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Hyperspectral Remote Sensing for Mine Waste Characterization and Critical Mineral Exploration

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*I knock at stone's front door.
"It's only me, let me come in.
I've come out of pure curiosity.
Only life can quench it.
I mean to stroll through your palace,
Then go calling on a leaf, a drop of water.
I don't have much time.
My mortality should touch you."*

Wisława Szymborska (Conversation with a Stone, 1962)

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Preface

This thesis presents original and independent work carried out by the author, Susanna Grita, under the supervision of Prof. Piero Boccoardo and Dr. Saeid Asadzadeh at the Polytechnic University of Turin and the University “La Sapienza” of Rome, within the National Ph.D. for Earth Observations framework. Some of the data used in this work was collected by third parties as indicated within the thesis.

Chapter 3 is a manuscript under revision for the *IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing (IEEE J-STARS)*, submitted on the 28th October 2025.

Part of the topics discussed in Chapter 4, relative to the samples collected in the field and EnMAP results, constitutes paper published on the journal *Remote Sensing (MDPI)* on the 3rd February 2026 (<https://doi.org/10.3390/rs18030499>).

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Abstract

The heavy reliance on few suppliers for the provision of rare earth elements (REEs), considered as critical raw materials (CRM), is a cause of vulnerability for Europe's economy, due to their importance in industrial applications. To counteract this issue, the European Union is resorting to the exploitation of historical mines and untapped reserves within its territory, by adopting sustainable mining practices. Therefore, legacy mining lands, which so far had been perceived as problems for their impacts on the environment and human health, now gain a pivotal role as potential secondary deposits of REEs. In this context, remote sensing emerges as a novel, non-invasive, time and cost-effective solution for geologically characterizing these deposits.

This Ph.D. project is an effort to show how imaging spectroscopy can aid in the characterization of mines and their residues as both sources of REEs and as potential causes of pollution. Structured on a case study basis, the thesis leverages multispectral and hyperspectral data in the visible-near infrared (VNIR) and shortwave infrared (SWIR) spectral interval to model REE concentrations at different scales, on the one hand, and to monitor sources of acidity deriving from mine residues, on the other.

In the first case study, a flexible, explainable and scalable Random Forest Regression approach was developed for quantifying individually Nd, Dy, Er, Sm and Pr, using 130 spectra of REE-bearing minerals and rocks. The Nd model's performance was tested on hyperspectral datasets acquired in the lab and on a satellite image, confirming its scalability. The results prove to be physically meaningful as the model uses REE-related spectral absorptions during the predictive process. Moreover, the approach is independent of mineralogy and robust against unharmonized datasets. In the second case study, secondary iron-bearing minerals are mapped using a polynomial fitting technique over the historical mining district of Montevecchio-Ingurtosu, in southwestern Sardinia, using different scales and sensors. Laboratory analyses of samples collected in the field are combined with Sentinel-2 and EnMAP images to derive spatial zonations of Fe(III) hydroxides and sulfates highlighting sources of acid drainage in mine residues and compositional variations in waterways affected by neutral drainage. The continuous acquisition of Sentinel-2 data in time allows to monitor the mineral paragenesis in different seasons with changing environmental conditions.

Throughout the thesis, two challenges are highlighted, whose mitigation could be the subject of potential future research: the effects of mineral masking and the effects of instrumental and atmospheric noise. Overall, this research project sets the baseline for ensuring remote sensing's role as an essential component in efficient and streamlined processes for sustainable, safe and cost-effective mining and post-mining operations.

Keywords: Remote Sensing, Random Forest Regression, Imaging Spectroscopy, REEs, AMD, Mine Wastes, Polynomial Fitting

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1. Introduction

1.1. Context - Critical Raw Materials, Mining and Climate Change

The XXI century is shaped by two major phenomena: the looming climate crisis and the digital revolution, also known as Industry 4.0 (Tortorella et al., 2023). A number of Intergovernmental Agencies, such as the IEA (International Energy Agency), IRENA (International Renewable Energy Agency), ITU (International Telecommunications Union) and UNIDO (United Nations Industrial Development Organization), greet Industry 4.0 as a key for mitigating climate change and as a means for achieving the targets outlined by the Paris Agreement (Tortorella et al., 2023). However, the implementation of Industry 4.0 requires an increasing amount of non-renewable critical material, defined by the European Commission as Critical Raw Materials (CRM). These are characterized by high demand and high supply risk in the global market and rare earth elements are among them (European Commission - Joint Research Center, 2023).

The distribution of primary reserves of critical minerals is uneven around the world. Besides its economic implications, this asymmetrical distribution has also direct environmental impacts, affecting greenhouse gas emissions (Golroudbary et al., 2022; Watari et al., 2022), land cover (Nakajima et al., 2017; Sonter et al., 2020) and water reserves (Bartlett, 2022; Golroudbary et al., 2022; Stefanović et al., 2023). At the same time, the mining industry is also vulnerable to climate change, as the traditional assumption of stationary climate conditions is not valid anymore, exposing mining projects to a wide range of challenges including increases in energy consumption (Meza et al., 2015) and geo-hydrological hazards (Nordstrom, 2009). Companies are thus urged to find novel solutions for adapting to new climate-induced conditions (Northey et al., 2017). All these factors contribute to increasing the CRM supply risk globally.

On the 16th March 2023, the European Commission published the Critical Raw Materials Act (European Commission, 2023). With the aim of enhancing its self-sufficiency with respect to critical and strategic minerals, the Act is developed around a set of principles intended to guarantee sustainable sourcing and management of CRMs (European Commission. Directorate General for Internal Market, Industry, Entrepreneurship and SMEs., 2021). These are subdivided into social, economic and environmental principles. The latter directly addresses the issues related to the impact of mining operations on land, water and the atmosphere, as well as the vulnerability they face with climate change. The social and economic principles touch on topics such as the commitment to ensure safe living conditions for concerned communities (principle 1c) and that of promoting a circular economy and the uptake of digital technologies in the production chain (principle 4b-d). There is therefore a push to innovate the mining industry, developing lean technologies and methods for making the CRM production chain safe, clean and cost-effective, while reducing its social and environmental impact, by increasing its resilience to climate change during its whole lifecycle (Valenta et al., 2023).

Mine waste management, in this context, becomes a key aspect for assuring the sustainability of CRM sourcing. Indeed, the lifecycle of a mine is limited in time. As the exploitation of a deposit continues, the ore eventually expires or its grade decreases until it is not cost-effective anymore (Venkateswarlu et al., 2016). At the same time, technological innovation makes the exploitation of deposits with increasingly lower grade economically convenient, consequently generating increasingly larger volumes of waste (West, 2011). This leads to a large number of exhausted or abandoned mines scattered across all continents. Europe has a centuries-old history of metals mining. Its legacy results in roughly 100,000 abandoned mines (Ashby and Van Etten, 2021), though an exact figure has not been calculated yet. The UK is estimated to have thousands of abandoned mines, while Sweden alone counts about 10,000 (Mayes et al., 2009). In Italy, the last census on abandoned mines was conducted in 2006 for mines active between 1870 and 2006, and the total number of them resulted in 3006, of which 438 only in Sardinia (Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici (A.P.A.T.), 2006). Each mine is accompanied by hundreds of cubic meters of waste. In Sardinia, the total volume of mine dumps is of 33,445 m³ (*Piano Regionale di Gestione dei Rifiuti - Piano di Bonifica di Siti Inquinati - Allegato 5*, 2003).

Mine wastes have a dual nature: on the one hand they pose a big threat to human health and ecosystems (Choe et al., 2008; Cidu et al., 2021; Da Pelo et al., 2009), due to their often acidic composition (Kopačková, 2014; Kopačková et al., 2012), the high concentration of heavy metals and the potential catastrophic failures of tailings dams (Hilsum, 2009). However, on the other hand, historical mines may also contain minerals of economic value within their tailings and stockpiles, including critical and strategic minerals, which were not considered useful in earlier times. Thus, the mine residues acquire an added value and can become secondary sources of critical raw materials. With a sustainable and circular approach to extractive waste management, it is possible to develop procedures that mitigate environmental risks along with the recovery of valuable materials.

Earth Observations is a particularly effective means for rapidly mapping and monitoring mines and their evolution in time. Multispectral and hyperspectral satellite sensors acquire images on a global scale with revisit periods varying from a few days (e.g. EMIT, Sentinel-2 or Landsat data) to daily frequencies (e.g. PlanetScope data), ensuring constant and periodic coverage on almost all land areas on Earth. In addition, the broad spectral range each sensor acquires in enables to detect different minerals at once, which would otherwise not be visible to the naked eye. There is extensive literature on how remote sensing can be used for mineral exploration (Asadzadeh et al., 2023; Corrado et al., 2025; Sabins, 1999; Santos et al., 2022; Sorrentino et al., 2024) and for mapping and monitoring acid mine drainage (AMD, see Section 2.3.3), but very few studies have attempted to map valuable metals from mine residues, in most cases using Sentinel-2 data (Guglietta et al., 2022; Kasmaeeyazdi et al., 2022), and more rarely with hyperspectral satellite data (Guglietta et al., 2025).

This dissertation proposes imaging spectroscopy and remote sensing as effective tools for conducting a geochemical and mineralogical characterization of mines and their residues in different phases of their

lifecycle. By analyzing the spectral signature of each pixel in an image, this work aims at reconstructing the potential of operational mines for the extraction of REEs, while at the same time tracking and monitoring potential sources of pollution in the form of mine drainage for mine wastes. A data-driven machine learning approach is applied to quantify REEs in mining areas using different imaging spectroscopy sensors and scales, while a knowledge-based polynomial fitting technique is used to identify Fe-bearing minerals, indicators of acid to neutral mine drainage. The thesis will delineate the advantages and limitations of these instruments and techniques setting the baseline for future implementation in operational contexts.

The two aspects of mine waste characterization are carried out in parallel in this dissertation. The next chapter is focused on providing a theoretical background on REEs and mine drainage, as well as the state of the art of remote sensing applications for these themes. Chapter 3 illustrates a Random Forest regression model developed for quantifying REE from reflectance spectra, while Chapter 4 describes the results of the characterization of mine residues located in Southwestern Sardinia for both REE hotspots identification and for detecting sources of acidity using secondary Fe-bearing minerals as indicators. Chapter 5 wraps up the experimental work carried out during the Ph.D. experience and draws up the conclusions and further research development paths.

1.2. Research Objectives

1.2.1. Objectives

The main aim of the project is to study the dual nature of mine residues using proximal and spaceborne imaging spectroscopy. The objectives of the project are defined as follows:

1. Develop a scalable method for quantifying REEs with reflectance spectroscopy to identify zones of higher concentration in rocks, mines with their residues, and deposits.
2. Develop a remote-sensing workflow for detecting and monitoring the evolution in time of sources of contamination in mine wastes.

1.2.2. Specific Research Questions

Here below are listed the questions this project would like to address:

1. How can Earth Observations be leveraged for distinguishing different minerals in mining environments?
2. How effective is the assessment of the environmental impact of mine residues through the detection of secondary minerals using remote sensing?
3. Can imaging spectroscopy be used for the recognition and reliable quantification of REEs?

1.3. Methodological Framework

As the aim presented in this dissertation is two-fold, two different approaches have been applied for addressing each of the aspects, both leveraging the fields of geochemistry and imaging spectroscopy. The methodological framework is illustrated in **Figure 1.1**. Specifically, to detect the potential of mines for REE exploitation, a machine learning approach, specifically Random Forest Regression, was developed to quantify selected REEs (Nd, Pr, Sm, Dy and Er) using reflectance spectroscopy and geochemical analyses (Chapter 3). While the models were trained on non-imaging spectra of rocks and minerals of synthetic and natural origin, especially the Nd model was applied to hyperspectral images of two minerals and a drill core, acquired in the lab, and an EnMAP image acquired over the REE mine of Mountain Pass, CA, USA. This area of interest is chosen because recent studies have shown that REEs are detectable in the mine site from space (Asadzadeh et al., 2024; Gadea et al., 2024).

On the other hand, the environmental impact of mining activity is assessed on a case study in southwestern Sardinia, the Montevecchio-Ingurtosu mining complex. This area of interest was selected because it represents an example of a relatively small historical mine by extent in a highly vegetated area with an irregular topography. The mine residues have been exposed to atmospheric phenomena and are subject to weathering. Several studies have reported the negative consequences of the oxidizing residues on the land and aquatic systems (Careda et al., 1999; Cidu et al., 2009; De Giudici et al., 2019, 2018; Frau et al., 2015), where heavy metal contamination and acidic drainage have been reported. Yet, in contrast with most literature on remote sensing applications for acid mine drainage mapping and as further detailed in Chapter 4, in this area, acid mine drainage is buffered by a siderite-ankerite gangue, therefore affected waterways are only slightly acidic to circum-neutral, though transporting large amounts of Pb, Cd and Zn. These characteristics make this an interesting case study, as the results obtained here could potentially be applied to other mining areas with similar characteristics in Italy and Europe. Moreover, a recent work has highlighted the potential of this mining district as a secondary source of critical raw materials, specifically rare earth elements and zinc (Sedda et al., 2023).

The methodology in this case consists in a bottom-up approach where samples are collected in the field, analyzed in the lab and then compared with imaging spectroscopy data, from laboratory to satellite scale. In order to analyze the polluting potential of the mining area, a polynomial fitting process is developed to map secondary iron-bearing minerals from both hyperspectral (i.e. EnMAP) and multispectral (i.e. Sentinel-2) images. These together with data collected in the field are used to identify hotspots of sources of acid mine drainage.

This framework provides two different tools based on remote sensing technology to characterize extractive environments with a rapid and non-invasive procedure. The framework also aims at highlighting the advantages and limitations of these techniques in the prospective of an operational implementation.

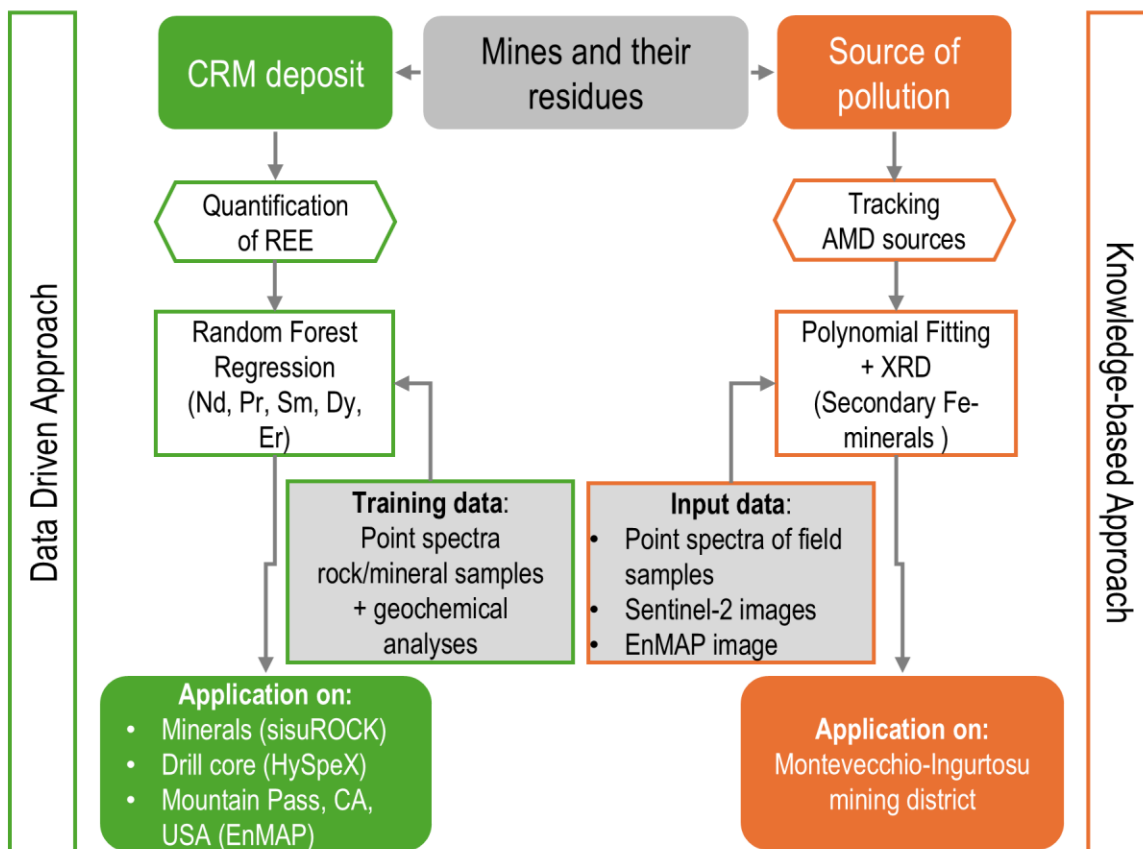


Figure 1.1 Flowchart of methodological framework of the research project. CRM=Critical Raw Materials, AMD=Acid Mine Drainage, XRD = X-Ray Diffraction.

2. Framing the Research Topic

2.1. Spectroscopy and Geological Remote Sensing

2.1.1. Principles of Spectroscopy in Geological Applications

Reflectance spectroscopy measures the reflection of light in the wavelength range between 250 to 2500 nm of the electromagnetic spectrum. This portion of the electromagnetic spectrum includes the upper section of the ultraviolet range (250-400 nm), as well as the visible (400-700 nm) and infrared (700-2500 nm) ranges (see **Figure 2.1**). In remote sensing, the infrared range is subdivided into near-infrared (NIR), between 700 and ~1000 nm, and shortwave-infrared (SWIR), from 1000 to 2500 nm (Clark, 1999). In laboratory conditions or with in-situ field measurements, the whole range of the visible-near and shortwave-infrared (VNIR-SWIR) range can be observed without interference. However, Earth's atmosphere, due to its composition, selectively absorbs part of the sun's incoming radiation at certain wavelengths. Therefore, when observing the Earth with a satellite system, reflectance spectra of target material are affected by noise where such atmospheric absorption occurs and are interpretable and useable only within the transmission windows, where the atmosphere is transparent or only partially absorbing radiation. As shown in **Figure 2.1**, the total absorption of the sun's radiation occurs in two areas: at about 1350-1500 nm and between 1800 and 1974 nm.

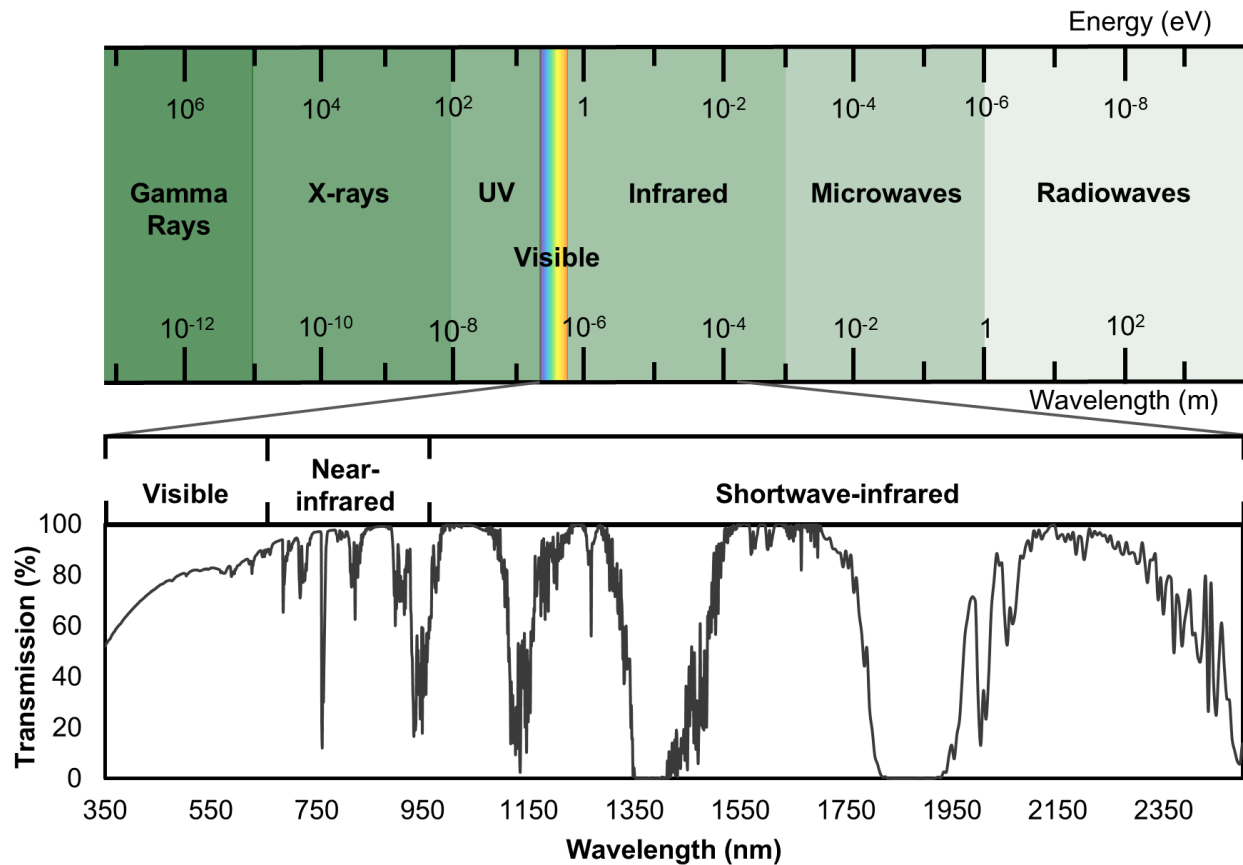


Figure 2.1 The electromagnetic spectrum based on energy and wavelength. In the bottom part of the figure is represented a subdivision of the visible-infrared range with a relative diagram of solar radiation transmission at Earth's surface, based on the ASTM G173-03 Reference Spectra (Air Mass 1.5) (G03 Committee, 2023).

In reflectance spectroscopy and therefore also in remote sensing, rocks and minerals can be distinguished based on their unique spectral signatures. These are characterized by absorption bands whose position, width and depth are diagnostic for the detection of different minerals. Absorption bands have a modified gaussian shape and are generated by electronic or vibrational processes occurring in the mineral's crystal structure. Depending on the spectral range, not all minerals are spectrally active. Some may be featureless in a specific portion of the electromagnetic spectrum, while others may have absorptions which are not diagnostic for univocally identifying a mineral or mineral class. In the VNIR-SWIR range, Fe-oxides and, clay minerals, hydroxides, carbonates and sulfates can be identified, while tectosilicates, such as quartz and feldspars do not have diagnostic absorptions in this range (Clark, 1999; Coulter et al., 2017).

Bands in the VNIR range represent processes tied to electronic transitions or crystal field effects and occur when minerals host transition metals or REE (Burns, 1993). Absorptions related to OH⁻, H₂O or CO₃²⁻ are visible in the range between 900 and 2500 nm (NIR-SWIR) and are due to overtones or combinations of fundamental vibrational modes visible at longer wavelengths (**Figure 2.2**). Specifically, a free water molecule has absorptions at 942, 1135, 1379, 1454 and 1875 nm. In minerals, instead, these absorptions are shifted based on the position of water in the crystal structure. If water is adsorbed or is

in a poorly ordered form, its absorption bands will be broad, while if water occupies a site in the crystal lattice, its absorption bands are sharp and narrow. There is only one fundamental vibration related to the OH anion, centered at around 2780 nm, that gives origin to two overtones visible in the VNIR (at 950 nm and 1400 nm) and absorptions in the range between 2000 and 2500 nm tied to combinations of stretching and bending of Metal-OH groups. Therefore, around 2200 nm, absorptions are related to combinations of Al-OH, at ~ 2300 nm to Mg-OH while at ~ 2290 to Fe-OH (Laukamp et al., 2021).

A spectral signature is the result of a material's spectral response when solicited by photons and of a continuous convex curve on which the absorption bands are overlain. This latter is called *continuum*. The physical origin of a continuum is not clear, but it is the result of a combination of processes including non-selective scattering related to the matrix effect, the Fresnel reflection and to minerals which are not spectrally active in the observed range, but with a constant reflectance (e.g. quartz) (Asadzadeh and de Souza Filho, 2016a; Clark et al., 1990; Sunshine et al., 1990). To compare spectra or to better observe absorption features, it is necessary to remove the contribution of the continuum. This makes absorption features of the target material more visible and allows to compare different spectral profiles. The most common technique used for continuum removal is the division or subtraction of a convex hull which approximates the continuum curve. The convex hull is built by identifying the 'highest points' in a spectral signature and connecting those points with straight lines tangent to the spectrum, thus defining the lowest convex hull above the spectral signature. The spectrum is then divided by the convex hull and the resulting spectrum is normalized to the value of one (Clark and Roush, 1984; Green and Craig, 1985). **Figure 2.3** shows the process of continuum removal.

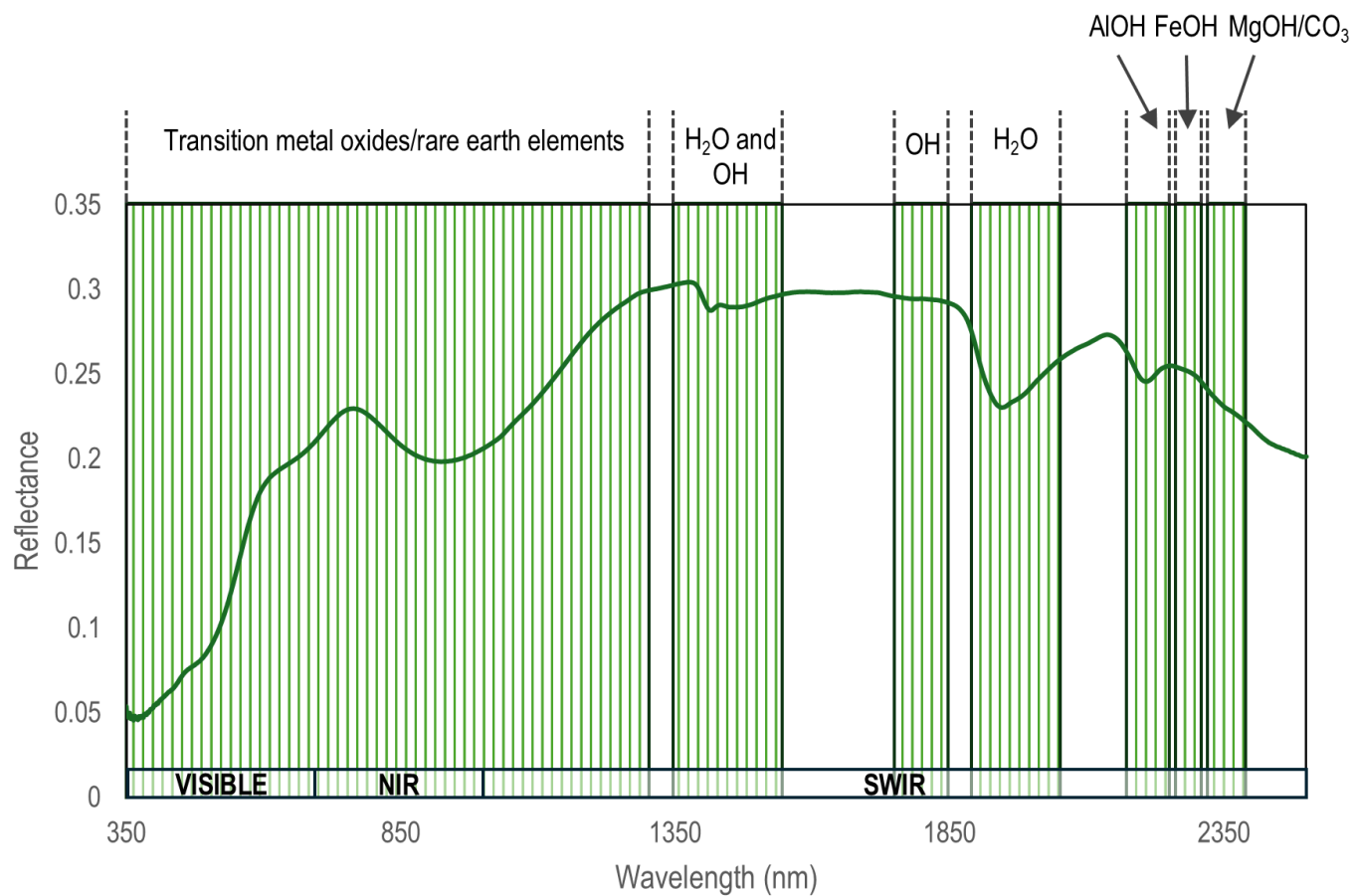


Figure 2.2 Wavelength intervals in the VNIR-SWIR range of common electronic and vibrational processes in a mineral reflectance spectrum.

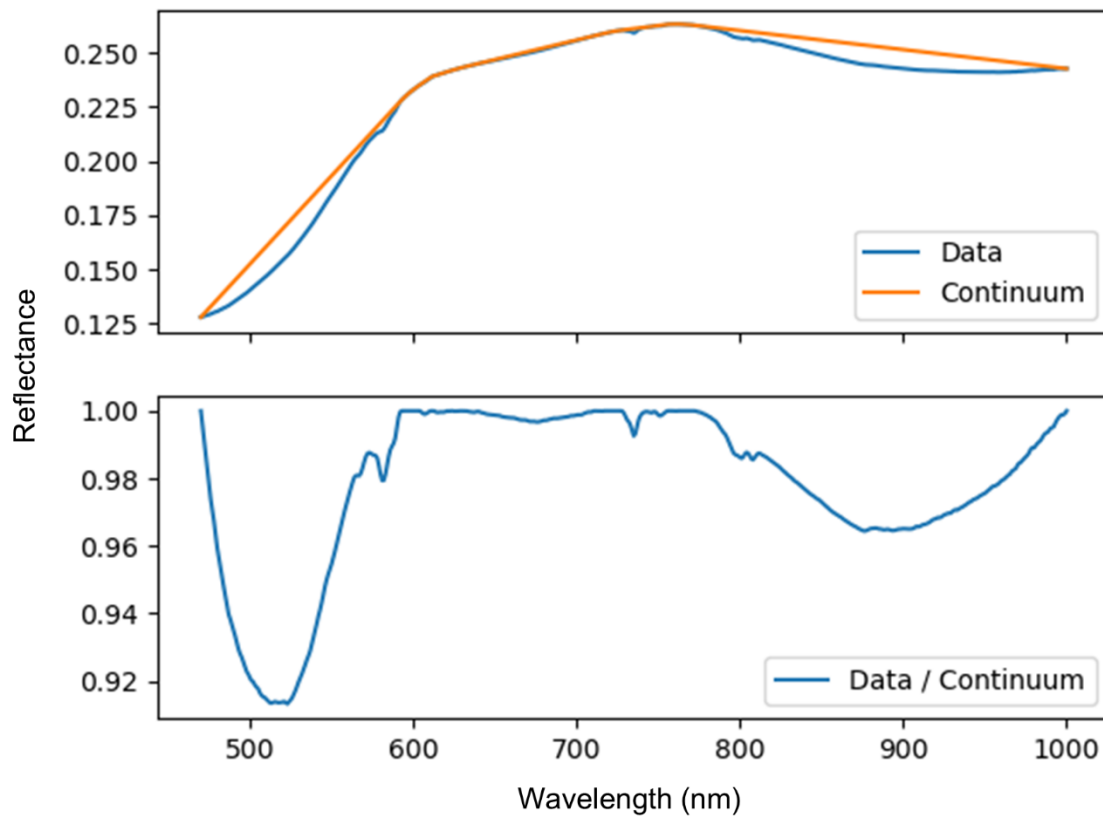


Figure 2.3 Top graph: a spectral signature of a mine tailing (blue) and its respective convex hull (orange). Bottom graph: the spectral signature of the mine tailing after the convex hull (or continuum) removal.

Once the spectrum has been continuum removed, it is possible to carry out quantitative considerations over the spectrum. The geometry of absorption features provides information on the type of material that generates such absorption. The position and symmetry allow to identify the type of mineral, the absorption depth is related to the abundance of a mineral or phase, while the width or full width at half maximum (FWHM) can be an indicator of the degree of crystallinity: the narrower the width, the more crystalline is the phase (Laukamp et al., 2021) (**Figure 2.4**) .

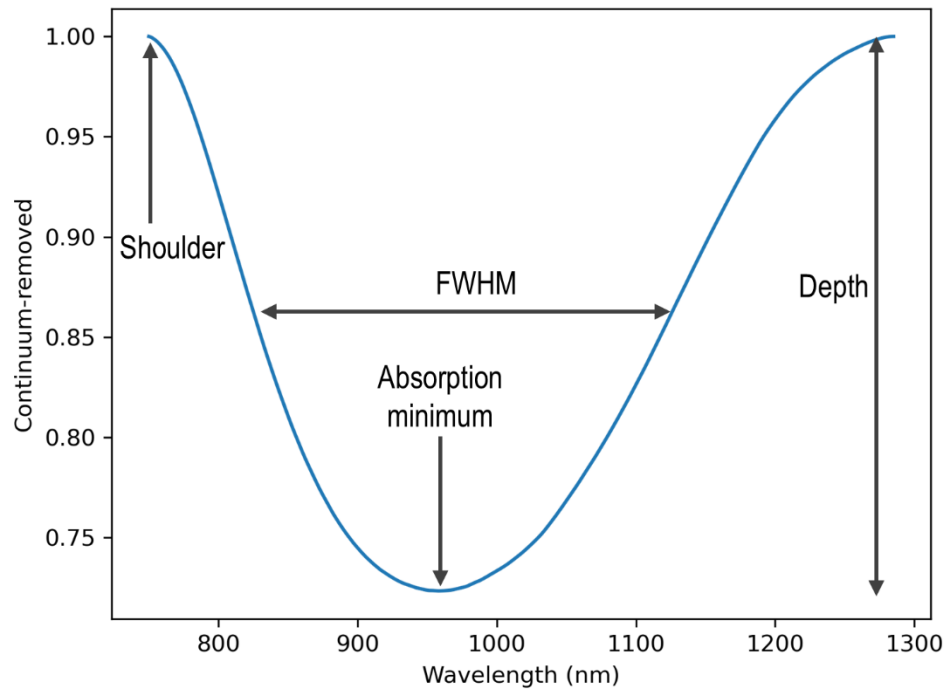


Figure 2.4 Geometrical characteristics of a spectral absorption feature.

2.1.2. Proximal and Remote Sensing Sensors

In this project, a number of imaging and non-imaging hyperspectral sensors have been used to obtain the results. Their technical characteristics are detailed in this section and examples of spectra for each sensor are illustrated in **Figure 2.5**.

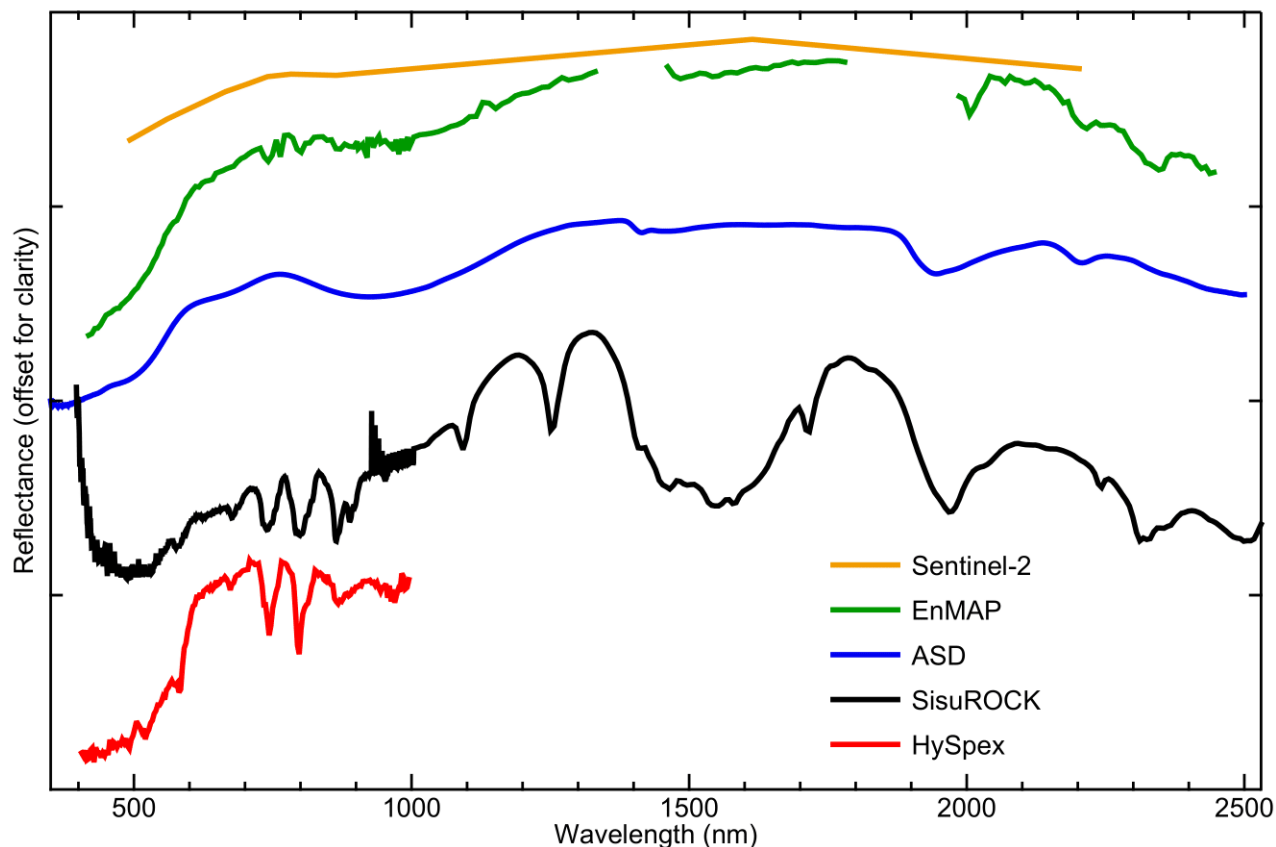


Figure 2.5 Example spectra of different imaging and non-imaging sensors. The material represented in each spectrum is as follows: HySpex = a monazite-bearing rock from a drill core of Catalao I mine, Brazil; sisuROCK = a bastnaesite mineral from Karonga, Burundi; ASD and Sentinel-2 = a flotation tailings sample collected from the Montevecchio mine, Sardinia, Italy; EnMAP = a bastnaesite bearing rock from the Mountain Pass mine pit.

2.1.2.1. Analytical Spectral Device (ASD) – FieldSpec-3

Samples collected in the Montevecchio-Ingurtosu area were measured spectrally with an ASD FieldSpec-3 spectroradiometer mounted in the lab and equipped with a contact probe. The FieldSpec-3 Spectroradiometer (Analytical Spectral Devices, Inc.) is a non-imaging portable device which has been designed for field and laboratory proximal sensing. It acquires data in the VNIR- SWIR wavelength interval (350-2500 nm) and measures reflectance, irradiance, transmittance or radiance. In this research project, spectral data was acquired only in reflectance mode. The spectral resolution is of 3 nm in the VNIR and 10 nm in the SWIR, while the sampling interval is 1.4 nm in the VNIR range and 2 nm in the SWIR range.

Before the acquisition of spectra, dark current effects are removed. The dark current is the current generated within the detector in the absence of light and varies with temperature and integration time. It adds up to the random instrumental noise in the spectra. To measure the dark current, a mechanical shutter blocks out all sources of light from the detectors, and the signal is measured. This is then automatically subtracted to the spectra. Reflectance is a normalized value of the intensity of light. It is

independent of the light source and, along with transmittance, it is a physical property of materials. Relative reflectance is obtained by measuring the white reference and dividing the intensity of light from it. This is carried out by measuring the reflectance on a 100% white reflectance panel called the reference panel.

Once these preliminary operations are carried out, the measurement of spectra is obtained by averaging several spectra within an acquisition, in order to reduce the effect of instrumental noise (Analytical Spectral Devices, 2005).

2.1.2.2. SPECIM sisuROCK

The sisuROCK system developed by SPECIM is designed to conduct hyperspectral scans of drill cores and rock samples. It is equipped with its own light source and two sensors covering the spectral interval between the VNIR (396-1003 nm) and the SWIR (928-2530 nm). The VNIR sensor has 784 channels with an average spectral resolution of 0.77 nm, while the SWIR sensor has 256 channels and a spectral resolution of about 6.26 nm (Turner et al., 2014a). The drill cores are loaded on a moving tray which allows to scan in push broom configuration. This system is able to scan a core box in a few seconds (Specim, 2025).

2.1.2.3. HySpex by Neo

The HySpex VNIR-1800 hyperspectral camera consists of a scientific CMOS detector that is actively cooled and stabilized. It acquires images in the VNIR spectral range, from 400 to 1000 nm using 186 channels with a spectral resolution of 3.2 nm. It is characterized by a high signal-to-noise ratio, which is above 255. In this study, acquisitions were obtained in laboratory configuration, in the premises of the Geological Department of the University of Campinas, however the sensor is designed to be mounted also on tripod, drone or plane (HySpex, 2025) .

2.1.2.4. Environmental Mapping and Analysis Program (EnMAP)

The Environmental Mapping and Analysis Program (EnMAP) is a hyperspectral Earth observations satellite, launched by the German Space Agency (DLR) in April 2022. Two sensors are mounted on the satellite together covering the VNIR-SWIR wavelength interval. The VNIR sensor (420-1000 nm) has a spectral sampling of 6.5 nm and a spectral calibration accuracy of 0.5 nm, while the SWIR sensor (900-2450 nm) has a spectral sampling of 10 nm and a spectral calibration accuracy of 1 nm. In total the satellite has 246 spectrally adjacent channels and the spatial resolution for both sensors is 30 m. In the VNIR the signal-to-noise-ratio (SNR) is 400:1 at 495 nm, while in the SWIR sensor it is of 170:1 at 2200 nm. The sensor's revisit time is 27 days in nadir-view and of 4 days in across track view (Chabrillat et al., 2024).

2.1.2.5. Sentinel-2A/B

The Copernicus Sentinel-2 mission, managed by the European Space Agency (ESA), consists of a constellation of two multispectral optical sensors. Sentinel-2A (launched on 23rd June 2015, now replaced by Sentinel-2C since 21st January 2025) and Sentinel-2B (7th March 2017). Each satellite holds a

multispectral imager which acquires in the VNIR-SWIR range in 13 bands. The sensors are designed to be a continuation of SPOT and Landsat missions, hence providing similar types of images. The satellites acquire continuously in a sun-synchronous orbit around the globe and are phased by 180° to each other. The satellite provides systematic coverage on all continental surfaces between latitudes 56° South and 82.8° North. Each satellite has a revisit time of 12 days and together they have a revisit time of 6 days. **Table 2.1** summarizes the spectral and spatial characteristics of Sentinel sensors.

Table 2.1 Spectral and spatial characteristics of Sentinel-2 (A, B and C) sensors. Wavelength indicates the central wavelength of each band, the FWHM is the band's full-width-half-maximum, SNR is signal-to-noise-ratio, while GSD is the ground sample distance.

Band number	S2A			S2B			S2C			GSD (m)
	Wavelength (nm)	FWHM (nm)	SNR	Wavelength (nm)	FWHM (nm)	SNR	Wavelength (nm)	FWHM (nm)	SNR	
1	442.7	20	129	442.2	20	129	444.2	21	894	20
2	492.7	64	154	492.3	65	154	489	65	162	10
3	559.8	35	168	558.9	35	168	560.6	36	189	10
4	664.6	30	142	664.9	31	142	666.5	30	175	10
5	704.1	14	117	703.8	15	117	707.1	15	192	20
6	740.5	14	89	739.1	14	89	741.1	15	169	20
7	782.8	20	105	779.7	20	105	784.7	21	161	20
8	832.8	118	174	832.9	115	174	834.6	114	174	10
8a	864.7	20	72	864	20	72	865.6	20	117	20
9	945.1	20	114	943.2	20	114	947.2	20	135	60
10	1373.5	30	50	1376.9	30	50	1372.2	33	301	60
11	1613.7	88	100	1610.4	93	100	1612	89	133	20
12	2202.4	179	100	2185.7	181	100	2191.3	182	141	20

2.1.3. Methods for Analyzing Mineral Spectra

This section is mainly summarized from van der Meer et al., (2012), and Asadzadeh and de Souza Filho, (2016a) with references therein.

The first applications of geological remote sensing were carried out using Landsat images. These were used for geological mapping obtained by specific band ratios, which allowed to discriminate between clay and non-clay minerals and identify ferric minerals. Another approach was to apply a selective Principal Component Analysis (PCA) to build a mineral map, otherwise known as the Crosta method (Crósta and De Souza Filho, 2009). This consists in selecting only bands containing geological information and applying the PCA on those. These methodologies were applied also on ASTER data, once it became available. The advantage of ASTER images is that these have narrow bands in the SWIR range and two bands in the thermal infrared range, allowing to shift from alteration indices to mineral maps. More

recent multispectral sensors include the Sentinel-2 constellation, which is particularly useful for detecting iron-bearing minerals, in continuity with ASTER data (van der Meer et al., 2014).

With hyperspectral data it is possible to better leverage the geometry of spectral signatures associated with each image pixel. Different analytical techniques exist and these can be broadly divided into knowledge-based or data-driven techniques (Asadzadeh and de Souza Filho, 2016a). The former are physics-based and require the user's expert knowledge. The latter are based on statistical and mathematical algorithms which need large sets of reference data to obtain results.

Knowledge-based techniques are generally focused on mapping absorption bands. Some approaches do not require continuum removal as a pre-processing step. Among these there is the already mentioned band-ratio approach and the relative band depth technique (Crowley et al., 1989). This is used in case of very defined absorption bands to measure the relative crystallinity of a mineral. The method consists in performing a ratio between the shoulders and the minimum of the absorption. Similarly, derivative analysis is generally used to find the position of the absorption minimum and its width. It consists in calculating the first or higher order derivatives of the spectrum through a method of finite approximation. This technique is highly sensitive to noise and further smoothing and de-noising of spectra prior to its application is required. Such a characteristic makes this technique not very suitable for airborne or spaceborne imaging spectroscopy, affected by strong instrumental noise.

Other techniques which require continuum removal are curve-fitting techniques, where the absorption is approximated to either a gaussian or a polynomial curve. An application of this approach is described in detail in Chapter 4. Parameters such as depth, minimum position and width are calculated with derivative analysis on the fitted curve instead of directly on the spectrum, allowing to significantly reduce the effects of noise. Deconvolution techniques are also very accurate and yet computationally intensive. However, they are particularly suitable for quantitative studies. The main assumption of this technique is that each absorption has a gaussian or modified gaussian shape and asymmetric absorptions are a combination of such curves. This is because the average bond length of electronic and vibrational transitions is a random variable (Sunshine et al., 1990). Wavelet analysis is similar to spectral deconvolution but is set in the frequency domain.

Data-driven techniques can be subdivided into two groups: pixel and sub-pixel approaches. The pixel-based techniques include methods based on spectral similarity, such as Spectral Angle Mapper (SAM) and Spectral Feature Fitting (SFF). SAM uses reference spectra from pure endmembers to compare the analyzed spectra. The algorithm considers the spectra as n-dimensional vectors, with n being the number of bands in a hyperspectral image and calculates the angle between the reference and the target spectra. The smaller the angle, the closer the target spectrum is to the end-member reference. SFF is instead based on minimum quadratic regression. Observing the absorption features of the spectra of each pixel, it tries to match them to an endmember of a spectral library. Unfortunately, a limitation of such statistical

matching techniques is that the matching degree is defined by a single value representing the whole spectrum, such that large spectral trends and absorptions dominate over single absorption features (Van Ruitenbeek et al., 2025). Increasing studies on remote sensing for geological applications are using Partial Least Square Regression (PLSR). It inherits some aspects tied to PCA analysis and multiple regression and establishes a linear regression with synthetic variables that optimize the trend of the parameter in analysis. It is a technique used to correlate a spectral signature to non-spectral parameters.

Machine Learning and Artificial intelligence are rapidly developing even in the remote sensing domain. These algorithms are suitable for learning sequences, generalizing them and applying them to new input data. They are used to obtain mineral classification maps and mineral abundance information. Among the different techniques there are Artificial Neural Networks (ANN) and Multilayer Perceptron. Non-parametric learning techniques include Support Vector Machine (SVM), Gradient Boosting algorithms, Decision Trees (DT) and more specifically Random Forest (RF) used for lithological mapping. Besides in applications for REE quantification, mentioned more in detail in Section 2.2.2, and further analyzed in Chapter 3, such algorithms coupled with reflectance spectroscopy have been used for mineral mapping and exploration purposes, as well as geochemical applications. Specifically, the Random Forest Classifier has been used for mapping REE and lithium bearing pegmatites (Santos et al., 2022), gold mineralization (Mohamed Sabri et al., 2025), tin-tungsten deposits (Mahboob et al., 2024), coal deposits (Begum et al., 2020), copper deposits and for alteration minerals, such as montmorillonite, kaolinite and talc (Agrawal et al., 2023). It has also been used for discriminating ores from waste effectively (Tuşa et al., 2020). Ye et al., (2023) used XGBoost for predicting As concentrations using hyperspectral data, while Dhoundiyal et al., (2025) have applied explainable machine learning (Random Forest and Gradient Boosted Trees) to classify different minerals from reflectance spectra. These techniques are particularly advantageous when having spatially distributed or noisy input datasets (Shirmard et al., 2022).

