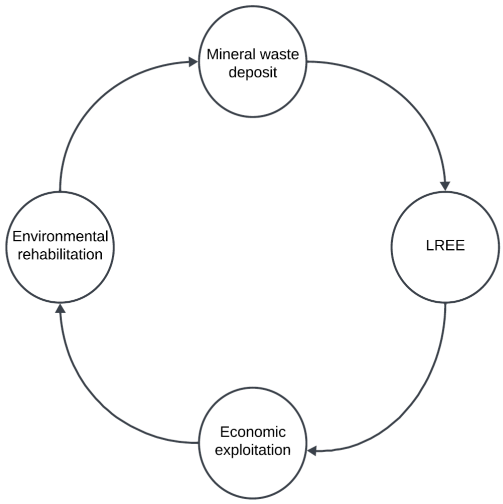

Figure 1 Flowchart synthetizing the concept of this study: mutual integration between circular economy through waste management, economic exploitation and ecosystem rehabilitation.

1 Introduction

The use of hyperspectral data has emerged as a critical tool in various scientific and industrial domains, particularly in geological and environmental applications [13]. A wide range of wavelengths across the electromagnetic spectrum can be analysed, allowing for the identification of different materials based on their spectral signatures. This unique capability has led to its increased deployment in remote sensing, with airborne, spaceborne, and ground-based sensors collecting vast amounts of hyperspectral data for diverse studies. A key element supporting the effective interpretation of hyperspectral data is the development of spectral libraries. These libraries serve as comprehensive databases of reference spectra for various materials, facilitating accurate data analysis and material identification. Spectral libraries play a critical role in geological mapping, mineral exploration, and environmental monitoring by enabling the precise characterization of rocks, minerals, vegetation, soils [14] and other natural objects. Very well-established examples include the USGS [9] ASTER and ECOSTRESS Spectral Libraries built by the Jet Propulsion Laboratory [1,8] at NASA, both based on spectroscopic remote sensing. Considering the widespread use of hyperspectral data, the importance of robust, well-calibrated spectral libraries continues to grow. At the same time, interest in research on rare earth elements (REEs) has significantly increased. In recent studies, many authors, have focused on utilizing remote and proximal sensing techniques for REE exploration [4, 3,6] particularly targeting Nd, which is regarded as a key indicator of Light Rare Earth Elements Enrichment [2, 5]. The applicability of reflectance spectroscopy for REE detection come from the pioneering efforts of several authors which, starting from the mid-900s, managed to identify small scale diagnostic features related to REEs presence [7,15, 11]. This field of research has continued to evolve, with many recent studies now focusing on exploring the properties and detection limits of spectroscopy-based methods for REE detection [10, 2]. In this context, Sardinia (Italy) offers an ideal case study due to its complex lithological structure and rich mining history. Sardinia was a historical mining region, characterised by mining activity that began in the Nuragic era and continued until the early 2000s. Mining activity has mainly focused on the extraction of base metals (Pb, Zn and Cu), metalloids (As and Sb), native elements (Au and Ag), fluorite and barite. This activity has left a legacy of around 70 million cubic metres of mining dumps which often represent a source of environmental contamination with the production of Acid Mine Drainage (AMD), produced by the oxidation of sulphide minerals. At the same time, these mining dumps can represent a source of Critical Raw Materials (CRMs), because they often contain different amounts of these elements (e.g.: REE, W, Ni, Co, etc.). However, despite the extensive geological research, no spectral analysis of these sites has yet been conducted. To bridge this gap, this study establishes the groundwork for creating a spectral library to support REE detection using spectral reflectance measurements collected in both field and laboratory conditions using an ASD-Fieldspec3 spectroradiometer. Although we had access to the entire VNIR-SWIR spectrum, we focused on the VNIR range, where the diagnostic absorptions of neodymium are present. Additionally, XRD and XRF techniques will be employed to provide complementary characterization of each sample. We believe that applying a comprehensive, fast, and cost-effective methodology to detect REEs in mining waste deposits is essential. This approach could serve as a crucial first step toward not only the economic recovery of valuable materials but also the environmental rehabilitation of these highly polluting sites

2 Methodology

The main part of the analyses focused on the acquisition of the spectral signatures of mine wastes samples to collect for creating a spectral library to support REE detection. Spectra have been acquired on the field and in laboratory conditions using an ASD Fieldspec3 portable spectroradiometer, which was equipped with a contact probe for the laboratory measurements. These were then supported by XRD and XRF techniques to obtain a complete mineralogical and elemental characterization of the samples analysed.