Sub-pixel analyses consist essentially in spectral unmixing techniques, be they total or partial. Partial unmixing assumes that not all the material contributing to a given spectrum is of interest to the user. Therefore, this technique focuses on identifying only the material of interest and its abundance. In this case, the unmixing problem consists in finding spectral signatures which match the target material. Among these methods there are Match Filtering, Mixture Tuned Match Filtering, Constrained Energy Minimization and Orthogonal Subspace projection. However, in geological applications these techniques are rarely used. Total unmixing instead decomposes the spectrum in a collection of spectra, each of which represents a pure endmember, and it estimates the relative abundance. The most common total unmixing process is linear unmixing. However, in geological applications spectra are generally the result of intimate mixtures and are thus non-linear combinations of end-member spectra (Clark, 1999).

2.2. Imaging Spectroscopy Applied to Rare Earth Elements

2.2.1. Overview of REEs

2.2.1.1. Occurrence in Nature

Rare earth elements (REEs) are a group of 17 chemically similar metallic elements. They consist of the lanthanide group (elements from Ce to Lu) but also include yttrium (Y, atomic number 39) and scandium (Sc, atomic number 21). All of them occur in nature except for promethium (Pm) which is unstable and decays to Nd-145 with a half-life of 17.7 years, that is too short for this element to be present on the Earth (Walters and Lusty, 2011). Because REEs have similar chemical and physical properties, specifically the same oxidation state and similar atomic radii, they naturally occur together and occupy the same positions in crystal lattices, making it hard to separate them. This means that a single mineral can have several REEs, but also that these are broadly dispersed on Earth's crust (Castor and Hedrick, 2006).

Lanthanides are divided into light rare earths (LREE, lanthanum to europium) and heavy rare earths (HREE, gadolinium to lutetium). The abundance of REEs varies widely, due to two main factors: on the one hand REEs with even atomic numbers are more abundant (from seven to two times more) than REEs with odd atomic numbers. On the other, LREE are more incompatible than HREE and tend to concentrate on the upper crust (Castor and Hedrick, 2006; Turner et al., 2015; Walters and Lusty, 2011).

REEs are lithophile elements and occur in different minerals including phosphates, silicates, halides, carbonates and are seldom found in sulfides. They rarely constitute their own minerals and more commonly substitute major elements such as Ca and Na. There are hundreds of minerals containing REEs, but the majority of REEs are mined from about 10 minerals, of which monazite, bastnaesite and xenotime are the most relevant.

Despite the name, these elements are not as rare as other critical metals such as gold or platinum, but their deposits are very rare. For example, Ce is more abundant than copper or lead, and all are more common than silver (Castor and Hedrick, 2006). REE deposits and mines are unevenly distributed around the world as shown in **Figure 2.6**. It is estimated that about 37% of REE are from China, followed by the Commonwealth of Independent States (19%), the USA (13%), Australia (6%), India (3%) and the remaining 22% from other countries, including Greenland, Brazil, Canada, Malawi and South Africa (European Commission - Joint Research Center, 2023; Maisel et al., 2023; Walters and Lusty, 2011). REE deposits can have igneous, sedimentary, or metamorphic origins. Primary deposits include igneous and hydrothermal processes which contribute to the enrichment of these deposits through fractionation. Secondary deposits are formed by surface weathering or sedimentary processes.

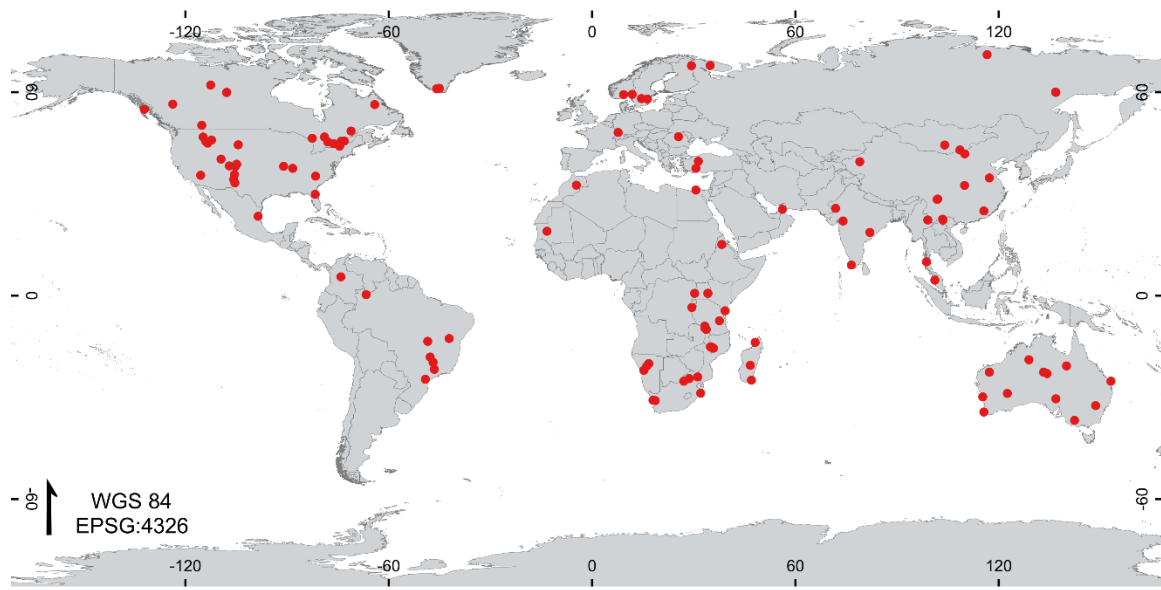


Figure 2.6 Distribution of REE deposits and mines worldwide. Map modified from Deady, (2021).

Since REEs are enriched in partial melts of magmas deriving from the upper mantle or of crustal origin, they can be associated with pegmatites, fluorite or quartz-bearing hydrothermal mineralized veins and skarns. The most commercially important deposits are those of alkaline magmas and of carbonatites. Carbonatites are igneous rocks poor in silica and rich in carbonate (more than 50%). They are formed from carbon-dioxide rich magmas deriving from the upper mantle. These occur in cratonic regions where there is major faulting or rifting and are often associated with alkaline igneous provinces. These types of deposits can be found in Scandinavia, Kola peninsula in Russia, Brazil, China, Canada, and the East African Rift zone (Walters and Lusty, 2011). The enrichment of REEs is often due to late stage carbothermal processes, when REEs are concentrated in mineralized dikes and veins (Neave et al., 2016). Alkaline igneous rocks are formed from magmas so enriched in alkalis that Na- and K-bearing and Si-poor minerals are precipitated. These rocks can be enriched in high-field strength elements (HFSE) such as Zr, Ti, Nb and REEs. The concentration of REEs in these kinds of rocks is relatively low- grade but are enriched in HREE. Such deposits occur in Greenland, in the Kola Peninsula, eastern Canada, Morocco and South Africa.

Among the secondary deposits, placers can contain an enrichment of REEs. These are deposits formed by river or coastal processes where heavy metals are concentrated along with sand and gravel. The most important ones are of tertiary and quaternary age. The largest ones are beach placers in Australia, rich in monazite, zirconium, and titanium. In tropical areas laterites deriving from carbonatites can be enriched in REEs to an economic grade. These are residual deposits deriving from in-place weathering of the host rock, whose dissolution causes leaching of elements such as Ca and Mg, and enrichment of less mobile ones such as Fe and Al. Finally, a third type of secondary deposits is residual deposits. These are present in southern China, where the weathering and leaching of granites mobilizes REEs which are adsorbed

on the surface of clays. These deposits are 3-10 m thick and are generally small (Dai et al., 2013; Tan et al., 2022; Walters and Lusty, 2011).

REEs often occur in association with actinide elements, principally uranium and thorium, due to similar physical and geochemical properties. For example, placer deposits in Malaysia contain xenotime with 2% U and 0.7% Th. This characteristic caused the REE industry to fail in Malaysia. Radioactivity can be a major environmental issue and, in some countries, such as China, Australia and Europe, the exploitation of placer deposits containing monazite has been banned (Jaireth et al., 2014; Walters and Lusty, 2011).

2.2.1.2. Physical Properties of REE mineralogy

REE are characterized by having $4f$ -orbitals which can accommodate 14 electrons in seven different orbital configurations. They are generally trivalent except for Eu^{2+} (divalent) and Ce^{4+} and Tm^{4+} which can be tetravalent. The $4f$ -orbitals of lanthanides (Ln^{3+}) are shielded by outer p and s orbitals which are complete. For this reason, the $4f$ -orbitals interact mainly with the outer shells and are largely non-participatory in bonding (Neave et al., 2016). Ln^{3+} ions are stripped of the $4f$, $5d$, and $6s$ electrons, leaving the $4f$ -orbitals to be sequentially filled. So, La has no electrons in the $4f$ -orbital, Gd has 7 unpaired electrons and Lu has the $4f$ -orbital full with 14 paired electrons. The Ln^{3+} series is also characterized by the so-called lanthanide contraction, for which with the increase of atomic number, the atomic radius decreases with La having the highest and Lu the smallest. Similar in size to Ca and actinides which have $5f$ -orbitals and include U and Th, they often co-occur in natural deposits (Turner et al., 2015).

In minerals, REEs occupy spacious and often distorted crystallographic sites. Because of the lanthanide contraction, generally HREE are predisposed to smaller sites (coordination 8), while LREE occupy sites with higher coordination (such as 11) and longer ligand distance (Turner et al., 2015). As a result, some minerals are more enriched in certain REEs than others. For example, the allanite group, bastnaesite and monazite are the primary source of LREE while xenotime is enriched in HREE.

2.2.2. Spectroscopy and Hyperspectral Imaging of REEs

This section has been modified from the introduction of a manuscript submitted to the *IEEE Journal of Selected Topics in Applied Earth Observations and Remote Sensing (IEEE J-STARS)* on the 28th October 2025.

Reflectance spectroscopy is practiced as both imaging and non-imaging techniques across various scales. It is based on the principle that when light interacts with a material with an ordered structure, such as a crystal lattice, a part of it is scattered and a part of it passes through the crystal and is selectively absorbed due to vibrational and electronic processes. These absorption bands at diagnostic wavelengths, which appear as drops in reflectance spectra, are more prominent the more the light interacts with the crystal (Clark, 1999; Turner et al., 2015). In most REEs, namely trivalent lanthanides (Ln^{3+}), absorptions are due to their unique electronic configuration, where deep-lying electrons in unfilled $4f$ orbitals are shielded by

filled outer shells, allowing for spin-orbit interactions, electrostatic repulsion, and crystal field effects (Adams, 1965; Turner et al., 2015). These are intraconfigurational transitions that occur within the $4f$ shells. For example, in a crystal field, the energy levels of a cation with unfilled orbitals are split into lower and higher excitation states, while still staying in the same orbital (Burns, 1993). Consequently, since absorption bands in Ln^{3+} rely on the presence of unpaired electrons, those with empty (La) or full (Lu) $4f$ orbitals are not spectrally active while the others present unique spectral signatures for each individual element, as shown in **Figure 2.7**. Ln^{3+} absorption patterns were traditionally assumed to remain unchanged, representing the corresponding element rather than the host mineral, because of their electronic configuration (Clark, 2013). However, recent studies have shown that subtle shifts can occur in the absorption features depending on the geometry and type of coordination sites occupied by REEs within mineral structures. Such shifts can be of the order of magnitude of ~10 nm in the VNIR range and ~80 nm in the SWIR range (Dijkstra et al., 2024; Turner et al., 2015, 2014a). This finding could potentially enable the spectral discrimination of REE mineralogy by observing the shifts in the reflectance minima of diagnostic absorption features ((Dijkstra et al., 2024; Turner et al., 2018, 2016, 2014a), Todd Hoefen, personal communication).

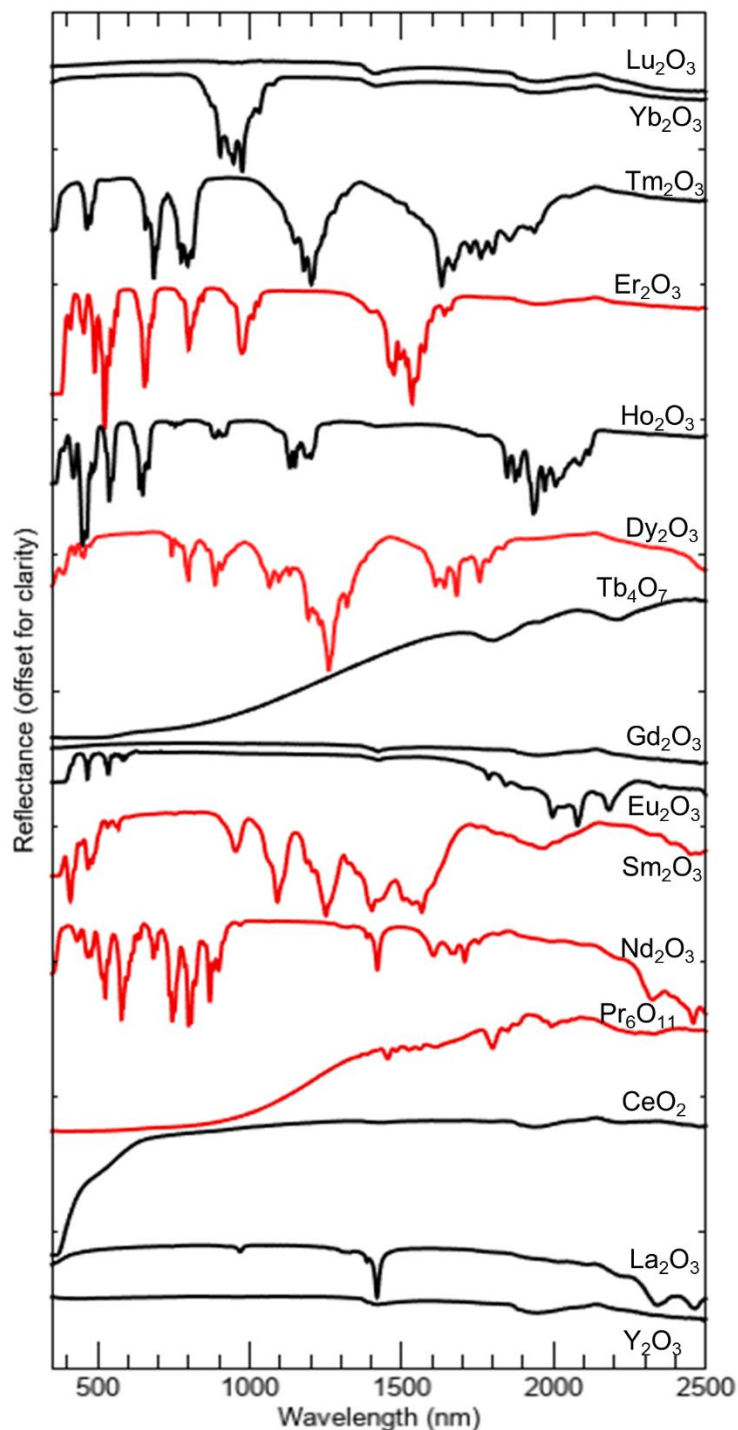


Figure 2.7 VNIR-SWIR spectral signatures of individual REE oxides (REacton®, 99.997% (REO), Alfa Aesar). The spectra in red are related to REEs analyzed in Chapter 3 of this work. Spectra are from Möller and Williams-Jones, (2018).

Since absorption features arise from electronic processes in elements, their intensity is expected to be directly related to REE concentration. Early studies have focused on quantifying Nd through its prominent absorption features at ~ 740 , ~ 800 , and ~ 870 nm, using this dominant element as a pathfinder

for other REEs. The methodology involved calculating the depth of spectral absorption feature (Boesche et al., 2015; Möller and Williams-Jones, 2018; Turner et al., 2014b) and area (Asadzadeh et al., 2024; Neave et al., 2016), as well as the second derivative of the recorded spectra to estimate the relative proportion of Nd (Tan et al., 2021). Others have applied band ratioing techniques to hyperspectral imaging data acquired in either transmittance (Daempfling et al., 2022) or reflectance modes (Gadea and Khan, 2023; Qasim and Khan, 2022). While these methods are straightforward to implement, they cannot provide quantitative estimations of Nd (and other REEs) concentrations analogous to geochemical analysis. This is because each noted absorption feature is often a composite of multiple overlapping absorption bands and because the relationship between Nd concentration and its absorption features is nonlinear (Boesche et al., 2015; Kopačková-Strnadová et al., 2021; Neave et al., 2016). An increasing number of studies are shedding light on factors that potentially hinder the effective quantification of REEs. For instance, the presence of Fe³⁺-bearing minerals, such as goethite and hematite, whose spectral signatures overlap those of Nd, negatively affects Nd estimation using spectral methods (Boesche et al., 2015; Tan et al., 2022, 2021). Grain size also affects the geometry of the spectra, as coarse grains seem to enhance the depth of diagnostic absorption features (Asadzadeh et al., 2024; Neave et al., 2016), making the detectability, and consequently the quantification, of REEs with spectroscopic methods and sensors to be deposit-specific (Booyesen et al., 2020). Moreover, in cases of co-occurrence of U and Th with REEs in the same mineral, the presence of U^{4+/5+}, as well as the development of radiation damage to the crystal structure and the eventual inclusion of water in the metamict crystals, is reflected in VNIR-SWIR spectra with absorptions interfering with REE-related features (Turner et al., 2018, 2016). The role of mineralogy in the quantification of Nd is more contentious. While Neave et al. (2016) and Möller and Williams-Jones (2018) demonstrated that Nd diagnostic features remain largely consistent across different natural samples, Kopačková-Strnadová et al. (2021) reached the opposite conclusion, highlighting the challenges of generating a universal model for various lithotypes.

Recent studies have employed machine learning (ML) to estimate REE concentrations. For this purpose, spectral derivatives (1st and 2nd-order), calculated from smoothed reflectance spectra, have been used as inputs to various algorithms, including multiple linear regression, partial least square regression, random forest, and backpropagation neural networks (Cheng et al., 2023; Huang et al., 2021; Ke et al., 2025; Kopačková-Strnadová et al., 2021; Wang et al., 2017), with the latter showing the most promising results. Machine learning generates parameterized models that are flexible and adaptable to input data, enabling the quantification of even low levels of REEs. Thanks to this capability, some models have focused on discriminating and quantifying nearly all REEs (Cheng et al., 2023; Wang et al., 2017), albeit not all REEs are spectrally active in the analyzed wavelength range (e.g., La, Lu, and Ce). It appears that only a subset of them, including Nd, Sm, Pr, Dy, Er, Ho, and potentially Eu and Tb, if present in sufficiently high concentrations, can be reliably estimated by reflectance spectroscopic methods in natural samples with naturally occurring concentrations (Dijkstra et al., 2024; Rowan et al., 1986; Turner et al., 2015; Todd Hoefen personal communication).

In several of these studies, the predictive models have been trained using the VNIR-SWIR full range spectral data (Huang et al., 2021; Ke et al., 2025; Kopačková-Strnadová et al., 2021; Wang et al., 2017), even though the majority of absorption features occur between 470 and 1000 nm. In other words, these predictions, if not suffering from overfitting, rely on indirect spectral signatures for concentration estimation, making them site-specific and non-transferable to other contexts. Another limitation of machine learning algorithms, including neural networks, is their complex architecture. In many cases, it does not allow for tracing the specific features contributing to final predictions and is effective only with large datasets (Dirks et al., 2023). Explainability is fundamental for the transferability of such models to operational applications. So far, only a few studies have exploited variable importance analysis to demonstrate the robustness of their results (Kopačková-Strnadová et al., 2021; Murer and De Souza Filho, 2026; Wang et al., 2017), thereby improving the understanding of the model's performance.

Several of such models are trained by low REE concentrations, whereas in geologic environments, REE concentrations can vary by several orders of magnitude. It remains to be seen whether these methods can handle such variability. To ensure the scalability of ML models, one should consider the effects of sensor noise. The use of derivative analysis as a preprocessing step (Cheng et al., 2023; Huang et al., 2021; Wang et al., 2017) can also make the models sensitive to noise (Asadzadeh and de Souza Filho, 2016a).

Being able to handle noise is crucial because a growing number of studies have shown the possibility of detecting REEs using imaging spectroscopic data acquired across various scales, spanning from proximal settings in the lab (Daempfling et al., 2022; Gadea and Khan, 2023; Murer and De Souza Filho, 2026; Qasim and Khan, 2022) to drone-borne (Boesche et al., 2015; Booyesen et al., 2020), airborne (Bedini, 2009), and spaceborne systems (Asadzadeh et al., 2024; Gadea and Khan, 2023; Kopačková-Strnadová et al., 2023; Neave et al., 2016). To ensure reliable performance, these models must account for sensor and atmospheric effects (Asadzadeh et al., 2024).

2.3. Imaging Spectroscopy Applied to Mine Drainage

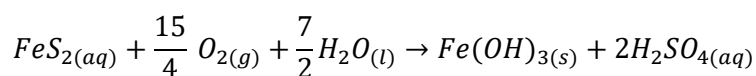
2.3.1. Acid and Neutral Mine Drainage – An Overview

Mining of metals and raw materials is fundamental for the social and economic development of humanity, and it has been practiced since ancient times. In recent years, the request for metals and critical minerals has increased due to the exponential flourishing of the technological industry. With the rapid improvement of mining techniques coupled with a growing demand for raw materials, deposits with increasingly lower grades are exploited, generating progressively larger volumes of waste material to be disposed of. These wastes, have significant impacts on land, air and water ecosystems, and consequently on health, as human bodies can take up mine waste particles and their toxic contaminants through different pathways (Plumlee and Morman, 2011). One of the major side-effects of metal mining is acid mine drainage (AMD). This is caused by mine waste piles enriched in non-economic metal sulfides that,

when interacting with groundwater, snowmelt or rainwater, can cause the oxidation of these sulfides and release high concentrations of sulfuric acid (Nordstrom and Alpers, 1999; Plumlee et al., 1997).

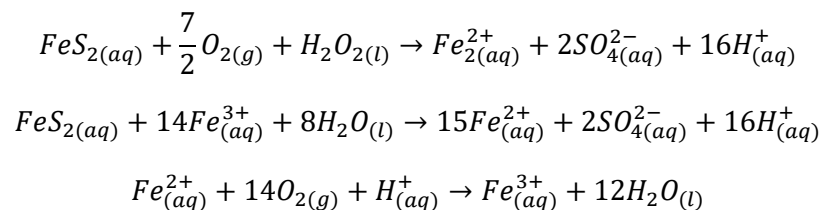
More in general, rock drainage is a hazard generally associated with the oxidation of pyrite and other sulfides. It may be deriving from natural outcrops, but it is often related to mine waste (smelter slag, tailings and mine workings) (Dold, 2017; Plumlee et al., 1997; Sares et al., 2004). Depending on the mine and residue composition or on the deposit type, drainage can be acidic, neutral or alkaline and with varying ranges of metal concentration (Plumlee et al., 1997). It is considered acid when pH is below 6, and neutral to alkaline for values above 6. Acid mine drainage is the most hazardous, though neutral mine drainage is still a significant source of pollution as it causes the mobilization of toxic metals and metalloids such as Pb, Ni, Cd and As.

In mine wastes, sulfide oxidation is more rapid as the processed material is often of finer grain size and more porous than a natural outcrop. The chemical reaction responsible for acid rock drainage is the following:



It essentially illustrates that one mole of oxidized pyrite generates a mole of iron-hydroxide and two moles of sulfuric acid. This is a simplified equation that summarizes several possible variants that occur during the slow oxidation process. The main factors affecting the formation of AMD are temperature, pH, gangue dissolution, types and structure of rocks, porosity, permeability, water flow paths, climate and precipitation/dissolution of efflorescent salts (Nordstrom and Alpers, 1999).

It has been proved that during the dissolution of pyrite, sulfur oxidizes more quickly than iron, which stays in its ferrous form (Fe^{2+}) in acid solutions. However, the presence of Fe^{3+} generally accelerates the dissolution of pyrite. Therefore, it is thought that pyrite oxidization is initiated by the presence of oxygen in near-neutral pH conditions, but as soon as pH is reduced to 4, the process is mainly governed by Fe^{3+} (Singer and Stumm, 1970). The whole process of AMD formation can therefore be better described according to the following three equations (Nordstrom and Alpers, 1999):



This process can also be catalyzed by the presence of bacteria, such as the *Thiobacillus Ferrooxidans* (Blowes et al., 1995). Rates of oxidation in nature and in mine contexts can vary significantly depending on environmental conditions. If microbial activity is present, the fastest reaction can be the oxidation of iron mediated by bacteria. However, the surface area and crystallinity of pyrite play a relevant role in the

AMD formation process. For example, it has been shown that framboidal pyrite will oxidize far more quickly than museum euhedral pyrite (Nordstrom and Alpers, 1999).

The oxidation of pyrite is an exothermal reaction that causes an increase in temperature. Waste rock piles can reach temperatures of 50 to 65°C while temperatures of drainage waters have been reported to be even 47°C (Nordstrom and Alpers, 1999).

The drainage, once formed, can interact with acid neutralizing minerals such as carbonates or aluminosilicates, which can shift the pH to more neutral values. The most effective neutralizing minerals are calcite and aragonite, while other carbonates are less reactive, and aluminosilicates are the least effective (Plumlee et al., 1997).

The above system creates the suitable conditions for the precipitation of a large variety of secondary minerals (Nordstrom and Alpers, 1999). Iron-bearing secondary minerals are stable in acidic conditions, becoming proxies for constraining the acidity of the environment without needing to directly measure the pH. AMD waters are characterized by low pH, high iron and aluminum content, high heavy metal concentrations and high sulfate concentrations. This is the reason why minerals stable at these conditions are hydrated Fe- or Al-sulfates. **Table 2.2** lists the major Fe-bearing secondary minerals that can be found in AMD environments (Alpers et al., 1994). In general terms, pH variations along AMD affected waters can be deduced by the presence of key iron-bearing oxides and sulfates. At varying pH different mineral phases can precipitate with varying degrees of crystallinity. For example, at pH above 2 ferric iron-bearing amorphous minerals precipitate, such as ferrihydrite, schwertmannite and jarosite. Specifically, jarosite forms at pH below 3, close to the sulfide source, while in ranges between 2.8 and 4.5 schwertmannite is stable. Ferrihydrite, together with schwertmannite will precipitate in less acidic environments with pH between 4 and 6.5. At mildly acidic to basic conditions, goethite and hematite are the most stable forms of hydroxides and oxides respectively. Ferrihydrite can transform to hematite in a pH range between 5 to 9, while out of this range it will transform to goethite. Aluminum starts precipitating at pH around 5. It may form a white crust along the drainage areas and can be considered as a reliable indicator of the acidity of the water. This crust is constituted by aluminum hydroxysulfates (Biggam et al., 1996; Nordstrom and Alpers, 1999). Fe^{2+} is more soluble than Fe^{3+} and in mine settings, it forms colloidal compounds in alkaline environments causing the partial oxidation of Fe^{2+} and the precipitation of 'green rust'. This kind of precipitation has been reported along the Irvi stream in correspondence to an area rich in carbonates (Frau et al., 2015).

It should be noted that the precipitation of iron hydroxides increases the acidity of the waters with the generation of hydrogen ions through metal hydrolysis reactions. The effect is that, along a mine drainage affected stream, pH can vary of several units, as for example along the Rio Irvi, further discussed in Chapter 4 (De Giudici et al., 2018; Frau et al., 2015; Plumlee et al., 1997).

Among the secondary minerals there are also highly soluble sulfate salts which also control the geochemistry of mine drainage waters. These are formed by evaporation in arid and semi-arid environments and can be found along mine drainage affected streams, or as efflorescences on mine walls and tailings. These are ephemeral minerals and rapidly dissolve with heavy rainfall events. They contain different metals including Fe (e.g. melanterite and copiapite), Mg (e.g. epsomite and starkeyite), Ca (e.g. gypsum) and Zn (e.g. goslarite and bianchite). The paragenesis of iron-bearing soluble salts allows to reconstruct specific environmental conditions such as oxidation, humidity and neutralization degrees (Jerz and Rimstidt, 2003). These minerals are important also because they can control the mobility of heavy metals. Indeed, different secondary minerals at formation selectively fix metals such as Pb, Zn and Cd. At metal concentrations higher than 10^{-6} molar and at progressively increasing pH, the sequence of precipitation is roughly the following: Fe^{3+} , Pb, Al, Cu, Zn, Fe^{2+} , Cd. However, these are ephemeral phases which act as sinks for acid and heavy metals in dry periods and release them in wet periods upon dissolution, causing cyclic pulses in the chemistry of water (Alpers et al., 1994; Frau, 2000; Hammarstrom et al., 2005; Jerz and Rimstidt, 2003).

As seen, the acidic conditions generated by the oxidation of sulfide minerals trigger a series of processes that are dynamically changing with the weather, temperature and other factors described above. Constant monitoring of such complex phenomena can be of great value for environmental managers and mining companies in order to reduce or prevent the formation of AMD.

Table 2.2 Common secondary Fe(II) and Fe(III)-bearing minerals. Modified from Alpers et al., (1994).

Soluble sulfates			Less soluble sulfates		Iron oxides/hydroxides			
Fe ²⁺	Melanterite	Fe ²⁺ SO ₄ .7H ₂ O			Magnetite Fe ²⁺ O.Fe ₂ ³⁺ O ₃			
	Ferrohexahydrite	Fe ²⁺ SO ₄ .6H ₂ O						
	Siderotil	Fe ²⁺ SO ₄ .5H ₂ O						
	Rozenite	Fe ²⁺ SO ₄ .4H ₂ O						
	Szomolnokite	Fe ²⁺ SO ₄ .H ₂ O						
Mixed Fe ²⁺ and Fe ³⁺	Halotrichite	(Fe ²⁺)Al ₂ (SO ₄) ₄ .22H ₂ O	Jarosite KFe ₃ ³⁺ (SO ₄) ₂ (OH) ₆		Hematite α-Fe ₂ ³⁺ O ₃			
	Copiapite	Fe ²⁺ Fe ₄ ³⁺ (SO ₄) ₆ (OH) ₂ .20H ₂ O						
	Bilinite	Fe ²⁺ Fe ₄ ³⁺ (SO ₄) ₄ .22H ₂ O						
	Roemerite	Fe ²⁺ Fe ₄ ³⁺ (SO ₄) ₄ .14H ₂ O						
	Voltaite	KFe ₅ ²⁺ Fe ₄ ³⁺ (SO ₄) ₁₂ .18H ₂ O						
Fe ³⁺	Coquimbite	Fe ₂ ³⁺ (SO ₄) ₃ .9H ₂ O	Fibroferrite Fe ³⁺ (SO ₄)(OH).5H ₂ O		Maghemite γ-Fe ₂ ³⁺ O ₃			
	Kornelite	Fe ₂ ³⁺ (SO ₄) ₃ .7H ₂ O						
	Rhombochase	HFe ³⁺ (SO ₄) ₂ .4H ₂ O					Amarantite Fe ³⁺ (SO ₄)(OH).3H ₂ O	
	Ferricopiapite	Fe ₅ ³⁺ (SO ₄) ₆ O(OH).20H ₂ O						
			Schwertmannite Fe ₈ ³⁺ O ₈ (SO ₄)(OH) ₆		Goethite α-Fe ³⁺ O(OH)			
					Lepidocrocite γ-Fe ³⁺ O(OH)			
					Ferrihydrite 5Fe ₂ ³⁺ O ₃ .9H ₂ O			

2.3.2. Spectroscopy of Iron-bearing Minerals

Ferric iron minerals, including iron alteration minerals, such as goethite, hematite and jarosite, are very common in soils and rocks and their occurrence is rather ubiquitous. In reflectance spectroscopy their presence is strongly revealed in the 400-1200 nm wavelength range (VNIR range). In this range, they have a trans-opaque behavior, meaning that they strongly absorb the blue and the green wavelengths, but reflect the red (Townsend, 1987). In oxides, iron is in octahedral coordination sites. The spectral absorptions are related to electronic processes involving Fe^{3+} or Fe^{2+} cations. Specifically, these processes are (i) charge transfer which involves the transfer of electrons from ligand to metal (in this case Fe^{3+} to oxygen), (ii) crystal field effects, which consist in the excitation of electrons from lower to higher energy states within the d -orbitals, because of variations in the octahedral electrostatic field and (iii) transitions due to the simultaneous excitation of magnetically-coupled Fe^{3+} cations occupying adjacent sites. These processes together make the interpretation of spectra rather complex (Cudahy and Ramanaidou, 1997; Sherman and Waite, 1985).

i. Ligand to metal charge-transfer

Occurring at higher energies compared to crystal field transition, this process consists in transferring electrons from ligands (i.e. oxygen atoms) to metal (i.e. Fe^{3+} cations). This process generates strong absorption bands centered at ~ 250 nm (Cudahy and Ramanaidou, 1997; Sherman and Waite, 1985).

ii. Paired excitation processes

This process is given by the magnetic coupling of paired Fe^{3+} cations which are simultaneously excited to an energy equal to the sum of two single Fe^{3+} ligand field transitions. These are responsible for the absorption edges between 400 and 600 nm (Sherman and Waite, 1985).

iii. Crystal field effects

Crystal field absorptions are due to energy changes of the d -shell orbitals. These are due to local compositional or crystallographic disorder in the crystal lattice which causes the splitting of the metal's d -orbitals in two states. The energy difference between these two states is the crystal field splitting energy. Types of lattice disorder can be lattice edge and dislocation effects due to ligand or cation substitution on a local level. In general, in isolated Fe^{3+} cations, these intraorbital energy jumps would be spin-forbidden. However, because of the strong magnetic coupling between adjacent Fe^{3+} ions in crystal fields, these changes do occur (Burns, 1993). Therefore, the smaller the iron oxide crystals the higher the crystal surface affected by lattice edge distortion, the higher the crystal field splitting energy. In ferric iron-bearing minerals, absorptions due to crystal field effects are superimposed on the ligand-to-metal charge transfer bands and on those of the paired excitations of magnetically coupled iron cations. These are characterized by a broad band centered at ~ 900 nm, one between 550 and 650 nm and a narrow band at around 450 nm. Minerals containing ferrous iron also have crystal field absorptions in somewhat

different wavelengths, but that can overlap with those of ferric iron. For example, there is an absorption between 900 and 1100 nm due to the $E_g \rightarrow T_{2g}$ transition of ferrous iron in the octahedral field, another centered at about 550 nm (${}^5T_{2g} \rightarrow {}^3T_{1g}$) and another at about 510 nm (${}^5T_{2g} \rightarrow {}^1A_{1g}$) and finally, one centered at 450 nm due to the ${}^5T_{2g} \rightarrow {}^3T_{2g}$ transition.

Distortion or changes of electronic configurations can affect the energy of these processes, which is expressed in a shift in wavelength of such absorptions. Changes include the distortion of the metal-ligand crystallographic site, change in valence state or coordination number, as well as the site symmetry. Also, variations of the metal-ligand distances may alter the position of the absorption feature. Such changes allow to discriminate different mineral phases (Cudahy and Ramanaidou, 1997).

Hematite, goethite and jarosite have been among the first minerals to be distinguished with reflectance spectroscopy. They are affected by the following crystal splitting energies: ${}^6A_1 \rightarrow {}^4A_1$ (380-440 nm), $({}^6A_1 + {}^6A_1) \rightarrow ({}^4T_1 + {}^4T_1)$ (480-550 nm), ${}^6A_1 \rightarrow {}^4T_2$ (640-730 nm), ${}^6A_1 \rightarrow {}^4T_1$ (850-1000 nm) (Scheinost et al., 1998; Sherman and Waite, 1985). The features of their spectra are interpreted as deriving from crystal field energy diagrams for cubic symmetry, although hematite, for example, can be assigned also to the trigonal symmetry and goethite has orthorhombic symmetry (Morris et al., 1985). Cudahy and Ramanaidou (1997) focused on the charge transfer shoulder at ~600 nm and the crystal field absorption centered at ~900 nm to obtain a hematite: goethite ratio.

Other studies have shown that it is in principle possible to discriminate different secondary iron-bearing minerals, namely oxides, hydroxides and sulfates, deriving from the alteration of pyrite. In reflectance spectra this is possible by analyzing not only the absorption bands related to electronic processes between 400 and 1300 nm, but also those related to vibrational processes of water molecules, hydroxyls and sulfate anions (Cloutis et al., 2006; Crowley et al., 2003). Because most of the minerals precipitating in AMD environments are hydrated, absorptions related to the vibration of OH^- and H_2O can be diagnostic for distinguishing different phases. Therefore, regions near 1400 and 1900 nm are related to the first overtones of O-H stretching fundamentals and the combination of O-H stretching and H-O-H bending in water molecules. In sulfates, weak absorption between 1700 and 1800 nm are related to combinations of H-O-H bending, O-H stretching and the first overtone of librational modes related to water. Another important region is the one between 2250 and 2300 related to Fe-O-H and Mg-O-H (Clark et al., 1990; Cull et al., 2014).

Here below are described the spectral features of some of the secondary minerals, which are mentioned in this work (Crowley et al., 2003).

2.3.2.1. Soluble mixed Fe(II)/Fe(III) sulfates

This category includes minerals such as copiapite and roemerite. These phases occur at high oxidation levels and in highly acidic conditions.

Copiapite ($Fe^{2+}Fe_4^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$)

In copiapite, Fe^{3+} octahedra form chains linked by OH^- and SO_4^- anions at the corners, while Fe^{2+} cations are isolated and are surrounded by six water molecules in octahedral coordination $[Fe(H_2O)_6]$. The Fe^{2+} octahedra occupy the center of the crystallographic unit cell. Copiapite and ferricopiapite have similar spectra, these are characterized by complex combinations of absorptions due to the presence of mixed valence iron. The major absorptions are centered at about 431, 541 and 868 nm, all related to crystal field effects of ferric iron (Fe^{3+}), which seems to be dominant with respect to ferrous iron. The absorptions at 1178, 1453, 1768 and 1941 nm are related to vibrational processes of water of hydroxyls. Copiapite forms in extremely acidic environments and is generally the results of the transformation of melanterite by dehydration and oxidation (Jambor et al., 2000).

2.3.2.2. Less soluble Fe(III) sulfates

Jarosite ($KFe_3^{3+}(SO_4)_2(OH)_6$)

The structure of jarosite consists of corner-sharing Fe^{3+} octahedra surrounded by six oxygens and bridged by OH^- and SO_4^{2-} anions, so as to form sheets separated by K^+ ions. This structural configuration gives rise to four electronic transitions due to crystal field effects of trivalent iron, visible also in crystalline jarosite. These include a band at ~ 435 nm and a broad band centered at about 920 nm, whose right shoulder is centered at about 1000 nm, causing this feature to be asymmetric. These are relatable to spin-forbidden transitions of edge-sharing or corner sharing Fe^{3+} octahedral sites (Cloutis et al., 2006). On the left side, the 920 nm feature is characterized by a weak shoulder centered around 650 nm. In addition, another diagnostic absorption feature centered at around 2265 nm is present and is due to Fe-O-H vibrations, while features associated with hydroxyls and adsorbed water are centered at about 1467, 1850 and a weak absorption at 1936 nm. The 435 nm feature is highly diagnostic for jarosite (Hunt and Ashley, 1979), because, compared to other minerals having this feature, it is enhanced by its crystal structure, which causes an antiferromagnetic coupling among the Fe^{3+} ions (Hunt and Ashley, 1979; Vilas et al., 1993). Jarosite forms solid solutions with other compounds, such as Pb (plumbojarosite), Na (natrojarosite) or even H_3O (hydronium-jarosite) based on the degree of depletion on K^+ and the availability of other cations in the site of formation (Basciano and Peterson, 2010; Öborn and Berggren, 1995). Hydronium-jarosite, specifically, though until recently considered a rare variety of jarosite (Jambor et al., 2000), can be found along with ferrihydrite in distal zones of acidic sources, where the soil is poor in alkali, rich in hydronium and sulfide oxidation is at its maximum (Velasco et al., 2005). Its spectral characteristics differ from those of K-jarosite in having deep and broad water related absorptions at ~1470 and ~1945 nm (Velasco et al., 2005). Jarosite precipitates from acidic, sulfate-rich solutions with $pH < 3$ and high oxidation rates (Nordstrom and Alpers, 1999). It forms with a general composition of $(K, Na, H_3O)Fe_3(SO_4)_2(OH)_6$ (Dutrizac and Jambor, 2000) and has as a common source of K trioctahedral micas such as biotite (Jambor et al., 2000).

Schwertmannite ($Fe_{16}^{3+}O_{16}(OH)_{12}(SO_4)_2$)

In schwertmannite there are two sites for Fe^{3+} . These are created by bridging SO_4^{2-} between edge-sharing octahedra surrounded by three oxygen atoms and three hydroxyls. These two sites cause a broad asymmetric absorption band at 900 nm and a strong absorption with a steep edge at wavelengths short of 500 nm. The spectral signature of schwertmannite is very similar to that of ferrihydrite. Schwertmannite is formed in conditions similar to jarosite but with slightly more moderate pH and oxidation conditions. This means that while jarosite generally forms at $pH < 2.8$, in ranges between 2.8 and 4.5 schwertmannite is favored. At less acidic conditions ($pH < 6.5$) ferrihydrite and schwertmannite tend to occur together, while at neutral to more alkaline pH there is the co-existence of goethite and ferrihydrite.

2.3.2.3. *Fe^{3+} Oxides*

Hematite ($\alpha - Fe_2^{3+}O_3$)

Hematite consists of edge sharing Fe^{3+} octahedra surrounded by six oxygens. The structure is hexagonal close packed (Burns, 1993). Because this mineral has strong antiferromagnetic properties between Fe^{3+} cations, these influence the electronic transitions and charge transfers. Therefore, there is a strong absorption below 550 nm, as can be observed by the significant drop in reflectance. Then, at about 872 nm there is a broad absorption characterized by a concave inflection between 900 and 950 nm.

2.3.2.4. *Fe^{3+} hydroxides*

Goethite ($\alpha - Fe^{3+}O(OH)$)

Goethite has sheets of edge-sharing octahedra. Single and paired electronic processes give rise to strong absorption at ~ 425 and 480 nm and a broad absorption between 900 and 1000 nm. This mineral can be of two different types, ochreous or vitreous. Ochreous goethite is fine grained and yellow and is spectrally characterized by a deep absorption at ~650 nm, which is instead lacking in vitreous goethite. Vitreous goethite is instead dark brown, crystalline and dense. Goethite, in its ochreous form, is a very common hydroxide in areas undergoing pyrite oxidation. It precipitates at pH between 2.5 and 8 often together with other hydroxides such as ferrihydrite or sulfates such as schwertmannite. The latter two are metastable phases and eventually transform to goethite (Nordstrom and Alpers, 1999).

Ferrihydrite ($5Fe_2^{3+}O_3 * 9H_2O$)

Ferrihydrite includes a group of minerals with varying states of lattice disorder (Cull et al., 2014). It forms in slightly acidic to alkaline solutions with high amounts of dissolved iron. It is a metastable phase which eventually transforms either to hematite or to goethite as both have the same structure (hexagonal close packed). Ferrihydrite is generally fine-grained, however, it may have differing levels of crystallinity: '2-line' (low) and 'six-line' (higher) crystallinity. The major diagnostic absorption features are a sharp drop in the visible-ultraviolet range and a crystal field absorption at around 970 nm. Because it is fine grained,

the edge positioned at around 600 nm remains invariant and is useful for distinguishing ferrihydrite from goethite and schwertmannite.

However, a number of factors can affect the spectra of iron-bearing minerals and may make identification of single species complex without complementary mineralogical and geochemical data. Some minerals have very similar spectral signatures and absorption band positions may overlap in natural samples. This is the case for example of goethite and schwertmannite (Scheinost et al., 1998). In intimate mixtures or in rock spectra, some minerals may mask the presence of other minerals even if the former are not the most abundant. For example, ferrihydrite and schwertmannite can mask goethite, goethite and/or hematite can mask jarosite; or in mixtures of goethite and hematite, the feature at 900 nm shifts as a single absorption feature without showing evidence of the single components in the spectra (Cudahy and Ramanaidou, 1997; Cull et al., 2014; Hunt and Ashley, 1979; Townsend, 1987). Also the substitution of Fe^{3+} with Al^{3+} causes the 900 nm absorption feature to shift to longer wavelengths, due to the collapse of the unit cell (Buckingham and Sommer, 1983; Cudahy and Ramanaidou, 1997). Moreover, differing grain sizes change the shape of the reflectance spectra. When particle sizes are larger than the wavelength of incident radiation, scattering decreases with increasing particle size, meaning that the reflectivity decreases. When the particle size is smaller than the wavelength, scattering increases with increasing grain size. Even the position of the ~ 900 nm band minimum varies with grain size. Generally, there is a shift to longer wavelengths with decreasing particle size in cases of particles smaller than the wavelength. The smaller the crystals the higher the crystal surface affected by lattice edge distortion, the higher will the crystal field splitting energy be (Morris et al., 1985). These effects all together can cause absorptions to shift up to 30 nm (Cudahy and Ramanaidou, 1997; Morris et al., 1985). Therefore, the spectral signature of iron oxides in the VNIR is due to a combination of physicochemical properties which can be challenging to identify in natural samples where the co-presence of other iron-bearing minerals and oxides is common.

Interpretation of spectra in the VNIR becomes more challenging when these are acquired from imaging sensors, where the spectral band pass is coarser. These systems are also affected by environmental and instrumental noise. Especially sensors mounted on aircraft or satellite are affected by instrumental noise at shorter wavelengths and in the region between 900 and 1200 nm, due to the transition from the VNIR to the SWIR sensor, as shown for example in **Figure 2.5** for both EnMAP and sisuROCK sensors. In addition, atmospheric effects can hamper the identification of important absorption features in regions close to 760 nm, where the O_2 absorption occurs and ~ 950 nm affected by water vapor absorption (Murphy et al., 2014).

2.3.3. Remote Sensing for Mapping Mine Drainage

In the last decades, there has been a growing interest among remote sensing geologists in analyzing legacy mining sites affected by acid drainage. This is because, thanks to the unique spectral signatures of

secondary iron-bearing minerals, reflectance spectroscopy and hence remote sensing are fast and non-invasive techniques that allow to analyze large areas at once, effectively supporting ground survey and remediation activities by considerably cutting down on time and resources.

While some studies have focused on sources of acid drainage, detecting one mineral as indicator of acidity (Farrand and Bhattacharya, 2021), others have mapped the entire paragenesis of acid-generating minerals and their transformations at neutral to alkaline environments (Buzzi et al., 2016; Quental et al., 2013; Riaza et al., 2011; Shang et al., 2009; Swayze et al., 2000; Zabcic et al., 2014). These maps are able to show zonations of hydrated Fe-bearing sulfates stable at different humidity and oxidation conditions within an affected area (Montero S. et al., 2005; Swayze et al., 2000; Zabcic et al., 2014). The pH of an area can be derived by mapping secondary minerals resulting from the oxidation of sulfides. pH models deriving from spectroscopy studies of secondary minerals have been developed (Flores et al., 2021; Kopačková, 2014; Ong and Cudahy, 2014; Zabcic et al., 2009). pH maps give information on the conditions of acidity of tailings and therefore provide insight on oxidation reaction, supporting remediation efforts for neutralizing such environments. Secondary mineral maps on the other hand are indicators, not only of pH, but also of metal and sulfate levels of an AMD solution and can help forecast future mineral precipitation and dissolution with changing environmental conditions (e.g. precipitation, humidity, temperature), ultimately giving information on heavy metal mobility in the affected area (Zabcic et al., 2014).

Legacy mines and acid mine drainage affected sites are strongly dependent of time and seasons, as these are extremely variable environments (Velasco et al., 2005). Remote sensing gives the possibility of constantly monitoring the same area on a seasonal and yearly basis (Jackisch et al., 2018; Riaza et al., 2011; Riaza and Müller, 2010). This aspect is fundamental for authorities responsible for mine site remediation, in order to monitor the effects of their mitigation efforts, but it is also a sensitive indicator of climate change (Riaza and Müller, 2010).

Depending on the type of sensor and processing method, it is possible to detect such secondary minerals with varying levels of detail.

Airborne hyperspectral remote sensing is the preferred approach for AMD mapping and monitoring, as most studies have used airborne HyMap (Kopačková, 2014; Ong and Cudahy, 2014; Riaza and Müller, 2010; Shang et al., 2009; Zabcic et al., 2014), AVIRIS (Farrand and Bhattacharya, 2021; Ferrier et al., 2007; Rockwell et al., 2005) and CASI (Davies and Calvin, 2017; Ferrier et al., 2007; Gläßer et al., 2011) sensors. This is because airborne hyperspectral data is characterized by having a high ground sample distance (~ 5 m in most HyMAP applications and ~ 20 m for AVIRIS) and a high spectral band pass (1-2 nm in the range between 350-2500 nm). Lately, new sensors such as HySpex are able to provide images at a spatial resolution below 1 m and a spectral resolution of 3 (VNIR) to 6 (SWIR) nm (Bautista Gascuña, 2020). However, in recent year there is an increasing use of hyperspectral sensors mounted on drones for

monitoring and mapping acid mine drainage at the mine scale (Barroso et al., 2025; Chalkley et al., 2022; Flores et al., 2021; Jackisch et al., 2018). The advantage of drone-borne hyperspectral sensors is that the spatial resolution is reduced to values below 1 m or 50 cm, though limiting factors may be the need to acquire permissions to fly these instruments and the relatively short lifespan of the battery which allows to fly the drones for only 20-50 minutes depending on the weight of the sensor (Flores et al., 2021).

Due to the coarse spatial resolution (between 30 to 60 m), there are very few applications of hyperspectral satellite-based AMD mapping as of today (Mielke et al., 2014). This is because mining areas are relatively small and fine details in mineral maps are lost at resolutions higher than 15-20 m and spectral mixing within the image cells deteriorates the results (Chalkley et al., 2022; Davies and Calvin, 2017). However, satellite images, though having limited potential are nevertheless fundamental for providing a preliminary map of potential sources of acidity in mining sites and natural environments (Davies and Calvin, 2017).

The major processing methods used with hyperspectral images are spectral matching techniques, such as Spectral Angle Mapper (Bautista Gascueña, 2020; Buzzi et al., 2016; Quental et al., 2013) or Spectral Feature Fitting (Kopačková, 2014) or the Tetracorder expert system (Rockwell et al., 2005; Swayze et al., 2000). Others include sub-pixel analyses such as unmixing (Kopačková et al., 2012; Riaza and Müller, 2010; Shang et al., 2009; Zabcic et al., 2014), while quantitative approaches include machine learning techniques such as partial least square (Ong and Cudahy, 2014) and Random Forest (Flores et al., 2021) regression models.

Even if ideal instruments for distinguishing AMD minerals are hyperspectral sensors, multispectral satellite data such as Sentinel-2 and the Landsat collection are often used in these applications. Their advantage is related their decadal archive which allows to carry out multitemporal analyses over a given area of interest from weekly to yearly intervals (Pereira et al., 2023; Pyankov et al., 2021). Moreover, the higher spatial resolution, between 10 and 20 m is suitable for investigating areas from mine (Mielke et al., 2014; Seifi et al., 2019) to regional scale (Pereira et al., 2023). Most of the studies using Sentinel-2 data leverage band ratios (Pereira et al., 2023) or indexes (Pyankov et al., 2021), or even Spectral Angle Mapper (Seifi et al., 2019). Hosseinjanizadeh et al., (2023) combined Landsat OLI with Sentinel-2 data to map acid mine drainage sources by applying a sub-pixel analysis. SAM and sub-pixel methods, however, rely on reference spectra of endmember minerals. Though reference spectra from spectral libraries are available, these rarely reflect the phases found in the specific case studies, making it difficult to create an ad hoc library without carrying out extensive fieldwork. On the other hand, band ratios and spectral indexes do not allow to distinguish single mineral phases and are not suitable for quantitative analyses, if not only at a qualitative level. Sentinel-2 is ideal for the identification of Fe(III)-bearing minerals, thanks to its 9 bands in the VNIR spectral range (van der Meer et al., 2014). Though it has been shown that it is possible to apply knowledge-based approaches to Sentinel-2 data (Van Der Werff and Van Der Meer, 2015), as of today, to the author's knowledge there is no application with this type of methodology. With this work

a polynomial fitting technique is applied to Sentinel-2 images in the effort to distinguish between main iron-bearing minerals.

Although still highly toxic, neutral to alkaline drainage is hardly addressed using reflectance spectroscopy and remote sensing. Though not having the acidic component, saline and alkaline drainage can alter the composition of surrounding soils and cause the salinization of groundwater, negatively impacting aquatic and terrestrial biota. Moreover, neutral to alkaline mine drainage often also contains heavy metals such as Pb, Cd and Zn, transporting them in waterways and contaminating the surrounding environment (Cidu et al., 2021; Kučerová et al., 2014). Williams et al., (2002) distinguished acid from near neutral mine drainage through the detection of schwertmannite, ferrihydrite and goethite, assigning a near neutral pH to ferrihydrite dominated sediments and an acidic pH to schwertmannite and goethite dominated sediments. Pfitzner et al., (2018) mapped magnesium sulfates in a uranium mine affected area, using field spectroscopy and hyperspectral airborne data. Other studies addressing efflorescent salts are mainly focused on applications in planetary geology (Cloutis et al., 2006; Hughes et al., 2023; Stack and Milliken, 2015). As illustrated in the following sections, efflorescent salts were extensively identified along the banks of the Rio Irvi in the Montevecchio-Ingurtosu mining area. These are investigated with reflectance spectroscopy with the intent of understanding the chemistry of stream water.

3. Rapid Quantification of Rare Earth Elements using Reflectance Spectroscopy and Machine Learning

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3.1. Summary

Rare Earth Elements (REEs) are critical to the green energy transition due to their unique physical and chemical properties. Ten trivalent lanthanides, in particular, exhibit sharp and narrow absorption features in the VNIR-SWIR regions of reflectance spectra. While these features correlate strongly with elemental concentration, systematic empirical studies exploring this relationship remain limited, with most previous work focusing primarily on Nd prediction. This study develops a reliable and scalable method to quantify individual REEs from their spectral signatures. Random Forest Regression was applied to continuum-removed spectra to estimate the concentrations of Nd, Pr, Sm, Dy, and Er. The models were trained on a dataset of 130 globally sourced samples characterized both geochemically and spectrally using point spectrometers (ASD FieldSpec) and an imaging system (sisuROCK scanner). Feature importance analysis confirms that predictions were driven by element-specific absorption features. Of the five REEs evaluated, the method reliably quantified four, with the Er model being negatively affected by Dy co-occurrences. Results show that the approach is largely independent of mineralogy and robust to heterogeneous datasets, though accuracy depends on the size of the training set. The scalability of the methodology was assessed by applying the Nd model to hyperspectral datasets acquired under laboratory conditions (HySpex and sisuROCK imaging systems) and to the EnMAP satellite data of the Mountain Pass area. Prediction maps were validated against independent geochemical measurements. Overall, this work demonstrates the potential and flexibility of machine learning for quantifying individual REEs across different spectral and spatial scales, laying the foundations for future advances in quantitative spectral remote sensing of REEs.

3.2. Materials and Methods

3.2.1. Sample Suite Spectra

3.2.1.1. Point Spectral Data and Geochemical Analyses

We used 130 reflectance spectra of REE-bearing samples from various external sources, accompanied by geochemical analysis, as training data for the model. A summary of the datasets is provided in **Table 3.1**. Most spectra derive from natural rocks and minerals collected by different research groups across the world (**Figure A1. 1** in Appendix I). A subset of the collection (n=41) comprises clay minerals synthetically enriched with REEs to simulate regolith-hosted, ion-exchangeable REE deposits. The dataset also includes spectra of a suite of REE-doped synthetic silica-based glasses (n=15) provided by the University of Edinburgh, with known REE concentrations (Cairns, E. et al., 2024). Aside from the synthetic samples (43% of the entire dataset), data from at least 17 different REE-bearing minerals are reported to be present, making it a diverse training dataset (**Table A1. 1** in Appendix I).

Although all samples contain REEs, not all elements were analyzed for every sample, resulting in variable availability of geochemical data. Therefore, we developed quantitative models only for a subset of spectrally active elements for which sufficient samples were available and whose spectral expression is detectable in natural minerals. These include Nd (n = 130), Sm (n = 97), Pr (n = 105), Dy (n = 104), and Er (n = 102), with “n” indicating the number of records in each collection.

Table 3.1 Overview of the number of sample spectra used in this study, their types, the analytical techniques used to characterize them, and their sources. A full description of the samples and the methods/protocols used for analysis is provided in the referenced sources. Analytical techniques include X-Ray Fluorescence Spectroscopy (XRF), Electron Microprobe Analysis (EMPA), Instrumental Neutron Activation Analysis (INAA), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES), and Secondary Ion Mass Spectrometry (SIMS).

No. samples	Type	Spectral measurement device	Geochemical analysis technique	Source/Reference
32	natural	ASD Fieldspec-3	XRF, EMPA, INAA	Neave et al., 2016
41	synthetic	ASD Fieldspec-3	ICP-MS	Tan et al., 2021
33	natural	SPECIM sisuROCK	EMPA	Turner et al., 2014, 2016, 2018
9	natural	ASD Fieldspec-3	ICP-AES	Boesche et al., 2015
15	synthetic	ASD Fieldspec-4	EMPA, SIMS	https://geosciences.ed.ac.uk/about/facilities/all/ionprobe/technical/standards/ree/composition

As illustrated in **Table 3.1**, most spectral measurements were carried out using the ASD FieldSpec instruments. However, samples from Turner et al., (2018, 2016, 2014a) were acquired using a SPECIM SisuROCK core logger. For this dataset, the spectra were resampled to a 1 nm resolution using a shape-preserving cubic spline algorithm (Akima, 1970) to ensure consistency with the rest of the dataset. Two

spectral ranges were defined for the analysis: the VNIR range (470–913 nm) for modeling Nd, Er, and Dy, and the SWIR range (1000–1705 nm) for Dy, Er, Pr, and Sm. Such ranges correspond to spectral intervals where REE-related absorptions appear and that are not affected by atmospheric or instrumental interferences in satellite data. **Figure A1. 2** shows the correlation matrix between the spectral variables for the VNIR (a) and SWIR (b) intervals, respectively, highlighting numerous interdependencies, especially between adjacent wavelengths. To normalize the data and make the resulting models transferable across scales, the spectral continuum in these ranges was removed using a segmented straight-line method. Examples of continuum-removed spectra from all sources are shown in **Figure A1. 3** (VNIR) and **Figure A1. 4** (SWIR). At wavelengths below 600 nm in the VNIR range, spectra appear to be noisy in most natural samples, while spectra in the SWIR range are less affected by instrumental noise.

3.2.1.2. Imaging Spectroscopy Data

To test its generalization effectiveness, the Nd model was applied to three image cubes acquired in two different labs and one hyperspectral satellite image. Two of the lab images are of samples dominated by synchysite and bastnaesite minerals with known concentrations of REEs (Turner et al., 2014a) and acquired as part of a Ph.D. thesis (Turner, 2015). For both minerals, these were obtained by Electron Microprobe Analysis (EMPA) on unzoned and compositionally unchanging fragments of the crystals represented in the image cubes, assuming that these would be representative of the whole sample. The synchysite sample, collected from Narsarsuk, Greenland, consists of ~25 euhedral crystals, each about 1 mm long, embedded in a feldspar-biotite-rich matrix. The bastnaesite sample, from the Diao Lou Shan area of Sichuan, China, is a single crystal measuring 3 × 3 × 2 cm. Both images were acquired with a SPECIM sisuROCK logger at the University of Alberta with a spectral range between 396 and 1003 nm, a spectral sampling interval of 0.77 nm and a spatial resolution of 0.079 mm/pixel in the VNIR (Turner et al., 2014a). The noise of the image spectra at lower wavelengths (between 470 and 600 nm) was reduced using a Savitzky-Golay filter with the following parameters: a window size of 5, a second-order polynomial, and no derivative. The third image, named LP144, depicts a carbonatite drill core of a porous carbonatite from the Catalão I mine in Goiás, Brazil. The sample was scanned for this work using a HySpex VNIR-1800 camera at the University of Campinas, Brazil, with an illumination angle of 45°, covering the spectral range between 400–1000 nm with 186 channels, a spectral sampling of 3.26 nm, and a pixel resolution of 0.22 mm.

The satellite data was acquired by the EnMAP (Environmental Mapping and Analysis Program) imaging spectrometer over the Mountain Pass area in California, USA. This location provides an ideal test site for the ML model, as it hosts the largest REE mine in the US (Mariano and Mariano, 2012), and Nd has previously been detected using satellite data (Asadzadeh et al., 2024; Gadea et al., 2024; Rowan and Mars, 2003). The Level 2A image used in this study was acquired on July 7th, 2022. Details on the imagery order setting and preprocessing are provided in Asadzadeh et al. (2024). The band centered at 763.7 nm was excluded from the analysis due to interference from O₂ absorption, affecting the 740 nm feature of Nd.

We also prepared a ground-adjusted reflectance product by using spectral measurements on the ground (Ivanpah playa) collected by the USGS, to remove the residual atmospheric effects from standard L2A data. In this data, we excluded the following bands from the original data: 756.35 nm, 771.3 nm, 808.9 nm, 816.6 nm, and 842.3 nm related to O₂ and water vapor interferences.

3.2.2. Random Forest Regression (RFR) Modeling

A Random Forest Regression (RFR) model was developed on Python 3 using the scikit-learn library (Pedregosa et al., 2011). The model was built following a three-stage workflow. In the first stage, the entire point spectral dataset is split into training and testing sets in an 80:20 ratio. Then, hyperparameters are optimized through a randomized cross-validation procedure applied to only the training data, which is internally split in a training and validation subset. In the third stage, the performance of the RFR model is evaluated on the testing set.

The RFR algorithm is based on developing an ensemble of decision trees during the training phase. Each tree starts from a root node and ends with leaf nodes. It is built by randomly sampling a subset of the data and considering only a random selection of features to split into branches. The final prediction is the average of predictions made by all trees, which helps reduce the overall variance of the model (Breiman, 2001).

Table 3.2 Number of spectral samples used for each REE model and their partition into training and testing subsets.

REE	Total No. Samples	No. Training Samples	No. Testing Samples
Nd	84	67	17
Dy	48	38	10
Er	32	32	32
Sm	43	34	9
Pr	49	49	49

The structure of a RFR model is defined by a set of hyperparameters that specify the number and characteristics of the single decision trees. In this study five hyperparameters were used to build the models: (i) the number of trees in the forest, (ii) the maximum number of features each tree can consider, (iii) the maximum tree depth which is the longest path from root to leaf in a tree, (iv) the minimum number of samples required to split a node and (v) the minimum number of samples per leaf node (see **Table A1. 2** in Appendix I). Using ML algorithms with small datasets can lead to undesirable effects, such as overfitting. This is particularly common when the same data is used to train and test the model, but it can occur even when a subset of data is held out for testing. In this case, overfitting may ‘leak’ into the test set because the model excessively tweaks the hyperparameters to fit the data, thereby compromising its generalization capacity. To mitigate this risk, cross-validation techniques are used to check the

model's performance and fine-tune its hyperparameters to identify the best configuration. In this study, two cross-validation methods were tested using the randomized cross-validation search function (Pedregosa et al., 2011): repeated k-fold and leave-one-out. Since both provided similar results and identified the same optimal hyperparameters (see **Table A1. 2**), all subsequent tests were carried out using repeated k-fold. This technique subdivides the training data into k-folds, where iteratively k-1 folds are employed for training and one fold is used for validation. This process is repeated a user-defined number of times (expressed by the repeats parameter), over which the model's performance is averaged out. Each randomized cross-validation iteration yields a score, the highest of which defines the hyperparameters of the final model. In this study, the following cross-validation parameters were used: 10 folds, 10 repeats, 10 iterations, and mean-squared error as the scoring method.

Random Forest Regression was chosen for its ease of use, flexibility, and successful performance in previous studies related to this topic (Huang et al., 2021). Moreover, it was selected because it retains information about the importance of each variable in the model through its feature importance property. This property describes how much each feature or variable contributes to the model's decision-making process, based on its relative importance. Each feature is automatically assigned a score (between 0, no importance, and 1, maximum importance) based on the Gini impurity of the nodes in each tree, so that the sum of all the feature importance scores is ~1 (Pedregosa et al., 2011).

Here the features are represented by the single bands of the spectrum, which in the selected VNIR range (470-913 nm) are 444 nm and in the SWIR range are 706 nm at 1 nm spectral resolution. Compared to the number of samples for each REE model, the number of features is significantly higher. For this reason, the maximum feature hyperparameter interval was selected between 20 and 80 through a trial-and-error procedure. Features subset sizes above 100 ppm impair the model's ability to predict concentration values correctly, causing it to assign a single value to data points with concentrations of the same order of magnitude. This is also reflected in the feature importance graph. Despite the importances maintain their position with varying subset sizes, the relative importance follows a step-like distribution rather than a continuous one with clear maxima.

The geochemical data associated with the point spectral samples used as training data (Section 3.2.1) span several orders of magnitude. Therefore, it was necessary to transform the REE concentrations to a logarithmic scale for use in the RFR model. In addition, as the doped glasses exhibit the highest REE concentrations, sometimes an order of magnitude higher than natural samples, the models were tested twice: once including and once excluding the synthetic glasses.

During modeling, only the samples containing more than 10 ppm of each individual REE were selected, aiming to establish a balanced distribution of data across the whole range. Excluding zero or close to zero concentrations guarantees that the model would not need to handle negative or infinite concentration values on a log scale. Besides, it ensured that the number of low-concentration samples was comparable

to that of higher-concentration samples. Moreover, of the synthetically generated samples, only the ones doped with the corresponding element were chosen, excluding all others irrespective of their composition. Trial tests on the full sample suite consistently misinterpreted instrumental noise as meaningful data, erroneously assigning REE concentrations above 100 ppm to samples that lacked them, thereby reducing the model's overall predictive accuracy.

Table 3.2 shows the datasets used to model each element. The smallest dataset belongs to Er, while Nd has the highest number of samples. The models were trained by splitting the dataset into training and testing subsets in an 80:20 ratio for most elements. Just for Er and Pr, the models were trained and tested using all samples, due to the small size of the dataset (Er) and the inconsistent results observed after splitting the dataset (Pr), as further detailed in Section 3.3.2. The lack of independent validation may expose the models to overfitting and reduce their generalization ability. These models are nevertheless showcased for comparison of the feature importance results with the other models and to verify the potential applicability of this technique on these REEs.

Model performances were evaluated using the coefficient of determination (R^2) and the root mean squared error (RMSE) metrics defined by the following equations:

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$$
$$RMSE = \frac{1}{n} \sqrt{\sum_{i=0}^{n-1} (y_i - \hat{y}_i)^2}$$

where y_i and $\hat{y}_i$ are the measured and predicted single REE concentrations, respectively, while $\bar{y}$ is the mean measured concentration, and n is the total number of samples.

3.2.3. RFR Model Application on Images

To evaluate the transferability and scalability of the developed models, the one trained for Nd was applied to the three hyperspectral image cubes acquired in the lab and to the EnMAP image (described in Section 3.2.1.2). Besides the larger dataset size, another reason for which Nd was tested is that it is generally the most dominant lanthanide visible with reflectance spectroscopy and is commonly used as a pathfinder for other lighter REEs in remote sensing applications.

The original model was adjusted to each image data by resampling the point spectral data to the image's spectral resolution using Akima's cubic spline interpolation (Akima, 1970), thus obtaining simulated spectra of each imaging spectrometer. The best hyperparameters were first found by adapting the value ranges to the images' spectral resolutions (**Table A1. 3**) and by splitting the resampled dataset into training and testing subsets. The final predictions were achieved by training the model with all the data.

Before applying the model to each image, REE-bearing pixels were isolated using either the Spectral Angle Mapper (SAM) technique (Kruse et al., 1993) (for the sisuROCK lab-based images) or a spectral matching technique by considering the diagnostic absorption features of Nd at 740 and 800 nm (for the EnMAP image). Only no data pixels were masked out from the HySpex image cube, extracted using SAM, while Nd concentrations were modeled on the entire drill core. The continuum was removed between 470 and 913 nm for lab data and between 470 and 885 nm for EnMAP data to avoid atmospheric interferences at longer wavelengths. The dataset used for training the model did not include the synthetic glasses spectra, as the model trained without them showed superior performance (see Section 3.3).

For the synchysite and bastnaesite images, Nd prediction maps were validated against independent EMPA analyses carried out on the same minerals by Turner et al. (2014a), while the EnMAP results were verified with geochemical analyses performed on rock samples collected in the same area by the USGS in 2018. These samples, were analyzed for trace elements using Inductively Coupled Plasma-Optical Emission Spectroscopy-Mass Spectroscopy (ICP-OES-MS) (Verplanck et al., 2022). Unfortunately, geochemical data associated with the drill core were not available, and results were compared with a monazite matching score map, calculated with a spectral matching technique based on high-order polynomial fitting (Asadzadeh et al., 2024). With this technique, besides obtaining a map of the distribution of Nd-bearing monazite, it also provides indirect information on its relative abundance in the sample, as high scores are correlated with high abundances.

3.3. Results

3.3.1. RFR Model Training Results

The evaluation metrics shown in **Table 3.3** and **Figure 3.1** and **Figure 3.2** refer to the performance of the final RFR models for each analyzed REE, obtained after the cross-validation process. **Figure 3.1** and **Figure 3.2** plot the predicted concentration values against the actual concentrations (True values) on the test data subset. The highest R^2_{Test} was obtained on models trained excluding the synthetic glasses, although those with the glasses present a lower relative $\text{RMSE}_{\text{Test}}$, which is the $\text{RMSE}_{\text{Test}}$ divided by the entire data range. Nevertheless, all yielded models show a relatively low variance, with a relative $\text{RMSE}_{\text{Test}}$ less than 20% (**Table 3.3**). The best model belongs to Nd, which is trained with the highest number of samples, followed by the Sm model over the SWIR range. The high scores obtained for the Er and Pr models are because the input data was not split into training and testing sets, likely affected by overfitting. This is indicated by the very high R^2_{Test} approaching 1.

The ability of the model to generalize is evident from the results of the cross-validation process. **Table 3.4** compares the RMSE of the validation fold from the repeated k-fold process within the best cross-validation score (RMSE_{cv}) with that of the final model ($\text{RMSE}_{\text{Test}}$). Since the cross-validation values are on a logarithmic scale, the $\text{RMSE}_{\text{Test}}$ values were transformed into the same scale for comparison. For all

modeled elements, the $RMSE_{cv}$ values are higher than those of the final model. This is generally expected, as cross-validation employs a smaller dataset for training the model. However, the differences for the Er model are significantly larger than the others, possibly because the dataset is too small to produce stable and reliable results.

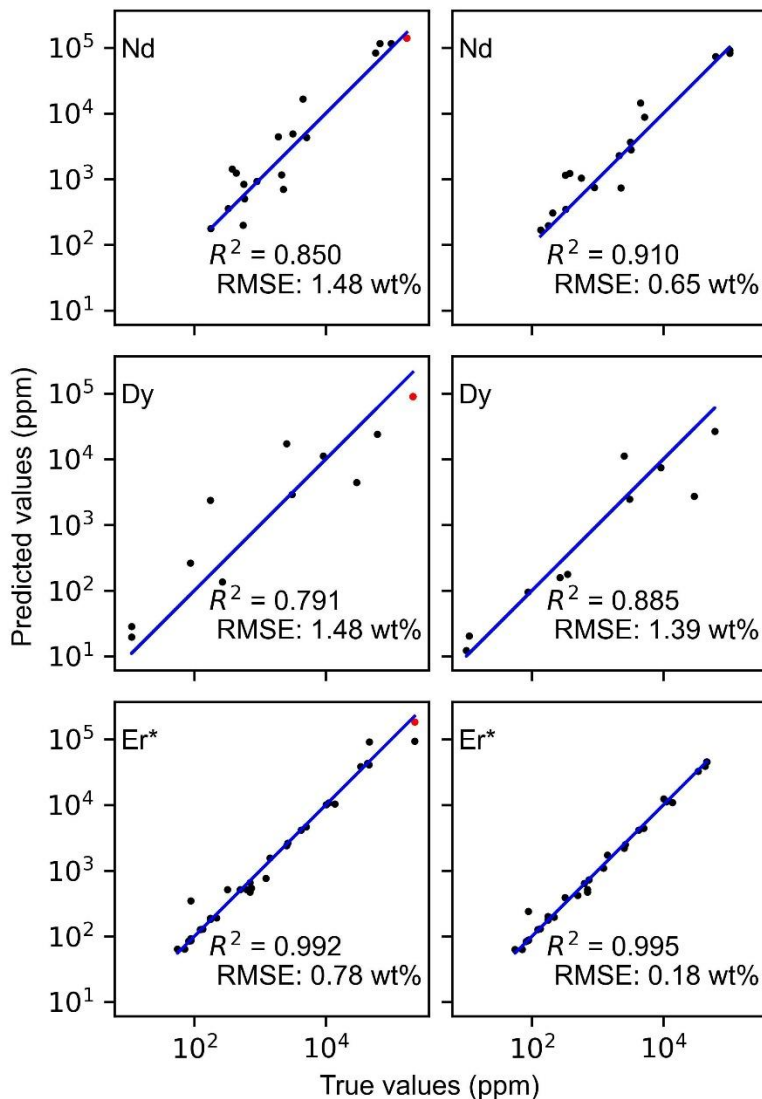


Figure 3.1 Regression plots of Nd, Dy and Er predictions on the testing data obtained from the final RFR model, using point spectral data above 10 ppm in the VNIR range. Left and right panels show results with and without the synthetic glasses, respectively. R^2 and RMSE are related to the test set. The red markers indicate the mono-lanthanide doped glass predictions. The Er model marked with an asterisk (*) was trained and tested using the entire dataset.

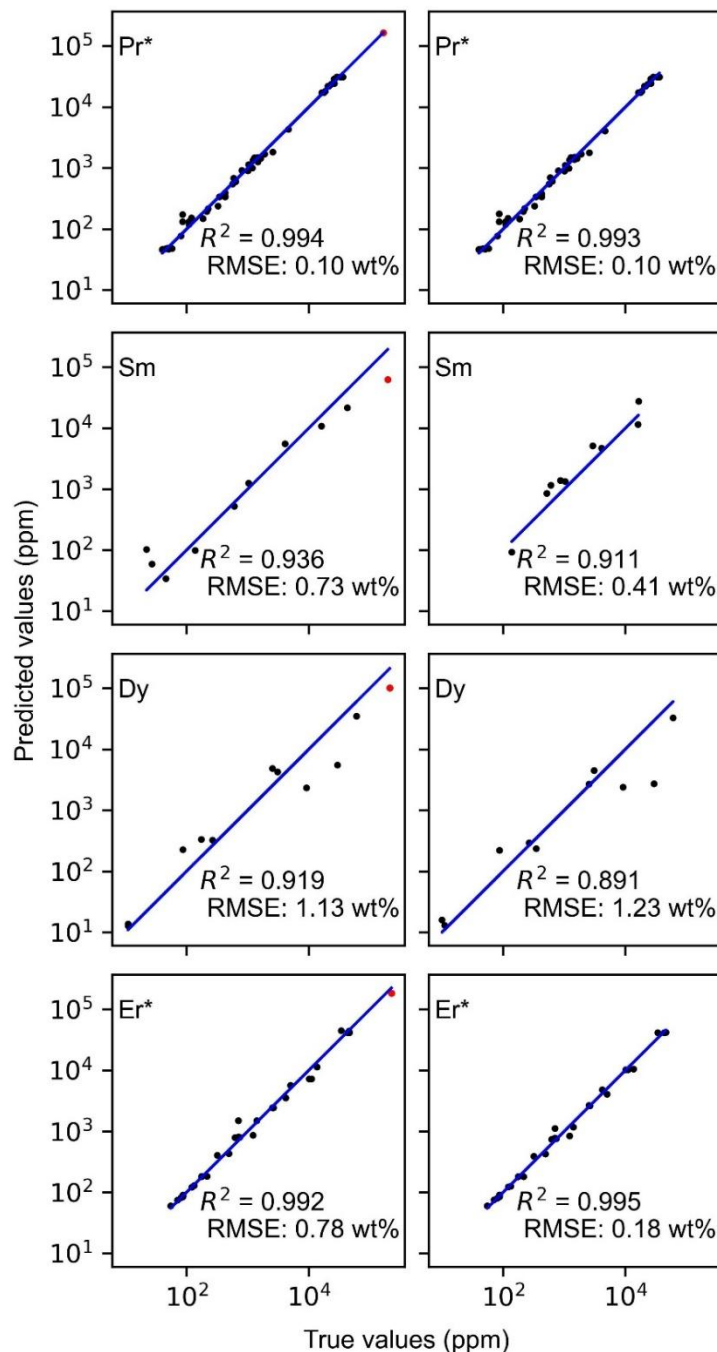


Figure 3.2 Regression plots of Pr, Sm, Dy and Er predictions on the testing data obtained from the final RFR model, using point spectral data above 10 ppm in the SWIR range. Left and right panels show results with and without the synthetic glasses, respectively. R^2 and RMSE are related to the test set. The red markers indicate the mono-lanthanide doped glass predictions. The models marked with an asterisk (*) was trained and tested using the entire dataset.

3.3.2. RFR Feature Importance

The feature importance of each REE model was compared to the spectral signature of natural minerals. Nd, Sm, and Pr were compared to a bastnaesite spectrum, while Dy and Er were compared to a xenotime

spectrum, both sourced from the USGS Spectral Library (v7) (Kokaly et al., 2017). **Figure 3.3** and **Figure 3.4** present feature importance results of models trained including glasses. Based on the feature importance results, the models select the appropriate features for estimating REE concentrations, all corresponding to known absorption features, demonstrating that the models are physically (and spectroscopically) meaningful and robustly constructed.

In the VNIR range (**Figure 3.3**), the models use features between 730 and 900 nm to predict Nd, Dy, and Er concentrations. The Nd predictive model relies primarily on multiple features around 740 nm and 860 nm, with some contributions from the features at 800 nm. The most important features of this element are located within the range of 860–868 nm, with a maximum at 863 nm, and within 732–745 nm, with a maximum at 736 nm. For Er and Dy, the most relevant features are concentrated around 800 nm. Whereas the Er model emphasizes features centered at 800 and 817 nm, the Dy model highlights features at 780 nm, corresponding to the right and left shoulders of the 800 nm absorption minima, respectively. Yet, the models differ in the way they use the composite absorption features at ~800 nm. Dy model relies heavily on the 800 nm peak itself. Er model incorporates multiple absorption bands to the left of the peak, along with several minor features beyond 820 nm. In summary, while all models use the composite feature at ~800 nm for their predictions, the specific usage varies, as reflected in the geometry of the feature importance distributions shown in **Figure 3.3b-c**.

In the SWIR range, the relative importance of features varies across the four models. Samarium highlights three sets of nearly equally important features, centered at 1087, 1559, and 1530 nm, and one strong importance at 1220 nm, not confirmed in the dataset without glasses (see **Figure A1. 5**). Similarly, the Er model emphasizes the range between 1554 and 1600 nm, with a maximum feature importance at 1558 nm, and partial contribution from a feature at 1015 nm. In contrast, the Dy model primarily extracts information from features between 1190–1300 nm, with additional contributions from features at 1420 nm. The Pr model extracts information primarily from a range between 1450 and 1490 nm. However, determining the feature importance for Pr proved challenging. When splitting the dataset into training and testing subsets, the feature importance results varied with each test, suggesting that the model struggled to identify specific wavelength ranges associated with Pr concentration, possibly due to insufficient training data. On the other hand, the RFR model may underestimate Pr concentrations, as these are obtained from absorption features deriving from Pr^{3+} . The possible presence of Pr^{4+} appears invisible in this spectral range. To address this, the model shown in **Figure 3.4d** was trained on the entire dataset, with the pattern remaining consistent with and without glasses.

The effect of glasses on the feature importance varies with the size of the training dataset (see **Figure A1. 5** and **Figure A1. 6**). In larger datasets (e.g., Nd and Pr and Dy-SWIR), the feature importance plots with and without glasses are very similar. For Sm, the positions of the feature importance maxima do not vary significantly, but the dataset with glasses gives higher importance to the feature at 1220 nm, followed by the ranges between 1527–1532 nm and 1084–1110 nm at almost equal importance. Instead, the dataset

without glasses does not consider the 1220 nm feature at all and focuses mainly on the 1084-1110 nm range. A similar behavior is observed in the Dy-VNIR model, where the features centered at 808 and 819 nm, followed by the 872 nm feature, are highlighted in the dataset without glasses. This relative importance difference may be due to slight absorption shifts of diagnostic features between the synthetic glasses and natural minerals. In contrast, the feature importance plots of Er (VNIR and SWIR) with and without glasses are quite distinct. The models trained without glasses have feature importance distributions very similar to Dy, such as the 909 nm feature or the features in the 1190-1300 nm range, suggesting that the Er model may be picking Dy diagnostic features for its predictions.

Table 3.3 Regression metrics of the final model applied on the test set after cross-validation, grouped by individual REE and wavelength intervals. The elements with an asterisk (*) were trained and tested using the entire dataset.

	REE	Without glasses			With glasses		
		R^2_{test}	RMSE _{test} (%wt)	Relative RMSE _{test} (%)	R^2_{test}	RMSE _{test} (%wt)	Relative RMSE _{test} (%)
VNIR	Nd	0.910	0.653	5.169	0.850	1.476	8.643
	Dy	0.885	1.392	16.388	0.791	1.480	7.035
	Er*	0.989	0.111	2.406	0.976	2.451	10.944
SWIR	Dy	0.891	1.232	14.502	0.919	1.129	5.368
	Er*	0.995	0.182	3.968	0.992	0.780	3.481
	Pr*	0.994	0.105	2.905	0.994	0.103	0.629
	Sm	0.911	0.408	9.576	0.936	0.726	3.721

Table 3.4 Comparison between the RMSE obtained on the best validation fold of the cross-validation (RMSE_{cv}) process and RMSE values for the final model on the test data (RMSE_{test}) on a logarithmic scale for all REE. Elements marked with an asterisk (*) were trained and tested using the entire dataset.

	REE	With glass			Without glass		
		RMSE _{cv}	RMSE _{test}	Difference	RMSE _{cv}	RMSE _{test}	Difference
VNIR	Nd	0.464	0.317	0.147	0.424	0.273	0.151
	Dy	0.656	0.582	0.074	0.533	0.429	0.104
	Er*	0.721	0.156	0.565	0.619	0.099	0.520
SWIR	Dy	0.606	0.363	0.243	0.573	0.419	0.154
	Er*	0.805	0.091	0.714	0.523	0.067	0.455
	Sm	0.421	0.289	0.132	0.289	0.196	0.093
	Pr*	0.430	0.076	0.354	0.369	0.078	0.291

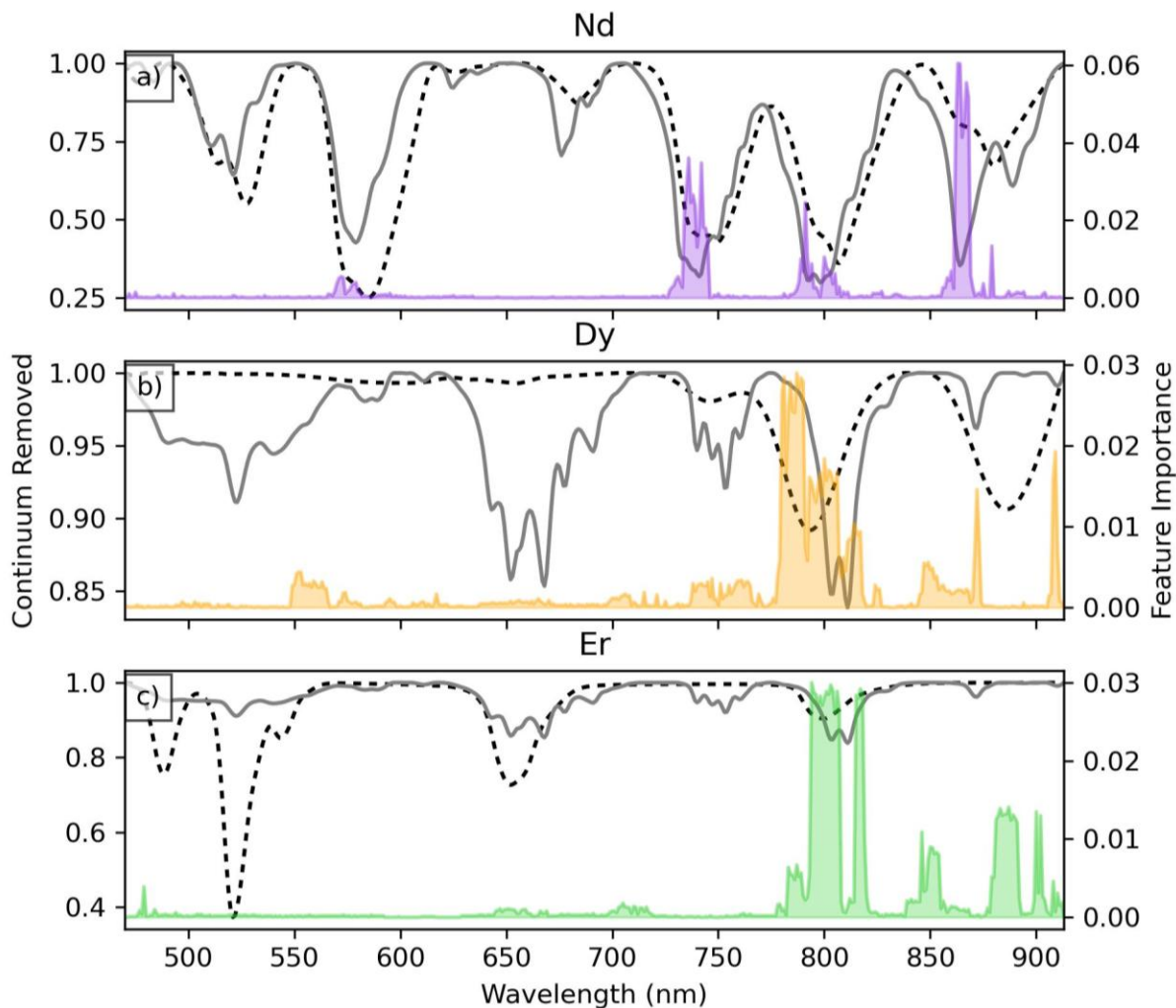


Figure 3.3 Feature importance of Nd, Dy and Er final models in the VNIR range. These are superimposed on the continuum-removed spectral plot of bastnaesite (a) and xenotime (b-c) sourced from the USGS spectral library, V7 (grey continuous line) and the continuum-removed spectrum of the related mono-lanthanide doped glass (dashed black line).

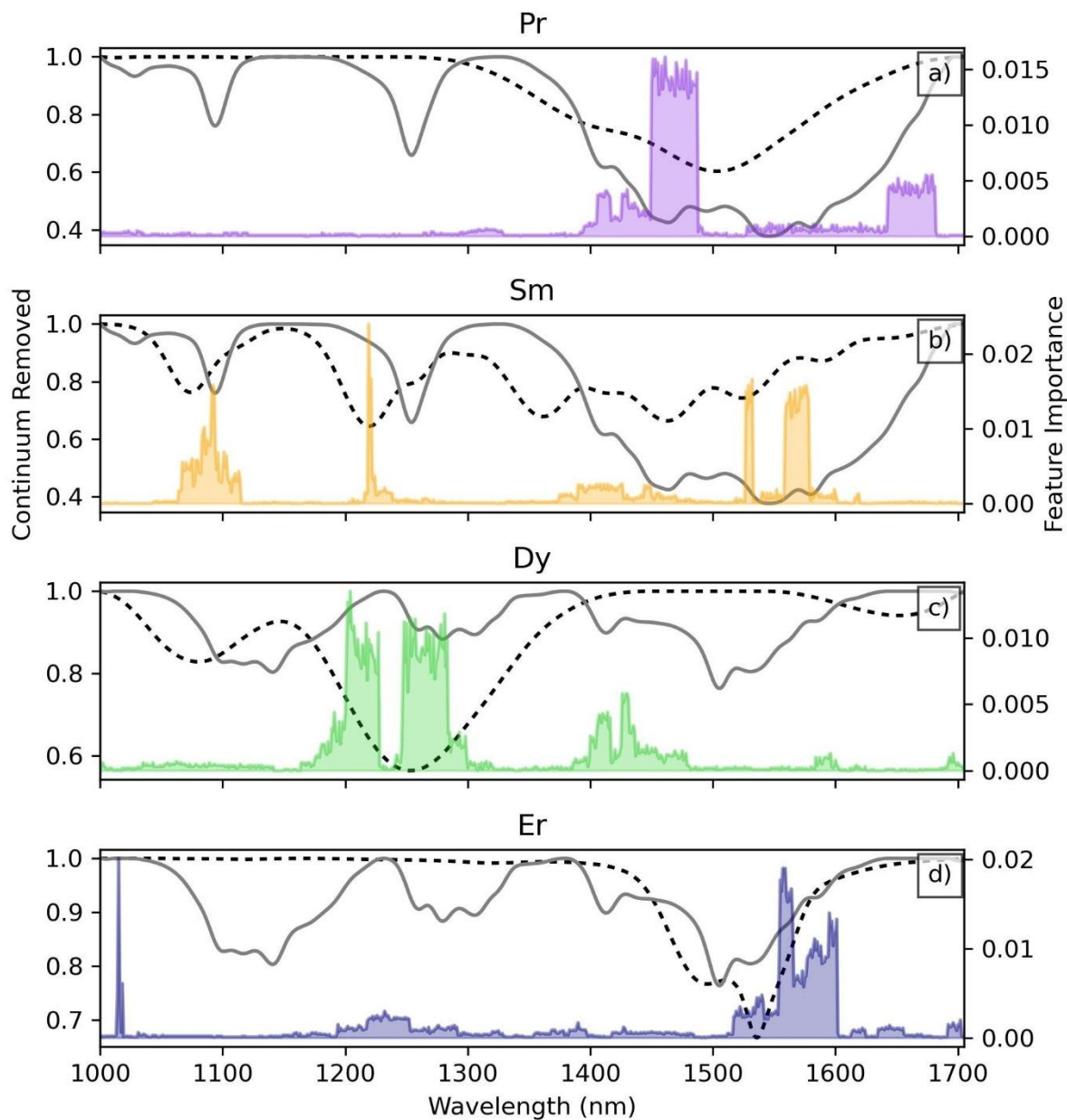


Figure 3.4 Feature importance of Sm, Pr, Dy and Er in the SWIR range These are superimposed on the continuum-removed spectral plot of bastnaesite (a-b) and xenotime (c-d) sourced from the USGS spectral library, V7 (grey continuous line) and the continuum-removed spectrum of the related mono-lanthanide doped glass (dashed black line).

3.3.3. RFR Model Applied to Images

3.3.3.1. Synchysite and Bastnaesite Images

The Nd predictive model applied to the two lab-based hyperspectral datasets (**Figure 3.5a-b**) revealed concentration values ranging from ~7000 ppm to >90000 ppm. The bastnaesite-rich sample shows greater concentration variability compared to the synchysite sample. This is displayed visually on the Nd

prediction maps (**Figure 3.5c-d**) but also on the histogram of their pixel values (see **Figure A1. 7**), where bastnaesite has a clear bivariate distribution. The level of noise in the imagery pixels appears to affect the predictions, with spectrally smoothed images yielding more consistent results, as highlighted in model performance (see Section 3.4). Analysis of the spectra of 4 random points selected from the prediction maps (**Figure 3.5e-f**) of both synchysite and bastnaesite samples indicates that the absorption depths at ~740, ~790, and ~870 nm increase with the increase of Nd concentration following a non-linear behavior. To assess the effectiveness of the mapped predictions, the mean Nd concentration over all analyzed pixels was calculated for both images and compared with the average concentration measured using the EMPA method (Turner et al., (2014a), see **Table 3.5** and **Table 3.6**). Based on this comparison, the models trained without synthetic glasses exhibit average concentrations closer to those obtained with EMPA. The addition of synthetic glasses causes the model to predict higher Nd concentration, by up to 10000 ppm (see **Figure A1. 7**). The average Nd concentration calculated for the synchysite sample closely matches the value reported in Turner et al. (2014a). In contrast, for bastnaesite, there is a relative difference of about 20% in the best performing model (i.e., trained without glasses and applied on the smoothed image). Although the EMPA concentrations are here considered as reference values, these are an average of measurements acquired in different parts of the same crystal, with the assumption of it being compositionally constant, while the model detected variations within the bastnaesite crystal. This could, in part, explain the larger offset between the RFR model results and the EMPA concentrations. The slight discrepancy between smoothed and unsmoothed images suggests that sensor noise has a negative influence on predictions.

Table 3.5 Average Nd concentration and its standard deviation predicted on the synchysite image data obtained from models trained with and without glass samples. The results are also compared with the EMPA data collected by Turner et al., (2014a), here considered to represent the reference value.

		Average concentration (%wt)	St. Dev. (%wt)	EMPA (%wt)
Glass	Smoothed	7.98	0.37	7.07
	Not smoothed	7.90	0.58	7.07
No Glass	Smoothed	7.02	0.32	7.07
	Not smoothed	7.33	0.55	7.07

Table 3.6 Average Nd concentration and its standard deviation predicted on the bastnaesite image data obtained from models trained with and without glass samples. The results are also compared with the EMPA data collected by Turner et al., (2014a), here considered to represent the reference value.

		Average concentration (%wt)	St. Dev. (%wt)	EMPA (%wt)
Glass	Smoothed	8.01	0.72	6.22
	Not smoothed	7.99	0.89	6.22
No Glass	Smoothed	7.40	0.72	6.22
	Not smoothed	7.46	0.82	6.22

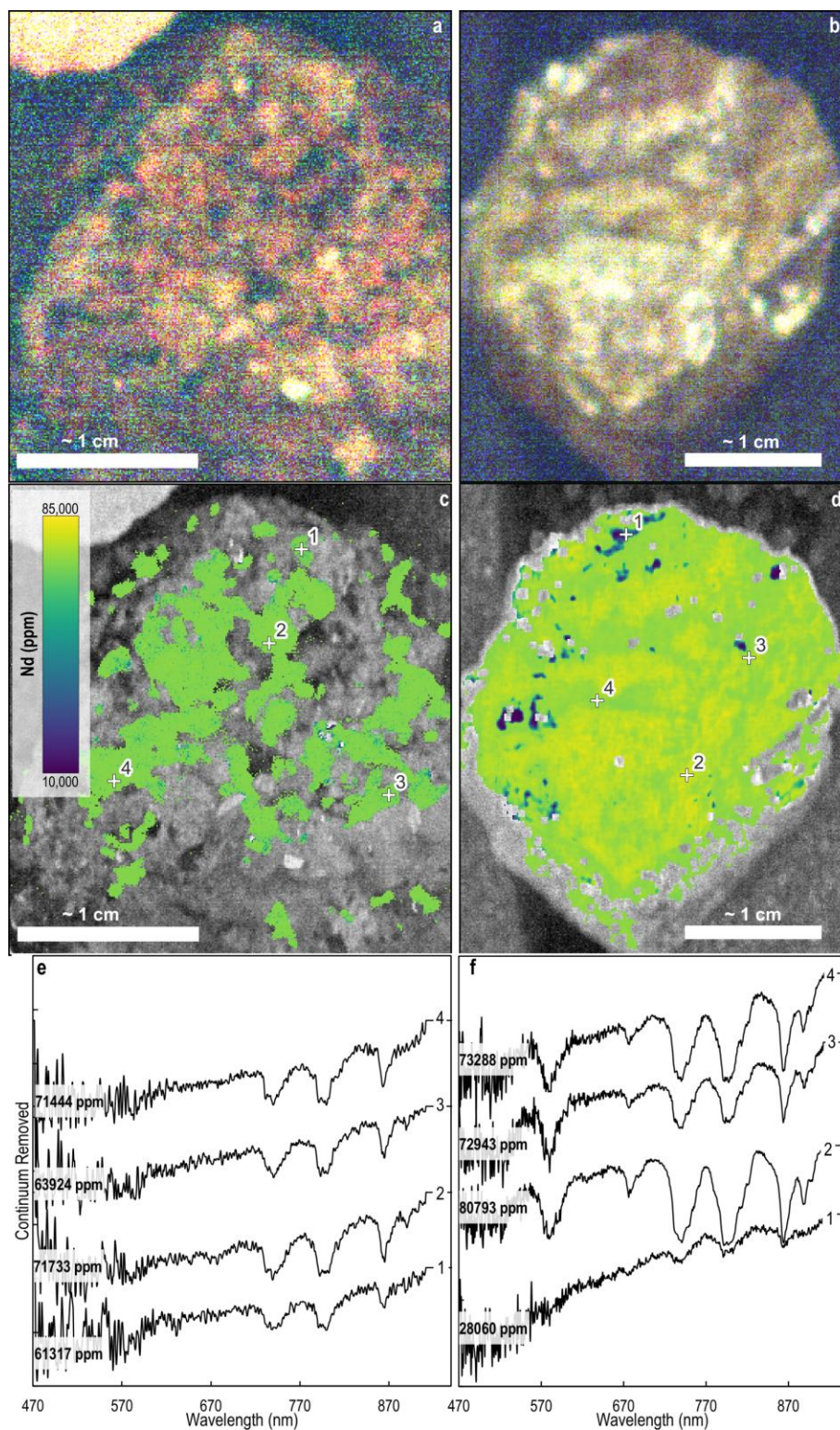


Figure 3.5 RGB images of (a) synchysite- and (b) bastnaesite-rich samples and their respective ML-based mapping of Nd concentration using continuum removed image data (c-d). The predictive model used was trained without glass samples. Spectra in (e) and (f) correspond to points indicated by a cross in (c) and (d), respectively showing pixel spectra with varying amounts of Nd contents.

3.3.3.2. *Carbonatite Drill Core Sample (LP144)*

Figure 3.6 presents the true-color image of the LP144 carbonatite drill core sample (a), its predicted map for Nd (b), and its comparison with the spatial distribution and relative abundance of monazite obtained through spectral feature matching (c). The results highlight a vein with high Nd concentrations extending from the upper-left to the lower-right section of the drill core. The estimated Nd content varies from approximately 600 ppm to over 65000 ppm. The spatial pattern obtained with the RFR model aligns well with the results obtained using the spectral matching technique. This is also confirmed by the spectra in **Figure 3.6d** referring to points represented in **Figure 3.6b-c**, where areas with high predicted concentrations show defined Nd diagnostic features at ~740 and 800 nm. However, there are some cases where the RFR model may overestimate Nd concentrations and does not match the monazite model. For example, point 3 has an estimated Nd concentration of 22385 ppm, while the very low monazite matching score and the related spectrum indicate the opposite. The model was also tested on another image cube of a drill core coming from the same mine and acquired with the same sensor but affected by higher noise levels. The results (not shown here) between the Nd predictions output by the RFR model and the monazite matching score did not converge as well as in the case depicted here. This suggests that the RFR model was not able to handle noise, overestimating Nd concentrations in areas where this was more prominent. However, the spectral feature matching technique only detects Nd features related to monazite, but not necessarily to other REE-bearing minerals within the sample, leading to a potential underestimation of the Nd concentrations.