2.1 Laboratory measurements

Laboratory measurements were conducted in a room with constant lighting and humidity conditions. Relative reflectance measurements were collected after taking white reference measurements using a Malvern Spectralon panel, with the samples placed on a non-reflective black surface. This process also included dark current measurements to suppress electrically derived noise. An ASD-Fieldspec-3 portable spectroradiometer equipped with a contact probe was used to collect the spectral signatures of the samples. To maximise the signal-to-noise (S/N) ratio, an average of 25 measurements was taken for each sample. Additionally, to eliminate any residual spectral anomalies caused by irregularities in the sample geometry, further post-processing averaging was performed. After averaging and analysing the spectra a quotient hull continuum removal procedure was applied to highlight REEs diagnostic spectral features. Then the spectra were confronted with existing literature data and stored in a spectral library.

2.2 X-Ray Diffraction (XRD)

XRD is a technique used to identify the crystalline structure of materials. It directs X-rays onto a sample, where the crystalline atoms cause the X-rays to diffract in specific directions. By measuring the angles and intensities of these diffracted rays, a diffraction pattern is generated, which can be analysed to determine the crystalline phases present in the analysed sample.

2.3 X-Ray Fluorescence (XRF)

XRF is used to determine the elemental chemical composition of a material. When a sample is exposed to high-energy X-rays, its atoms become excited and emit secondary (fluorescent) X-rays at characteristic energies specific to each element. By measuring these energies, XRF can identify and quantify the elements present in the sample.

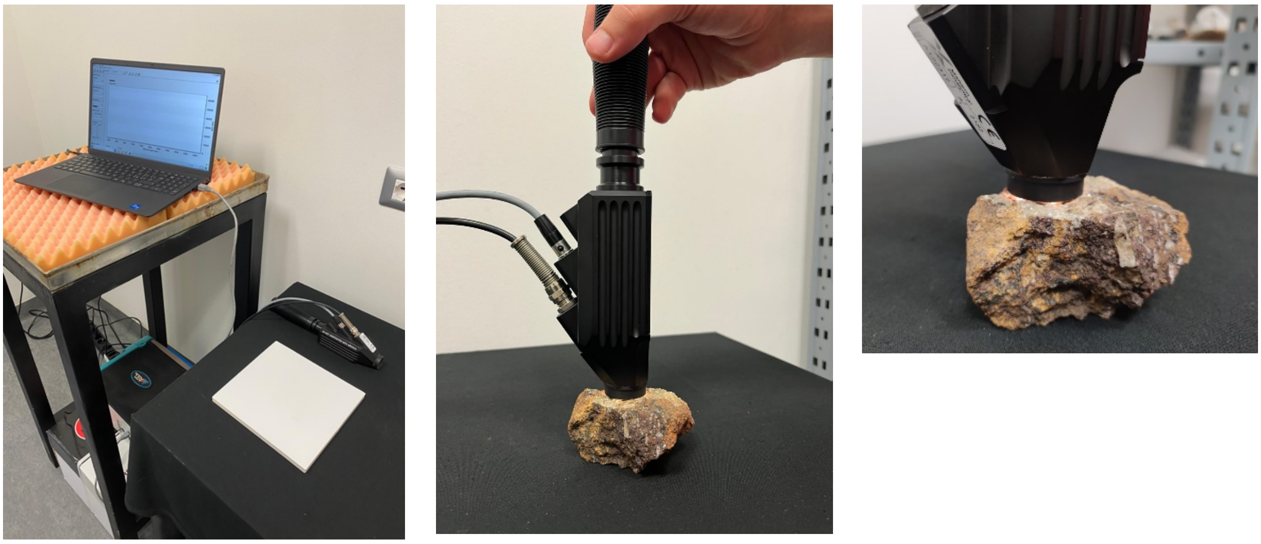

Figure 2 Laboratory setup for spectral signatures acquisitions

3 First results

Here are presented some of the first results of this study. Clear Neodymium diagnostic narrow and deep absorption features commonly found at ~580 nm, ~740 nm, ~800 nm (Figure 3) are showed in the spectra of 2 Sardinian mine waste samples, mimetite (MMT) and cerussite (CER) in both raw reflectance and quotient hull continuum removal (Figure 4). These look very promising as Neodymium detection is commonly used in literature as a proxy for LREE presence.