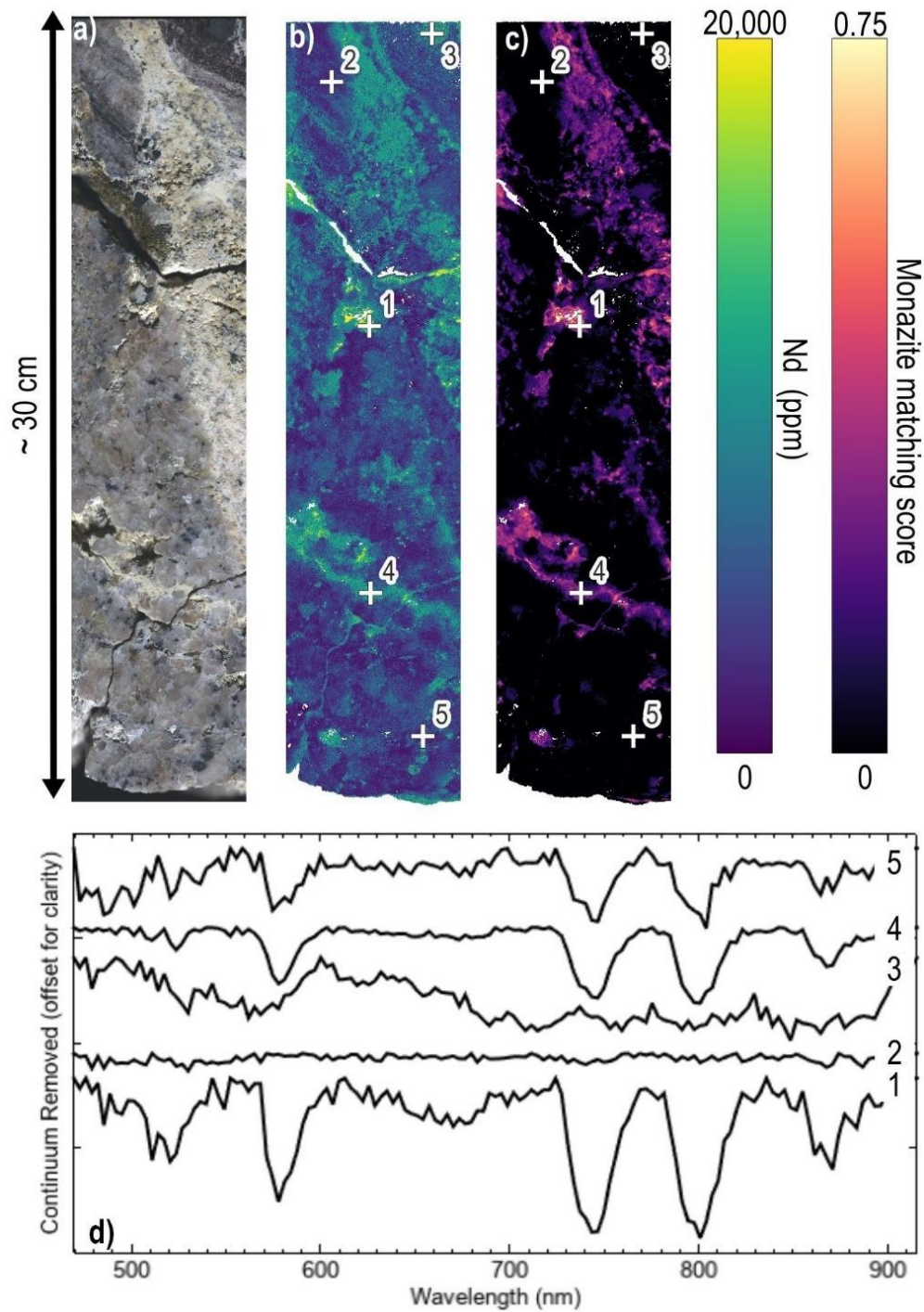


Figure 3.6 (a) RGB image of a carbonatite drill core scanned using HySpex imaging system in the lab. (b) RFR-based mapping of Nd concentration and (c) is the map of possible distribution and relative abundance of monazite obtained through a spectral matching technique. The higher the monazite matching score, the closer the pixel spectra are to the monazite reference spectrum. (d) Spectral plots corresponding to the pixels marked by a cross in (b) and (c).

3.3.3.3. EnMAP Satellite Data

Figure 3.7a is an image of the Mountain Pass mine. **Figure 3.7b** shows the predictive map for Nd concentrations over the Mountain Pass mining district using the EnMAP L2A data. Areas of higher Nd are located within the open pit and near the crusher and tailings. Points 1 and 2 exhibit the highest Nd concentrations, as evidenced by their corresponding spectra containing strong absorptions at 740 and 800 nm (**Figure 3.7c**). The spatial distribution of Nd content in **Figure 3.7b** aligns with the findings of Asadzadeh et al. (2024).

To evaluate whether the quality of atmospheric correction affects the performance of the model, we applied the same model to ground-adjusted reflectance data (not shown here). However, the results were significantly lower than those obtained with the standard reflectance data. We speculate that this discrepancy arises from the exclusion of key spectral bands near the O₂ absorption feature at 760 nm, which likely impairs the model's ability to accurately predict Nd concentration. In other words, standard reflectance data from EnMAP should be sufficient for remote sensing-based concentration mapping for Nd.

A comparison between the model-predicted values per pixel and the bulk-rock geochemistry of samples collected in the field during 2018 is shown in **Figure 3.8**. The predicted values for Nd concentration appear to be systematically underestimated, with a correlation coefficient of 0.58 between the predicted and measured values. However, the model seems to perform reasonably well for medium to low Nd concentrations but severely underestimates higher concentrations, even though the pixel values fall at the upper end of the prediction range. The systematic underestimation may be attributed to several factors, but primarily the point-scale properties of the samples compared to a 30x30 m image pixel, which aggregates multiple non-REE-bearing geological features. Moreover, the Nd quantities provided by bulk-rock geochemistry relate to the volume of the hand samples, while the predictions obtained from the satellite data refer to geological materials at the surface of the Earth. Additionally, there is a gap of over four years between the sample collection and the image acquisition, particularly over the mining area, where activities are quite dynamic. Despite this, the results obtained are reasonable and follow the same patterns observed in field data. Indeed, while the average predicted Nd concentration over the mine pit is 4003 ppm, the maximum estimated value is 12000 ppm, which is comparable to the average Nd concentration measured on the hand samples collected in the same pit (10595 ppm).

As highlighted in the literature, the diagnostic absorptions of Nd that are most useful for remote sensing mapping are those centered at ~740 and ~800 nm, with those at lower and higher ends affected by chlorophyll and water vapor absorptions, respectively (Asadzadeh et al., 2024; Clark et al., 2003). To test this, a spectral subset of the data between 700 and 885 nm was used to predict Nd concentrations. Results indicated that the model's R² slightly decreases to 0.86, with an RMSE of 0.95%wt. A pixel-by-pixel comparison revealed that the differences with the VNIR full-range are 25%, on average, while

maintaining the same spatial pattern. When compared with ground data, the correlation coefficient of the subset model improved to 0.6, but the mapped pattern shown in **Figure 3.8** remained unchanged.

As reported by Asadzadeh et al. (2024), the evaporation ponds to the north of the mine show anomalous Nd concentrations. Attempts to estimate the Nd concentration over this area were hampered by the presence of water, as the model was not trained to cope with water-containing spectra. Consequently, the results were excluded from the map in **Figure 3.7**.

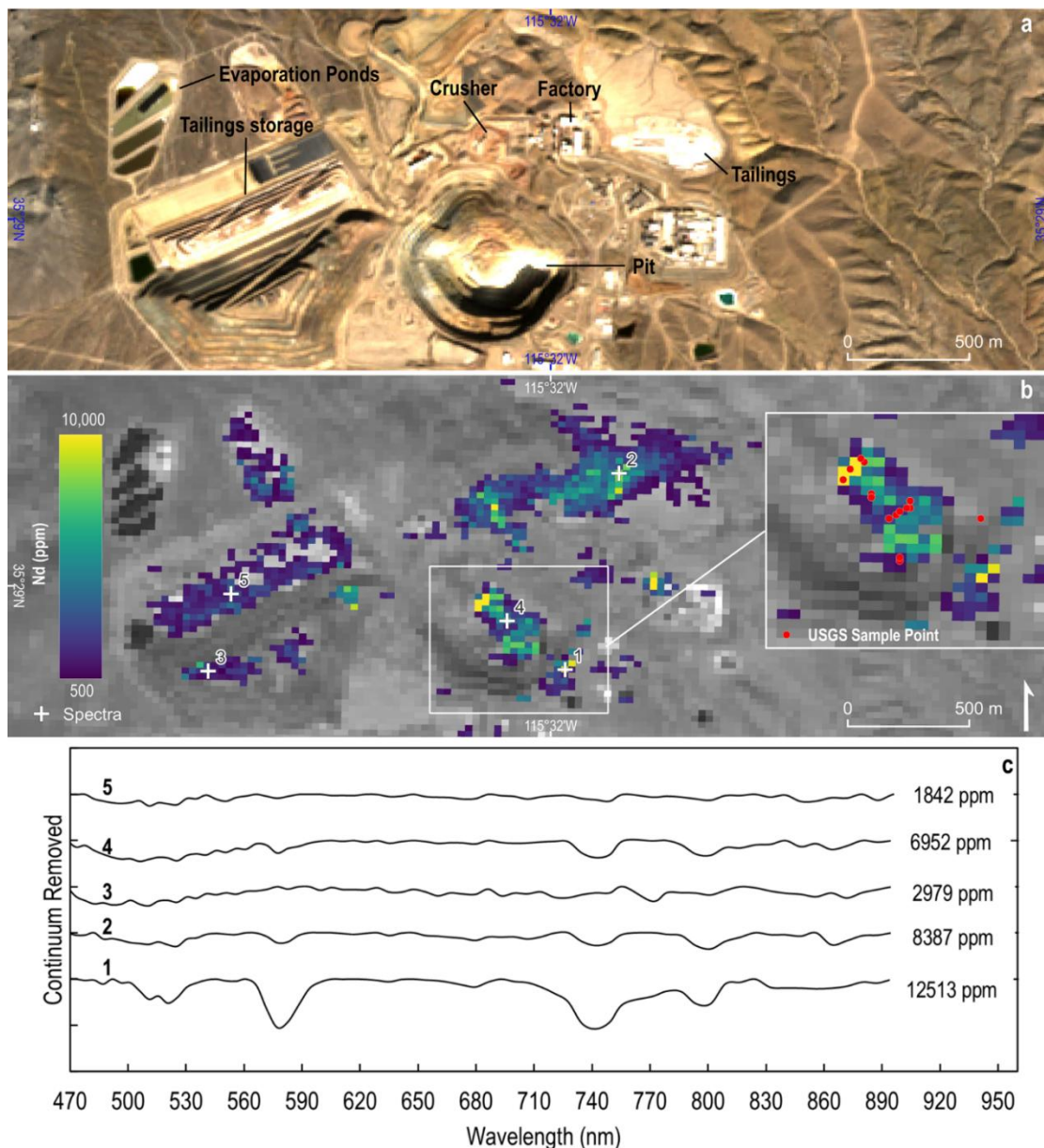


Figure 3.7 (a) True color Sentinel-2 image of 17/12/2025 of the Mountain Pass mine. (b) RFR-based mapping of Nd concentrations, expressed in ppm, over the Mountain Pass mining area using EnMAP hyperspectral data. The inset map indicates the locations of the samples ($n = 22$) used to validate the model, collected by the USGS (Verplanck et al., 2022). (c) the EnMAP pixel spectra corresponding to points marked by cross in (b) with numbers matching each other.

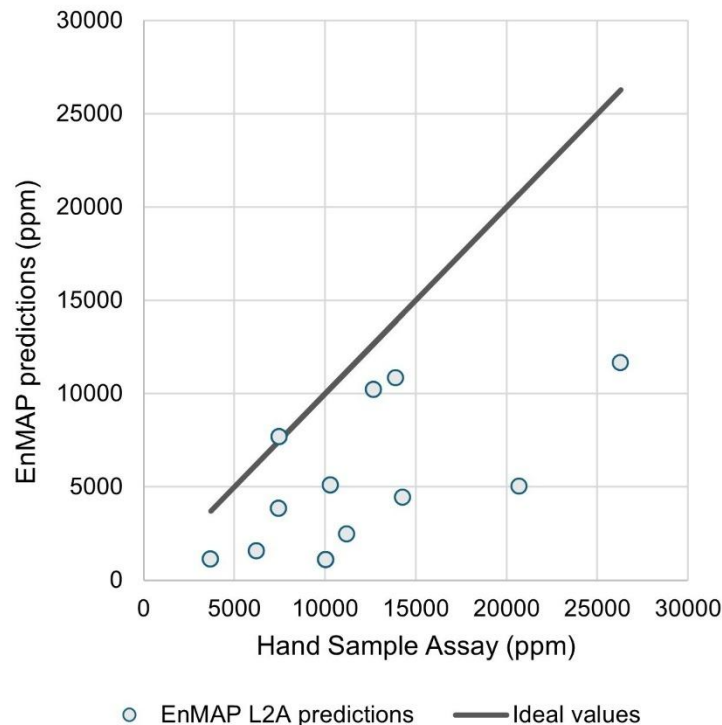


Figure 3.8 Comparison of EnMAP-based model predictions vs. measured Nd concentrations from rock samples collected in the corresponding locations. The 1-to-1 line is shown in solid black.

3.4. Discussion

3.4.1. Advantages of the Method

The strength of ML lies in its ability to estimate complex non-linear patterns from a dataset through a learning process, without the need for a data distribution assumption (Zuo, 2017). This study confirmed findings of previous studies, where RFR proved to be effective for this purpose in geochemical and mineralogical applications (Dhoundiyal et al., 2025; Huang et al., 2021; Qasim and Khan, 2022; Schnitzler et al., 2019). Here, we obtained a model that is relatively insensitive to data variability and therefore generalized for each analyzed REE. Samples had strongly differed REE concentrations spanning from 0 to more than 100,000 ppm. In addition, the input dataset is a collection of spectrs from 17 different minerals from diverse deposits across the world. With these conditions, satisfactory results have nevertheless been obtained in this work, despite recent studies that have emphasized the critical role of mineralogy in controlling the shape and positions of absorption features of REEs (Dijkstra et al., 2024; Turner et al., 2014a), and its influence on quantitative modeling (Kopačková-Strnadová et al., 2021).

However, the key factor that determines the success of this approach is the introduction of expert knowledge in the workflow. Cropping reflectance spectra to only significant wavelength ranges drives the RFR model to select features related to specific absorptions, which are a direct expression of REE

physical properties. This effect is evident when observing the feature importance results. A comparison between these and the crystal field absorption features of synthetic xenotime and monazite, as studied by Dijkstra et al. (2024), reveals a strong correspondence between the ML model's highlighted features and the REE-specific absorptions of individual elements (see **Figure 3.9**). This demonstrates the effectiveness of the model in extracting physically meaningful information from spectral data. Notably, the features with the highest importance often correspond to persistent absorption features observed in several minerals.

Though, as evident in **Figure A1. 2**, spectral data at different wavelengths are highly correlated, the ML model selected only features that are unambiguously associated with Nd, Sm, and Pr. In some cases, however, the model also highlighted features shared by multiple REEs, suggesting that predictions in these regions may reflect groups of elements (e.g., Dy and Er, or Sm and Pr). One reason is the inherent correlation between different REEs in natural samples (**Figure A1. 8**). For elements that are highly correlated and overlap spectrally, such as Er and Dy ($R = 0.96$), the more abundant element is also spectrally dominant, exerting a stronger influence on quantification estimates. Consequently, the feature importance diagrams for these elements are very similar (**Figure 3.9a**). Some REEs such as Eu, Gd, Tb, Ho, Er and Lu, are almost never dominant in any mineral because their absolute abundance is too low compared to other members of the lanthanide series and there are no geochemical processes that separate and concentrate these individual elements to form their own minerals. This aspect further contributes to explaining the poor separability of Er with Dy, though further analyses should be conducted with a larger dataset to confirm this hypothesis. On the other hand, elements that are highly correlated but spectrally distinct, such as Nd with Sm (0.77), Pr with Nd (0.99), and Sm with Pr (0.72), remain spectrally separable, allowing for accurate quantification. Pairwise correlation plots of predicted REE concentrations closely align with those of the original input data in terms of both correlation coefficient and patterns, as well as the concentration distribution of each single element. Correlation between Dy predictions in the VNIR and SWIR ranges are very high (approaching >0.9), indicating that predictions are consistent across the spectral ranges. This is an indication that the models accurately reproduce the relationships among different REEs present in the input dataset (see **Figure A1. 9**). One other reason for shared features could be the limited spatial resolution of the instrument, preventing it from distinguishing the very narrow absorption features of individual elements.

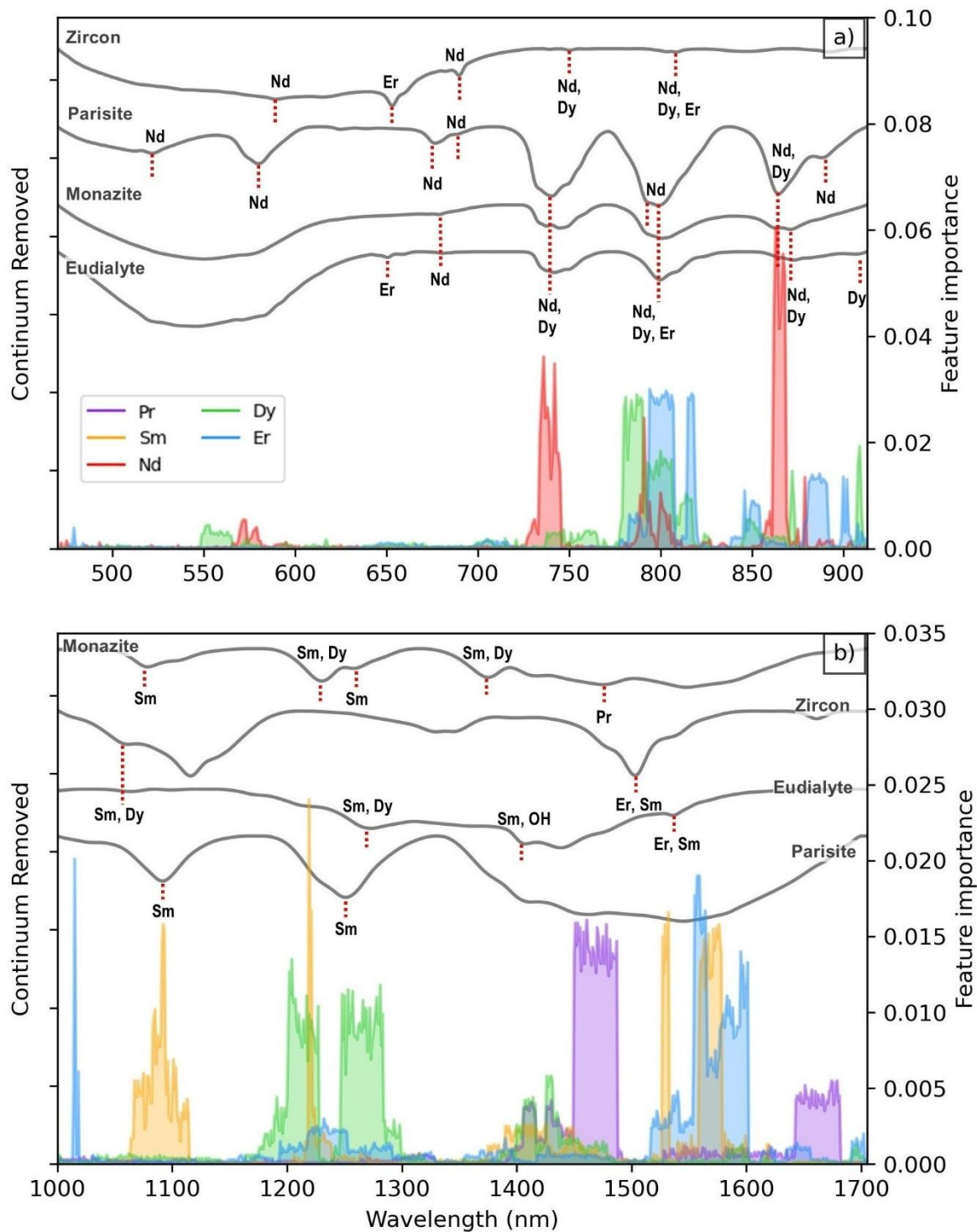


Figure 3.9 Feature importances of Nd, Dy and Er in the VNIR range (a) and of Pr, Sm, Dy and Er in the SWIR range (b) overlain with the spectra of different REE-bearing minerals from the Canadian National Mineral Reference Collection (NMC) (Percival et al., 2023). Probable origins of the features are noted based on studies by Dijkstra et al. (2024), Turner et al. (2014a, 2016, 2018) and Möller and Williams-Jones (2018).

Spectral and spatial resolution are known to have a considerable impact on the model's performance. Generally, higher spectral resolution can lead to improved predictions. This is particularly evident in **Figure 3.10a**, where the coefficient of determination is plotted against the RMSE for each simulated sensor type used in this study. Among them, while the R^2_{test} is similar for all sensors (between 0.90 and 0.91), simulated spaceborne EnMAP spectra (with a 6.5 nm spectral sampling interval in the VNIR) exhibit, as expected, a slightly higher RMSE value. Of the laboratory datasets, ASD spectra perform best, followed by simulated HySpex (with 3 nm spectral interval in the VNIR) and sisuROCK instruments (**Figure 3.10a**). The effects of spectral sampling interval are also evident in the relative importance of features used for the model construction (**Figure 3.10b**), with broader intervals relying on fewer features to construct the model (e.g., EnMAP). In contrast, high-resolution sensors like ASD can better resolve the complexity of crystal field absorptions, increasing the number of features useful to the prediction, yet spreading the importance scores over a broader range in the plot. The positions of features and their relative importance remain consistent across all sensors. This consistency demonstrates the model's scalability to coarser spectral resolutions, as demonstrated in this study. Spatial scalability is also evident: EnMAP's coarse spatial resolution (30 m pixel size) is the main reason for the underestimation of Nd concentrations in some pixels, since its spectra are the result of heterogeneous surfaces containing various minerals and materials of different sizes and orientations. Even so, the predicted relative concentration maps align reasonably well with field data.

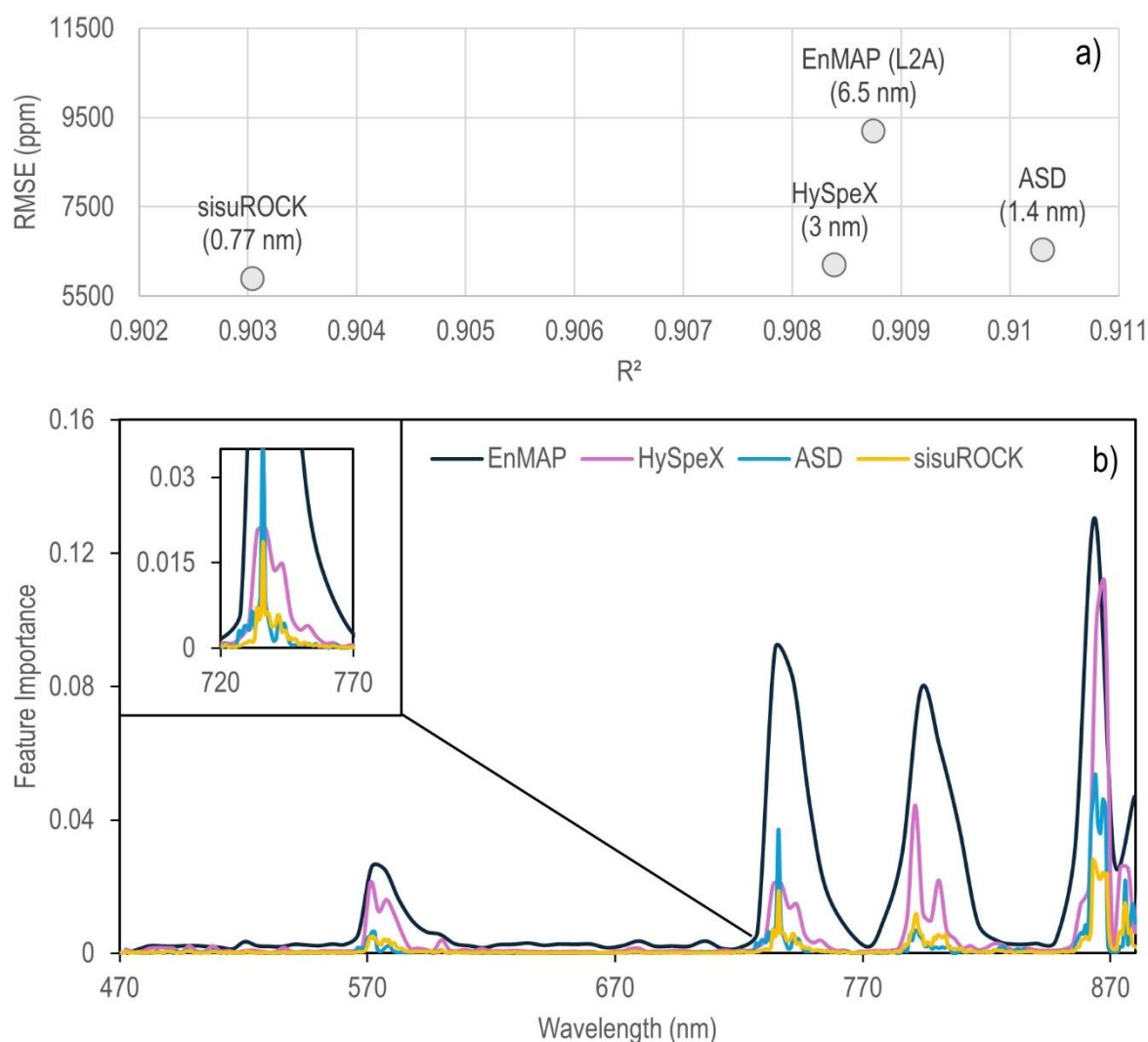


Figure 3.10 (a) Graph showing the coefficient of determination (R^2_{test}) plotted against the $RMSE_{test}$ for Nd models obtained from resampling the data to different sensors and spectral sampling distances. (b) Comparison of Nd feature importance across different sensor systems. As a rule of thumb, larger spectral sampling interval corresponds to broader peaks and higher feature importance values.

3.4.2. Limitations of the Method

From this study, a number of potential limiting factors to the method's performance emerged. These include the training dataset size and characteristics, the presence of iron oxides in the input dataset, and the influence of atmospheric and instrumental noise.

The small dataset for training and testing the single REE models posed a major challenge in this work, and in REE studies in general. ML techniques typically require hundreds of data points to generate high-quality outputs. However, in the literature, there are few natural REE-bearing samples available that have been measured geochemically and spectrally. Moreover, the broad dispersion of REE

concentrations in the datasets is not evenly distributed across the range, causing an imbalance in the modeling step. This aspect highlighted the importance of data cleaning, consisting of excluding training samples at the extremes of the range (e.g., the doped glasses and samples with concentrations below 10 ppm), thus further reducing the size of the dataset. Here, the best modeled REE was Nd, which had the highest number of samples (87 in total). In contrast, the most problematic models were developed for Er and Pr, where splitting the data into testing and training was not possible, leading to predictions prone to overfitting. This is also reflected in the feature importance results for Er, where two features (between 900-902 nm and 1015-1018 nm) are not associated with any apparent absorption. Despite being aware of the unreliability of models trained and tested on the same dataset, from the feature importance results, we show that these models could be robust if implemented with a sufficient number of samples.

Though having shown that it is possible to build models independent of mineralogy, the latter has an undeniable influence on the feature importance. Absorption features related to different REEs in overlapping wavelength ranges, such as the case of Dy and Nd or Dy and Sm, cannot be discriminated even if the shape of such features differs considerably and the correlation between these elements is low. This effect is less pronounced in minerals enriched in either light or heavy REEs, where the concentration differences between them are significant. However, in minerals with a broad range of REE compositions in their structure, such as eudialyte, zircon, and kainosite, which are reported as outliers in the Dy models illustrated in this study, overlapping feature importance can lead to miscalculations in element concentrations. Moreover, Ln^{3+} diagnostic absorption features in different minerals are subject to subtle shifts of up to 10 nm in the VNIR and 80 nm in the SWIR range (Turner et al., 2015). An analysis of the diagnostic absorption positions in Nd-bearing samples reveals that the highest feature importance scores correspond to the positions of Nd^{3+} absorptions related to the most frequent minerals in the dataset (i.e., the Nd-doped synthetic kaolinites). This suggests that groups with consistent mineralogy are likely to have more weight in the prediction process.

The analysis of outliers in the Nd model revealed the effect of iron oxides on prediction accuracy. The Nd model highlighted pyrochlore-bearing samples containing iron oxides in either goethite or hematite form. In these samples, the ferric iron absorptions completely obscure the diagnostic features of Nd (Neave et al., 2016), leading to overestimation in samples with high Nd concentrations and underestimation in those with low concentrations. The spectral interference of iron oxides is a well-documented issue in REE spectroscopy (Rowan et al., 1986). Even small quantities (i.e., 5 wt%) of iron oxides can hinder the detectability of REEs or render the quantification attempt invalid (Boesche et al., 2015; Li et al., 2024; Tan et al., 2021). The models developed here derive their predictions from the continuum-removed reflectance spectra at each wavelength but are unable to differentiate between the broad iron absorption features and sharp REE features, likely due to inadequate training data.

A systematic analysis of the effects of data quality on the developed model is out of the scope of this study. However, insights from the algorithm's development and testing highlighted several key points.

First, noise significantly degrades the quality of the predictions. This was particularly noticeable in the bastnaesite and synchysite images (**Figure 3.5**) in which smoothed data produced more accurate results, but also on the drill core image predictions (**Figure 3.6**), where pixels affected by noise diverged from spectral feature matching results. Noise, even in spectral bands with low feature importance, was observed to adversely affect predictions. Consequently, the Nd model for EnMAP was applied to a spectral range of 470–885 nm, deliberately excluding the noisy bands in the 900–1000 nm range. Second, when applying the model to satellite data, proper atmospheric correction is essential. The exclusion of multiple bands close to water vapor and oxygen's absorption at 720 and 760 nm tends to deteriorate the efficiency/accuracy of the model. Finally, with the current experimental setup, the model is unable to return null value to a pixel containing no REEs. This is partly due to the fact that samples with 0 ppm concentration were excluded from the training set, but also because the model cannot distinguish between 10 and a few hundred ppm (generally around 350 and 600 ppm), probably because the diagnostic absorption features with these concentrations are comparable with the instrumental noise.

3.4.3. Recommendations

The limitations highlighted in this work are strictly tied to the characteristics of the data available for developing the models. However, with more data availability in the future, the modeling results are expected to improve dramatically, and most of the limitations could potentially be mitigated. For example, training separate models for each mineralogic category and thus obtaining a more homogeneous mineralogic association could improve the prediction accuracy and the overall model performance. External validation could be carried out by selecting blind test cases at various scales (from rock sample to deposit) where to apply the models. Accuracy and reliability of the RFR model could also be improved by incorporating SNR information during the training phase, to allow the model to distinguish REE-bearing minerals from noise. Moreover, further research, such as measured mineral mixtures (e.g., following the notion given by Mustard and Pieters, (1989)), is required to develop techniques for mitigating the negative effects of ferric iron oxides more effectively. A further step forward could be the measurement of samples using spectrometers with very high spectral resolution.

Random Forest Regression was chosen because of its successful application in other geochemical analyses (Huang et al., 2021; Qasim and Khan, 2022; Schnitzler et al., 2019), its feature importance property, and its robustness in cases of limited data (Parsa, 2021) and noisy inputs (Buccione et al., 2023). Several other ML techniques are also available, including Support Vector Machine, Convolutional Neural Networks (which could potentially be coupled with algorithms such as SHAP to explain their outputs (Guerra Prado et al., 2023; Lundberg and Lee, 2017)), and XGBoost. The latter has been shown to be a reliable technique in many geochemical and mineral exploration studies, often outperforming other methods in terms of both accuracy and speed (Buccione et al., 2023). Given the limited number of studies

addressing the use of ML and spectroscopy for REE quantification, a comparative study of different algorithms is necessary to better understand of their specific strengths and limitations.

Finally, because this technique relies on spectroscopic data, quantification estimates refer only to trivalent lanthanides present at the surface of the analyzed sample, and not within its volume, implying that such models should be considered as rapid, preliminary estimates of REE concentrations, suitable for identifying areas of economic interest, but not as a replacement for geochemical analyses.

3.5. Conclusion

A machine learning (ML) approach based on Random Forest Regression (RFR) was developed to rapidly estimate the concentration of five spectrally active REEs (Nd, Dy, Er, Pr, and Sm) in natural and synthetic samples using reflectance spectroscopy. The study leveraged a diverse collection of datasets, in terms of mineralogy and geographical origin, with each dataset obtained using different analytical techniques and protocols for spectral and geochemical analysis. The constructed models were shown to be robust, independent of mineralogy and to select physically meaningful wavelength ranges and diagnostic absorption features for quantifying the concentrations of multiple spectrally active REEs, beyond Nd. The study also demonstrated that the models are transferable to different sensors and resolutions, by applying the resampled models to hyperspectral imaging data acquired under laboratory conditions and with the EnMAP satellite system.

In this work we prove that ML, and more broadly artificial intelligence, are powerful approaches for REE quantification, provided these are integrated with expert knowledge. A growing number of studies addresses the theme of REE quantification using reflectance and imaging spectroscopy, but few of these share the data, hampering the ability to reproduce the experimental work. In order to further pursue this research field and obtain generalizable and accurate models, an increasing amount of spectral data accompanied by high quality geochemical analyses should become publicly available.

Despite the impact of the SNR and the spectral resolution on the results, the adaptability of the technique to satellite systems makes it a potentially useful and cost-effective tool for REE exploration at a regional scale, providing preliminary information of their abundance in a target area. At the same time, at a deposit or mine scale, where it is possible to use sensors with a higher spectral and spatial resolution, as well as acquire a mineralogically more homogeneous site-specific training dataset, the method could provide a rapid estimation of individual REE concentrations with greater detail and accuracy than the models presented in this study, effectively supporting mining operations and exploration procedures.

One of the major limitations highlighted in this work is the masking effect of ferric iron minerals. Especially in natural environments, many REE deposits are coated with an alteration patina rich in iron oxides, which could potentially cause an underestimation or a wrong assessment of REE concentrations with this technique. This work should be considered as a first step for applying a non-invasive method

to REE exploration, but more research on mitigating the effect of iron is essential for implementing this approach in an operational context.

Finally, while this study focused on only five spectrally active REEs, with sufficient training data, this methodology could be extended to other spectrally active elements such as Ho, Tm, and potentially Yb, whose diagnostic absorption features primarily occur in the VNIR region.

3.6. Author Contributions (CredIT)

Susanna Grita: Conceptualization, Methodology (RFR model development), Investigation (individual REE model training and testing and application to images), Formal analysis, Visualization, Writing – Original Draft;

Saeid Asadzadeh: Conceptualization, Supervision, Formal analysis (Monazite index calculation over the carbonatite drill core LP144), Writing – Review & Editing;

David Turner: Resources (provision of point spectra of REE-bearing minerals and bastnaesite and synchysite images along with geochemical data), Writing – Review & Editing;

Carlos Roberto de Souza Filho: Resources (provision of the carbonatite drill core LP144 image), Writing – Review & Editing;

Sabine Chabrilat: Writing – Review & Editing, Funding acquisition;

Piero Boccardo: Writing – Review & Editing, Funding acquisition.

4. Characterization of Mine Dumps and Tailings in the Montevecchio-Ingurtosu District

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4.1. Summary

The climate crisis and the need for a rapid transition to renewable energy systems, as well as the continuous innovation in technological applications in almost all industrial and production sectors, have contributed to a pressing demand for critical raw materials. As a result, new and old deposits have been targeted for exploration of critical minerals. Potential sources are identified in legacy mine wastes in the form of stockpiles, tailings, and slag. Europe is estimated to have hundreds of thousands of abandoned mines within its territory, and among them large volumes of mine residues. As of today, only part of these mining areas have been characterized from a mineralogical point of view, and a more in-depth assessment is needed to better understand their impact on the environment and on the health of communities living nearby. Many scientific studies have shown the usefulness of proximal to satellite-based hyperspectral remote sensing data for monitoring and assessing the pollution potential generated by mine dumps affected by acid mine drainage. Fewer studies have used this technique for monitoring areas affected by neutral mine drainage.

This study aims to assess the effectiveness of imaging spectroscopy for deriving the mineralogical and geochemical composition of residues of an abandoned carbonate-buffered sulfide mine as a source of pollution for the environment. The Montevecchio-Ingurtosu mining district in southwestern Sardinia was analyzed by combining proximal sensing, with point spectral measurements acquired in the lab using an ASD spectroradiometer, multispectral (Sentinel-2) and hyperspectral (EnMAP) satellite-based remote sensing, and complementary mineralogical analyses carried out with powder X-Ray Diffraction (XRD). Point spectra and EnMAP data reveal areas with a spatial zonation of Fe(III) hydroxides and sulfates, highlighting sources of acid drainage in mine residues and compositional variations in neutral drainage affected waterways. The continuous acquisition of Sentinel-2 data in time allows to map dominant iron-bearing phases in different seasons, despite being limited by its low spectral resolution.

The combined use of different sensors is therefore leveraged to track subtle compositional variations indicative of changing environmental conditions.

4.2. Geographic and Geological Setting of the Area

The Montevecchio and Ingurtosu mines are on the south-western coast of Sardinia, surrounded by the cities of Guspini and Arbus and the Mediterranean Sea (**Figure 4.1**). The Montevecchio mines include the Piccalinna and Sanna areas, whose residues are investigated in this study, while the Ingurtosu mine is southwest of Montevecchio. As shown in **Figure 4.1**, it is a hilly area and the mine dumps appear to be distributed along three main valleys: the Montevecchio valley, where the Piccalinna impoundment is, the Rio Roia Cani valley, where the Sanna residues are located, and the Rio Naracauli, which crosses the Ingurtosu mine dumps. From the Casargiu mine, located northeast of Ingurtosu, a stream flows to the Rio Irvi system and then directly to the Mediterranean Sea. These mines were exploited mainly for lead and zinc, extracted from mostly galena and sphalerite sulfides since Roman times. From the Middle Ages, exploitation was conducted under the Pisan and Aragonese dominations, but modern industrial activity started in 1848 and lasted 150 years until its closure in 1991 (Marcello et al., 2004). The area is characterized by dry climatic conditions throughout the year, with periods of intense heat and drought from May to September and a short rainy period during the winter, especially in November and December, which are the wettest months. Between 2018 and 2023 the average annual precipitation measured by the Guspini-Montevecchio rain gauge was 873 mm/year, with an average of 230 dry days per year (ARPA Sardegna, 2023), while in the period between 1922-2010 the average precipitation measured with the same rain gauge was 735 mm/year with an average of 283 dry days (Frau et al., 2015). The mean annual temperature is about 15°C.

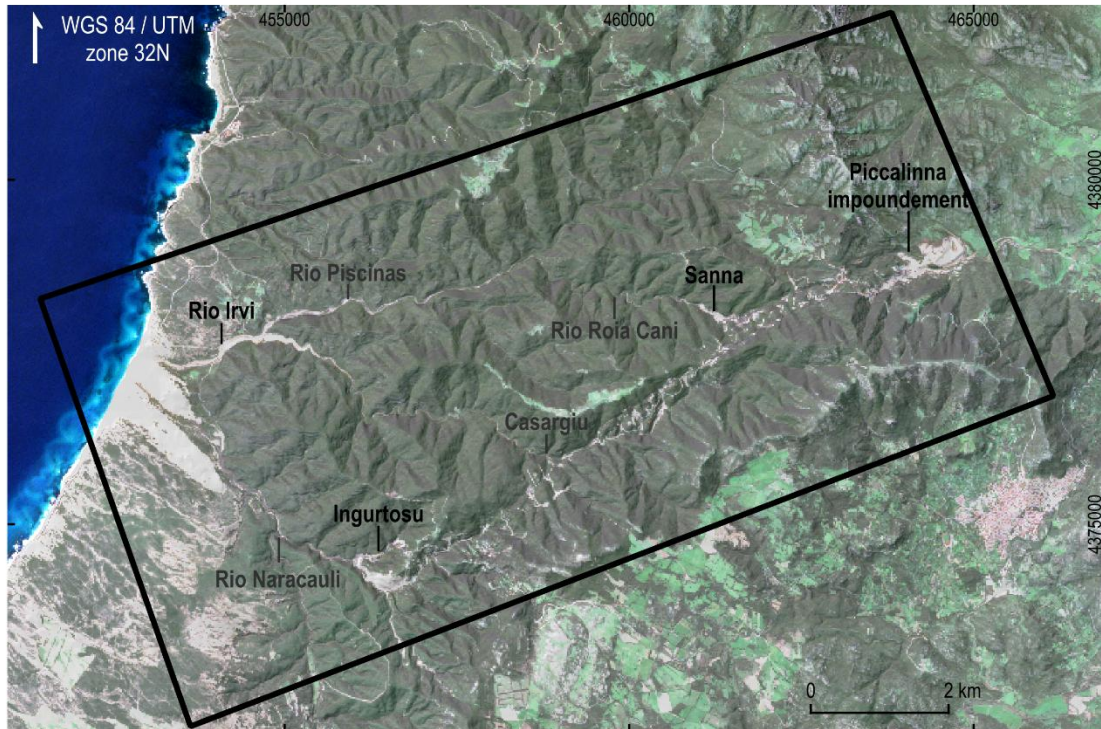


Figure 4.1 Area of interest: Montevecchio-Ingurtosu mining district located in SW Sardinia. Labels in black are the residues and areas analyzed in this study, while those in grey are mentioned but not investigated in this work. In the background is a true color composite from a Sentinel-2 image of 21/01/2024, and the hillshade derives from the Tinitaly v1.1 dataset (Tarquini et al., 2023).

The ore is in polymetallic mineralized veins that are part of the peripheral sector of the Arbus pluton. The latter intruded the Variscan metamorphic basement between 309 and 304 Ma and has a roughly concentric structure, with leucogranite at the core and pyroxene-bearing biotite granodiorite at the border (Moroni et al., 2019; Secchi et al., 1991). Radial fractures characterize the igneous complex, which are filled by mafic and felsic dykes, while sulfide-bearing metalliferous veins of hydrothermal origin, containing metals such as Zn, Pb, and Ag, run roughly parallel to the outer border of the batholith and are hosted in phyllites of the Arburese Unit (Marcello et al., 2004; Moroni et al., 2019) (see **Figure 4.2**). The Montevecchio and Ingurtosu mines exploited veins extending in a NNE-SSW direction for c.a. 12 km in the northern sector of the Arburese igneous complex (Medas et al., 2017).

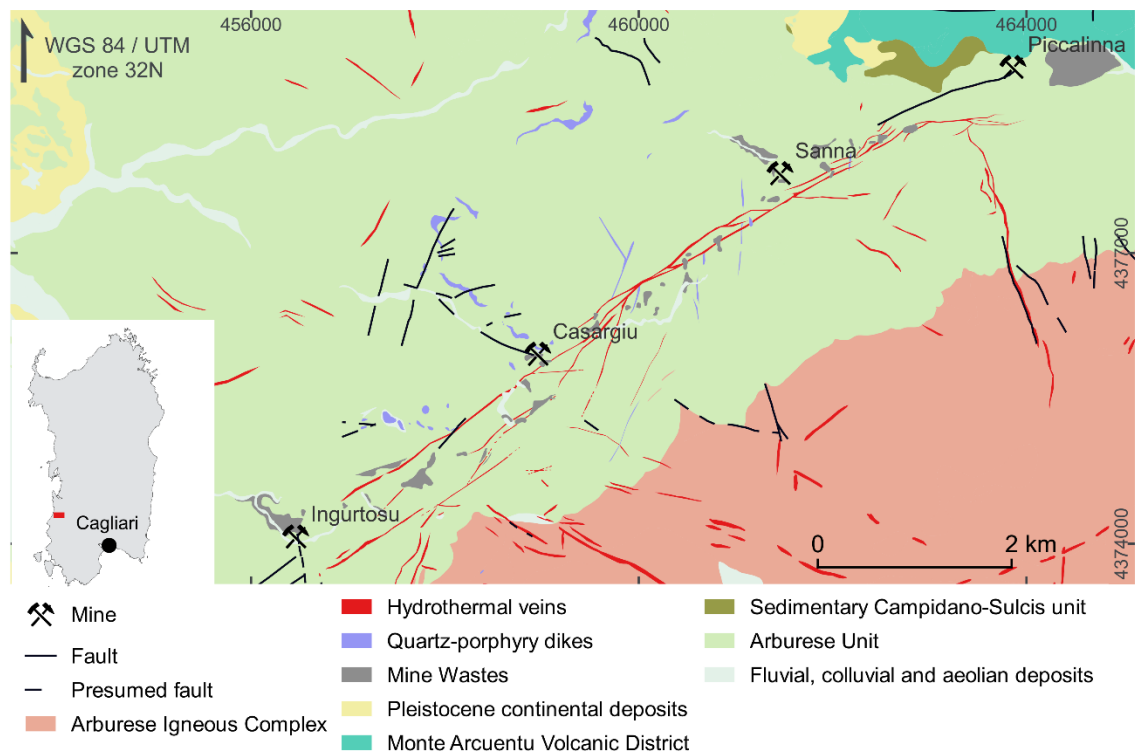


Figure 4.2 Simplified geological map of the Montevecchio-Ingurtosu mining district. The geological dataset is obtained from the Base Geological Map of Sardinia in a 1:25 000 scale (Regione Autonoma della Sardegna, 2008).

The primary ores are mainly composed of galena and sphalerite, with minor but still significant amounts of silver and chalcopyrite, and arsenopyrite. Alteration products of minerals include smithsonite (often iron-bearing), hemimorphite, goslarite, hydrozincite, greenockite, pyromorphite, and cerussite. Gangue minerals include quartz, barite, siderite, and minor amounts of ankerite and calcite. **Table 4.1** summarizes the mineral occurrence for each vein system (Moroni et al., 2019).

Table 4.1 Mineral occurrence in the vein mineworks by locality (modified from Moroni et al., 2019).

Locality	Primary Ore	Supergene Ore	Gangue Minerals
Montevecchio Levante - Piccalinna	Galena, Sphalerite (chalcopyrite)	Fe-smithsonite, hemimorphite, goslarite, hydrozincite, cerussite (anglesite, greenockite, pyromorphite, massicot, plattennite and silver, pyrite, marcasite) Cerussite, smithsonite, hemimorphite,	Quartz, barite, siderite (ankerite, calcite)
Montevecchio Ponente - Sanna	Sphalerite, galena (chalcopyrite, tetrahedrite- tennantite group, arsenopyrite)	goslarite, hydrozincite, Fe-smithsonite, anglesite, cuprite, malachite, azurite, brochantite, greenockite, plattennite, massicot (pyromorphite, fosgenite, pyrite, marcasite, galena)	siderite, ankerite, quartz (barite, calcite, dolomite)
Montevecchio -Casargiu	Sphalerite, galena (chalcopyrite,	Cerussite, smithsonite, hemimorphite, goslarite, hydrozincite, Fe-smithsonite,	Quartz, siderite, ankerite, calcite,

Ingurtosu - Brassey	tetrahedrite- tennantite group, arsenopyrite) Sphalerite, galena (chalcopyrite, tetrahedrite- tennantite group, arsenopyrite, Ni- Co arsenides and sulfoarsenides)	anglesite, malachite, azurite, greenockite, plattennite, massicot (pyromorphite, pyrite, marcasite, galena)	dolomite, (barite)
		Cerussite, smithsonite, hemimorphite, goslarite, hydrozincite, Fe-smithsonite, anglesite, malachite, azurite, greenockite, plattennite, massicot (pyromorphite, pyrite, marcasite, galena)	Quartz, siderite, ankerite, calcite, dolomite, (barite)

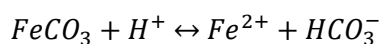
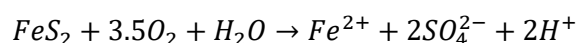
When the mines closed, waste rock dumps and mine tailings were left along the banks of the Casargiu, Ingurtosu, and Irvi rivers, exposed to atmospheric weathering. At the time, the consequences of the abandonment of mine residues to atmospheric agents for the environment and for human health were underestimated (Frau et al., 2015). Since then, these deposits have continuously contaminated the aquatic system and the soils in the area (Cidu et al., 2011; De Giudici et al., 2019, 2018, 2014; Frau et al., 2015). To the easternmost side of the area of interest lies the Piccalinna mine tailings impoundment. The material of the impoundment is composed of three-fourths by flotation muds and one-fourth by sandy mining products. The mineral composition of the tailings is quartz, siderite, ankerite, white mica, and barite as major constituents and pyrite, dolomite, sphalerite, and galena as minor minerals. Secondary minerals deriving mainly from atmospheric weathering are: cerussite, anglesite, and pyromorphite deriving from the alteration of galena; hemimorphite, smithsonite, and hydrozincite deriving from the alteration of sphalerite; while the breakdown of iron sulfides, such as pyrite and marcasite leads to the formation of oxyhydroxides and hydroxy-sulfates such as ferrihydrite, schwertmannite and jarosite which then transform into goethite and hematite. Efflorescent salts have been observed on the walls of the impoundment and in the Rio Montevecchio stream below; these are mainly composed of gypsum, epsomite, starkeyite, boyleite, gunningite, and Al- and Zn-copiapite and precipitate mostly in the dry season (Cidu et al., 2011).

A few kilometers west of the Piccalinna impoundment are the mine residues related to the Sanna vein and its processing plant. This vein is characterized by having a composition dominated by supergene minerals such as anglesite, cerussite, Fe-oxyhydroxides, and Zn- and Cu-bearing secondary minerals. Gangue is mainly constituted by siderite and quartz. The mine's waste rock and tailings are dumped along the Rio Roia Cani and are affected by erosion and slope instability. The residues can be distinguished between tailings and jigging waste based on granulometry. The former are composed of fine material, from sands to clays, while the latter have a coarser granulometry, varying from gravel to coarse sand. Such material is continuously transported downstream by the Rio Roia Cani, as proved by the occurrence of white patinas identified as biomineralizations of hydrozincite and reddish sediments in the riverbed (Sedda et al., 2023).

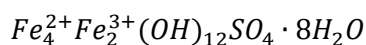
Seawards are the residues related to the Brassey Lavery, used to process ore from the Ingurtosu vein. The residues consist of gravimetric tailings with material of grain sizes larger than 2mm and of flotation tailings, consisting of finer material (sands to clays). A high concentration of Pb and Zn was observed in the finer flotation tailings. The mineralogy of these anthropic deposits consists of sphalerite, pyrite, and galena, along with secondary minerals, such as anglesite, cerussite, ankerite, siderite, quartz, barite, and dolomite. Minor occurrences of zircon, ilmenite, monazite, and corundum are present. Finally, concretions of sulfate salts are common, generally composed of gypsum and Zn-rich epsomite and hexahedrite (Caboï et al., 1993).

In this area, the hydrologic system is severely affected by the presence of the mine residues (see **Figure A2. 1** in Appendix II), with streams having varying levels of pollution due to the high concentration of heavy metals (Pb, Zn, and Cd mainly). The alteration of sulfides can cause the development of acid mine drainage. However, due to the presence of carbonates in the host rock, such as siderite, ankerite, and dolomite, the acidity is buffered, and the pH of the streams is slightly acidic to circum-neutral.

For example, the Rio Irvi has its main source of water deriving from the Casargiu adit, which directly connects with a now flooded mining tunnel. From a geological point of view, the Casargiu mine is an eastern offshoot of the Ingurtosu vein, but it was operationally considered as part of the Montevecchio mine. As indicated in **Table 4.1**, the main mineralization is sphalerite along with an ankerite-siderite gangue (Frau et al., 2015). When the Caragiu mine closed, the underground workings were filled with flotation tailings, and after that, with the arrest of the underground pumping system, the mine tunnel was flooded with groundwater. At the adit, pH is 5.8 and, after a slight increase to pH 6.4 in the first few hundred meters, it progressively decreases non-linearly to 4.0 after the confluence with Rio Piscinas, downstream (De Giudici et al., 2018; Frau et al., 2015). The quasi-neutral pH at the source is due to the buffering effect caused by siderite, according to the following set of chemical reactions:



The stream is very rich in iron, as can be seen from the high abundance of ochreous precipitates in the riverbed, also visible with satellite images. These are amorphous Fe(III)-oxyhydroxides which then evolve into low crystallinity goethite or hematite. In the upstream part of the Rio Irvi, an amorphous phase, due to the flocculation of colloidal particles into layers, can be observed in the waters. This is called 'green rust' and consists of layered Fe(II)/Fe(III) oxy/hydroxides with varying types of anions such as chloride, sulfates, or carbonate. In the Irvi stream, the interlayer is composed of water molecules and sulfate (Frau et al., 2015). The ratio between Fe(II) and Fe(III) is not constant and ranges from 0.5 and 3, but for sulfate green rust, it is 2. Its general formula is:



The crystal structure is trigonal, consisting of stacked oxide sheets $[Fe_4^{2+}Fe_2^{3+}(OH)_{12}]^{2+}$ (brucite type of layer) alternated with two interlayers of H_2O and SO_4^{2-} (Simon et al., 2003). Green rust in atmospheric conditions eventually oxidizes and precipitates in Fe(III)-hydroxides (De Giudici et al., 2018; Frau et al., 2015; Simon et al., 2003). This river is also characterized by having the highest concentrations of zinc of all the other mine-affected streams of the area. It is estimated that it discharges in the Piscinas coast about 2370 kg/day of zinc, 1580 kg/day of which are from the Casargiu adit (De Giudici et al., 2018; Frau et al., 2015).

Finally, Rio Naracauli is characterized by the precipitation of biological hydrozincite along the riverbed, due to the presence of cyanobacterial communities. This characteristic is due to the presence of alkaline groundwater. The chemistry of the water is tied to the emplacement of flotation muds rich in unexploited carbonates, which occurred around 50 years ago. Also, this river has a near-neutral pH between 6.63 and 7.98 (De Giudici et al., 2014).

4.3. Material and Data

4.3.1. Field Samples

In total, 105 samples were collected during two field campaigns, which took place between 23rd January and 3rd February 2024 and between the 21st and 26th July 2024, respectively, in the area of interest. In the first campaign, Piccalinna and Sanna mine residues were assessed, while in the second one, Ingurtosu mine residues and Rio Irvi samples were collected. Waste rock, flotation tailing, and jigging tailings samples were collected in the areas of Piccalinna impoundment, Ingurtosu, and Sanna dumps, as well as efflorescent salts and precipitates along the mine drainage-affected riverbed of Rio Irvi-Piscinas (**Figure 4.3**). Only the upper surface of the exposed soils was collected to ensure that the samples could be comparable to the satellite images. Samples collected in the areas of Piccalinna and Sanna mines were mineralogically characterized using X-Ray Diffraction (XRD). All samples were analyzed with reflectance spectroscopy in the visible to shortwave infrared (VNIR-SWIR) wavelength range.

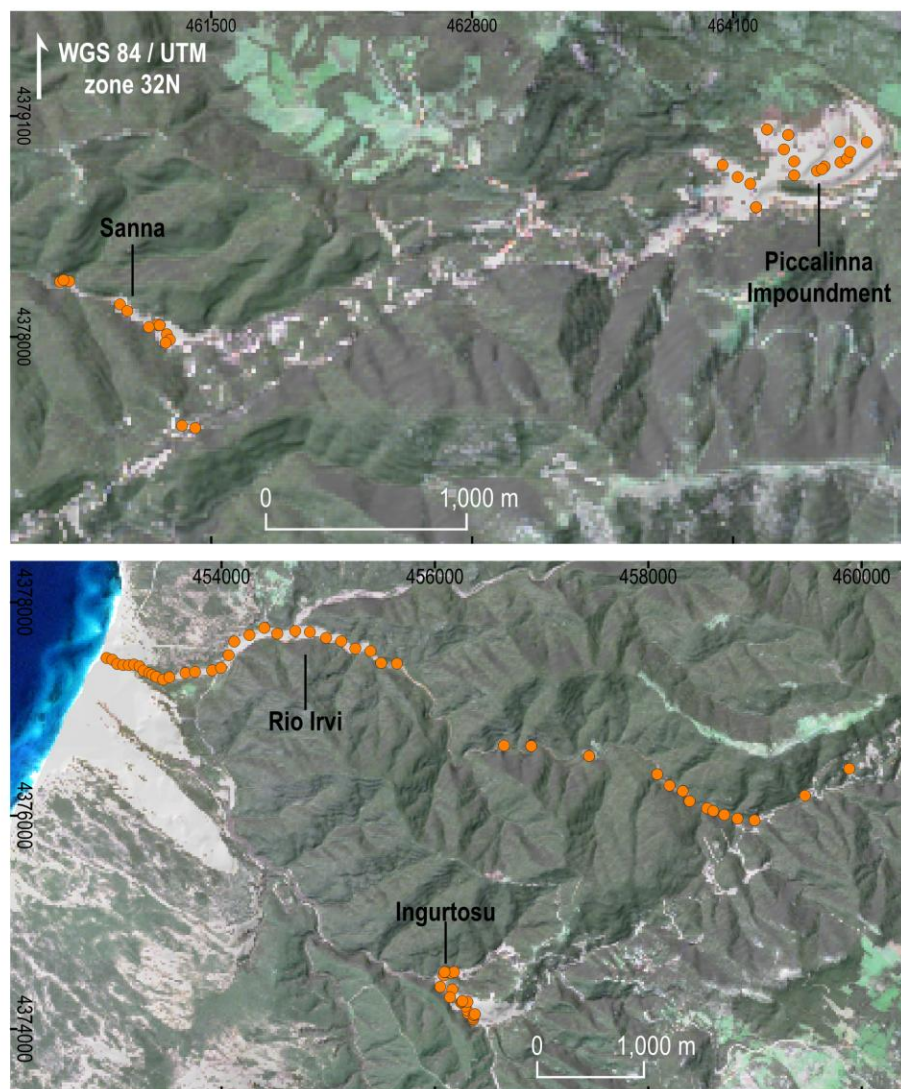


Figure 4.3 Location of samples collected in January 2024 (top) and July 2024 (bottom).

4.3.1.1. XRD Measurements

An X'Pert Pro PANalytical diffractometer (Malvern Panalytical, Malvern, UK) from the Department of Chemical and Geological Sciences of the University of Cagliari was used to analyze the mineralogy of 31 samples collected in the Piccalinna impoundment and in the Sanna residues. The instrument is equipped with an X-ray tube with Cu anticathode (Cu-K α 1) with a wavelength of 1.54060 Å, a nickel monochromator filter, and X'Celerator detector. All diffractograms were acquired at 40kV and 40 mA in an angular range of 5-70° 2 θ . Mineral phases on the single diffractograms were identified with the software HighScore, which is a search-match algorithm that provides a list of candidate minerals through the comparison of profile data, accompanied by a matching score. End-members with the highest score were considered as being part of the sample's mineral composition.

4.3.1.2. VNIR-SWIR Reflectance Spectroscopy

All samples were measured with a portable spectroradiometer in VNIR-SWIR wavelength range. The instrument is an Analytical Spectral Device (ASD) FieldSpec®-3 (Malvern Panalytical) mounted in the laboratory premises of the Helmholtz Center for Geosciences (GFZ), Potsdam, Germany. A contact probe was placed over each sample, and every measurement was the average of 50 scans, acquired with an integration time of 17 ms. To convert to reflectance, a white reference was initially measured and further collected every three samples. Three spectra were acquired for each sample and averaged to reduce random noise effects. For further noise removal, a Savitzky-Golay (Savitzky and Golay, 1964) smoothing filter was applied to the spectra with a window size of 5, and second-order polynomial. Due to logistical reasons, reflectance spectra of the samples were acquired several weeks after their collection. Specifically, for those collected in January, the measurements occurred on the 23rd April 2024, while those collected in July were measured on the 22nd August 2024. This delay may have caused transitions of metastable phases within the samples, as further discussed in Section 4.6.4.

4.3.2. Satellite Images

Four satellite images (**Table 4.2**) were used to cover the Montevecchio-Ingurtosu district. Specifically, a cloudless EnMAP image of 28/04/2024 was acquired from DLR's EOWeb® portal (<https://planning.enmap.org/>) with 2A processing level with the following parameters: atmospheric correction for land surfaces in the summer season with cirrus and haze removal, and ozone value of 330 in Dobson Units. Additionally, three level-2A Sentinel-2 images were acquired from CNES's GEODES portal (<https://geodes.cnes.fr/>). Atmospheric and topographic correction for these was carried out with the MAJA algorithm, developed by CNES. Indeed, these same images were also initially downloaded with processing level 2A from the Copernicus Browser (<https://browser.dataspace.copernicus.eu/>), which stores images corrected with ESA's Sen2Cor algorithm. However, these resulted in being affected by significant artifacts, which limited their use for the scope of this study (see Section 4.6.4). As indicated in **Table 4.2**, two of the Sentinel-2 images were acquired on dates close to the two field campaigns, and one of them on a date close to the EnMAP image.

Table 4.2 Satellite images used in this study and their technical specifications.

Sensor	Date	Cloud cover	Spatial resolution	Number of bands	Spectral range
Sentinel-2A	21/01/2024	0%	20 m	13	VNIR-SWIR
Sentinel-2A	26/07/2024	0%	20 m	13	VNIR-SWIR
Sentinel-2B	05/05/2024	16.4%	20 m	13	VNIR-SWIR
EnMAP	28/04/2024	0%	30 m	224	VNIR-SWIR

4.4. Methodology

4.4.1. Iterative Polynomial Fitting for ASD Point Spectra

Spectra of the samples collected in the field were analyzed with an iterative polynomial fitting technique described in Asadzadeh and de Souza Filho, (2016b). This technique allows for the extraction of spectral parameters, such as position, depth, and FWHM, of absorption features by modeling this via a polynomial curve. In cases of absorptions resulting from the combination of more than one feature, it identifies only the deepest one.

A polynomial curve is defined by the following formula:

$$P(\lambda) = p_n x^n + p_{n-1} x^{n-1} + \dots + p_2 x^2 + p_1 x^1 + p_0$$

Where $p_n \dots p_0$ are constants, and n is the order of the polynomial. The minimum of the polynomial is defined as the point where the first derivative of the curve is equal to zero and the second derivative is positive. The depth of the feature is then calculated as

$$Depth = 1 - P(x_0)$$

where $P(x_0)$ is the value of the polynomial curve at its minimum. The full width at half maximum is calculated as the difference between the values of the polynomial to the left and right of the absorption feature at its half-depth.

This technique follows a three-step workflow: in the first stage, the user provides a wavelength interval within which the absorption feature of interest is expected to occur. The algorithm iteratively performs a straight-line continuum removal on the given range, each time refining the position of the feature's shoulders on which to apply the continuum removal. In the second stage, a high-order polynomial (in this study, a 5th-order polynomial) is fitted to the absorption feature, and all its relative minima and maxima are extracted. The aim of this procedure is to assess the number of minima occurring within the feature. If more than one is detected, each local minimum is fitted separately in the final stage. In the last stage, the actual polynomial fitting occurs. This is an iterative procedure, where each time the parameters $p_0 \dots p_n$ are optimized through a least squares routine to generate a fourth-order polynomial, until the residual error between the original and the fitted curve is below a specific threshold. For this study, the threshold was set to 0.0003, whose value was obtained by trial-and-error and represents the smallest magnitude above the instrumental and random noise appearing in spectra. At each iteration, a smaller wavelength interval around the absorption minimum is selected until it is compliant with the threshold conditions. Once the curve is found, the position, full width at half-maximum, and depth are calculated accordingly.

In this study, all the absorption features present in the spectra from 350 to 2500 nm were analyzed using this technique. Then, by comparing them with the USGS v7 (Kokaly et al., 2017) and NASA's RELAB (Brown University, 2014) spectral libraries as well as with earlier works (Crowley, 1991; Cull et al., 2014), each feature was assigned to a specific mineral or phase. **Table 4.3** describes the diagnostic absorption features used here to identify minerals within every spectrum.

Table 4.3 Positions of spectral absorption features used to identify the listed minerals, accompanied by the references reporting on the physical processes relating to such absorptions. Features flagged with an asterisk (*) indicate the position of the VNIR reflectance shoulder. Wavelengths in bold indicate the most relevant and used features for mineral identification in this work.

Mineral	Diagnostic features (nm)	References
Goethite	425, 490, 670, 760* , 965 , 1450, 1935	(Brown University, 2014; Crowley et al., 2003; Cull et al., 2014; Kokaly et al., 2017)
Ferrihydrite	484, 770* , 980-1000 , 1437, 1920	(Brown University, 2014; Crowley et al., 2003; Cull et al., 2014; Kokaly et al., 2017; Leone et al., 2011)
Hematite	545, 660, 745* , 880	(Brown University, 2014; Crowley et al., 2003; Kokaly et al., 2017)
Jarosite	380, 435, 721* , 925 , 1467, 1848, 2264	(Brown University, 2014; Cloutis et al., 2006; Crowley et al., 2003; Cull et al., 2014; Kokaly et al., 2017)
Copiapite	430, 700* , 860 , 1450, 1937	(Brown University, 2014; Cloutis et al., 2006; Crowley et al., 2003)
Epsomite	988, 1203, 1453, 1577-1620 , 1975, 2400	(Crowley, 1991; Kokaly et al., 2017)
Goslarite	1480, 1680 , 1955	(McConachy et al., 2007)
Gypsum	990, 1200, 1447, 1488, 1530 , 1740, 1940, 1970, 2219, 2270 , 2430	(Brown University, 2014; Cloutis et al., 2006; Crowley, 1991; Kokaly et al., 2017)
Chlorite	1390-1400, 2250, 2330 , 1450, 1550, 2000, 2100 , 2290, 2350, 2400	(Kokaly et al., 2017; Lypaczewski and Rivard, 2018)
Siderite	1050, 1260 , 1950, 2330	(Bishop et al., 2021; Gaffey, 1987; Kokaly et al., 2017)
Biotite	2250, 2330, 2385-2390	(Brown University, 2014; Kokaly et al., 2017; Lypaczewski and Rivard, 2018)
Muscovite/Illite	1412, 2200, 2345, 2440	(Kokaly et al., 2017)

4.4.2. Polynomial Fitting on Sentinel-2 Images

4.4.2.1. Sentinel-2 Analysis

The study area was analyzed using Sentinel-2 multispectral images. While having a lower spectral resolution than the ASD spectra or a hyperspectral sensor, Sentinel-2 has the advantage of having a frequent revisit time (10 days for each individual satellite and 5 days for the constellation). Mining environments are highly dynamic contexts within which the mineralogy of secondary precipitates and efflorescent salts varies by seasonal changes in precipitation and humidity (Riaza and Müller, 2010). Sentinel-2, with its high temporal resolution, can be useful for time series analyses of this phenomenon. Previous studies have also proved its effectiveness in geological remote sensing applications and specifically, for mine-affected areas (Pereira et al., 2023; van der Meer et al., 2014). Here, Sentinel-2 data is used to detect and map the spatial distribution of goethite, hematite, jarosite, and potentially copiapite.

The images were clipped to the area of interest, and water and vegetation masks were applied to them. Specifically, the Normalized Difference Vegetation Index (NDVI) was used for masking vegetation, and a Normalized Difference Water Index (NDWI) was used for masking water bodies. The masks were obtained through the following relations:

$$NDVI = \frac{NIR - Red}{NIR + Red} \leq 0.15, \quad \text{where } NIR = B8A, Red = B4$$
$$NDWI = \frac{Green - NIR}{Green + NIR} < -0.05, \quad \text{where } NIR = B8A \text{ and } Green = B3$$

The thresholds were chosen by trial and error, in order to exclude all water bodies and vegetated areas. Also, the coastal dunes were masked out as they are out of the scope of this study.

The reflectance shoulder centered at around 760 nm was modeled through polynomial fitting thanks to the nine bands centered in the VNIR wavelength range (see **Table 2.1**). Bands 1 to 7 and 8A have a comparable bandwidth, being between 20 and 30 nm. These were therefore used in the polynomial fitting procedure, where a polynomial curve passing through the reflectance values of bands 4,5,6,7, and 8A approximates the target reflectance feature. A previous study successfully modeled the broad absorption feature centered at ~900 nm typical of Fe-bearing minerals (Van Der Werff and Van Der Meer, 2015) with a second-order polynomial on simulated Sentinel-2 data. However, this approach did not apply to level 2A images, where band 10, centered at around 1374 nm, is lacking, as it is used solely for atmospheric correction.

The approach used for polynomial fitting is a similar, but simplified version of the workflow used with the laboratory spectra. The reflectance shoulder is treated as an absorption feature, and thus the spectrum is inverted for further processing. A straight-line local continuum removal is then applied in the wavelength range between 650 and 900 nm. In this case, the continuum is not iteratively refined, as the spectra deriving from Sentinel-2 images are too coarse. A fourth-order polynomial curve passing through

bands 4,5,6,7, and 8A is modeled (**Figure 4.4a**). Then a derivative analysis is carried out to determine if the modeled curve contains more than one maximum. In that case, it is excluded from further processing, not being considered as a spectral feature related to iron-bearing minerals. If the curve contains only one maximum (or minimum in the inverted spectrum), the wavelength position is calculated by assessing the point where the first derivative of the curve is equal to zero and the second derivative is larger than zero on the inverted spectrum.

This procedure is calculated for each grid cell of the masked Sentinel-2 image. Only grid cells with shoulder positions between 690 and 830 nm were taken into consideration, as this is the wavelength range where the reflectance maxima occur for goethite, hematite, ferrihydrite, jarosite, and copiapite.

Before applying it to Sentinel-2 images, the workflow was first tested on the sample spectra resampled to Sentinel-2 resolution using a spectral response function convolution applied through the QGIS plugin EnMAP-Box 3 (EnMAP-Box Developers, 2019) (**Figure A2. 2** in Appendix II). The test proved that the shoulder position of the resampled spectra matched that of the original ones with an R^2 of 0.84, an average difference of 4 nm, and a maximum difference of 16 nm, proving that this procedure is robust (**Figure 4.4b**). These results were also used to validate the classification results obtained on Sentinel-2, as described in Section 4.4.2.2.

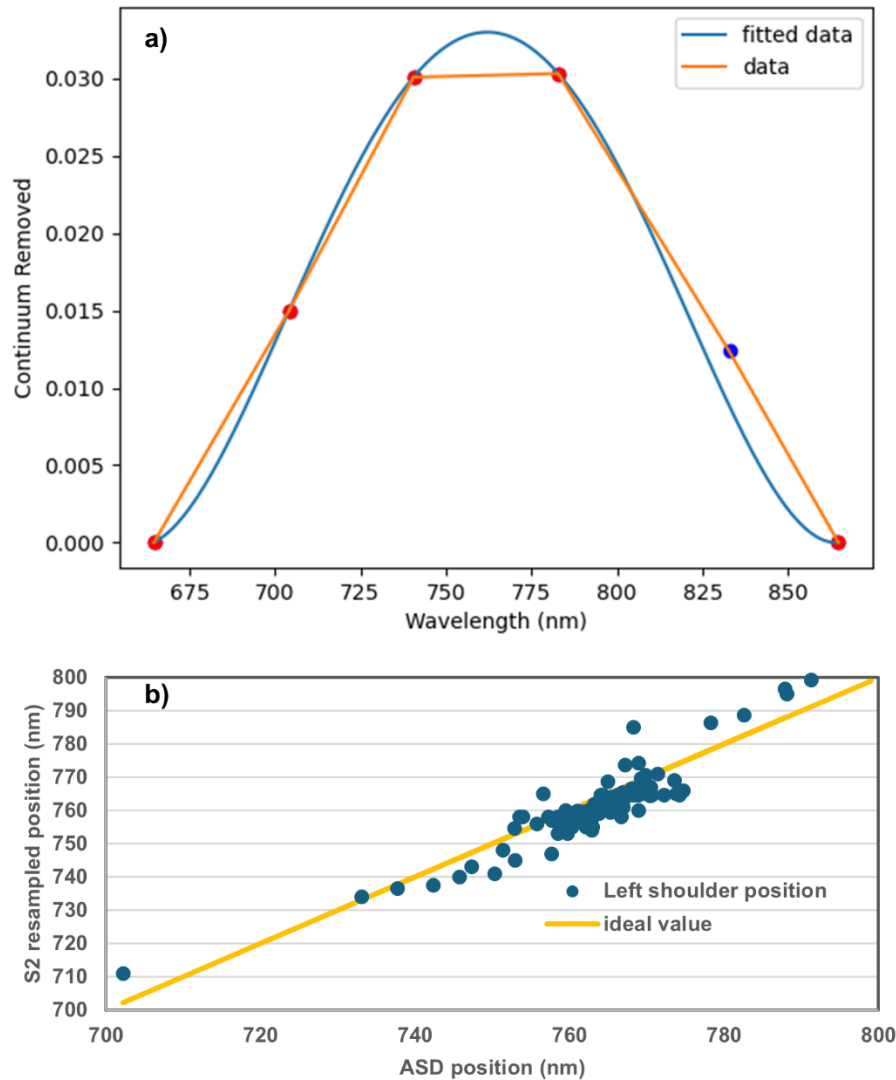


Figure 4.4 (a) modeled VNIR reflectance shoulder based on polynomial fitting of Sentinel-2 resampled spectra. The red markers indicate the fixed bands the polynomial passes through. (b) Comparison between the reflectance shoulder position in the original ASD spectra and in the Sentinel-2 resampled version.

To define the different mineral classes, the shoulder positions of spectra of pure goethite, ferrihydrite, hematite, copiapite, and jarosite from different spectral libraries (Brown University, 2014; Crowley et al., 2003; Kokaly et al., 2017) (**Table A2. 1**) were calculated through polynomial fitting. This allowed us to select physically meaningful thresholds for the mineral map. The final thresholds are described in **Table 4.4**.

On the Sentinel-2 images, pixels with a shoulder depth greater than 0.01 and full width at half maximum (FWHM) greater than 65 nm were considered, to filter out spectra not related to iron-bearing minerals or affected by artifacts related to atmospheric and topographic correction. These are the minimum values of the depth and FWHM, respectively, of all the sample spectra resampled to Sentinel-2 resolution.

Table 4.4 Mineral classification criteria based on the VNIR reflectance maximum.

Mineral	Reflectance shoulder ranges
Copiapite	690-710 nm
Jarosite	710-735 nm
Hematite	735-750 nm
Goethite/Ferrihydrite	750-780 nm

Although some studies have differentiated goethite and ferrihydrite by their reflectance shoulder positions (Williams et al., 2002), here they are classified together, as ferrihydrite was not detected in the point spectra, and the shoulder positions of the analyzed pure ferrihydrite spectra were overlapping those of goethite.

The Sentinel-2 results were related to precipitation data over the area of interest obtained from NASA’s Integrated Multi-satellitE Retrievals for GPM (IMERG v07) dataset, derived from the Global Precipitation Measurement (GPM) (Precipitation Processing System (PPS) At NASA GSFC, 2023). A time series of calibrated precipitation data starting from 01/01/2024 to 31/12/2024 was retrieved using Google Earth Engine. The hourly precipitation values were cumulated daily, and dry days were defined as days having less than 5 mm of rainfall.

4.4.2.2. Comparison with Samples Collected in the Field

The classification results obtained from the Sentinel-2 images were validated with the spectra of the samples collected in the field resampled to the Sentinel-2 resolution (see Section 4.3.1.2). The sample spectra were classified based on the criteria shown in **Table 4.4** and compared with the image acquired on the closest date to the time of their collection from the field. A confusion matrix was built by comparing the image cell overlapping or closest, within a range of 10 meters, to the sample location. Only classified pixels were considered in the confusion matrix.

4.4.3. Polynomial Fitting of EnMAP Image

An EnMAP image was analyzed over the same area. The image was clipped to the area of interest and masked using NDVI>0.15, obtained from bands 48 (Red) and 75 (NIR), respectively. In total, four features were taken into consideration: the VNIR reflectance shoulder at around 750 nm for comparison with Sentinel-2 data, the ferric iron absorption feature at ~ 900 nm, the 435 nm and 2265 nm absorption features to locate potential areas of jarosite occurrence. As the reflectance shoulder and the ferric iron absorption feature are strongly affected by instrumental and atmospheric noise, these features were mapped with a 4th-order polynomial fitting using fixed points, as for the Sentinel-2 images. The other two features were fitted with a 4th-order polynomial without using fixed points. Only features with an RMSE of less than 0.003 between the original and fitted curve were considered. The fixed points and the continuum removal ranges are shown in **Table 4.5**. As illustrated, the fixed bands used for the VNIR reflectance shoulder calculation are centered at wavelengths as close as possible to the Sentinel-2 image bands. The additional

rules, such as the thresholds related to the FWHM and wavelength position (λ), are based on the ranges found in the spectra of the samples collected in the field.

Table 4.5 Techniques and parameters used to analyze spectral features on EnMAP. CR = Continuum Removal.

Feature	CR range (nm)	Method	Fixed bands (nm)	Additional Rules
750 nm reflectance	650-900 (on inverted spectrum)	Fixed points PF	666.6, 706.6, 749.06, 793.6, 839.98, 871.68	$\begin{cases} Depth \geq 0.01 \\ FWHM > 65 \text{ nm} \end{cases}$
900 nm absorption	750 -1300	Fixed points PF	801.248, 871.683, 1025.66, 1081.79, and 1128.11	$\begin{cases} Depth \geq 0.01 \\ 870 \leq \lambda \leq 1050 \end{cases}$
435 nm absorption	418-460	PF (RMSE threshold: 0.003)	N/A	$\begin{cases} Depth \geq 0.01 \\ 16 \leq FWHM \leq 24 \\ 432 \leq \lambda \leq 440 \end{cases}$
2265 nm absorption	2240-2285	PF (RMSE threshold: 0.003)	N/A	$Depth > 0.0$

4.5. Results

4.5.1. Point Spectra

Figure 4.5, **Figure 4.6** and **Figure 4.7** show the final spectra of all the samples collected in this study. These appear smooth and not affected by instrumental noise except at wavelengths below 500 nm. Most samples are iron bearing as evident by the prominent reflectance drop towards the ultraviolet wavelength range and by the broad absorption at about ~ 900 nm. Most also contain water in the form of H₂O and OH⁻, as can be observed by the presence of absorption features centered at 1400 and 1900 nm.

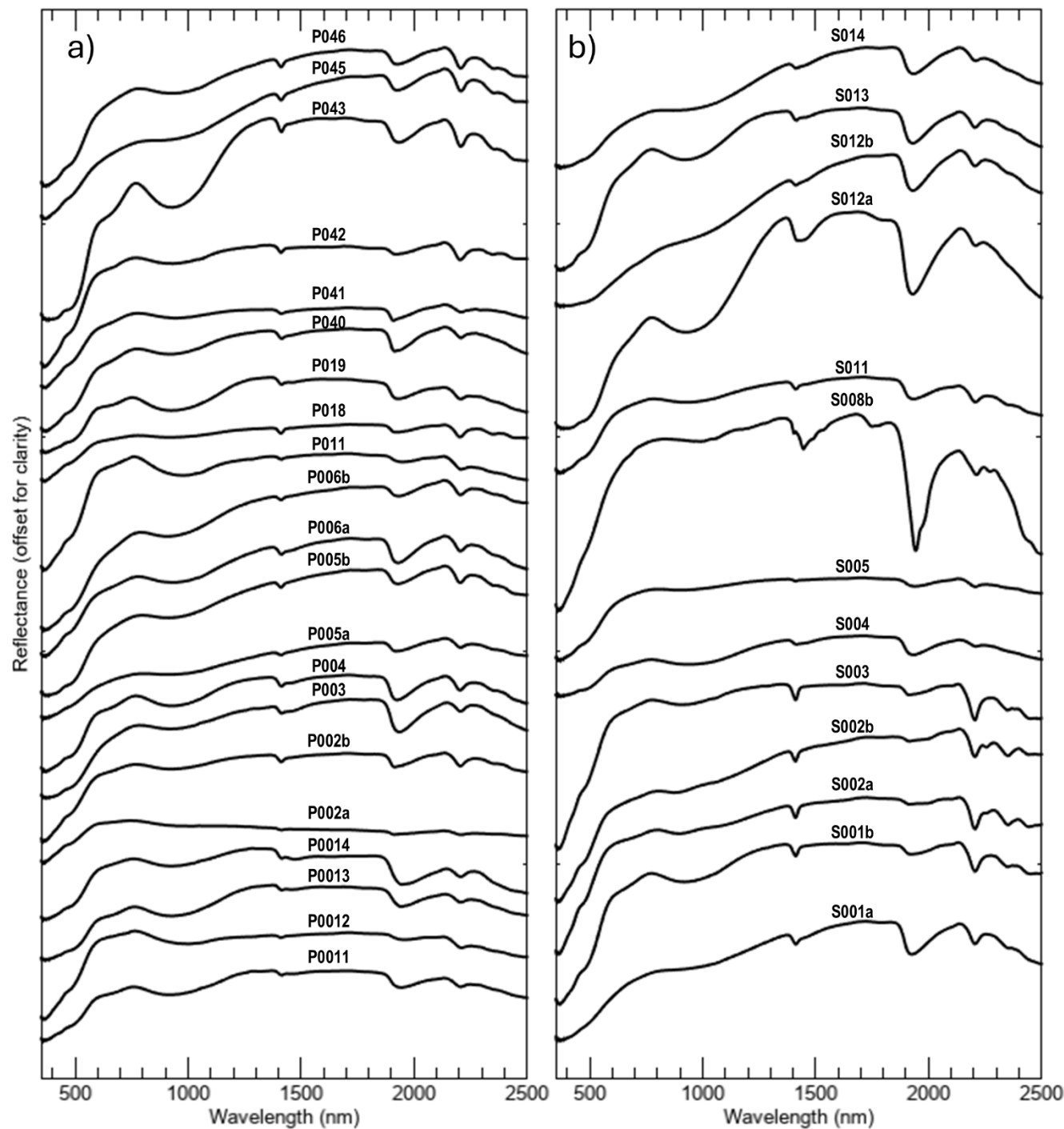


Figure 4.5 Spectra of samples collected in the Piccalinna impoundment (a) and in the Sanna minesite (b).

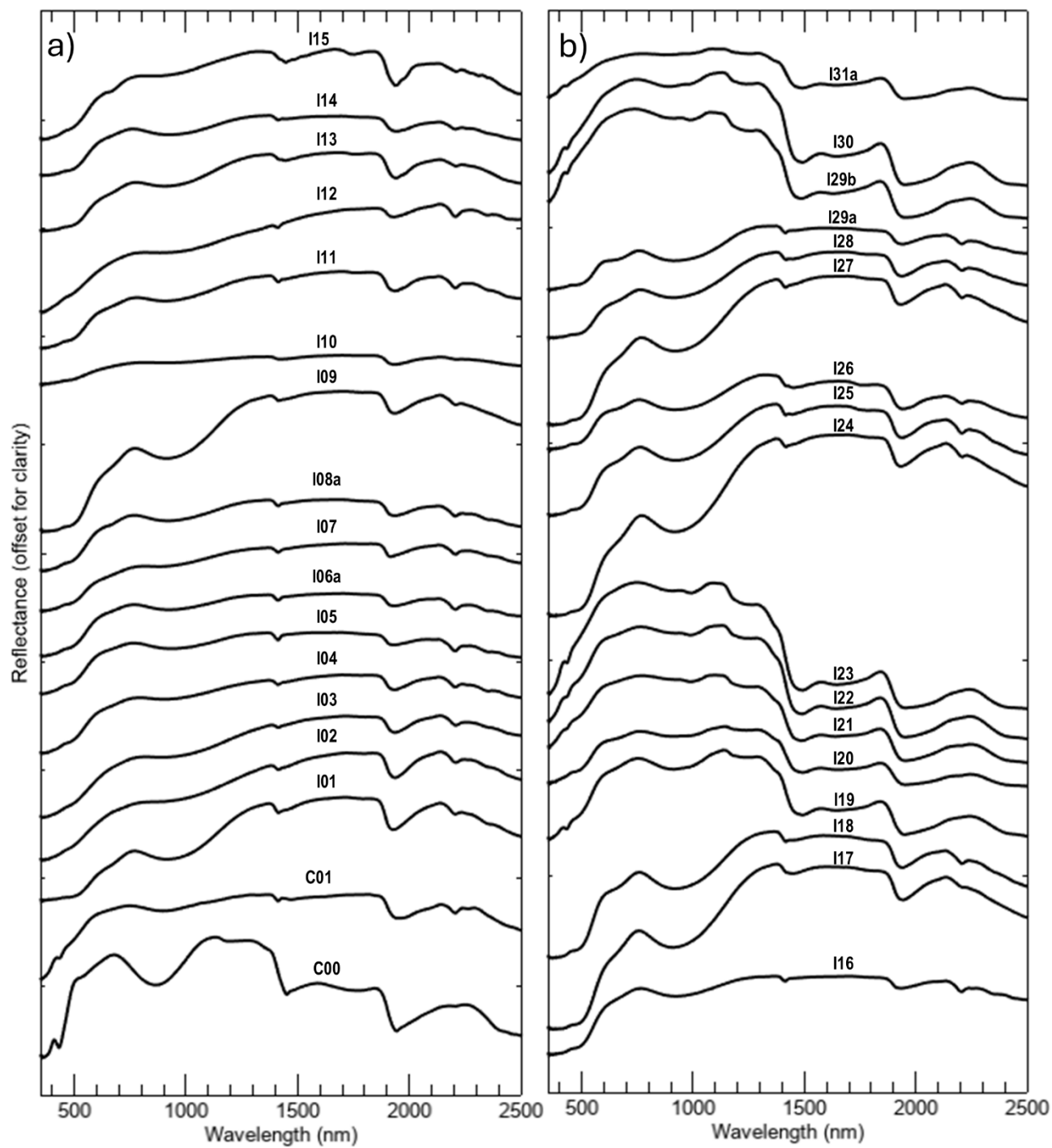


Figure 4.6 Spectra of samples collected in the Casargiu mining area (a) and along the Rio Irvi (a-b).

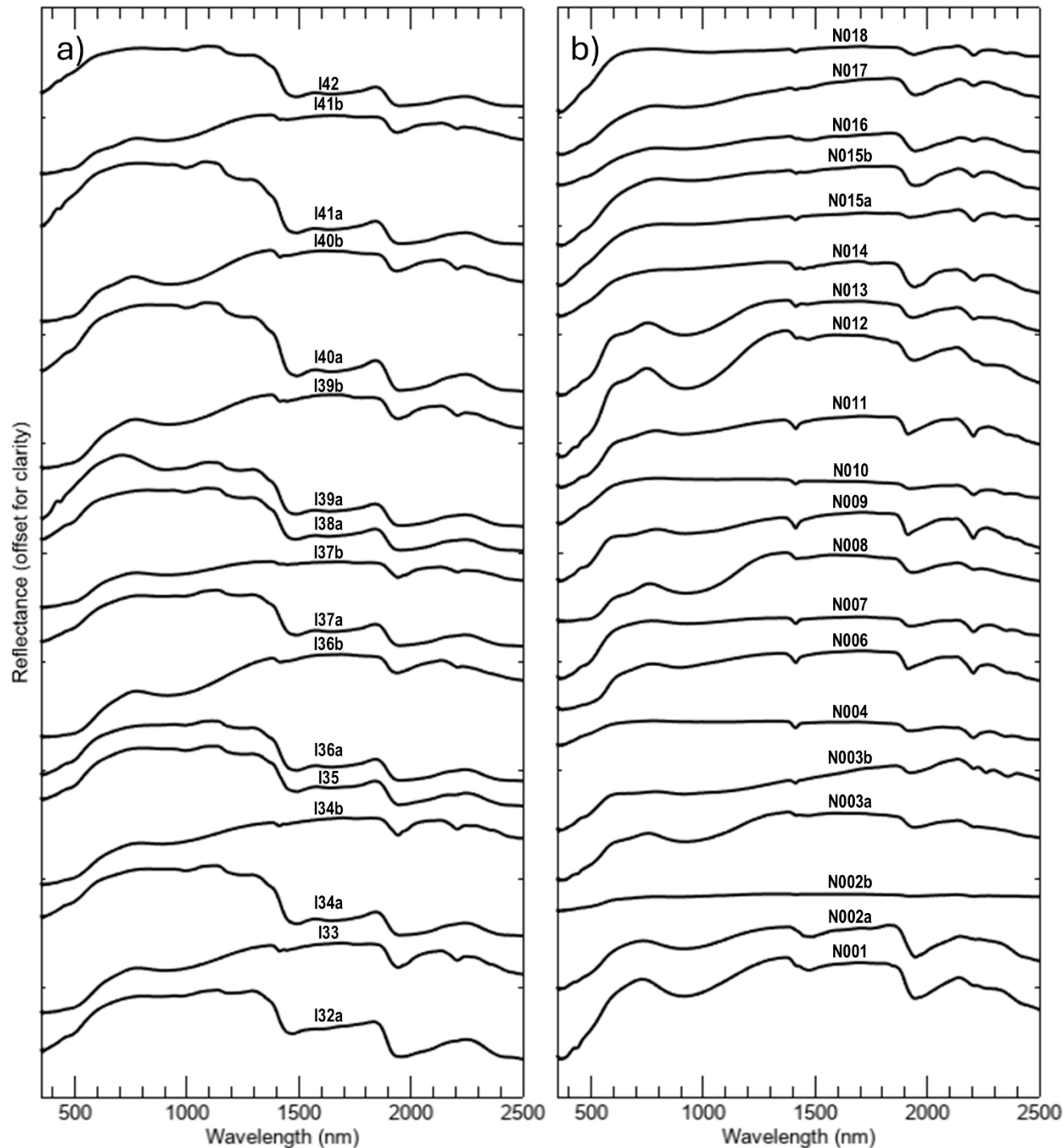


Figure 4.7 Spectra of samples collected along the Rio Irvi (a) and in the Ingurtosu minesite (a-b).

4.5.1.1. Sanna and Piccalinna Mine Residues

Table 4.6 illustrates the occurrence of minerals identified in the samples collected in the Piccalinna impoundment and in the Sanna mine site. The most abundant minerals identified with XRD in the Piccalinna and Sanna areas are quartz, white mica, in the form of muscovite or illite, and anglesite (see

also Appendix III). These are the main constituents of the gangue, while ore minerals, such as galena and sphalerite, appear in minor amounts. Reflectance spectroscopy also revealed a widespread occurrence of goethite and ferrihydrite, as well as a relatively consistent presence of jarosite and siderite. This mineralogical assemblage reflects the results obtained on the same mine wastes in previous studies (Cidu et al., 2011; Sedda et al., 2023).

Table 4.6 Mineral occurrence per sample in the Piccalinna impoundment (MVL_*) and Sanna (MVP_*) tailings. Colored boxes represent spectrally active minerals, identified with reflectance spectroscopy only (dark green), XRD only (orange) and in both techniques (light green). The last column indicates non-spectrally active minerals identified with XRD. Gt=goethite, Sch=schwertmannite, Jar=jarosite, Fhyd=ferrihydrite, Eps=epsomite/bianchite, Gyp=gypsum, Chl=chlorite, Sid=siderite, Mic=micaceous minerals (illite, muscovite and/or biotite and phlogopite), Kaol=kaolinite, Mtm=montmorillonite, Arg=Aragonite, Qtz=quartz, Art=anorthite, Ang=anglesite, Tet=tetrahedrite, Alb=albite, Bar=barite, Ank=ankerite, Galb=galenobismuthinite, Nkt=nanokite, Gal=galena, Sph=sphalerite, Frk=franklinite, Cup=cuprite, Ten=tennantite, Zin=zincite, Lit=litharge, San=sanidine, Bis=bismuthinite, Cer=cerussite, Hem=hemimorphite.

Geographic Coordinates		Other Minerals												
Sample Name	(WGS84)	Gt	Sch	Jar	Fhyd	Eps	Gyp	Chl	Sid	Mic	Kaol	Mtm	Arg	identified with XRD
MVL_P002a	8.585663, 39.558194													Qtz, Art, Ang, Tet, Alb
MVL_P002b														Qtz, Ang, Alb, Bar
MVL_P003	8.585659, 39.558815													Qtz, Ank
MVL_P004	8.585063, 39.559353													Qtz, Ang, Galb
MVL_P005a	8.585303, 39.560002													Qtz, Galb
MVL_P005b														Qtz
MVL_P006a	8.584081, 39.560241													Qtz, Ang, Bar
MVL_P006b*														
MVL_P0011*	8.583460, 39.556748													
MVL_P0012														Qtz, Nkt, Gal, Ang
MVL_P0013														Qtz, Gal, Sph, Ang
MVL_P0014														Qtz, Sph, Frk, Ang
MVL_P011	8.588314, 39.559705													Qtz, Sph, Gal, Bar, Ang
MVL_P018	8.581508, 39.558638													Qtz, Art
MVL_P019	8.583118, 39.557806													Qtz, Sph, Gal, Ang
MVL_P040	8.587275, 39.558475													Qtz, Ang, Cup, Alb
MVL_P041	8.586984, 39.558398													Qtz, Art, Ang, Alb
MVL_P042	8.587426, 39.558593													Qtz, Ten, Cup
MVL_P043	8.588347, 39.558785													Qtz
MVL_P045	8.588904, 39.559255													Qtz
MVL_P046	8.589863, 39.559693													Qtz, Zin, Cup, Lit
MVP_S001a	8.549254, 39.550542													Qtz
MVP_S001b														Qtz
MVP_S002a	8.548900, 39.551324													Qtz, San
MVP_S002b														Qtz, Alb, Art
MVP_S003	8.548900, 39.551324													Qtz, Sph
MVP_S004	8.548830, 39.551324													Qtz, Ang, Sph, Gal
MVP_S005	8.548761, 39.551350													Qtz, Sph, Gal, Bar, Bis
MVP_S008b	8.549498, 39.550678													Qtz, Ank, Zin
MVP_S011*	8.546593, 39.552251													
MVP_S012a	8.543308, 39.553332													Qtz, Cer
MVP_S012b														Qtz, Cer
MVP_S013	8.543111, 39.553255													Ang, Qtz, Hem
MVP_S014*	8.543637, 39.553277													

Reflectance Spectra Reflectance Spectra & XRD XRD

 Reflectance Spectra
  Reflectance Spectra & XRD
  XRD

As can be noticed, iron-bearing minerals are not easily identified using the XRD technique, partly due to the fluorescence effect generated when the copper target is used on iron, which significantly increases the background noise (Ali et al., 2022), and partly because many of the iron-bearing minerals in this area are amorphous (e.g. ferrihydrite) or poorly crystalline (newly formed goethite and schwertmannite). Kaolinite has diagnostic absorption features in the SWIR spectral range, but it was not detected on reflectance spectra because of its low abundance compared to muscovite and illite. **Figure 4.8** shows some examples of continuum removed spectra and the absorption features used to identify different mineral phases. It is evident that some minerals partially mask the absorption features of others, as can be seen for goethite or schwertmannite, partially covering absorptions related to siderite at 1050 and 1260 nm. Similarly, in the sample containing jarosite, the ferric iron feature is shifted to longer wavelengths (~960 nm) due to the spectral dominance of goethite.

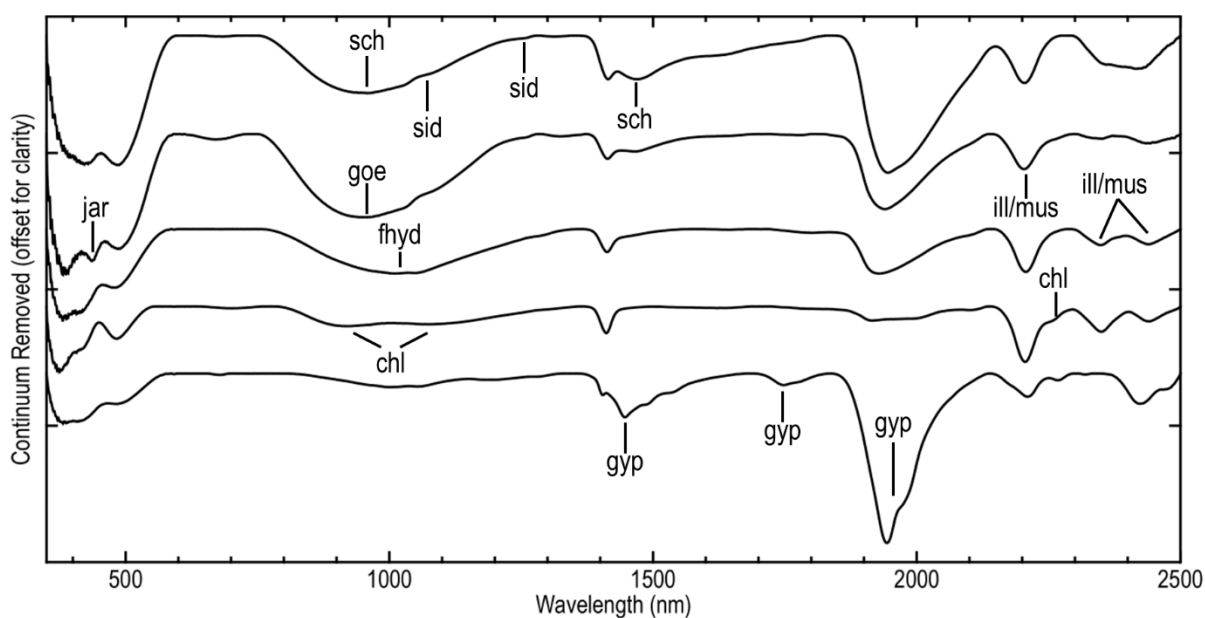


Figure 4.8 Examples of continuum removed spectra from Piccalinna and Sanna mines: goe = goethite, sch = schwertmannite, sid = siderite, ill/mus = illite/muscovite, chl = chlorite and gyp = gypsum.

Figure 4.9 shows the distribution of secondary minerals in the Piccalinna and Sanna areas. Goethite (b-c) is widespread across all residues, while ferrihydrite occurs close to the tailing ponds in the Piccalinna impoundment and mainly along the banks of the Rio Roia Cani in Sanna. Schwertmannite was identified only at one point of the Piccalinna impoundment (b), though it is probably underestimated due to the spectral similarities with goethite and ferrihydrite. Jarosite (d-e) occurs mainly in the north-eastern part of the Piccalinna impoundment and along the banks of the Roia Cani stream in Sanna, where flotation tailings outcrop due to the stream's erosional effect. Gypsum (f-g) was instead detected in the south-western part of the impoundment and in the eastern part of the Sanna tailings, in the upstream sector of the Rio Roia Cani.