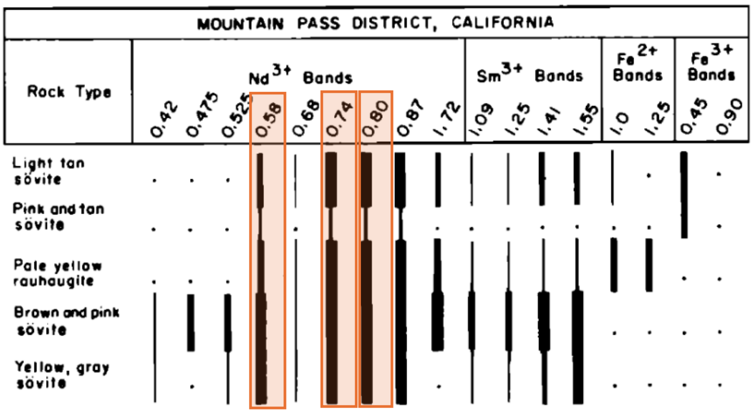

Figure 3 Wavelength Position (um) and Relative Intensities of Nd3+ related absorption features found in different rocks. The most intense ones have been highlighted in orange. Modified from Rowan L.C. et al, 1986.

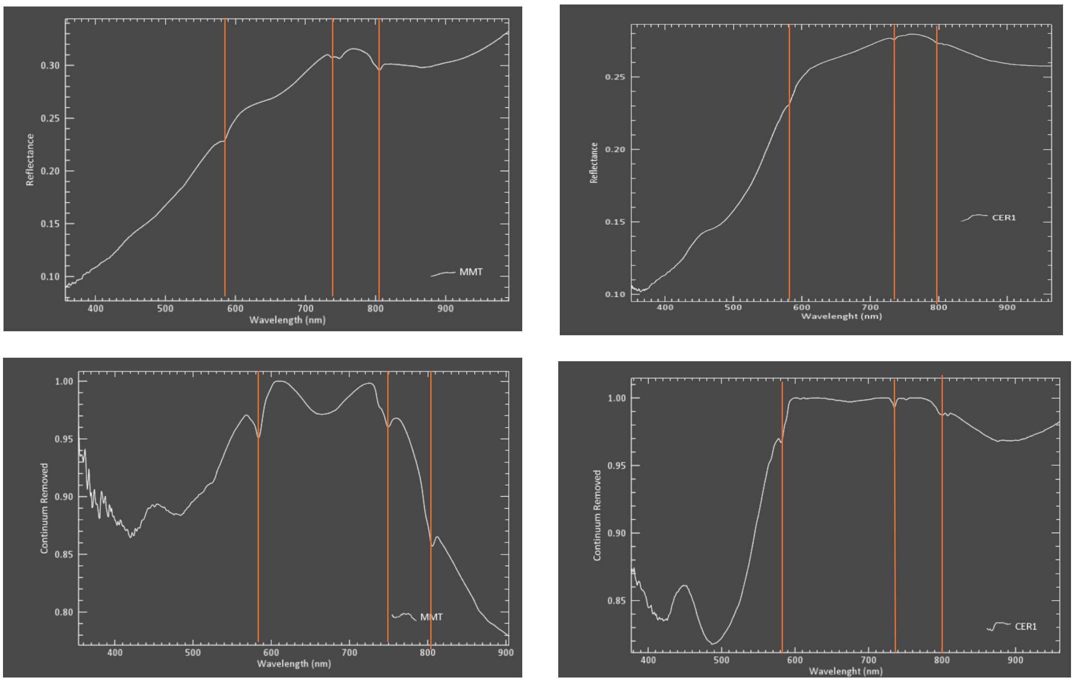

Figure 4 Spectral signatures of mimetite and cerussite samples from Sardinian mine waste deposits showing strong Nd related absorption features.

4 Conclusions

The preliminary results obtained highly encourage the future development of this study. The presence of Nd and the possible enrichment of the selected samples in LREEs will be further investigated through the complementary measurements discussed in this methodology. Furthermore, we aim to improve the methodology and extend the study area to cover and characterize more mineral waste deposits. We strongly believe that the creation of a spectral library containing comprehensive information about the analysed samples will provide important new insights toward the development of effective environmental rehabilitation strategies for these highly polluted sites.