Mapping the position of the ferric iron absorption feature (at ~ 900 nm) of each sample in the Piccalinna area, it is possible to observe a progressive shift longwards in wavelength towards the north-eastern sector of the impoundment, with greatest values closest to the tailing ponds (**Figure 4.10a-c**). This is accompanied by a progressive wavelength shift and eventual disappearance of the 670 nm absorption feature (the 'yellowness feature' (Haest et al., 2012)) and a steepening of the edge centered at 550 nm (**Figure 4.10b**).

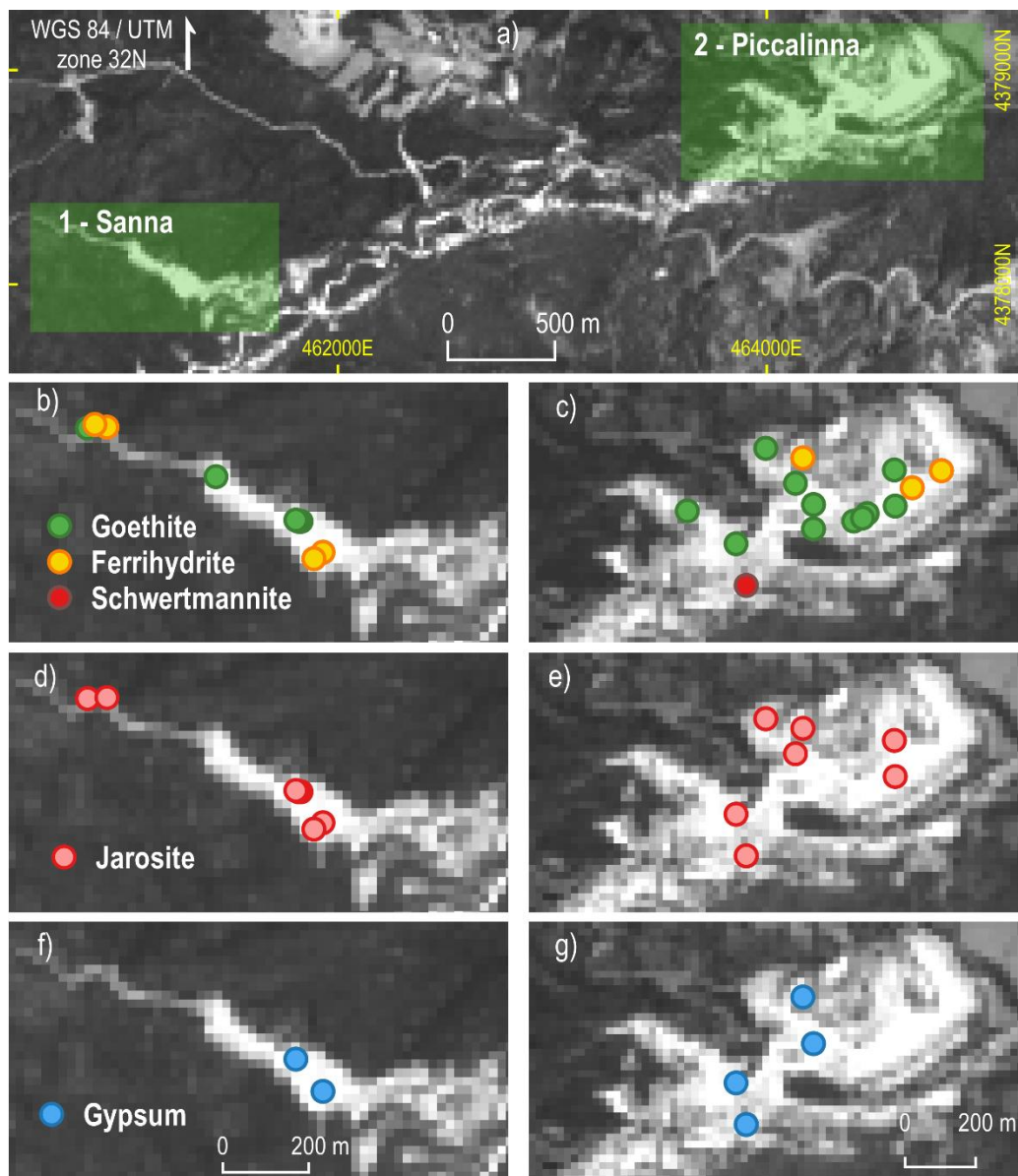


Figure 4.9 distribution of samples where, respectively, goethite and ferrihydrite (b-c), jarosite (d-e), and gypsum (f-g) were identified in the Sanna (left column) and Piccalinna (right column) mine residues.

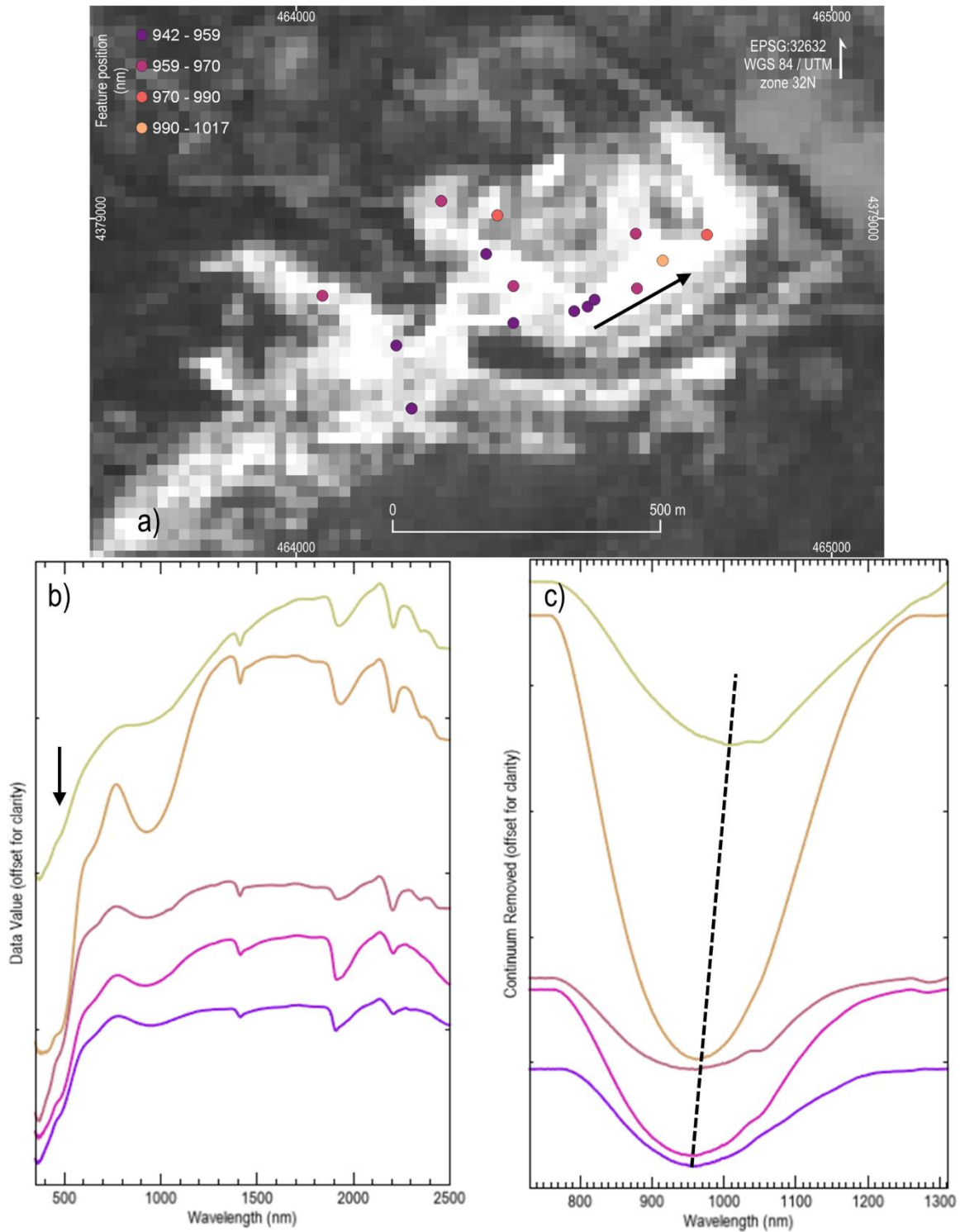


Figure 4.10 (a) Variation of the 900 nm feature position for samples in the Piccalinna impoundment. The arrow indicates the 5 samples whose spectra are represented in (b) and (c). (b) Spectra of selected samples shown in (a). The arrow indicates the steepening of the edge at 550 nm. (c) The continuum removed subset of the spectra shown in (b), representing the ferric iron absorption. The dashed line shows the variation of the absorption position towards longer wavelengths.

4.5.1.2. Rio Irvi and Ingurtosu Areas

For samples collected along the Rio Irvi and in the Ingurtosu area only spectral data is available, while XRD could not be carried out due to logistical reasons and limited funding. **Figure 4.11(a-c)** shows the distribution of sediments and efflorescences along the river (a-b) and their mineral assemblage detected through VNIR-SWIR spectroscopy. The samples of the riverbed sediments are dominated by goethite with additional muscovite and illite, as well as gypsum. Ferrihydrite may be underestimated, as samples were measured about one month after they were collected, allowing for the transformation of ferrihydrite to goethite.

The efflorescent minerals found along the stream are soluble sulfates as shown by the general shape of the spectra. In the VNIR range these spectra also show the presence of iron, identified by the drop in the ultraviolet range (e.g. samples I36a **Figure 4.7a**) and by a sharp absorption at 435 nm accompanied by a broader, though quite shallow absorption at 880-900 nm (e.g. sample I39a, **Figure 4.7a**). The latter feature's position variation along the stream has a bimodal distribution, with features positions centered at wavelengths greater than 900 nm in some cases, especially at the confluence with Rio Piscinas and towards the estuary, while in others centered between 880-890 nm (see **Figure A2. 3** in Appendix II). Spectra bearing the 435 nm feature refer to samples collected along the entire stretch of Rio Irvi, even in areas where 'green rust' was observed (but not sampled, see **Figure 4.12a**, **Figure 4.13**) and at pH varying from slightly acidic to neutral values. Those with the 435 nm feature and a ferric iron feature above 900 nm are hypothesized to be containing jarosite, which, as shown in **Figure 4.12b**, occur only downstream of the confluence with Rio Piscinas, with the 435 nm feature depth progressively decreasing upstream. In the rest of the samples the position and depth of this feature remain quite constant along the stream, with the position oscillating between 434 and 436 nm and slightly dropping below 434 nm towards the estuary, and the depth always below 0.1. The interpretation of the efflorescent minerals is rather complex and are further discussed in-depth in a dedicated section (see Section 0).

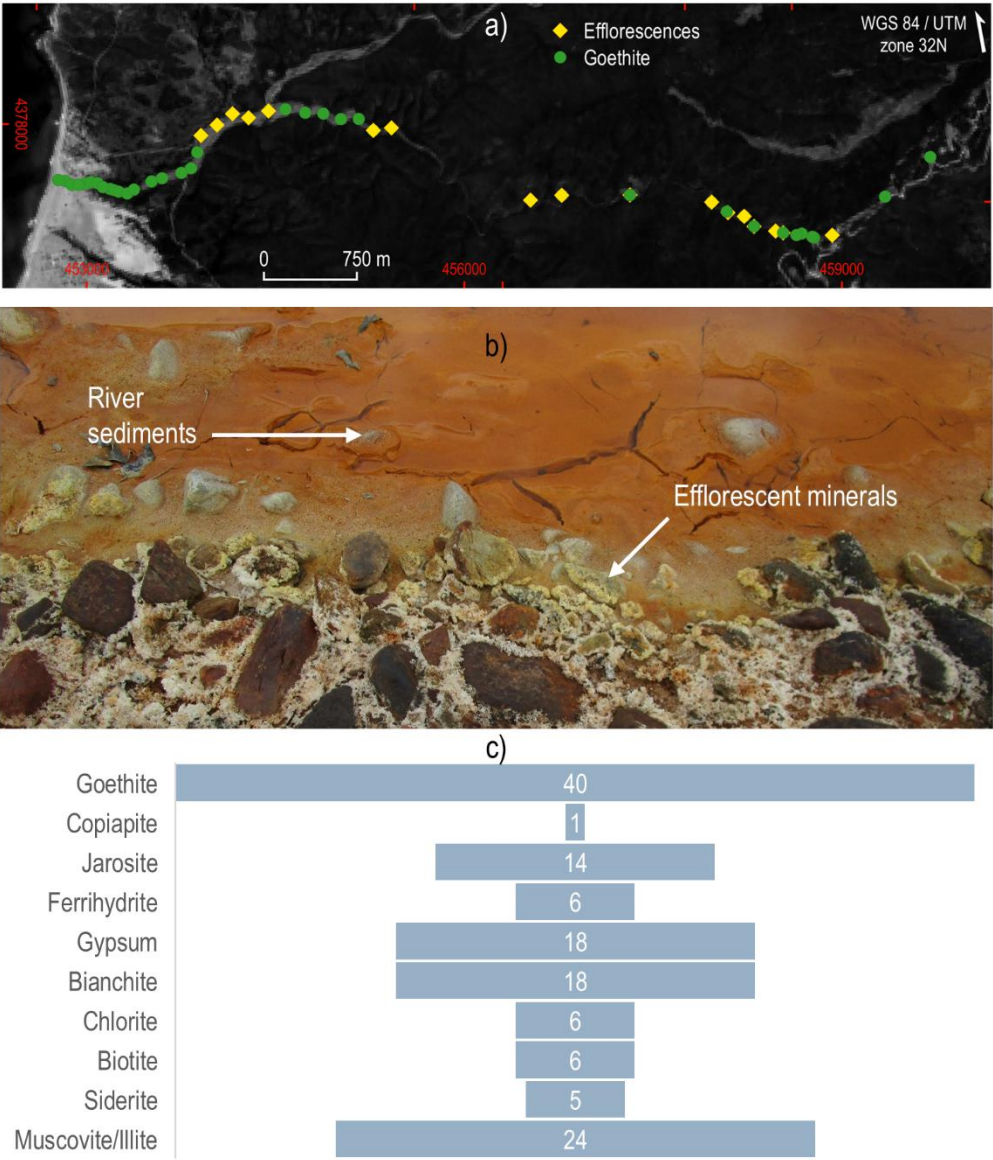


Figure 4.11 (a) distribution of samples containing sediments of the Irvi riverbed and efflorescent minerals. The former is mainly composed of goethite while the latter is mainly a soluble sulfate. (b) Photo of types of samples collected along the Rio Irvi. (c) Other minerals found in association with these sediments. The jarosite occurrence includes also the Fe-bearing phase found in the efflorescences.

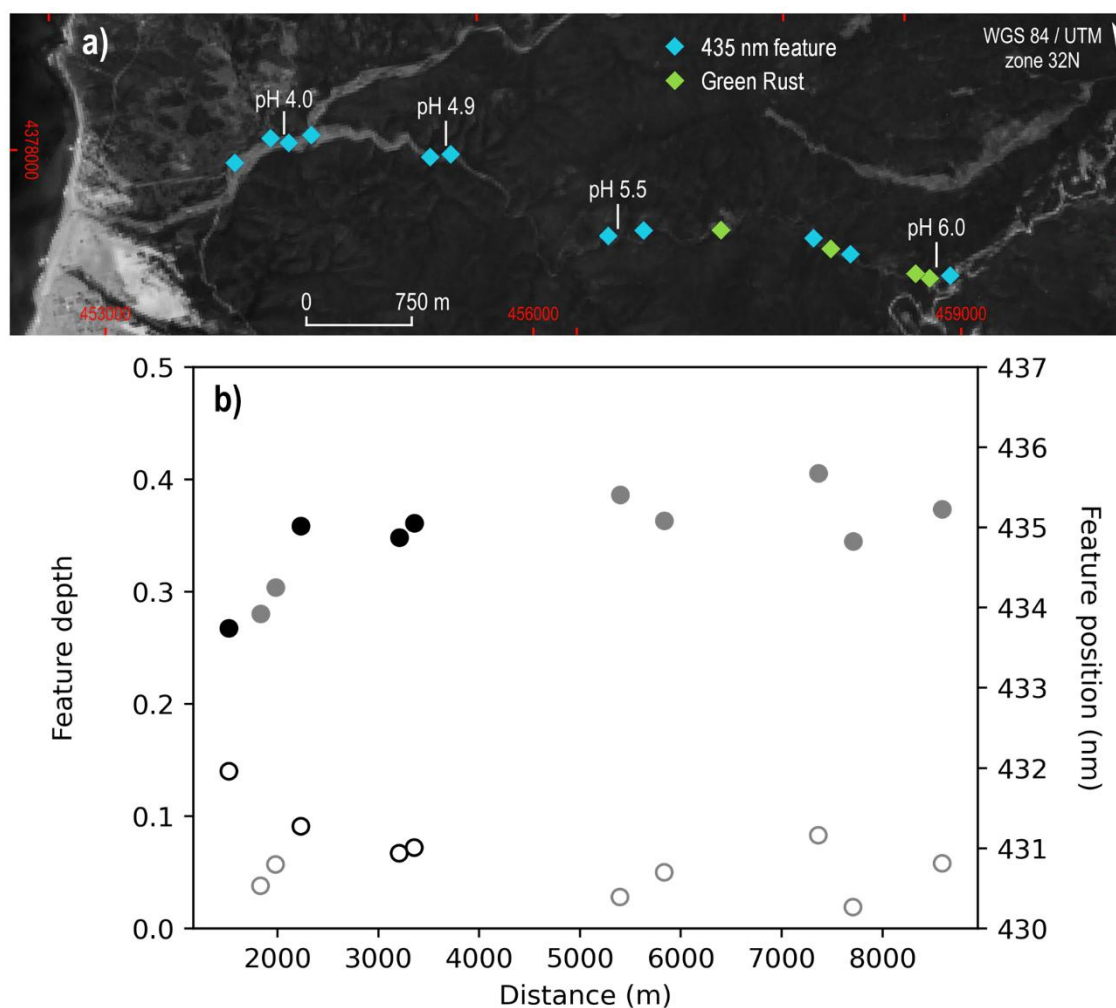


Figure 4.12 (a) location along Rio Irvi of efflorescent mineral samples containing the ~ 435 nm absorption feature and points where green rust was observed in the stream waters. pH values are from earlier studies (De Giudici et al., 2018; Frau et al., 2015) (b) Variation of the position (full circles) and depth (open circles) of the 435 nm feature with distance from the estuary. Black markers refer to samples where jarosite occurrence is hypothesized (i.e. spectra having the ferric iron absorption feature > 900 nm).



Figure 4.13 Rio Irvi with waters containing 'green rust', while the red sediments are hydroxide precipitates, such as ferrihydrite and goethite, and the white minerals along the banks are efflorescences, likely a Zn-sulfate.

The 2265 nm feature was also tracked along the Rio Irvi. This feature was found only in streambed sediment samples and never in the efflorescent minerals samples. As illustrated in **Figure 4.14**, the feature position oscillates between two wavelengths, one centered at ~ 2255 nm and another at ~2265 nm. The latter appears only close the confluence with Rio Piscinas and is most likely related to the presence of jarosite, while the former can be identified constantly up to the confluence with Rio Piscinas, then this feature is not detected anymore. The feature centered at 2255 nm may be associated with detrital phyllosilicates, such as chlorite or biotite, and its depth is quite constant along the stream.

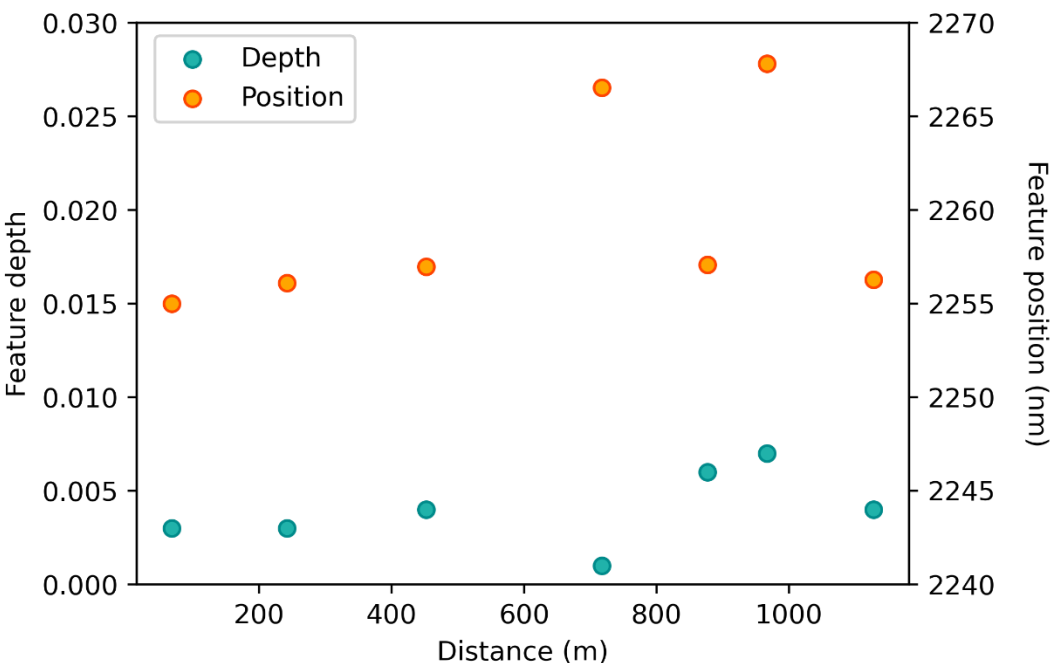


Figure 4.14 variation with distance from the Rio Irvi estuary of the 2265 nm feature position (orange points) and depth (green points).

The Ingurtosu mining area, at the Brassey lavery, is principally composed of clay minerals, mainly illite and muscovite, but also traces of montmorillonite, and gypsum. While present also here iron-bearing minerals, their abundance is far lower than in the other areas analyzed in the case study, as seen by the shallower depth of iron-related absorption features (e.g., the broad absorption centered at ~900 nm). Siderite and chlorite are quite abundant here, while jarosite was detected in only 5 samples. These were mainly found in correspondence with flotation tailings layers, exposed in erosional rills present along the slopes of the waste dumps or by the Naracauli river. Two samples (N001, N002a) contain jarosite in the form of hydronium jarosite, as the spectra contain the characteristic prominent absorptions at ~1470 and 1945 nm (Velasco et al., 2005). The 435 nm absorption feature present in these jarosite samples is slightly shifted longward, probably due to small structural differences compared to those found along the Irvi stream (Cloutis et al., 2011; Russell et al., 2001; Vilas et al., 1993). **Table 4.7** describes the minerals found in each sample point within the Ingurtosu area.

Table 4.7 Mineral assemblage in the Ingurtosu area, detected with reflectance spectroscopy.

Sample Name	Minerals
N001	h-jarosite, gypsum, muscovite/illite
N002a	h-jarosite, gypsum, muscovite/illite
N002b	goethite, , gypsum, siderite, illite/muscovite
N003a	goethite, jarosite, gypsum, muscovite/illite
N003b	goethite, gypsum, siderite, anorthite
N004	muscovite/illite
N006	hematite, goethite, muscovite /illite
N007	goethite, muscovite/illite
N008	goethite, gypsum, muscovite/illite
N009	goethite, siderite, muscovite/illite
N010	goethite, chlorite, muscovite/illite
N011	goethite, siderite, muscovite/illite
N012	goethite, jarosite, gypsum, chlorite
N013	goethite, jarosite, gypsum, chlorite, muscovite/illite
N014	goethite, gypsum, muscovite/illite
N015a	gypsum, chlorite, siderite, muscovite/illite
N015b	gypsum, siderite, muscovite/illite
N016	goethite, gypsum, siderite, muscovite/illite, montmorillonite
N017	goethite, gypsum, siderite, muscovite/illite
N018	gypsum, chlorite, siderite, muscovite/illite, nontronite

4.5.2. Sentinel-2 Images – Multitemporal Analysis

The results deriving from the VNIR reflectance shoulder classification show a progressive increase of Fe(III)-bearing minerals from January to July (**Figure 4.15** and **Figure 4.16** and **Table 4.8**). The most dominant Fe(III) bearing mineral in the analyzed area appears to be goethite/ferrihydrite, followed by hematite, while jarosite appears in very small concentrations in a handful of pixels within the Piccalinna impoundment and the Irvi stream. The technique successfully discriminates subtle feature positions in the spectra (**Figure 4.17**). In point spectra, goethite and ferrihydrite were distinguished mainly by the position of the ferric iron absorption at ~ 900 nm and the presence or absence of the “yellowness” feature (~ 650 nm). The VNIR reflectance shoulder, instead, is not as sensitive as these other features, as there is a strong overlap of its position in the pure endmembers (see **Table A2. 1**). Thus, we preferred to map goethite and ferrihydrite together under the class ‘goethite’. The increase in the extent of areas containing Fe(III)-bearing minerals (**Table 4.8**) is in line with the seasonal and climatic conditions, where the peak of secondary mineral precipitation occurs in the late summer, when the weather has been dry for several consecutive days (Riaza and Müller, 2010). Moisture in soils also drastically reduces the general reflectance of spectra and may have an impact on the results of this classification (Riaza et al., 2011). However, the continuum removal applied before the polynomial fitting should mitigate these effects.

Observing the IMERG rainfall time-series over the area of interest, the image with the greatest number of classified pixels corresponds to the one acquired after 44 consecutive dry days. Jarosite occurs principally in the Piccalinna impoundment, along the Rio Irvi, close to the confluence with the Rio Piscinas, and in the Ingurtosu area, in correspondence with the mine dump slopes furrowed by erosional rills, where the flotation tailings are exposed. It slightly decreases from January to July, especially in the Rio Irvi and Ingurtosu areas, probably due to a slight overrepresentation in the January image related to atmospheric correction artifacts (see Section 4.6.4, **Figure 4.16a, d**). May and July images, instead, show a relatively stable occurrence of jarosite. In different seasons, hematite seems to alternately replace goethite.

Validation results represented by the overall confusion matrix in **Table 4.9** show that the technique performs well when compared with independent data, with an overall accuracy of about 73%. Omission and commission errors are highest for jarosite and hematite, but this is also because most of the field sample spectra were classified as goethite, which is the dominant phase. Therefore, there is a low representation of validation points for these two classes. Nevertheless, goethite shows a very low commission error, while the omission errors are mostly related to a misclassification with hematite. Jarosite, instead, is seldom a dominant phase, so it was not possible to successfully validate it. The overall matrix includes validation of both January and July images. Single-image confusion matrices (**Table A2. 2** and **Table A2. 3** in Appendix II), confirm the results of the overall one, having overall accuracies of 63.64% and 75.76% respectively.

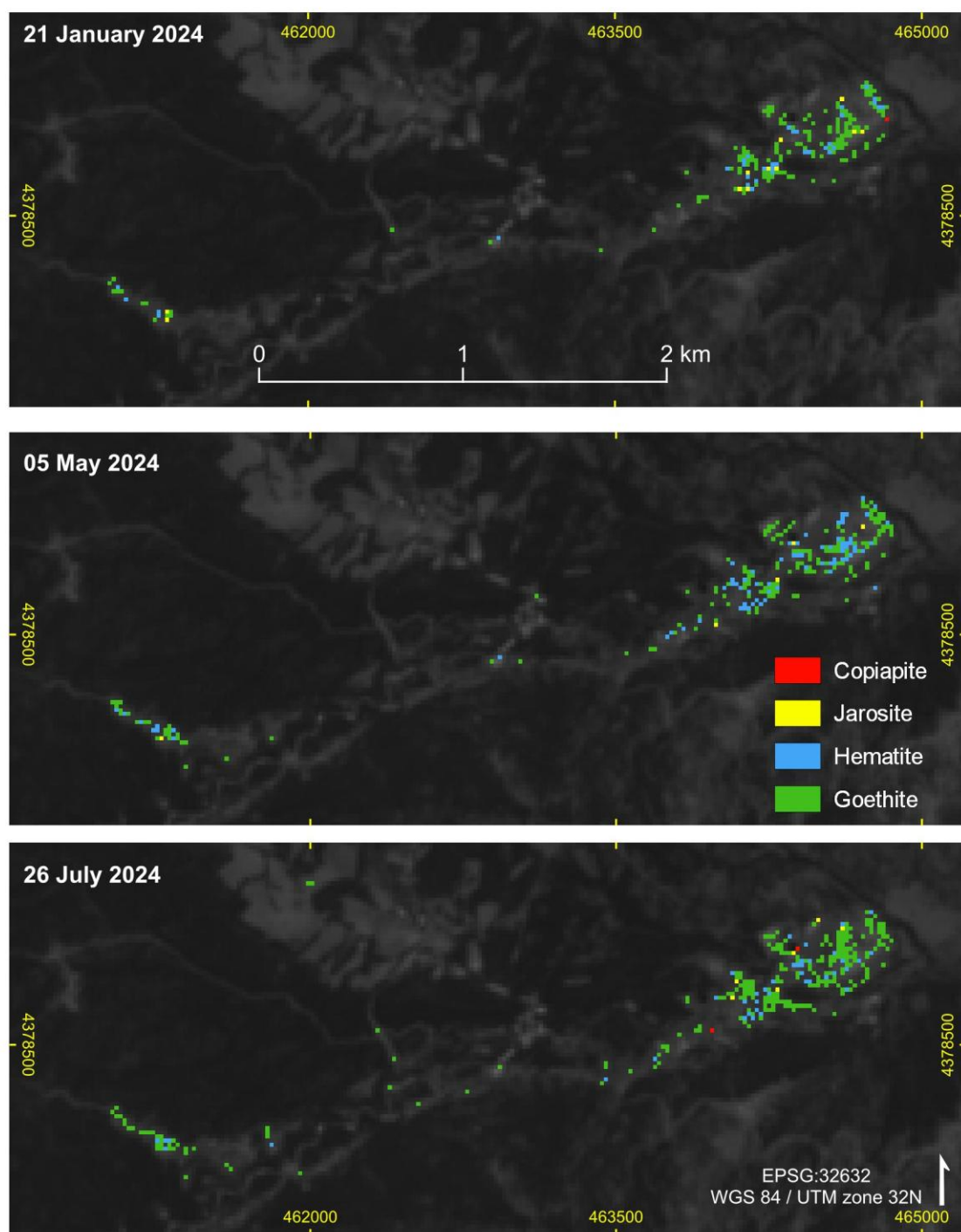


Figure 4.15 Polynomial fitting-derived mineral classification on Sentinel -2 images in the Piccalinna and Sanna mining areas.

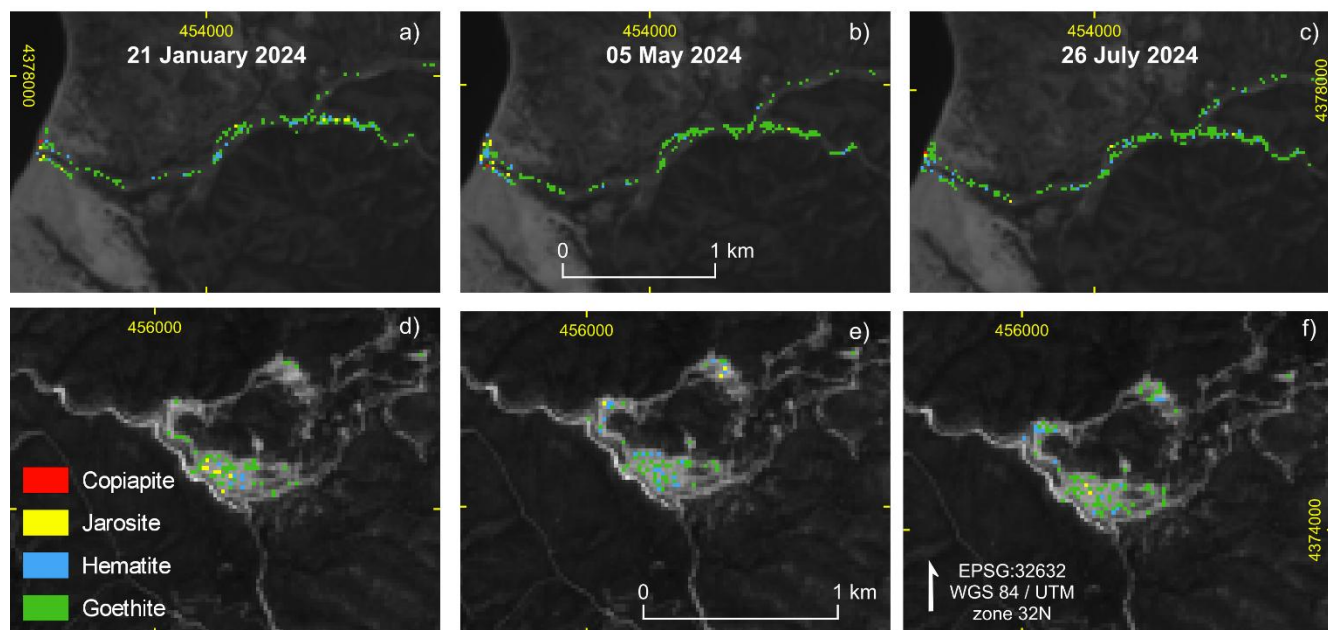


Figure 4.16 Polynomial fitting-derived mineral classification on Sentinel-2 images along the Rio Irvi (a-c) and the Ingurtosu (d-f) mining area.

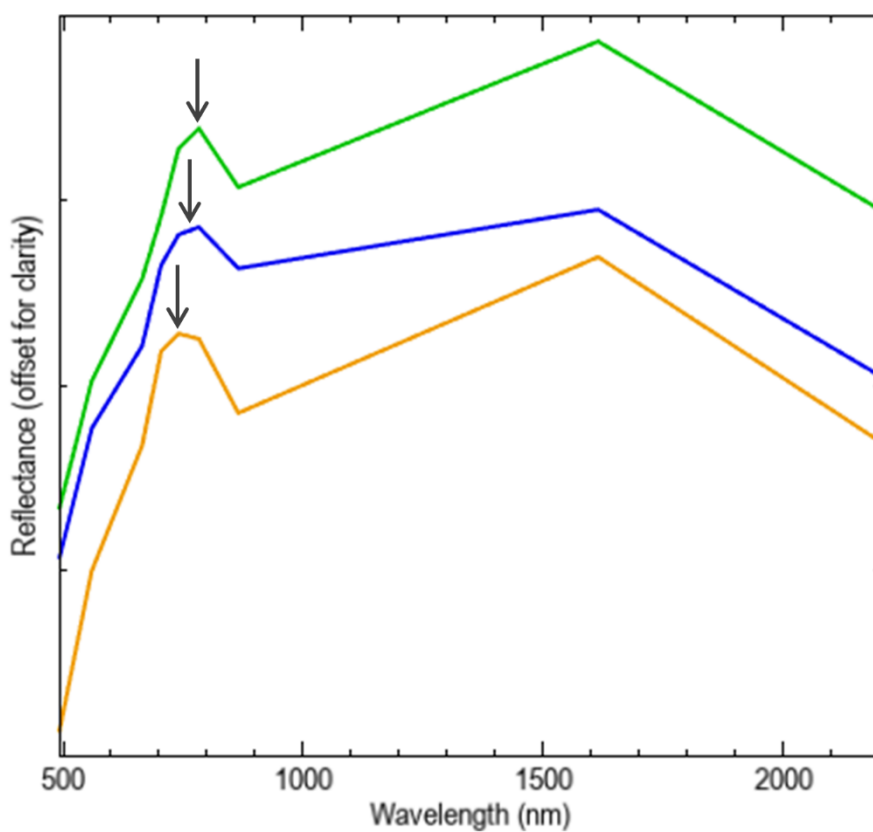


Figure 4.17 Example spectra of goethite (green), hematite (blue), and jarosite (orange) spectra from the Sentinel-2 image of 21st January 2024. Arrows indicate the reflectance maxima for each spectrum.

Table 4.8 Total area covered by each mineral class for the three Sentinel-2 images. The number of dry days is the number of preceding days with precipitation below 5 mm according to the NASA GPM IMERG v07 dataset.

Area (m ²) Mineral	21-Jan-24	5-May-24	26-Jul-24
Copiapite	800	400	1,200
Jarosite	10,800	6,800	6,000
Hematite	26,400	47,200	35,600
Goethite/Ferrihydrite	132,800	152,000	209,600
Total	170,800	206,400	252,400
No. Dry days	0	4	44

Table 4.9 Overall confusion matrix of the mineral classification applied to Sentinel-2 images. Samples collected in the January campaign were compared with cells from the Sentinel-2 image of 21st January 2024, while samples collected in July were compared with the image acquired on the 26th July 2024.

		Sentinel-2					Omission Errors	Commission Errors
		Copiapite	Jarosite	Hematite	Goethite	Total		
Reference	Copiapite	0	0	0	0	0	N/A	N/A
	Jarosite	0	0	0	0	0	N/A	100.00%
	Hematite	0	0	1	3	4	75.00%	85.71%
	Goethite	0	3	6	31	40	22.50%	8.82%
	Total	0	3	7	34	44	Overall Accuracy	72.73%

4.5.3. EnMAP Image Analysis

The iron-bearing mineral distribution obtained from the EnMAP image and based on the polynomial fitting of the VNIR reflectance shoulder, results in being essentially goethite or ferrihydrite (**Figure 4.18**). The lack of other minerals, such as hematite and jarosite, compared to the Sentinel-2 image acquired in May, can be related to the lower spatial resolution.

This VNIR reflectance shoulder allows for the identification of only the dominant Fe-bearing phase present in each image cell. However, by leveraging the sensor's high spectral resolution, it is possible to observe other minor minerals, such as jarosite. This mineral was investigated by observing the 435 nm and 2265 nm absorption features independently, although, as also observed on the spectra of the samples collected in the field, these two features, when associated with jarosite, may not appear together. **Figure 4.19** highlights them in continuum-removed EnMAP spectra. As shown, these features are quite small and sharp, often having a depth that is less than 0.1 and a width of a few tens of nanometers.

Figure 4.20 and **Figure 4.21** show the distribution of image cells containing these bands. At a glance, it emerges that these features represent slightly different phases. Indeed, the 2265 nm feature is more widespread than the 435 nm one and has a greater positional variability (20 nm as opposed to 7 nm for

the 435 nm feature). This suggests that the 2265 nm feature is probably related to more than one mineral phase. In the Piccalinna impoundment (**Figure 4.20a**), the 435 nm feature appears mainly in the central and north-eastern part of the impoundment, close to the tailing ponds. The 2265 nm (**Figure 4.20b**) feature instead can be found in the whole impoundment, but the feature position shifts longward in wavelength as we move closer to the tailing ponds, and in a small area in the southwestern part of the impoundment. The difference between the two features is particularly evident in the Ingurtosu area (**Figure 4.20c-d**), where the 435 nm feature is totally absent, while the 2265 nm feature is present in most of the waste dumps.

Along the Rio Irvi, these features show similar patterns (**Figure 4.21**): the 2265 nm feature upstream and close to the estuary has features centered at lower wavelengths, while in the surroundings of the confluence and for about one kilometer downstream, the feature is shifted to higher wavelengths (2263-2268 nm, **Figure 4.21a** and **c**). The 435 nm feature is most present in the surroundings of the confluence with Rio Piscinas and tends to have also wavelength position values closer to 434-436 nm (**Figure 4.21b** and **d**). The FWHM of the 2265 nm feature graph (**Figure 4.21e**) reveals a double trend, pixels with values between 19-25 nm relative to features centered at around 2265 nm, and others with values between 15 and 17 nm with features centered below 2260 nm. The distribution of depth values (**Figure 4.21g**) is instead harder to interpret, likely because this feature comprises more than one type of mineral. There, however, seem to be three points of maximum depth: at the estuary, slightly downstream of the confluence, and at about 3000 m from the estuary. **Figure 4.21f** for the 435 nm feature shows a more scattered trend, but generally depth values are higher close to the Piscinas confluence and progressively decrease non-linearly towards the estuary of the Irvi stream. The confluence area is also where there is a higher density of pixels containing the 435 nm feature. The FWHM (**Figure 4.21h**) instead remains relatively constant throughout the length of the stream. The spatial pattern defined by the union of image cells containing the 435 and the 2265 nm features is similar to the one shown in **Figure 4.9e** and **Figure 4.12a**, relative to the samples collected in the field.

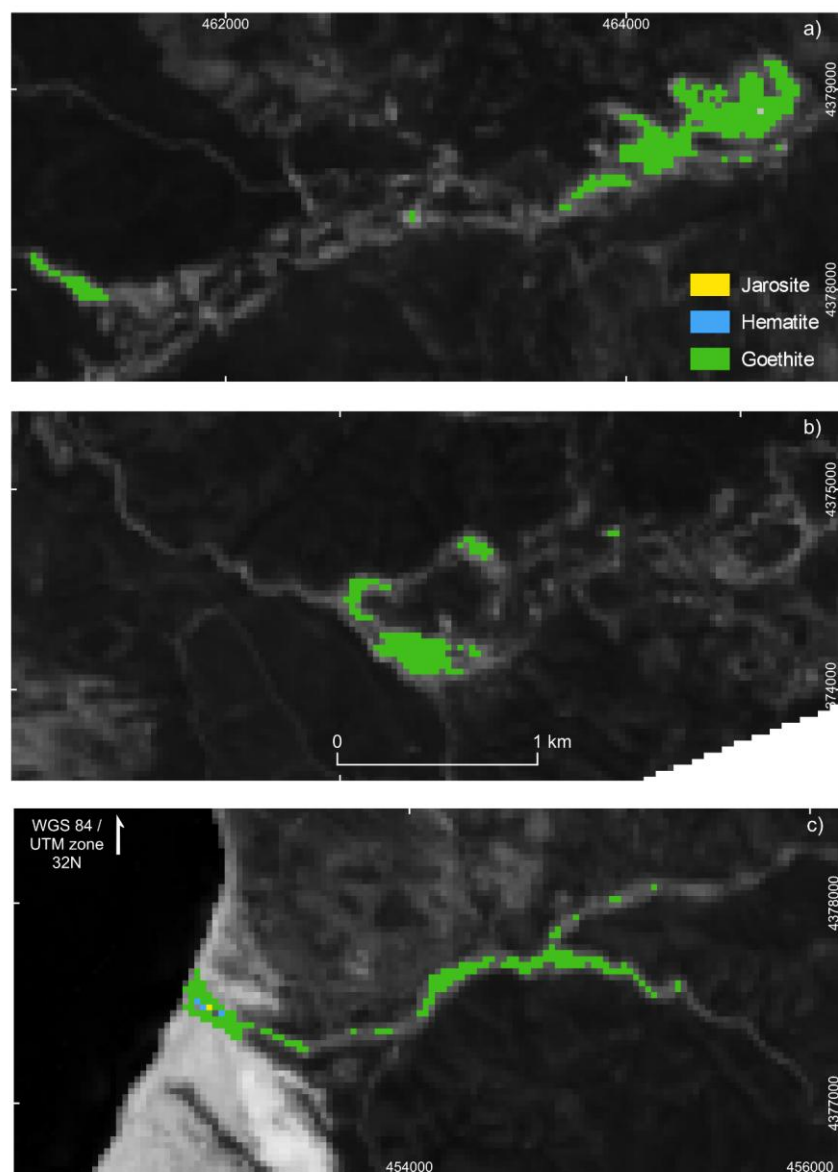


Figure 4.18 Fe(III)-bearing mineral classification based on the VNIR reflectance shoulder (at ~ 760 nm) carried out with EnMAP over the Piccalinna and Ingurtoisu mining dumps (a, b) and along the Rio Irvi (c).

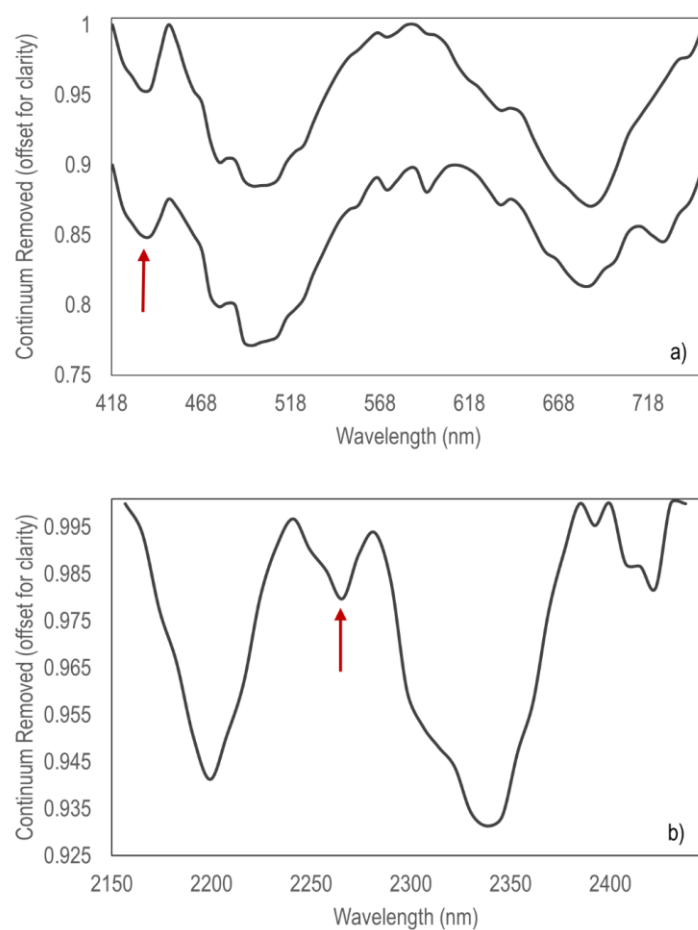


Figure 4.19 Continuum removed EnMAP spectra of the 435 nm feature (a) and the 2265 nm feature (b).

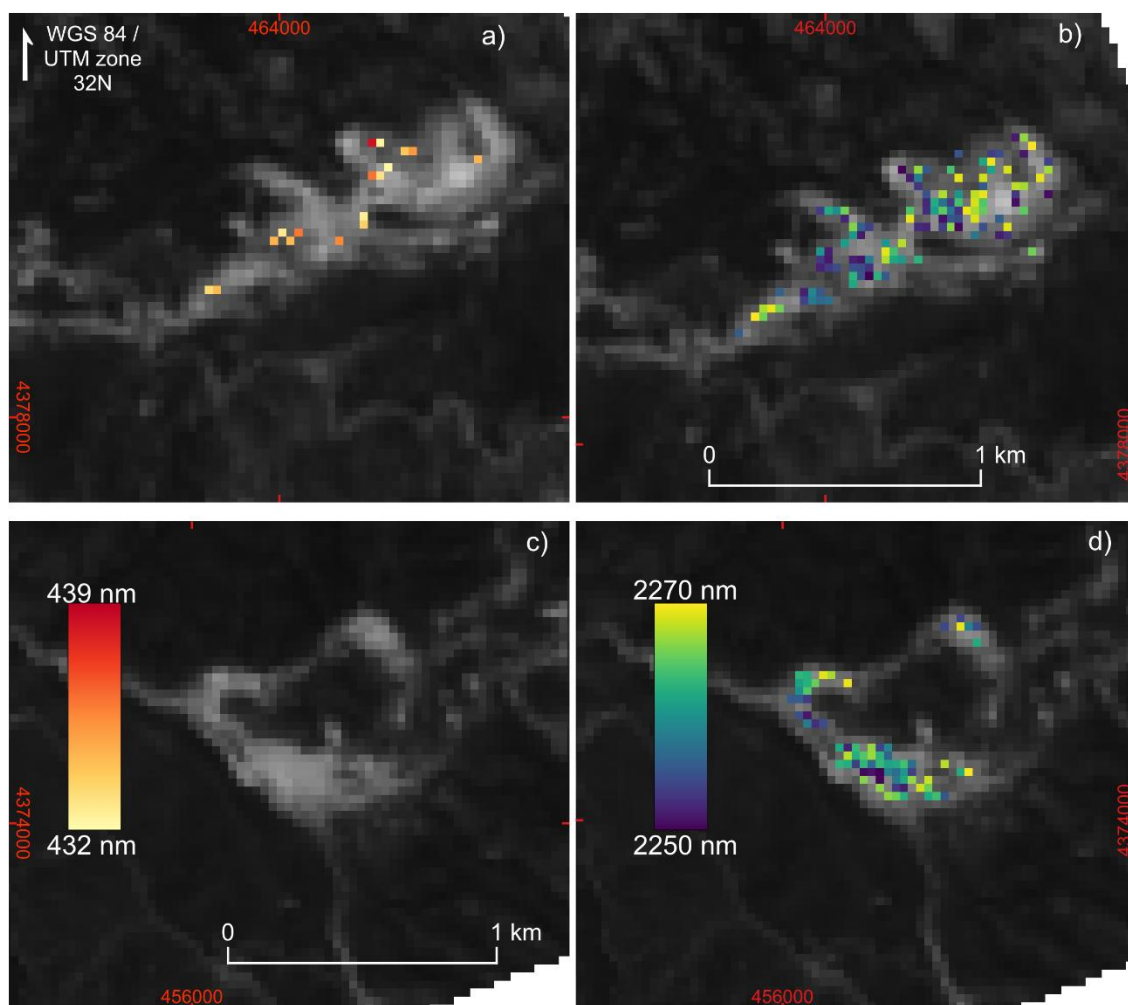


Figure 4.20 Mineral detection analysis carried out with an EnMAP image over the Piccalinna impoundment (a-b) and the Ingurtoosu mining dumps (c-d). (a, c) Occurrence and position of 435 nm absorption feature, diagnostic for jarosite. (b,d) Occurrence and position of the 2265 nm feature.

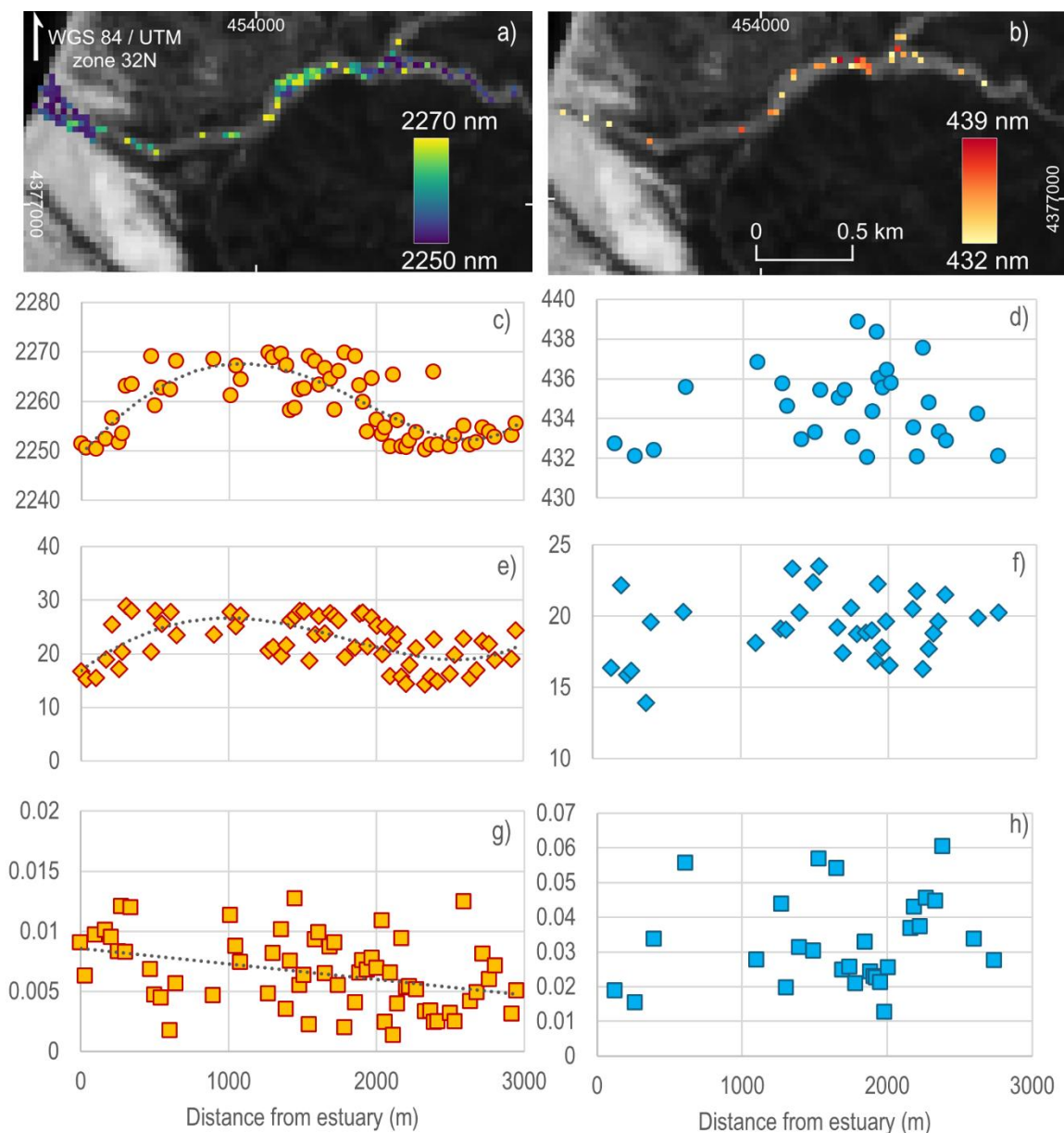


Figure 4.21 Occurrence of the 2265 nm (left column) and the 435 nm (right column) features along the Rio Irvi. The graphs indicate the variation of the feature position (a-d), FWHM (e-f), and depth (g-h) with distance from the Rio Irvi estuary.

The position of the ferric iron feature modeled on EnMAP with polynomial fitting highlights spatial variations within the Piccalinna impoundment and in the Rio Irvi area (**Figure 4.22**). In the former, a clear spot characterized by phases that have a ferric iron position shifted towards ~ 1000 nm emerges. This result matches those obtained from the samples collected in that same area (**Figure 4.10**). Rio Irvi, instead, shows a progressive longward wavelength shift towards the estuary. The Ingurtosu area is instead almost totally lacking this feature. This result is in line with the spectra of samples collected in that area, which were mainly dominated by clay minerals and lacked or showed shallow iron-related features (see **Figure 4.7b**).

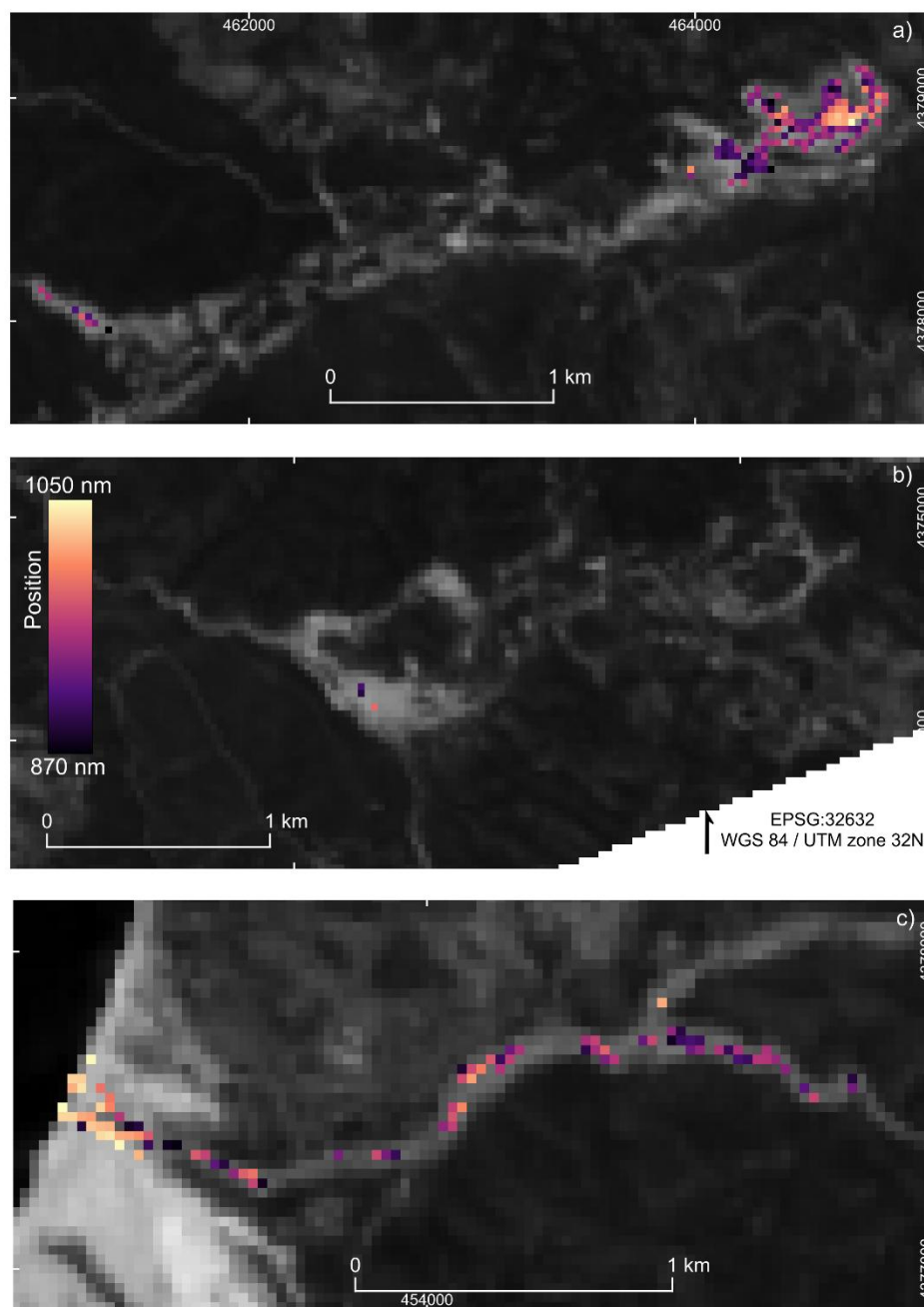


Figure 4.22 Position of the modeled ferric iron absorption feature (~900 nm) in the Piccalinna and Sanna areas (top), the Naracali (middle), and the Rio Irvi (bottom) areas.

4.6. Discussion

With this study, we wanted to show the potential of hyperspectral remote sensing and spectroscopy for the geochemical characterization of mine residues in a challenging test site. The area of interest is difficult to analyze with this technique, as it is highly vegetated and characterized by an articulated topography. An in-depth analysis of the iron-bearing minerals themselves allowed for reconstruction of the chemistry

and dynamic environmental conditions of the area. In this section are discussed the interpretation of spectral signatures encountered in this work, geochemical implications, as well as technical and methodological advantages and limitations and future research developments.

4.6.1. Interpretation of Analyzed Spectral Features

The Montevecchio-Ingurtosu area was analyzed with satellite data by leveraging four main spectral features: the ferric iron absorption feature (at ~ 900 nm), the 435 and 2265 nm absorption features as potential indicators of jarosite, and the 760 nm reflectance peak to discriminate between different iron-bearing minerals.

The spatial pattern shown on the EnMAP image by mapping the ferric iron feature is remarkably in agreement with the spectra of samples collected in the field. In the Piccalinna impoundment, the progressive positional shift to longer wavelengths of the ferric iron feature towards the tailing ponds can be interpreted as an indication of a decrease in grain size of the iron-hydroxide phases towards the north-eastern sector of the impoundment (Morris et al., 1985) and a progressive transition from a goethite to a ferrihydrite-dominated zone. This is confirmed also by the progressive reflectance decrease at wavelengths below 500 nm, due to the trans-opaque nature of iron-hydroxides in VNIR range (Cudahy and Ramanaidou, 1997), and the progressive migration to longer wavelengths and reduction in depth of the 'yellowness feature' towards 700 nm (Crowley et al., 2003; Scheinost et al., 1998). Along Rio Irvi, the shift of the ferric iron feature to longer wavelengths at the estuary could be an indication of a transition to a more neutral to alkaline water chemistry, which favors the precipitation of ferrihydrite, but also the oxidation of other iron-bearing minerals including clay minerals and silicates.

The 2265 nm feature, when associated with jarosite, is quite constant and is related to the combination of stretching of the hydroxyl anion and of bending of the Fe-OH group (Clark et al., 1990), appearing around 2263 and 2267 nm (Bell et al., 2010; Farrand et al., 2009). Yet, this feature overlaps with a similar one centered between 2248 and 2261 nm, associated with di-octahedral and tri-octahedral sheet silicates such as biotite and chlorite, which is related to a combination of stretching and bending of the Al(Mg, Fe²⁺)OH group and whose position depends on the Mg/Al ratio (Laukamp et al., 2021; Lypaczewski and Rivard, 2018). In this case, end-members rich in iron (e.g., chamosite) shift the feature to longer wavelengths. Therefore, the great variability of this feature's position in all the mine residues could be an indication that the feature represents different mineral phases. Where the feature is centered at about 2265 nm it is likely related to jarosite, while positions at lower wavelengths are indicative of phyllosilicates such as chlorite and biotite, present as detrital minerals. It emerges that jarosite mainly occurs close to the tailing ponds in Piccalinna and at the confluence with Rio Piscinas along the Rio Irvi. At the same time, the lack of a spatial pattern in the Ingurtosu dumps is a clear indication that the feature represents phyllosilicates, where areas with features centered close to 2265 nm could be indicative of Fe-bearing phyllosilicates, such as biotite, though the possibility of finding jarosite should not be ruled out completely. These

findings are also confirmed by the spatial distribution of the 435 nm feature, which occurs in the same areas where the jarosite-related 2265 nm feature appears.

Finally, the 760 nm reflection peak was here used to produce a map of iron-bearing minerals, both on Sentinel-2 and EnMAP images. The technique proved to successfully discriminate different minerals, especially goethite, hematite and jarosite, by subtle feature position variations in the spectra (**Figure 4.17**). With this method, two minerals, hematite and copiapite, were identified on Sentinel-2 data that were not detected in the spectra of samples collected in the field. Copiapite, in almost all cases, appears as a false positive, most likely the result of an artifact generated during atmospheric correction or due to mixed land-water spectra (Jewell et al., 2024). Copiapite is probably too sparse, if present, to be detected in this area of interest, despite having been found in one sample collected in the July campaign (C00) and reported in previous studies (Cidu et al., 2011). Hematite, though not found in any of the samples collected in the field, is nevertheless quite extensive in the area, as reported by some authors, especially in the Piccalinna area (Cidu et al., 2011). Poorly crystalline hematite forms as a result of ferrihydrite or goethite dehydration (Nordstrom and Alpers, 1997), but may also seasonally transform to goethite with varying temperature and humidity (Kämpf and Schwertmann, 1983). Yet, it should also be noted that the reflectance shoulder position between hematite and goethite is quite similar and would be better distinguished using the ~ 900 nm absorption feature (Crowley et al., 2003). More extensive fieldwork and mineralogical analyses should be carried out to verify the presence of hematite and better calibrate the classification workflow.

4.6.2. Spectral Interpretation of the Efflorescent Minerals

The efflorescent minerals found along the stream are soluble sulfates of either the epsomite or the hexahydrite group. This can be deduced by the general shape of the spectra (Lane et al., 2015; Pfitzner et al., 2018), specifically by the geometry of the single absorption features between 1400 and 2000 nm, which are distinguishable from other less hydrated groups (Crowley, 1991; Drake, 1995). However, the positions of such features are shifted compared to pure hexahydrite or epsomite, at 1465, 1673 and 1952 nm respectively. Because Rio Irvi is very rich in Zn, the sulfate phase detected in the samples is likely Zn-bearing, and therefore it is probably goslarite, whose spectral signature is reported in only one previous work (McConachy et al., 2007) or bianchite. Unfortunately, an end-member reference from a spectral library or database is not available, and further mineralogical analyses should be carried out to confirm the validity of this hypothesis. Bianchite is a common efflorescent mineral in Zn-bearing mine residues and generally forms in the summer period where the temperature is between 15 and 40° C and the relative humidity is between 50-85%, while goslarite is stable at lower temperatures (Bril et al., 2008; Chou and Seal, 2005). Natural bianchite can contain up to 45 mol% of Fe (Chou and Seal, 2005; Jambor et al., 2000). Because the spectra of efflorescent minerals show the presence of iron, it is likely that the phase is bianchite-bearing. However, the 435 nm feature is highly diagnostic for jarosite (Hunt and Ashley,

1979), and spectra with this feature appear also in co-occurrence with green rust, in circumneutral waters and in suboxic conditions (Frau et al., 2015). These environmental conditions are not favorable to the precipitation of this mineral (Jambor et al., 2000; Nordstrom and Alpers, 1997). However, observing the position of the ferric iron feature, it is hypothesized that the 435 nm feature present in the efflorescences' spectra are related to two different phases: to oxidized iron-bearing bianchite, in samples with the ferric iron absorption at 880 nm, and to a jarosite-bianchite mixture in samples with the ferric iron absorption feature centered longward of 900 nm. Samples bearing jarosite occur only at the confluence with Rio Piscinas, where pH drops to 4, a pattern also confirmed by the results obtained with EnMAP. Though the section of the stream where jarosite occurs is more acidic than upstream, pH conditions are, in principle, not ideal for its formation. However, the high Fe^{3+} content dissolved in Rio Irvi contributes to the increase in water acidity. Thus, this factor, coupled with a high evaporation rate, may create localized extremely acidic microenvironments in sediment pore-water along the banks of the stream, perhaps mediated by bacterial activity (Dockrey et al., 2014; Frau, personal communication), ultimately favoring the precipitation of iron-bearing sulfates in a dynamic equilibrium (Nordstrom and Alpers, 1997).

4.6.3. Other Geochemical Implications

By tracking Fe-bearing minerals' grain size and detecting the transition between goethite and ferrihydrite, as well as the spatial distribution of jarosite, it is possible to map zones of higher Fe^{3+} activity and sources of acid mine drainage within tailings. By observing the results from all sensors presented in this work, a zonation of secondary minerals can be delineated in the Piccalinna impoundment (**Figure 4.23**). The zonation is obtained by visual analysis of the results combined with the author's knowledge of the area of interest and outlined manually, summarizing the results in a single graphic. The zonation reflects the pH-controlled precipitation of minerals described in other works (Bigham et al., 1996; Montero S. et al., 2005; Swayze et al., 2000; Zabcic et al., 2014). Specifically, in areas where jarosite is the main Fe^{3+} -bearing mineral, there is a higher concentration of sulfides and pH is expected to be below 3.5. The presence of water facilitates ferric iron activity thus enabling the precipitation of jarosite. Radially from the source, a jarosite and ferrihydrite (pH between 3-4) or jarosite and goethite (pH<4) zone follows, while the most external zone is characterized by goethite only (pH>4). As shown, the most acidic hotspots are located close to the tailing ponds, or by the Principe Tommaso lavery and the Sant'Antonio mineshaft. Schwertmannite is most likely present in this area, as the environmental conditions favor its precipitation (Cidu et al., 2011). However, this phase was not detected despite being, in principle, possible to identify it with reflectance spectroscopy, because its spectral signature is similar to that of ferrihydrite and goethite, hampering its discrimination in mixed spectra (Crowley et al., 2003; Williams et al., 2002).

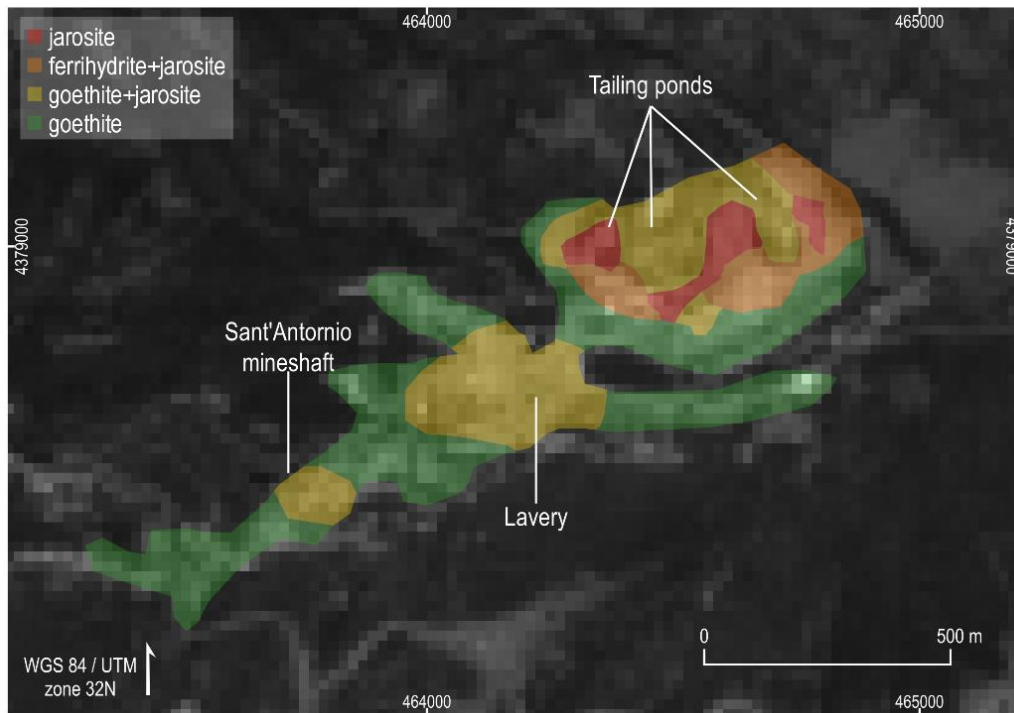


Figure 4.23 Secondary Fe-bearing mineral zonation in the Piccalinna impoundment derived by the combination of results obtained from spectra of samples collected in the field, Sentinel-2, and EnMAP images.

The efflorescent salts detected along the banks of the Rio Irvi reflect the chemistry of the water in the stream (Frau, 2000; Romero et al., 2006). Bianchite generally precipitates when the concentration of Fe^{3+} in the waters decreases with the formation of oxides, hydroxides, and sulfates. Besides Zn, these minerals tend to incorporate in their crystal structure also other metals, such as Cd (Romero et al., 2006). Equally, green rust and the phases it precipitates in are considered temporary sinks for a large number of metals and contaminants, such as Zn, Cd, Ni, Co, and Mg. As these minerals are highly soluble, they could generate peaks in metal loads in the waters at the end of the dry season, with the first rain showers (Bril et al., 2008; Frau et al., 2015). Therefore, monitoring of precipitation and dissolution pulses of these minerals allows to reconstruct the dynamics of contaminant mobility, thus providing essential information for preventing or tackling river and soil contamination.

4.6.4. Technical and Methodological Implications

i. Methodological Strengths

The results of this study underscore the effectiveness of adopting a multi-sensor and multi-scale approach for analyzing mine residues. Imaging and non-imaging hyperspectral sensors, such as ASD systems and EnMAP images, fully capture the geometry of reflectance spectra through which minerals and their chemical and mineralogical characteristics take shape. At laboratory level, reflectance spectroscopy proves to be superior to other techniques for the detection of certain minerals, confirming

its relevance in the characterization of geological targets. For instance, while powder XRD technique used in this work is optimal for identifying sulfides and tectosilicates, which are transparent in the VNIR-SWIR spectral region (Coulter et al., 2017), optical reflectance spectroscopy has a higher sensitivity for iron-bearing minerals in both crystalline and amorphous structures (Balsam et al., 2014; Scheinost et al., 1998; Shen et al., 2006), clays (Sadrian et al., 2022), and gypsum (Crowley, 1991; Drake, 1995). At a remote sensing scale, the same physical principles of reflectance spectroscopy and methods are leveraged for observing vast regions at once, making this technique extremely time- and cost-effective.

With the use of polynomial fitting, we have shown that low spectral resolution of multispectral sensors can partially be compensated, while still maintaining a high spatial resolution. This technique allowed to make reflectance and absorption feature maps, carried out with multispectral systems, comparable to those conducted on hyperspectral ones. The only requirement is to have a minimum of three to five bands centered within the range of the feature of interest to apply the polynomial interpolation (Crowley et al., 1989; Van Der Werff and Van Der Meer, 2015). Thus, based on the same reflectance feature (i.e. the 750 nm shoulder), Sentinel-2 with a 20 m GSD revealed subtle variations in the area of interest, which EnMAP, despite its high spectral resolution, could not detect. This advantage unlocks the potential of conducting systematic temporal analyses on a monthly, seasonal (as presented in this study), or multi-year scale. Until today, very few studies have attempted to use remote sensing for monitoring AMD affected areas (Ong and Cudahy, 2014; Riaza and Müller, 2010), and none using Sentinel-2 data. Monitoring these variations is of fundamental importance, since some of the secondary ephemeral minerals, such as bianchite (or other Zn-sulfates) and ferrihydrite, adsorb contaminants upon precipitation, but are also able to rapidly release them in the waterways as the first heavy rainfall event of the season occurs (Das et al., 2011; Romero et al., 2006). Though changes in these environments are very rapid, the large data collection represented by Sentinel-2 could still reveal seasonal patterns in the mineral distribution of post-mining areas.

In parallel, in cases where multispectral data is lacking, hyperspectral data can complement. This is the case of the 900 nm absorption feature which cannot be mapped with Sentinel-2 images due to a lack of bands in that range, while it was possible to reconstruct it on EnMAP, despite the strong instrumental noise. This feature, together with the 750 nm reflectance shoulder, allowed to identify the spatial distribution of different secondary minerals and detect areas of higher acidity. The instrumental noise occurring in the spectral region between 900 and 1000 nm is common to most optical satellite data. However, next-generation satellites such as the already mentioned Sentinel-2 NG and ESA's CHIME hyperspectral sensor (European Space Agency, 2025) are expected to overcome this issue thanks to technological improvements to the sensors.

ii. Methodological Limitations

There are, however, challenges and limitations when adopting this technique for post-mining environmental analyses. Despite the level of detail obtained from EnMAP and Sentinel-2 images, this is still too coarse for operational applications, since legacy mining lands are spatially inhomogeneous, with variations occurring within a meter or less. Ideally, sensors should have a spatial resolution of 2.5-15 m, meaning that aerial and drone hyperspectral acquisitions are more suitable than satellite data (Chalkley et al., 2022; Davies and Calvin, 2017). However, it is expected that, once operational, sensors such as Sentinel-2 Next Generation (Kirsches et al., 2024) and Landsat-Next generation (European Space Agency - ESA, 2025; Portela et al., 2025) which have 26 bands in the VNIR-SWIR range with a spatial sample distance of 5 or 10 m, will enable the generation of more accurate mineral maps. Atmospheric correction too plays a critical role in correctly interpreting mineral spectra. It has already been shown how different atmospheric corrections provide different results on the same images (Riaza et al., 2011). In this case as well, two different atmospheric correction algorithms were tested on Sentinel-2 images, sen2Cor (developed by ESA) and MAJA (developed by CNES). The classification results were very different with ESA's Sentinel-2 data having an overall accuracy of just 16.5% compared to the over 72% accuracy presented in this study. With the Sen2Cor atmospheric correction, artefacts were introduced in the spectra, causing an overestimation of the copiapite class over the others (see **Figure A2. 4** in Appendix II). On the other hand, results with MAJA algorithm showed greater consistency in time, as it is tailored for time-series analyses, ensuring that images acquired on different dates are comparable (Colin et al., 2023). Nevertheless, as historical and operational mine sites are variable landscapes both spatially and spectrally, it may be considered opportune to apply a tailored atmospheric correction to these sites for more accurate results.

Sentinel-2 classification results did not always match results obtained in point spectra (e.g. presence of hematite, not reported in Sentinel-2) or with EnMAP data (e.g. the extensive iron presence in Ingurtosu, not detected on the 900 nm feature map) This fact begs the question: How reliable is a classification based on just the VNIR reflectance shoulder? Previous studies have leveraged this feature for a characterization of an AMD-affected site (Cuadros et al., 2020), others used the 900 nm absorption band to discriminate between different iron oxy/hydroxides (Cudahy and Ramanaidou, 1997). Yet, both features shift considerably if in intimate mixture with goethite and ferrihydrite (Clark, 1999; Hunt and Ashley, 1979). Even in the SWIR range the 2265 nm jarosite absorption may disappear in co-existence with muscovite (Farrand and Bhattacharya, 2021; Montero S. et al., 2005). Using just one feature for mineral classification is often not enough to accurately identify target minerals, and results must be confirmed by the presence of other diagnostic features or independent analytical techniques. This implies that an in-depth knowledge of the geology of the area is still necessary for a correct interpretation of the results (Riaza et al., 2011; Zabcic et al., 2014).

Time between sample collection and laboratory analyses plays a critical role in comparing field data with satellite images. In this study, the significant delay between the field campaigns and the spectral measurements of the samples may be a reason for the discrepancy between these and the Sentinel-2 results. For instance, ferrihydrite may have transformed to goethite as the samples were removed from the original environment (Das et al., 2011; Kämpf and Schwertmann, 1983; Lagroix et al., 2016; Yee et al., 2006). **Figure A2. 5** illustrates how spectra can vary after being acquired several months after their collection from the field. The efflorescences (**Figure A2. 5a**) show the greatest difference, with the broad feature between 1600 and 1800 changing geometry, probably due to a loss of water molecules and therefore the phase transition to a less hydrated Zn-sulfate mineral. **Figure A2. 5(b-c)** shows an increase in depth of the 480, 960 and 1950 nm features, probably indicating a further transformation from poorly crystalline to crystalline goethite, while the general increase in reflectance in a and c is likely due to a loss in humidity of the samples.

Other factors which may contribute to omission and commission errors in mineral classifications are: a) intimate mixtures with non-geological materials within a pixel (Jewell et al., 2024), b) adjacency effects: especially in highly vegetated areas such as the present case study, the adjacent image cells contribute to some extent to the geometry of the spectrum, leading to possible misclassifications of pixels. Further research on such effects on each mineral class should be carried out to find ways to mitigate them in the future.

4.6.5. Future Research developments and Recommendations

Though this work demonstrated the potential of combined multi-platform remote sensing for deriving the geochemistry and mineralogy of legacy mining areas, the knowledge gap between the state of the art and an operational implementation is still relatively large. The main reason lies in the low spatial resolution of freely available satellite-based sensors. These, though useful for preliminary assessments, are insufficient for providing products with the required level of detail. Therefore, drone or aerial-based hyperspectral acquisitions are more suitable for this kind of application. Even the timing between repeat acquisitions is critical: ideally, especially in fluvial systems, acquisitions should reflect changes in river flow rates, to better understand pulses of pollution tied to the precipitation/dissolution dynamics of heavy metal and acidity-bearing minerals. This means that the six-day revisit time of Sentinel-2 is still too low for properly addressing these issues.

Nevertheless, with the growing collection of Sentinel-2 and Landsat data, as well as with the upcoming CHIME mission, expected to acquire continuously in hyperspectral mode on a global scale, time series analyses also in mining environments become increasingly interesting themes to conduct research in. Earlier studies on Sentinel-2 data have shown that mineral indices are not invariant, but change based on illumination, humidity and weather (van der Werff et al., 2022). In the coming years, attention should be paid on ensuring that mineral targets observed in time with remote sensing data are comparable

throughout different seasons and years, in order to improve both classification and mineral quantification studies.

This study emphasized the challenges related to intimate mixtures and mineral masking effects, particularly in the VNIR range. Investigations on AMD-affected environments reveal that an in-depth knowledge on geometrical changes in spectral mixtures of different iron-oxy/hydroxides with varying relative abundances is still lacking. Further research developments in this field could greatly improve the accuracy of spectroscopy-based results for such geochemically dynamical contexts, and better support mining companies and reclamation institutes in mitigating environmental impacts.

Finally, though AMD-affected areas have been extensively investigated with remote sensing technologies, secondary minerals generated from Pb-Zn mines have seldom been analyzed. There is therefore a lack of spectral reference data referring to Zn and Pb sulfates, oxides, hydroxides and salts, which significantly affects the possibility of studying these geological environments with imaging spectroscopy means. With the increasing use of hyperspectral systems in the mining and geological exploration domains, it is of great importance to continue developing extensive spectral libraries of more metal-bearing minerals of primary, secondary and tertiary generation, present in mining environments.

4.7. Conclusion

With this work, we demonstrated how the combined use of proximal sensing and multispectral and hyperspectral satellite data can describe the mineralogy and geochemistry of a legacy mining site with a high level of detail. With this study, we proved the usefulness of reflectance spectroscopy and remote sensing for analyzing an area affected by mine drainage with different degrees of acidity, by tracking secondary iron-bearing minerals and Zn-bearing efflorescences. Specifically, we highlighted AMD sources in land (Piccalinna) and water (Rio Irvi), while allowing to exclude other non-acid generating areas (Ingurtoosu dumps). Challenges related to the use of satellite data in a relatively small area and with a lush vegetation were partially overcome by the combined use of Sentinel-2, with its high spatial resolution, and EnMAP images, characterized by a high spectral resolution. Though the spatial resolution of satellite images is not suitable to detect details below 20 or 30 m, maps derived from such sensors are still useful for providing authorities with a preliminary understanding of the mineral distribution of a mine site and potential sources of pollution and effectively guide more detailed assessments.

However, certain aspects emerged as key factors determining the quality of the work. Firstly, polynomial fitting on multispectral and hyperspectral data is highly sensitive to noise and artifacts, and an accurate atmospheric correction is of fundamental importance in this kind of application. Secondly, time plays a significant role in the accuracy of laboratory analyses on secondary minerals, as these are highly metastable and quickly transform into different phases within a few days or weeks. Therefore, in future investigations, samples collected in the field must be analyzed within a few hours, in order to then be compared with satellite data. Then, a major challenge is the impact of mineral mixtures on the

detectability of specific phases and the correct interpretation of the results. Diagnostic absorption features may not be unique to a single mineral, and mixtures of Fe-bearing minerals with overlapping features in the visible to near infrared (VNIR) wavelength range may cause significant positional shifts of these features, leading to potential misclassification of mineral maps. This demonstrates that an in-depth knowledge of the geology of the area still remains an essential condition for the correct interpretation of spectroscopic results. Further research on the mitigation of the spectral masking effect by iron oxides should be carried out, as it is a strongly limiting factor for the use of remote sensing in operational contexts. Finally, though an extensive collection of reference spectra of Fe-bearing minerals related to AMD environments is available, reference spectra for Zn-bearing minerals are lacking, limiting the possibility of using remote sensing in non-sulfide Zn mining sites or, more generally, in neutral mine drainage contexts. Further research will be focused on developing a spectral library of such minerals to allow their detection from space as well.

In conclusion, for the first time, a remote sensing investigation was carried out on a historical mining site affected by near-neutral mine drainage. This study highlights the potential of such a technique also in these environments, setting a benchmark for further research in this domain.

4.8. Author Contributions (CredIT)

Susanna Grita: Conceptualization, Methodology (polynomial fitting workflow development), Software, Investigation (image download and preprocessing, point spectra preprocessing, fieldwork), Validation, Formal analysis (spectral interpretation of laboratory samples and images), Data curation, Writing – original draft preparation, Visualization.

Lorenzo Sedda: Investigation (fieldwork, XRD measurements and diffractogram interpretations), Validation, Resources (XRD lab permission), Writing – review and editing.

Marco Casu: Investigation (fieldwork), Writing – review and editing.

Saeid Asadzadeh: Investigation (point spectral measurements of samples), Resources (spectral lab permission), Writing – review and editing, Supervision.

Piero Boccardo: Writing – review and editing, Supervision, Funding acquisition

5. Concluding Remarks

This Ph.D. project demonstrates the high value-added given by imaging spectroscopy and remote sensing in supporting different phases of mining activities, from early-stage exploration to post-mining monitoring. For the early-stage exploration and the extractive phases, we have developed a robust, flexible, scalable and explainable method, based on Random Forest Regression, to estimate the concentration of spectrally active REEs. Recent studies have employed machine learning to quantify or map the distribution of REEs using major element concentrations in bauxite deposits (Buccione et al., 2023), phosphorites (Tahar-Belkacem et al., 2024), iron-oxide apatite (Zaremotlagh and Hezarkhani, 2017) and coal (Chatterjee et al., 2024) deposits. However, these techniques rely on indirect features, limiting the generalization potential of these models to other deposits, while the modelling approach presented in this thesis relies on direct element-specific spectral properties. Therefore, for the first time we were able to consistently quantify not only Nd, but also other four REEs (Dy, Er, Pr and Sm) independently. We also hypothesize that, should more training data be available, other elements such as Ho, Tm and Yb could potentially be quantified with this approach, provided their concentration is sufficiently high. This aspect, along with the method's flexibility and scalability allows to apply the model not only to geological contexts but also to other scientific domains (Kaegi et al., 2021; Yamamoto et al., 2001; Zheng et al., 2025).

In support of post-mining operations, and specifically environmental impact monitoring, we here propose a multi-platform method for mapping sources of acid mine drainage. Indeed, the area of Montevecchio-Ingurtosu has been previously investigated by collecting a discrete number of samples from the field, allowing for data gaps within the area (Cidu et al., 2011; De Giudici et al., 2018, 2014; Frau et al., 2015). Here for the first time, we provide a spatially continuous dataset which provides valuable information on the geochemistry and mineralogy of the mine dumps and the affected waterways. The unprecedented application of polynomial fitting on actual Sentinel-2 data allows to extract with precision the position, depth and width of diagnostic features related to Fe-bearing minerals, at a level comparable to hyperspectral remote sensing. Though this work showed a seasonal monitoring over a single year, it is possible to leverage Sentinel-2 and potentially other multispectral sensors' high temporal resolution to build detailed weekly, seasonal, annual and decadal time series of mining areas' environmental conditions at a vast scale. Instead, in previous studies the actual revisit time over AMD affected areas was years (Buzzi et al., 2016; Ong and Cudahy, 2014) or, at best, months (Riaza and Müller, 2010). Moreover, we here prove that the mapping of secondary minerals as indicators of mine drainage is effective also in carbonate-buffered environments, where pH levels are near neutral, an environment seldom studied with imaging spectroscopy. The approach adopted in this work could potentially be applied to monitoring post-disaster events as well, such as tailings dam failures (Ammirati et al., 2022; Cheng et al., 2021) The results obtained with this study can help shed more light on the dynamics of transport and mobilization of heavy metals in legacy mining environments (Choe et al., 2008).

Both data driven and knowledge-based techniques have been adopted in this research project, proving the success of the two approaches in different contexts. It emerges that none of the approaches is superior to the other, but rather these complement each other based on the specific geological applications. For instance, machine learning and artificial intelligence succeed in addressing non-linear relationships between variables, thanks to their extremely flexible structure. Therefore, besides being used for mineral quantification problems, these techniques could prove effective in modelling endmember spectral signatures from spectra of intimate mixtures. Likewise, knowledge-based methods show great accuracy in tracking subtle mineralogical and geochemical variations in a geological environment. Nevertheless, as demonstrated in this study and as also shown in Van Ruitenbeek et al., (2025), the integration of knowledge-based steps in a data-driven workflow is an efficient strategy for improving the interpretability of results and guaranteeing consistency over time.

The project also highlighted the difficulties of CRM detection, as in the case of REEs, in mine residues using remote sensing, due to the strong masking effect of certain minerals, highlighting how this technology is not yet mature in addressing this issue. Problems related to mineral masking have been extensively observed within the scientific community, though research on methods to address them is still very limited. However, with the available technology and current computational power there is potential to solve this issue. Findings in this field are key for enabling the identification of less abundant, but economically relevant phases using imaging spectroscopy, and it is recommended that future research should be carried out in this direction.

Another limiting factor in using imaging spectroscopy for mineral exploration and mapping is spectral versus spatial resolution. As highlighted in this project, though Sentinel-2 has a lower GSD than EnMAP, its applications are only limited to Fe-bearing mineral detection. Hyperspectral satellite systems available today have a medium spatial resolution (30 m in the case of EnMAP and PRISMA, 60 m for EMIT). This makes them sub-optimal for analyzing open pit mines or small deposits, while being particularly suited for regional scale mapping, a theme amply covered by scientific literature. For this reason, satellite-based imaging spectroscopy is seldom used during the extractive phases, where drone or ground-based spectral surveys are more effective (Koerting et al., 2024). Nevertheless, despite the limited extent of the areas analyzed in this Ph.D. project, we show that satellite hyperspectral imagers are still able to provide a preliminary overview of relative (for Fe-bearing minerals) and absolute (for REEs) abundances of target mineral phases and spatial compositional hotspots on which to constrain further assessments. Moreover, recent studies are developing super-resolution techniques for improving the spatial resolution of hyperspectral sensors, while preserving their spectral detail (Naik et al., 2025). This methodology could potentially be beneficial for identifying compositional patterns with higher detail within the small areas. Therefore, research with satellite data should continue, considering that airborne and drone-based systems, though being the ideal compromise between spatial and spectral resolution, are limited by the battery lifetime and the costliness of their surveys, allowing to cover only relatively small areas.

Concluding Remarks

In line with the EU's Critical Raw Material's Act, Italy is currently developing a national inventory of active and ceased non-energy mining activities (Lucarini et al., 2020). The methodologies presented in this work could greatly support this effort, by allowing to rapidly provide an initial characterization of several mining sites scattered in the national territory. More in general, remote sensing is a powerful tool for supporting responsible mining practices. The case studies presented in this project suggest that such applications, if integrated into the production line, could be used for measuring indicators of sustainability within mining operations. For example, the ability of hyperspectral remote sensing of quantifying mineral phases and areas where these are concentrated is a valuable tool for reducing exploratory drilling and digging, thus potentially reducing energy consumption, and therefore also greenhouse gas emissions (Gorman and Dzombak, 2018). Equally, the provision of remote sensing-based maps of acid mine drainage sources have proved to be time and cost-effective, accelerating cleanup efforts by years and reducing costs of millions of U.S. dollars, as exemplified in Swayze et al., (2000). The constant remote monitoring of pollution and contamination levels generated by active or past mining activities can significantly ensure safer working conditions during both remediation operations or within the extractive process. Though imaging spectroscopy has proved to be flexible and effective in several sectors of the mining industry, it is limited by the inconstant acquisition repeats over the same area. As Nordstrom, (2009) mentions, climate change is a driver for exacerbating acid and metal loading pulses from mine wastes, obliging remediation activities to consider extreme rather than stationary climatic conditions. In the author's opinion, the temporal aspect of remote sensing can be a valuable tool for monitoring changes in mine drainage fluctuations and relating them to climatic conditions, as well as providing useful data for future modelling of AMD dynamics during extreme drought and rain events. Therefore, future research and development should focus on ensuring a constant and regular coverage of hyperspectral images over key areas and refine current mineral quantification models to be comparable in time.

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Appendix I

Table A1. 1 Name, description and origin of the samples used in this study. The bibliographical reference provides further details on each sample.

Sample number	Type	Descriptiton	Origin	Reference
CR-01	Rock	Disseminated Monazite Stage	Bayan Obo, China	Neave et al., 2016
CR-02	Rock	Banded Ore	Bayan Obo, China	Neave et al., 2016
CR-03	Rock	Fluorite Stage	Bayan Obo, China	Neave et al., 2016
CR-04	Rock	Barite Stage	Bayan Obo, China	Neave et al., 2016
CR-05	Rock	Carbonatite	Uyaynah, UAE	Neave et al., 2016
CR-06	Rock	Carbonatite	Uyaynah, UAE	Neave et al., 2016
CR-07	Rock	Carbonatite	Uyaynah, UAE	Neave et al., 2016
CR-08	Rock	Carbonatite	Uyaynah, UAE	Neave et al., 2016
CR-09	Rock	Carbonatite	Uyaynah, UAE	Neave et al., 2016
CR-10	Rock	Carbonatite	Fort Portal, Uganda	Neave et al., 2016
CR-11	Rock	Microsyentite	Motzfeldt, Greenland	Neave et al., 2016
CR-12	Rock	Microsyentite	Motzfeldt, Greenland	Neave et al., 2016
CR-13	Rock	Microsyentite	Motzfeldt, Greenland	Neave et al., 2016
CR-14	Rock	Biotite-rich calcite carbonatite	Oka, Canada	Neave et al., 2016
CR-15	Rock	Biotite-rich carbonatite	St. Honoré, Canada	Neave et al., 2016

CR-16	Rock	Monazite carbonatite	Kangankunde, Malawi	Neave et al., 2016
CR-17	Rock	Calcite carbonatite	Fen, Norway	Neave et al., 2016
CR-19	Rock	Calcite carbonatite	Kaiserstuhl, Germany	Neave et al., 2016
CR-20	Rock	Banded carbonatite	Tundulu, Malawi	Neave et al., 2016
CR-21	Rock	Banded carbonatite	Tundulu, Malawi	Neave et al., 2016
CR-22	Rock	REE-rich ankerite carbonatite	Songwe, Malawi	Neave et al., 2016
CR-23	Rock	Carbonatite	Songwe, Malawi	Neave et al., 2016
CR-24	Rock	Calcite carbonatite	Songwe, Malawi	Neave et al., 2016
CR-29	Rock	Carbonatite	Tororo, Uganda	Neave et al., 2016
CR-31	Rock	Carbonatite	Sukulu, Uganda	Neave et al., 2016
CR-33	Rock	Apatite carbonatite	Chilwa Island, Malawi	Neave et al., 2016
CR-36	Rock	Carbonatite	Mountain Pass, USA	Neave et al., 2016
CR-37	Rock	Phlogopite pyrochlore carbonatite	Panda Hill, Tanzania	Neave et al., 2016
CR-38	Rock	Altered carbonatite with large pyrochlores	Panda Hill, Tanzania	Neave et al., 2016
CR-42	Rock	Phyrochlore sovite	Sokli, Finland	Neave et al., 2016
CR-43	Rock	Coarse sovite	Sokli, Finland	Neave et al., 2016
CR-46	Rock	Kakortokite	Ilímaussaq, Greenland	Neave et al., 2016
Nd-Kaolinite-100	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-200	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-300	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-500	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-600	Clay	Kaolinite	synthetic	Tan et al., 2021

Nd-Kaolinite-700	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-900	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Kaolinite-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Pr-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Pr-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Pr-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Pr-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Sm-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Sm-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Sm-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Sm-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Eu-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Eu-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Eu-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Eu-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Dy-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Dy-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Dy-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Dy-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Ho-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Ho-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Ho-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Ho-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Er-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Er-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Er-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Er-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Tm-Kln-400	Clay	Kaolinite	synthetic	Tan et al., 2021
Tm-Kln-600	Clay	Kaolinite	synthetic	Tan et al., 2021
Tm-Kln-800	Clay	Kaolinite	synthetic	Tan et al., 2021
Tm-Kln-1000	Clay	Kaolinite	synthetic	Tan et al., 2021
Nd-Smectite-1000	Clay	Smectite	synthetic	Tan et al., 2021
Nd-Illite-1000	Clay	Illite	synthetic	Tan et al., 2021
Nd-Halloysite-1000	Clay	Halloysite	synthetic	Tan et al., 2021
Bastnaesite_Sichuan	Mineral	Bastnaesite	Sichuan, China	Turner et al., 2014
Bastnaesite_Karonga	Mineral	Bastnaesite	Karonga, Malawi	Turner et al., 2014

Bastnaesite_Madagascar	Mineral	Bastnaesite	Madagascar	Turner et al., 2014
Bastnaesite_Burundi	Mineral	Bastnaesite	Burundi	Turner et al., 2014
Parisite_Muzo	Mineral	Parisite	Muzo, Columbia	Turner et al., 2014
Parisite_SB	Mineral	Parisite	Snowbird Mountain, USA	Turner et al., 2014
Synchysite_UBC3376	Mineral	Synchysite	Narsarsuk, Greenland	Turner et al., 2014
Monazite_SerraVerde	Mineral	Monazite	Serra Verde, Brazil	Turner et al., 2016
Monazite_ElkMountain	Mineral	Monazite	Elk Mountain, USA	Turner et al., 2016
Monazite_UofA	Mineral	Monazite	Unknown location	Turner et al., 2016
Britholite_Kipawa	Mineral	Britholite	Kipawa, Canada	Turner et al., 2016
BritholiteY_Kipawa	Mineral	Britholite	Kipawa, Canada	Turner et al., 2016
Xenotime_SerraVerde	Mineral	Xenotime	Serra Verde, Brazil	Turner et al., 2016
Xenotime_NovoHorizonte 1131C	Mineral	Xenotime	Novo Horizonte, Brazil	Turner et al., 2016
Xenotime_NovoHorizonte 1131J	Mineral	Xenotime	Novo Horizonte, Brazil	Turner et al., 2016
Xenotime_GunterQuarry	Mineral	Xenotime	Gunter Quarry, Canada	Turner et al., 2016
Cerite_Bastnas	Mineral	Cerite	Bastnas, Sweden	Turner et al., 2018
Mosandrite_Kipawa	Mineral	Mosandrite	Kipawa, Canada	Turner et al., 2018
Kainosite_LongLake	Mineral	Kainosite	Long Lake, USA	Turner et al., 2018
Zircon_StPetersDome	Mineral	Zircon	St. Peter's Dome, USA	Turner et al., 2018
Zircon_MtMalosa	Mineral	Zircon	Mount Malosa, Malawi	Turner et al., 2018
Zircon_NorthBurgess	Mineral	Zircon	North Burgess, Canada	Turner et al., 2018

Zircon_Mudtank001	Mineral	Zircon	Mudtank, Australia	Turner et al., 2018
Zircon_GreenRiver	Mineral	Zircon	Green River, USA	Turner et al., 2018
Eudialyte_Kipawa CMN_F92_23	Mineral	Eudialyte	Kipawa, Canada	Turner et al., 2018
Eudialyte_Kipawa_002	Mineral	Eudialyte	Kipawa, Canada	Turner et al., 2018
Eudialyte_Kipawa UofAfragment	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
Eudialyte_CMNOC476	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
Eudialyte_CMNOC478	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
Eudialyte_CMN37104	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
Eudialyte_CMNOC2045	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
Eudialyte_CMN_88_79	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
Eudialyte_CMNC72_24	Mineral	Eudialyte	Mt Saint-Hilaire, Canada	Turner et al., 2018
1H	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015
2H	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015
3H	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015
4M	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015
5M	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015
6M	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015
7L	Rock	Siderite-bearing carbonatite	Fen, Norway	Boesche et al., 2015
8L	Rock	Siderite-bearing carbonatite	Fen, Norway	Boesche et al., 2015
9L	Rock	Calcite carbonatite	Fen, Norway	Boesche et al., 2015

glassCe	glass	glass	synthetic	This study
glassDy	glass	glass	synthetic	This study
glassEr	glass	glass	synthetic	This study
glassEu	glass	glass	synthetic	This study
glassGd	glass	glass	synthetic	This study
glassHo	glass	glass	synthetic	This study
glassLa	glass	glass	synthetic	This study
glassLu	glass	glass	synthetic	This study
glassNd	glass	glass	synthetic	This study
glassPr	glass	glass	synthetic	This study
glassSm	glass	glass	synthetic	This study
glassTb	glass	glass	synthetic	This study
glassTm	glass	glass	synthetic	This study
glassY	glass	glass	synthetic	This study
glassYb	glass	glass	synthetic	This study

Table A1. 2 Value ranges for Random Forest Regression hyperparameter optimization. For each single REE the final parameters were chosen based on the randomized cross-validation search function available in the scikit-learn library.