References

1. Baldridge, A.M., Hook, S.J., Grove, C.I., Rivera, G., The ASTER spectral library version 2.0, Remote Sensing of Environment, Volume 113, Issue 4, 711-715 (2009).
2. Boesche, N., Rogass, C., Lubitz, C., Brell, M., Herrmann, S., Mielke, C., Tonn, S., Appelt, O., Altenberger, U., Kaufmann, H., Hyperspectral REE (Rare Earth Element) Mapping of Outcrops—Applications for Neodymium Detection. Remote Sensing 7, 5160–5186 (2015).
3. Boesche, N.K., Rogass, C., Mielke, C., Herrmann, S., Körting, F., Papenfuß, A., Lubitz, C., Brell, M., Tonn, S., Altenberger, U., Chapter 16 - Hyperspectral Rare Earth Element Mapping of Three Outcrops at the Fen Complex, Norway: Calcitic, Dolomitic, and Ankeritic Carbonatites, in: Lima, I.B.D., Filho, W.L. (Eds.), Rare Earths Industry. Elsevier, Boston, 235–265 (2016).
4. Booysen, R., Zimmermann, R., Lorenz, S., Gloaguen, R., Nex, P.A.M., Andreani, L., Möckel, R., Towards Multiscale and Multisource Remote Sensing Mineral Exploration Using RPAS: A Case study in the Lofdal Carbonatite-Hosted REE Deposit, Namibia. Remote Sensing 11, 2500 (2019).
5. Booysen, R., Jackisch, R., Lorenz, S., Zimmermann, R., Kirsch, M., Nex, P.A.M., Gloaguen, R., Detection of REEs with lightweight UAV-based hyperspectral imaging. Sci Rep 10, 17450 (2020).
6. Desikan, R., Rajendran, K., Exploring Rock Phosphates Using Hyperspectral Remote Sensing & Field Spectroscopy, 9th Workshop on Hyperspectral Image and Signal Processing: Evolution in Remote Sensing (WHISPERS), Amsterdam, Netherlands, 2018, pp. 1-5.
7. Jassie, L B., Diffuse reflectance spectra of ten rare earths, Spectrochimica Acta Volume 20, Issue 2, 169-177, (1964).
8. JPL Spectral Library, https://speclib.jpl.nasa.gov/documents/jpl_desc#1.0%20INTRODUCTION, 2024/10/15.

9. Kokaly, R.F., Clark, R.N., Swayze, G.A., Livo, K.E., Hoefen, T.M., Pearson, N.C., Wise, R.A., Benzel, W.M., Lowers, H.A., Driscoll, R.L., and Klein, A.J., USGS Spectral Library Version 7 Data: U.S. Geological Survey data release (2017).
10. Neave, D.A., Black, M., Riley, T.R., Gibson, S.A., Ferrier, G., Wall, F., Broom-Fendley, S., On the Feasibility of Imaging Carbonatite-Hosted Rare Earth Element Deposits Using Remote Sensing. Economic Geology 111, 641–665 (2016).
11. Rowan, L.C., Kingston, M.J., Crowley, J.K., Spectral reflectance of carbonatites and related alkalic igneous rocks; selected samples from four North American localities. Economic Geology 81, 857–871, (1986).
12. Sanborn, P., Sellitto, V.M., Sudduth, K.A., Rawlins, B.G., Walter, C., Winowiecki, L.A., Hong, S.Y., Ji, W., A global spectral library to characterize the world's soil, Earth-Science Reviews, Volume 155, 198-230 (2016).
13. Van Der Meer, F.D., Van Der Werff, H.M.A., Van Ruitenbeek, F.J.A., Hecker, C.A., Bakker, W.H., Noomen, M.F., Van Der Meijde, M., Carranza, E.J.M., Smeth, J.B.D., Woldai, T., Multi- and hyperspectral geologic remote sensing: A review. International Journal of Applied Earth Observation and Geoinformation 14, 112–128 (2012).
14. Viscarra Rossel, R.A., Behrens, T., Ben-Dor, E., Brown, D.J., Demattê, J.A.M, Shepherd, K.D, Shi, Z., Stenberg, B., Stevens, A., Adamchuk, V., Aïchi, H., Barthès, B.G., Bartholomeus, H.M., Bayer, A.D., Bernoux, M., Böttcher, K., Brodský, L., Du, C.W., Chappell, A., Fouad, Y., Genot, V., Gomez, C., Grunwald, S., Gubler, A., Guerrero, C., Hedley, C.B., Knadel, M., Morrás, H.J.M., Nocita, M., Ramirez-Lopez, L., Roudier, P., Rufasto Campos, E.M., Sanborn, P., Sellitto, V.M., Sudduth, K.A., Rawlins, B.G., Walter, C., Winowiecki, L.A., Hong, S.Y., Ji, W., A global spectral library to characterize the world's soil, Earth-Science Reviews 155, 198-230 (2016).
15. White, W. B.. Diffuse-Reflectance Spectra of Rare-Earth Oxides. Applied Spectroscopy 21, 167 – 171 (1967).