Hyperparameter optimization			
	Nd, Dy (SWIR), Er (NIR)	Dy (NIR), Er (SWIR), Sm	Pr
number of trees	1000, 4000, 9000, 10000	1000, 4000, 9000, 10000	1000, 4000, 9000, 10000
maximum number of features	20 - 80 (step size: 10)	20 - 200 (step size: 10)	20 - 80 (step size: 10)
maximum tree depth	5-15 (step size: 1)	5-30 (step size: 1)	5-20 (step size: 1)
minumum number of samples per split	3, 5, 7, 10	3, 5, 7, 10	3, 5
minimum number of samples per leaf	1, 2	1, 2,3	1, 2

Table A1. 3 Value ranges for Random Forest Regression hyperparameter optimization for Nd by sensor. The final parameters were chosen based on the randomized cross-validation search function available in the scikit-learn library.

Nd Hyperparameter optimization for images			
	SPECIM sisuROCK	HySpex	EnMap
number of trees	1000, 4000, 9000, 10000	1000, 4000, 9000, 10000	1000, 4000, 9000, 10000
maximum number of features	20 - 80 (step size: 10)	20 - 80 (step size: 10)	10 - 40 (step size: 10)
maximum tree depth	5-30 (step size: 1)	5-30 (step size: 1)	5-15 (step size: 1)
minumum number of samples per split	3, 5, 7, 10	3, 5, 7, 10	3, 5, 7, 10
minimum number of samples per leaf	1, 2	1, 2	1, 2

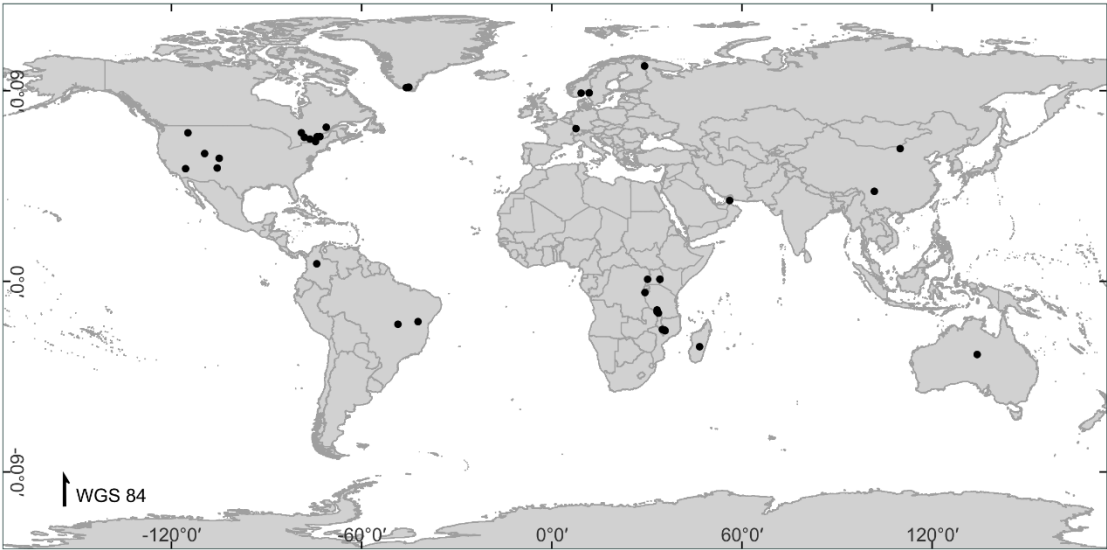


Figure A1. 1 Locations of origin of natural REE-bearing samples used in this work.

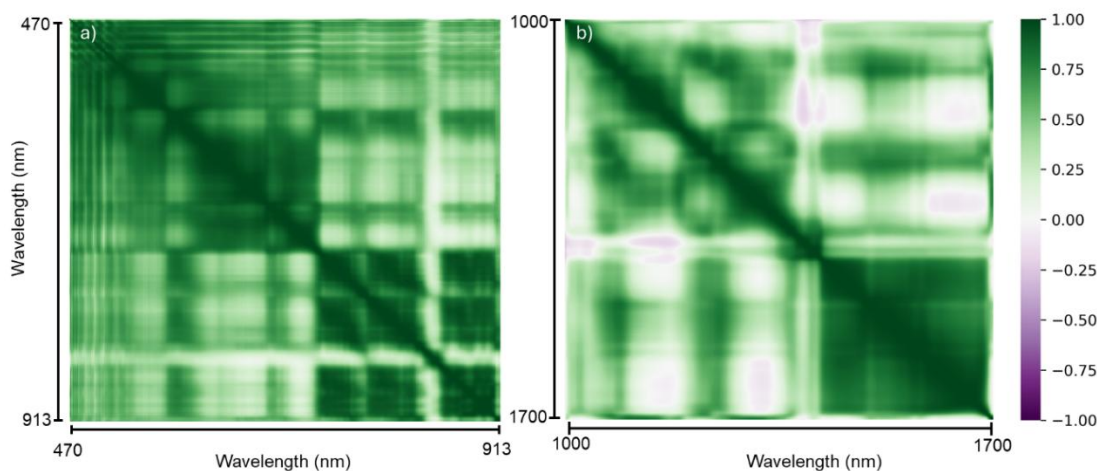


Figure A1. 2 Correlation heatmap of spectral data from samples used in the Random Forest Regression model, in the VNIR (a) and SWIR (b) wavelength range.

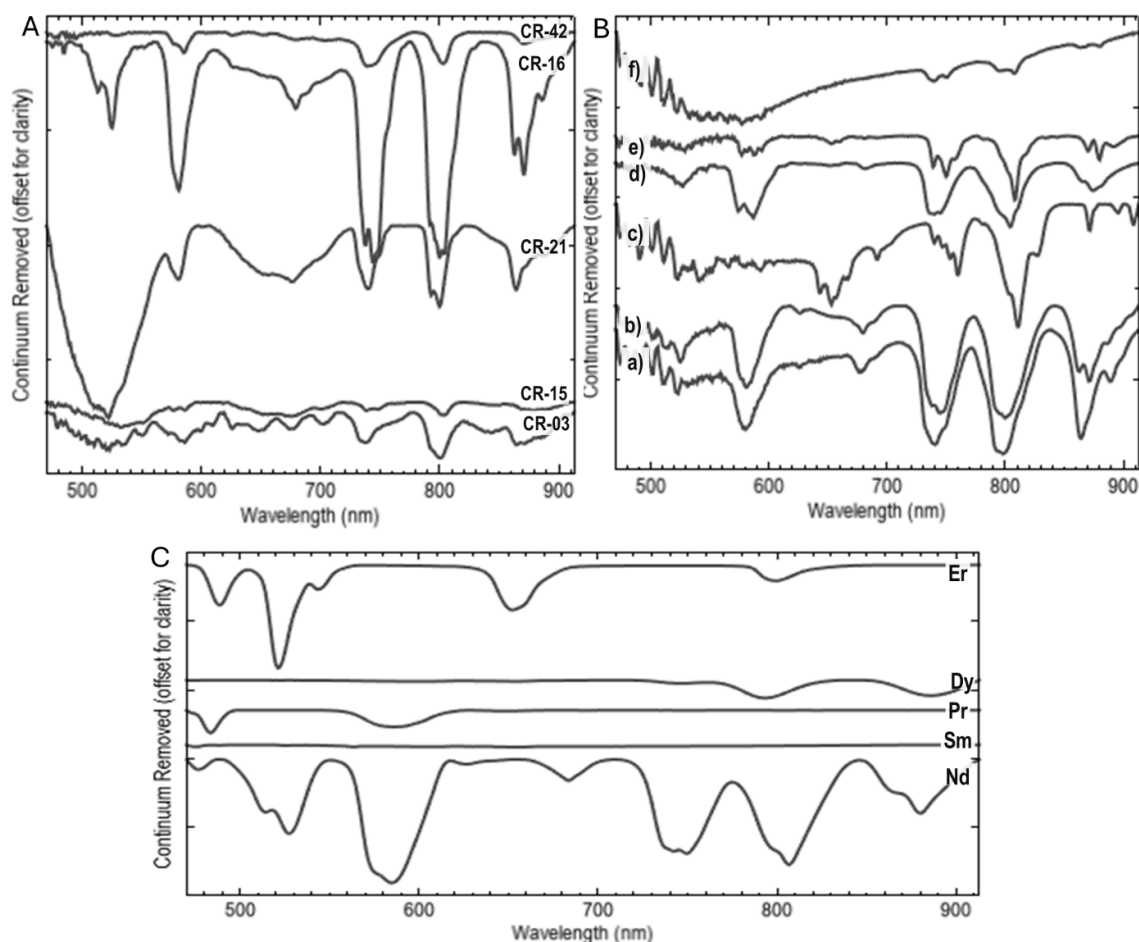


Figure A1. 3 Continuum removed spectra of the samples used to train the single REE models in VNIR spectral range (470-913 nm). Spectra include examples from the collection of Neave et al. (2016) (A), Turner et al. (2014a, 2016, 2018) (B) and synthetic doped glasses (C). In graph B: a = Parisite_SB, b = Monazite_ElkMountain, c = Xenotime_NovoHorizonte_1131J, d = Mosandrite_Kipawa, e = Zircon_MtMalosa, f = Eudialyte_CMN37104.

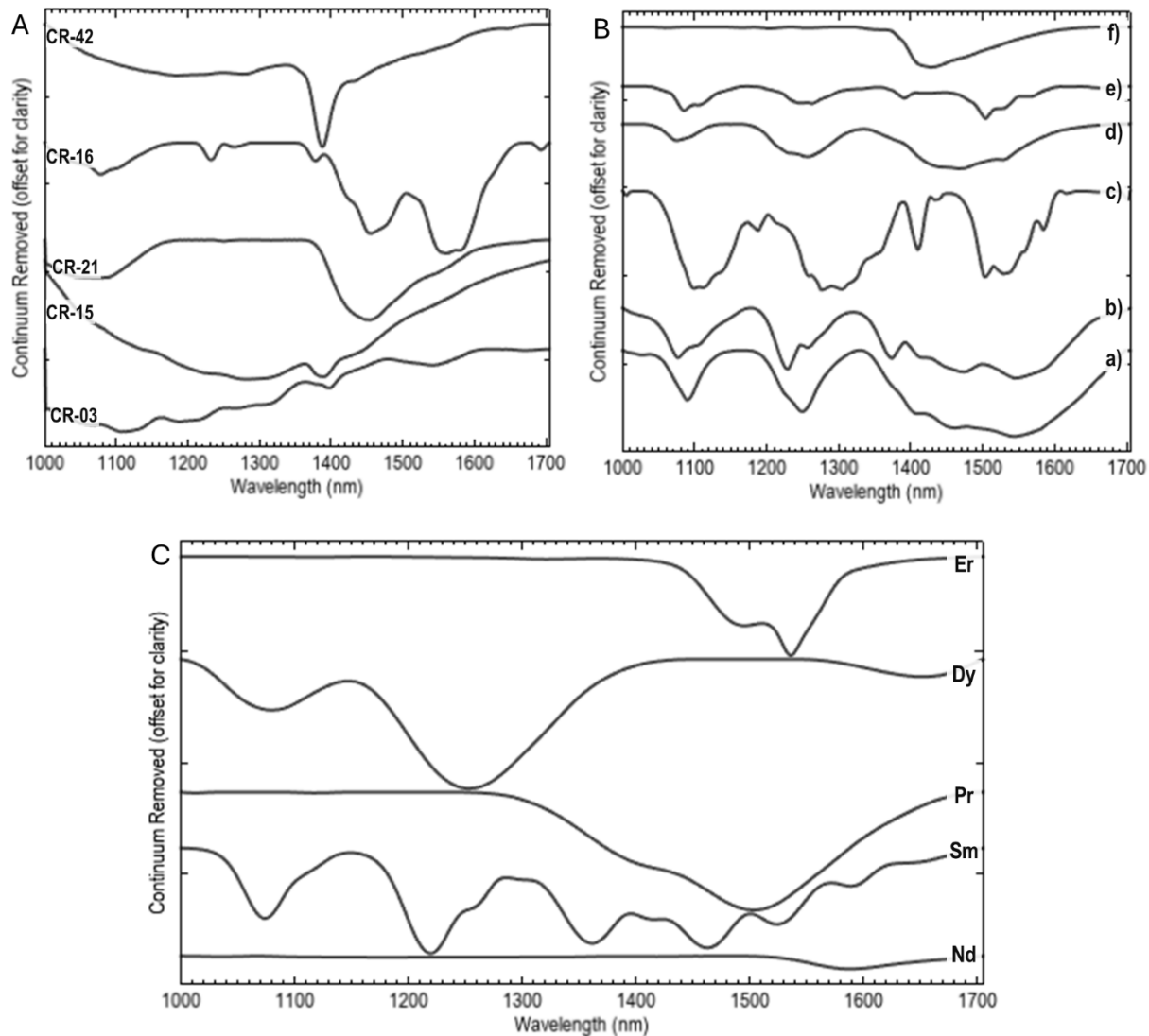


Figure A1.4 Continuum removed spectra of the samples used to train the single REE models in SWIR spectral range (1000-1700 nm). Spectra include examples from the collection of Neave et al. (2016) (A), Turner et al. (2014a, 2016, 2018) (B) and synthetic doped glasses (C). In graph B: a = Parisite_SB, b = Monazite_ElkMountain, c = Xenotime_NovoHorizonte_1131J, d = Mosandrite_Kipawa, e = Zircon_MtMalosa, f = Eudialyte_CMN37104.

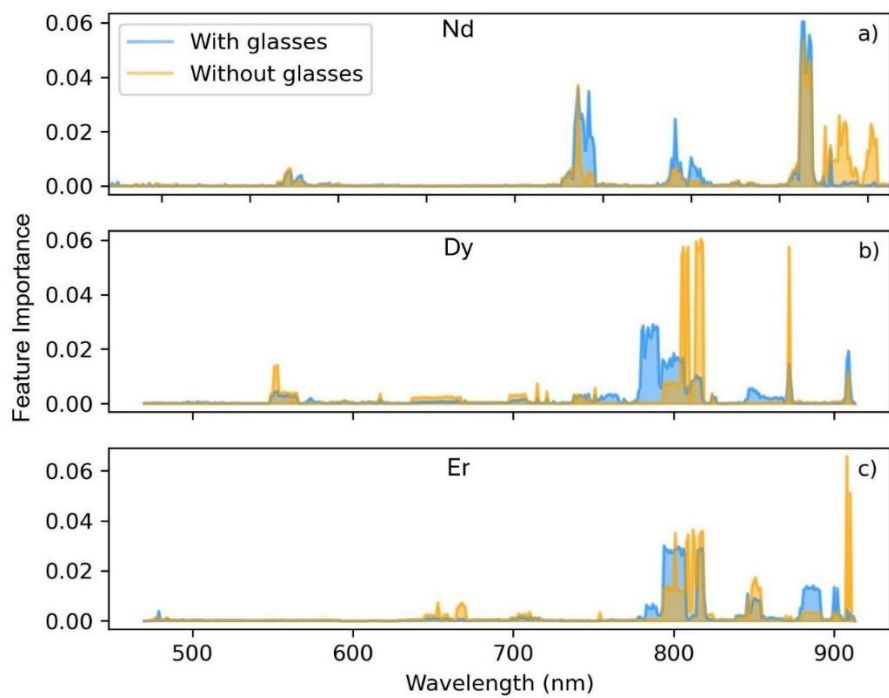


Figure A1. 5 Feature importance comparison between models trained with or without glasses for single REEs in the VNIR range.

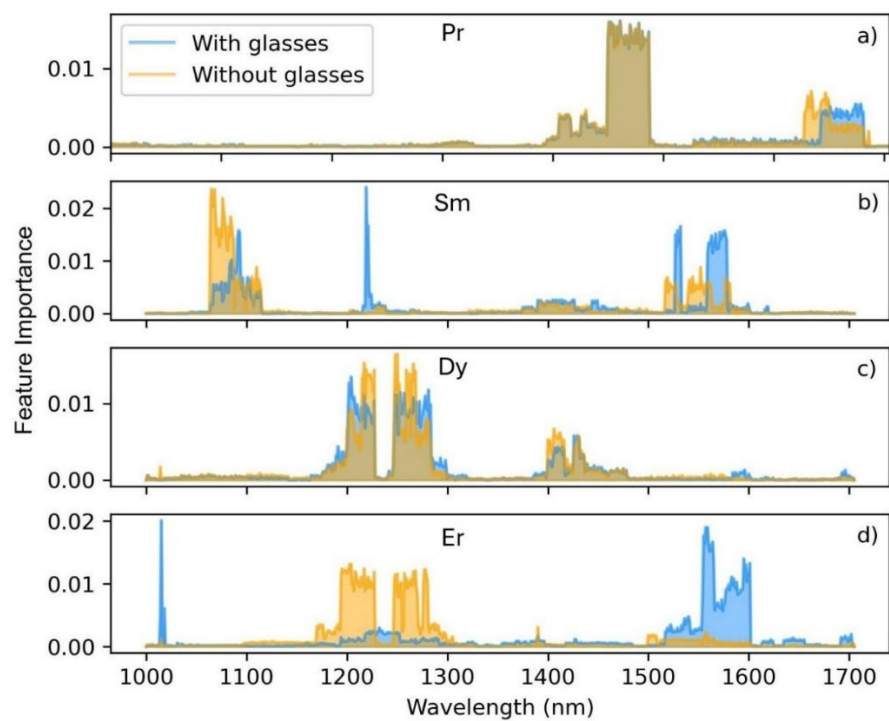


Figure A1. 6 Feature importance comparison between models trained with or without glasses for single REEs in the SWIR range.

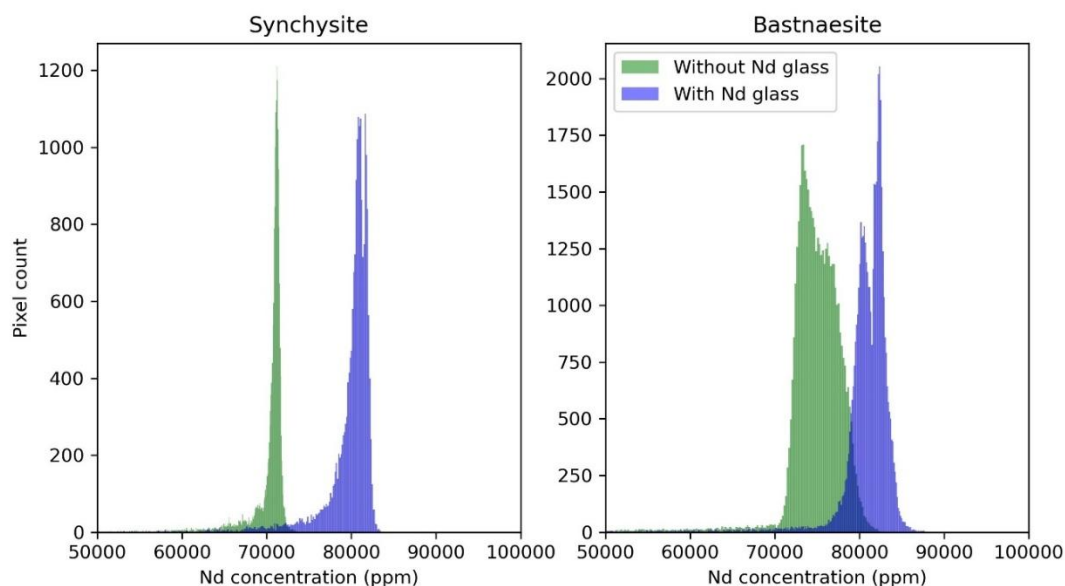


Figure A1. 7 Histogram of pixel values of Nd prediction maps for the synchysite and bastnaesite datacubes with and without glasses after the application of a Savitzky-Golay smoothing filter (window size 5, polynomial order 2 and no derivative).

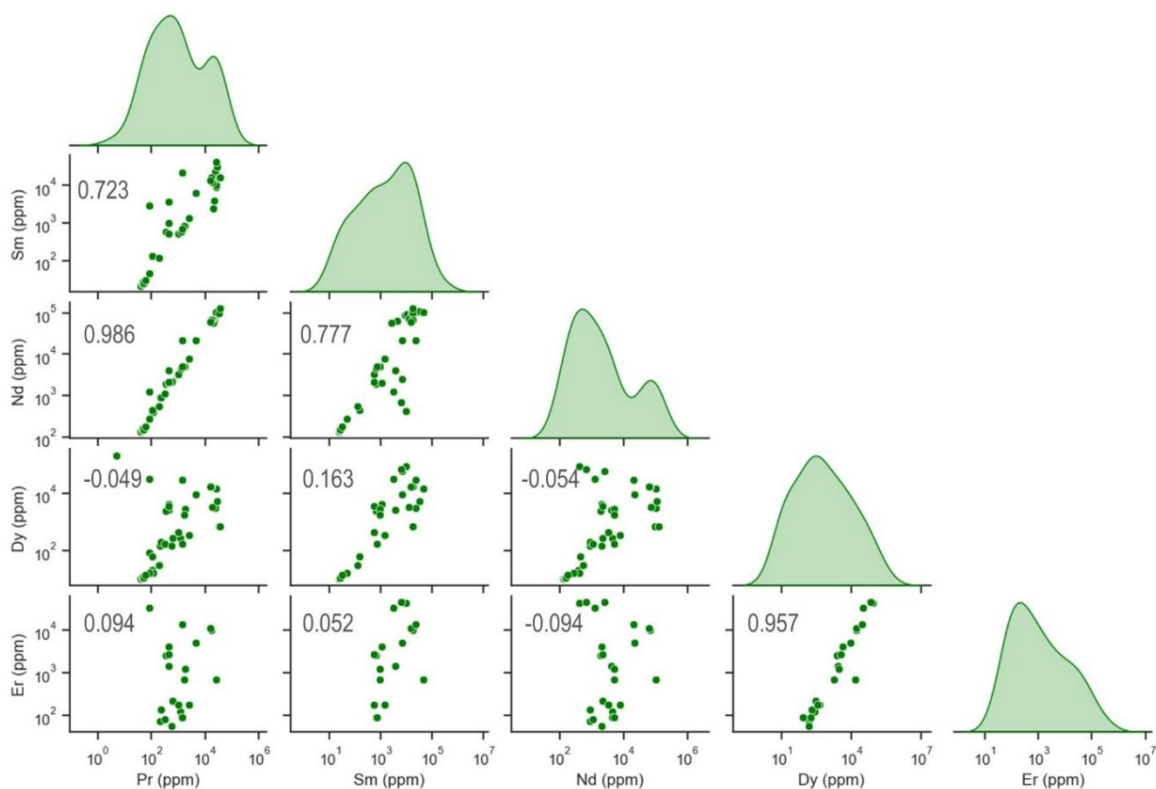


Figure A1. 8 Correlation plots between single REE with concentrations above 10 ppm. The number reported in each plot is the corresponding correlation coefficient. The distribution plots above each column represent the concentration data distribution of the corresponding element.

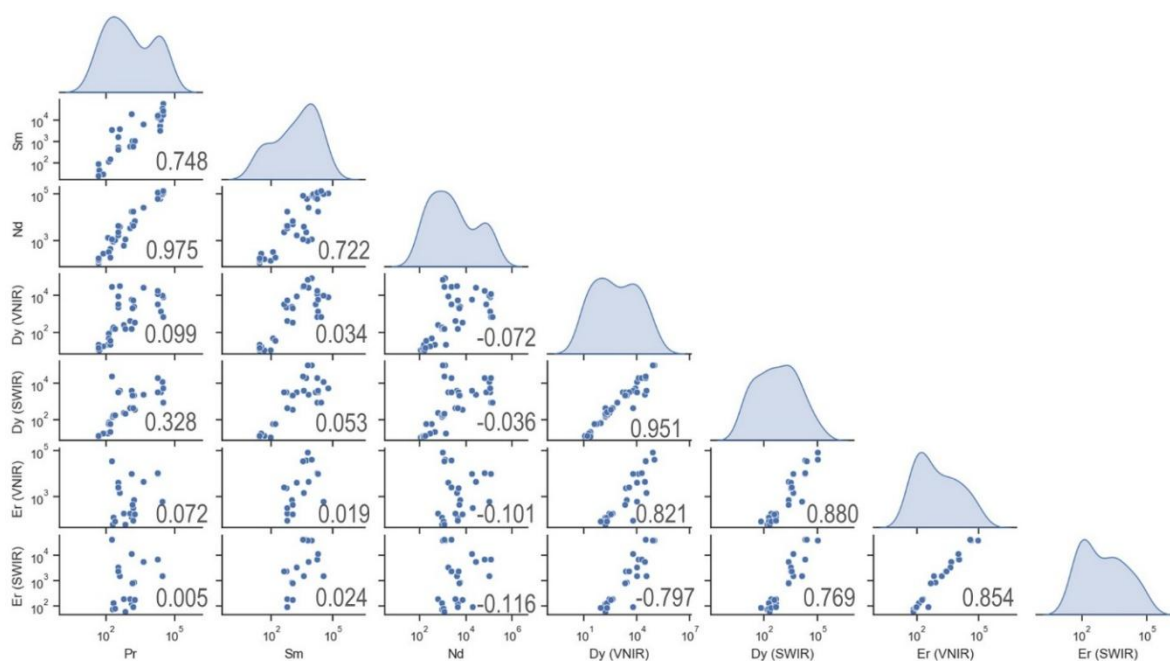


Figure A1. 9 Correlation plots between single REE with predicted concentrations from the RFR model. The number reported in each plot is the corresponding correlation coefficient. The distribution plots above each column represent the concentration data distribution of the corresponding element.

Appendix II

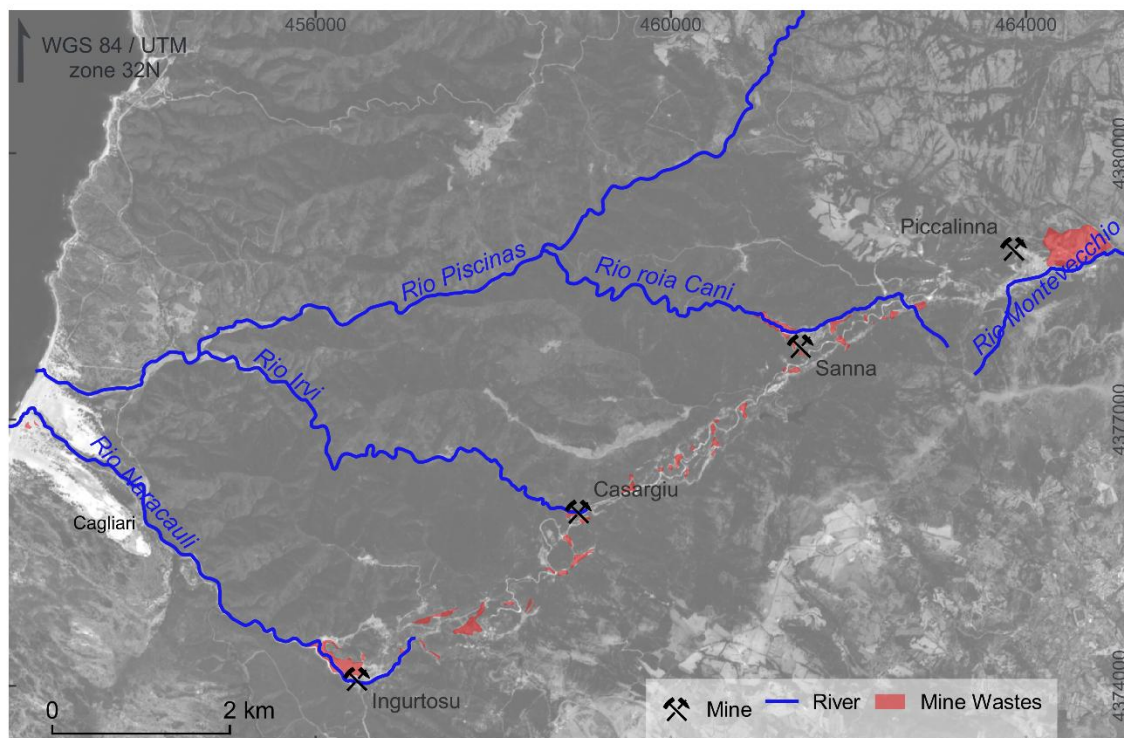


Figure A2. 1 Map of streams affected by the presence of mine residues in the Montevecchio-Ingurtosu mining district. Stream data is from the “Database Geo-Topografico” (Regione Autonoma della Sardegna, 2025) and mine waste data is from (Regione Autonoma della Sardegna, 2008).

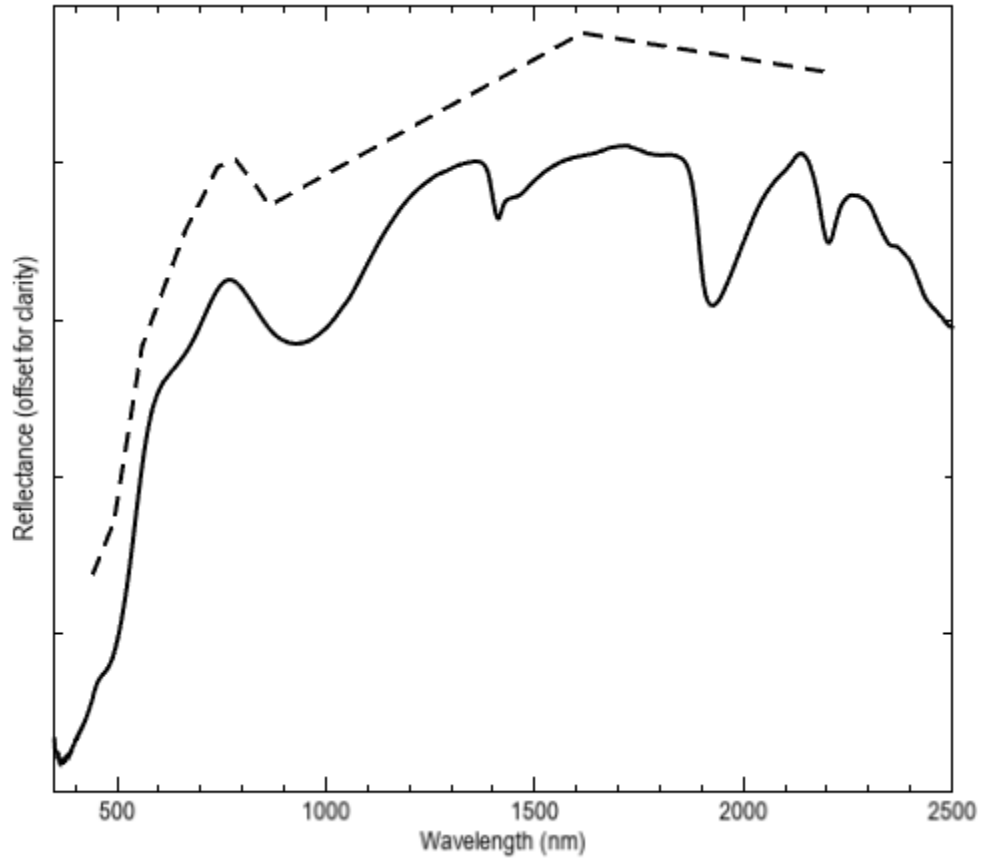


Figure A2. 2 Comparison between the original ASD spectrum (solid line) and the resampled to Sentinel-2 spectrum (dashed line) of sample MVL_P004.

Table A2. 1 Endmember spectra used as reference for VNIR shoulder position and the ferric iron feature position. Samples are from three sources, the NASA RELAB database (Brown University, 2014), the USGS Spectral Library v7 (Kokaly et al., 2017) and the Spectral library from Crowley et al. (2003, (Crowley et al., 2003)).

Sample Name	VNIR Shoulder (nm)	Ferric Iron feature (nm)	Source
Goethite			
c1cy08_goethite	759.5	925	NASA RELAB
c1go01_goethite_lessthan_125um	760.08	970	NASA RELAB
c1jb47_goethite	762.45	940	NASA RELAB
c1jb55_ferrihydrite_goethite	766.78	970	NASA RELAB
goethite	799.45	964	Crowley
Goethite_GDS134_ASDFRb	762.44	977	USGS
Goethite_HS36.3_BECKb	763.42	949	USGS
Goethite_MPCMA2-B_FineGr_adj_BECKb	760	956	USGS
Goethite_MPCMA2-C_M-Crsgrad2_BECKb	764.19	957	USGS
Goethite_WS219_(limonite)_BECKc	760.63	981	USGS
Goethite_WS220_BECKc	766.07	949	USGS

Goethite_WS222_Coarse_Gr_BECKa	755.29	1005	USGS
Goethite_WS222_Medium_Gr_BECKa	763.03	949	USGS
Goethite0.02+Quartz_GDS240_BECKa	758.19	957	USGS
c2hy14_goethite_coating	762.68	980	NASA RELAB
Hematite			
Hematite_Coatd_Qtz_BR93-25B_BECKa	742.024	892.95	USGS
Hematite_Coatd_Qtz_BR93-34C_BECKa	740.247	915.06	USGS
Hematite_Coatd_Qtzt_BR93-25A_BECKa	739.7	904	USGS
Hematite_Coatd_Qtzt_BR93-25C_BECKa	745.019	904	USGS
Hematite_Thin_Film_GDS27_BECKa	742.111	865.47	USGS
Hematite_FE2602_BECKb	746.47	894	USGS
Hematite_GDS27_BECKa	744.166	896.47	USGS
Hematite_HS45.3_BECKb	751.564	871	USGS
Hematite_WS161_BECKb	743.362	871	USGS
Nanohematite_BR93-34B2_BECKb	755.286	898.72	USGS
Hematite.02+Quartz.98_GDS76_BECKa	749.868	885.8	USGS
c1cy11_hematite	745.543	899.08	NASA RELAB
cijb256_hematite	742.372	897.5	NASA RELAB
cahe01_hematite	743.287	892.37	NASA RELAB
hematite	743.27	880.63	Crowley
Ferrihydrite			
ferrihydrite	762.228	976	Crowley
c1jb45_synthetic_ferrihydrite	766.634	1005	NASA RELAB
c1jb46_synthetic_ferrihydrite	773.961	995	NASA RELAB
Ferrihydrite_GDS75_Syn_F6_BECKb	770.757	1016	USGS
Jarosite			
Ammonio-Jarosite_SCF-NHJ_BECKa	713.65	920.55	USGS
c1cy16_jarosite	721.28	927.11	NASA RELAB
c1jb53_jarosite	738.28	937.5	NASA RELAB
c1jb709_jarosite	741.35	935.23	NASA RELAB
Goeth+qtz.5+Jarosite.5_AMX11_BECKb	723.96	930.06	USGS
jarosite	730.24	922.13	Crowley
Jarosite_GDS24_Na_BECKb	717.66	930.55	USGS
Jarosite_GDS98_K_90C_Syn_BECKa	712.54	900.88	USGS
Jarosite_GDS99_K_200C_Syn_BECKa	716.48	938.21	USGS
Jarosite_GDS100_Na_90C_Syn_BECKa	710.98	891.33	USGS
Jarosite_GDS101_Na_200C_Syn_BECKa	715.97	915.37	USGS
Jarosite_GDS635_Na_Cyprus_ASDNga	717.91	926.12	USGS
Jarosite_GDS636_K_Penalt325um_ASDNga	726.49	930.79	USGS
Jarosite_GDS732_K_200CSyn6hr_ASDNgb	719.3	928.42	USGS

Jarosite_JR2501_(K)_BECKb	726.03	937	USGS
Jarosite_NMNH95074-1_(Na)_BECKb	726.93	928.5	USGS
Jarosite_on_Qtzite_BR93-34A2_BECKa	739.15	967	USGS
Jarosite_Rhyolite_CU91-20A_BECKa	691.78	930.37	USGS
Jarosite_SJ-1_H3O_10-20_BECKb	712.38	923.41	USGS
Jarosite_Thin_Film_GDS243_BECKb	737.34	929.73	USGS
c1jbb81_hydronium_jarosite	725.9	913.99	NASA RELAB
c1jbb82b_natrojarosite	717.24	927.99	NASA RELAB
Siderite			
siderite_c1cy24	772.488		NASA RELAB
siderite_less56um_c1gr03	760.464		NASA RELAB
siderite_less45um_c1jb287	770		NASA RELAB
chalcosiderite_c1jb747	744.377		NASA RELAB
siderite_c1jbe62A	769.926		NASA RELAB
siderite_c1jbe62b	758.211		NASA RELAB
siderite_c1jbe62c	749.553		NASA RELAB
siderite_c1jbe62d	747.033		NASA RELAB
siderite_c1jbe62e	738.676		NASA RELAB
siderite_c1jbe62f	729.363		NASA RELAB
siderite_c1jbe63a	788.692		NASA RELAB
siderite_c1jbe63b	783.952		NASA RELAB
siderite_c1jbe63c	780.092		NASA RELAB
siderite_c1jbe63d	777.156		NASA RELAB
siderite_c1jbe63e	769.992		NASA RELAB
siderite_c1jbe63f	765.26		NASA RELAB
siderite_ankerite_c1mg23	771.87		NASA RELAB
siderite_ankerite_c1mg24	765		NASA RELAB
siderite_ankerite_c1mg25	766.58		NASA RELAB
siderite_ankerite_c1mg26	759.131		NASA RELAB
siderite_ankerite_c1mg27	757.489		NASA RELAB
siderite_FeDolomite_c1mg28	761.653		NASA RELAB
siderite_FeDolomite_c1mg29	755.485		NASA RELAB
siderite_FeDolomite_c1mg32	751.237		NASA RELAB
siderite_FeDolomite_c1mg33	762.5		NASA RELAB
siderite_FeDolomite_c1mg34	754.902		NASA RELAB
siderite_ankerite_c1mg35	757.692		NASA RELAB
siderite_FeDolomite_c1mg38	759.613		NASA RELAB
siderite_cacb08	789.04		NASA RELAB
siderite_cacb67	788.812		NASA RELAB
siderite_cacb69	745		NASA RELAB

siderite_cacb71	762.147		NASA RELAB
siderite_cacb73	797.643		NASA RELAB
siderite_cacb74	779.018		NASA RELAB
siderite_cbc08	759.331		NASA RELAB
siderite_cbcc07	732.601		NASA RELAB
Siderite-coarse-c09a	724.5		NASA RELAB
Siderite-fine-c09a	762.5		NASA RELAB
Siderite-medium-c09a	736.5		NASA RELAB
Siderite_HS271.1B_ASDFRa	796.59		USGS
Siderite_HS271.2B_ASDFRa	800.645		USGS
Siderite_HS271.3B_ASDFRa	785.07		USGS
Siderite_HS271.4B_ASDFRa	777.818		USGS

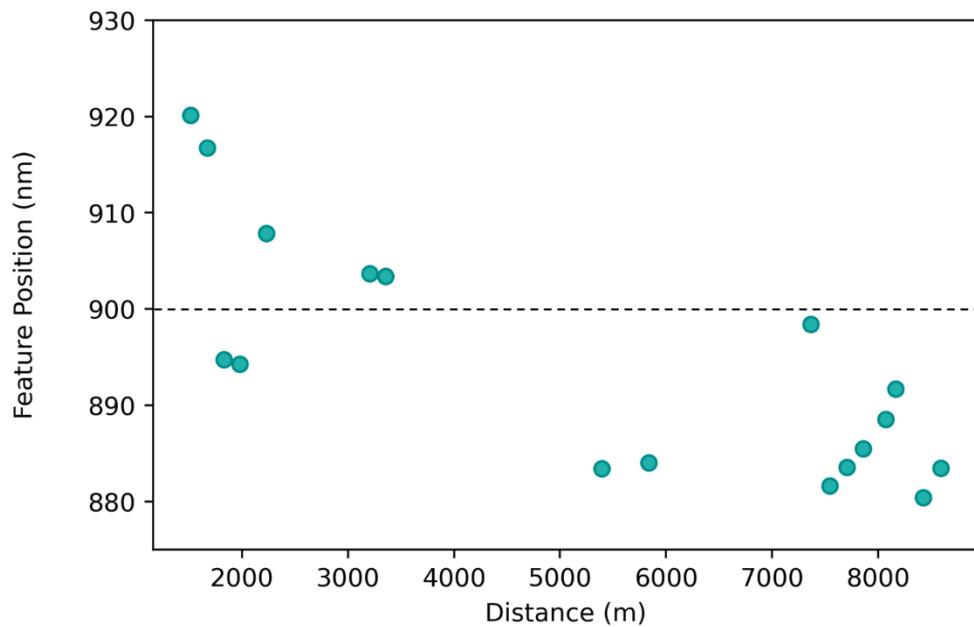


Figure A2. 3 Variation of the position of the ferric iron absorption feature in efflorescent salt samples along Rio Irvi with distance from the estuary. The dashed horizontal line indicates the threshold above which samples are considered to be jarosite-bearing.

Table A2. 2 Confusion matrix of the mineral classification applied on the Sentinel-2 image acquired on the 21st January 2024 .

		Sentinel-2 21/01/2024						
		copiapite	jarosite	hematite	goethite	Total	Omission Errors	Commission Errors
Reference	copiapite	0	0	0	0	0	N/A	N/A
	jarosite	0	0	0	0	0	N/A	100.00%
	hematite	0	0	0	0	0	N/A	100.00%
	goethite	0	1	3	7	11	36.36%	0.00%
	Total	0	1	3	7	11	Overall accuracy	63.64%

Table A2. 3 Confusion matrix of the mineral classification applied on the Sentinel-2 image acquired on the 26th July 2024 .

		Sentinel-2 26/07/2024						
		copiapite	jarosite	hematite	goethite	Total	Omission Errors	Commission Errors
Reference	copiapite	0	0	0	0	0	N/A	N/A
	jarosite	0	0	0	0	0	N/A	100.00%
	hematite	0	0	1	3	4	75.00%	75.00%
	goethite	0	2	3	24	29	17.24%	11.11%
	Total	0	2	4	27	33	Overall accuracy	75.76%

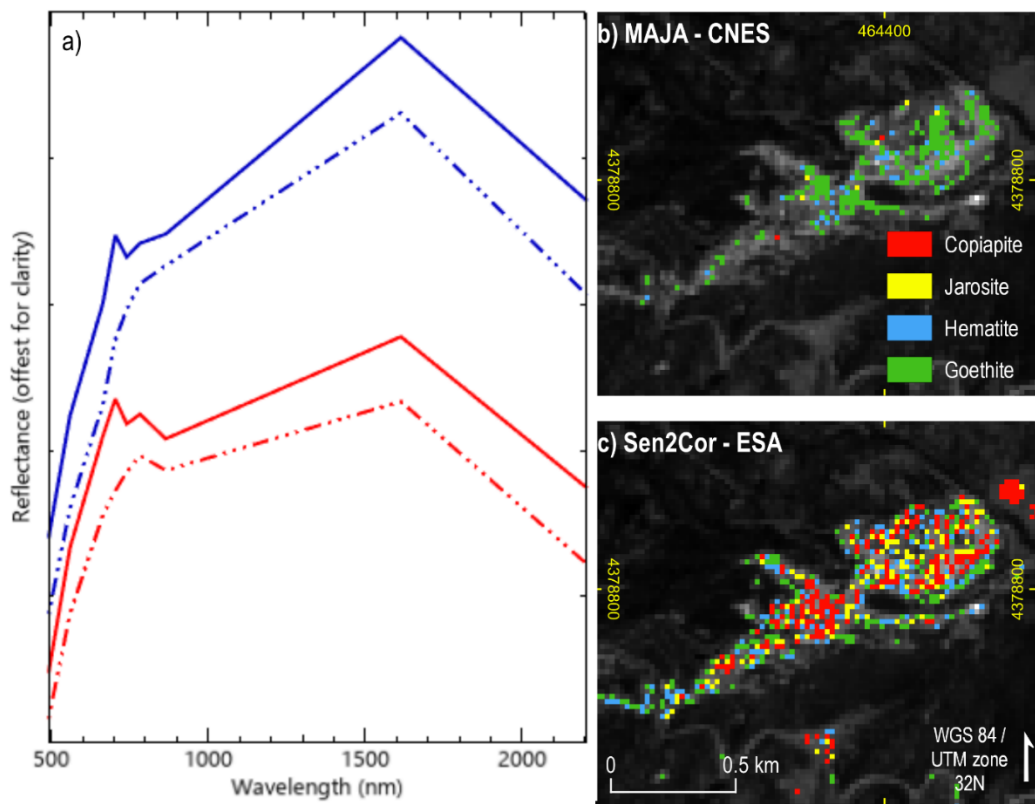


Figure A2. 4 Comparison of the mineral classification applied on the Sentinel-2 image acquired on the 26th July 2024 and corrected with the MAJA and Sen2Cor atmospheric correction algorithms. a) Example of spectral difference between MAJA (dashed lines) and Sen2Cor (solid lines) atmospheric correction. b-c) Mineral map of the Piccalinna impoundment obtained with the MAJA (b) and Sen2Cor (c) corrected image.

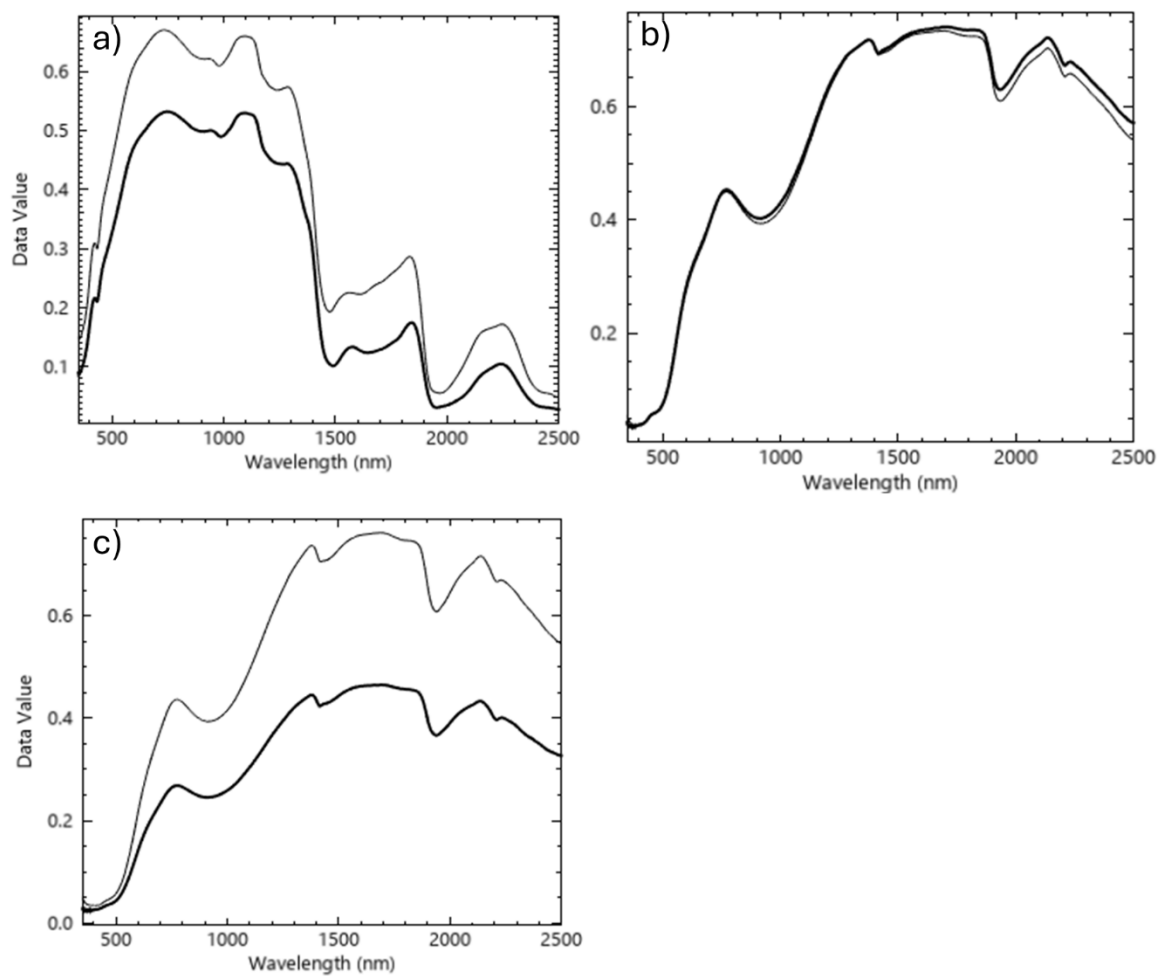


Figure A2. 5 Spectra acquired 1 month (thick line) and 6 months (thin line) after the collection of samples. The samples here shown are: (a) I23, (b) I09, (c) I36b.

Appendix III

This section shows the X-Ray diffractograms obtained from the samples collected in the Piccalinna impoundment (P-samples) and the Sanna tailings (S-samples). The colored bars represent the peaks used by the software HighScore to identify the different minerals phase. Micaceous minerals (muscovite, illite, biotite and phlogopite) in this study are considered as a unique class, due to the limitations of this technique to distinguish them.

