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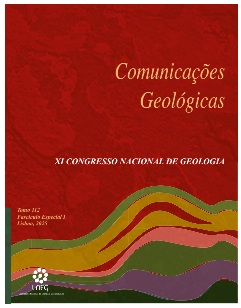
Mineralogical and geochemical characterization of surface soils and waste piles collected in the Preguiça-Vila Ruiva mining area

Caracterização mineralógica e geoquímica de solos superficiais e escombreiras coletados na zona mineira Preguiça-Vila Ruiva



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Abstract: The Preguiça and Vila Ruiva mines, located in the Ossa Morena Zone, Beja district, were explored for Fe-Zn-Pb in the early and mid-20th century. This study aims to reassess their mining potential by creating geochemical maps using modern exploration techniques combined with petrographic and mineralogical analyses. These maps resulted from field measurements obtained by portable X-ray fluorescence (XRF-P) equipment. The geochemical mapping shows that the Zn, Pb, and Fe anomalies correspond to the waste rock piles presenting, however, variations in their spatial distribution. Spatially concordant anomalies of Fe, Co, Cr, and V were detected in the soil NW of the Preguiça mine.

Keywords: Preguiça, Vila Ruiva, portable X-ray fluorescence, metadolomites, supergene deposits.

Resumo: As minas da Preguiça e Vila Ruiva, localizadas na Zona de Ossa Morena, distrito de Beja, foram exploradas pelo seu conteúdo em Fe-Zn-Pb no ínicio e meados do século XX. Este estudo tem como objetivo reavaliar o seu potencial mineiro através da criação de mapas geoquímicos com o auxílio a técnicas modernas de prospeção, complementados com análises petrográficas e mineralógicas. Estes mapas foram gerados com medições obtidas por equipamento portátil de fluorescência de raios-X. A cartografia geoquímica mostra que as anomalias em Zn, Pb, e Fe correspondem às escombreiras das minas apresentando, no entanto, variações na sua distribuição espacial. Foram detadas anomalias espacialmente concordoantes de Fe, Co, Cr, e V a NW da mina da Preguiça.

Palavras-chave: Preguiça, Vila Ruiva, fluorescência de raio-X portátil, metadolomias, depósitos supergénicos.

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1. Introduction

The Preguiça and Vila Ruiva mines are situated within the Ossa Morena Zone (OMZ), specifically in the Moura-Ficalho region, where several mineralizations of the Zn-Pb(-Ag-Sb-Au) type are present. The Preguiça and Vila Ruiva ores are composed of secondary minerals, exhibiting significant zinc (Zn) enrichment. Both deposits were exploited for Fe-Zn-Pb during the early and mid-20th century.
The objective of this study is to contribute to the reassessment of the mining potential of the Preguiça and Vila Ruiva mines by integrating new exploration techniques with conventional methods. This involved conducting a petrographic characterization of the host rock and a mineralogical analysis using X-ray diffraction (XRD) on the gossans, host rock, and soils within the Preguiça-Vila Ruiva mining area. Later, a surface geochemical mapping was performed for Zn, lead (Pb), iron (Fe), vanadium (V), manganese (Mn), cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), arsenic (As), cadmium (Cd), and antimony (Sb), all measured by portable X-ray fluorescence (XRF-P).

2. Geological setting

Located within the Magnetitic Zinciferous Belt (Montemor-Ficalho sector; Figura 1), the Preguiça and Vila Ruiva mining area is situated on the southwestern margin of the OMZ. This mining area is characterized by the occurrence of massive sulfide deposits, associated with dolomitic limestones of the Lower Cambrian age (Figura 2), as well as intermediate-acid volcanites of probable Early Cambrian age (Piçarra *et al*., 2007). Recent research has reclassified the host carbonate rocks in the Preguiça-Vila Ruiva mining area as Lower Cambrian metadolomites with evidence of karstification (Mateus *et al*., 2013).

The genesis of the primary sulfide ore occurring in Preguiça and Vila Ruiva remains a subject of debate. Some researchers, such as Piçarra *et al*. (2007) and Mateus *et al*. (2003), propose a sedimentary-exhalative origin similar to Irish-type deposits. However, Tornos *et al*. (2004) suggest a primary VHMS (volcanic-hosted massive sulfides) origin, with stratiform massive sulfides occurring in metacarbonates and metavolcanites, affected by intense, albeit heterogeneous, hydrothermal alteration.

The (exploited) deposits of Preguiça and Vila Ruiva correspond to highly enriched secondary ores, particularly rich in Zn. These ores were formed through intensive processes of supergene enrichment and *in situ* oxidation of primary sulfides (Tornos *et al*., 2004). A Zn-enriched gossan that extends over 40 meters in depth is present in the Preguiça mine. This gossan was the primary focus of past mining activities.

The reported main mineralogy of the Preguiça mine is extensive, consisting of iron oxyhydroxides (hematite, magnetite, lepidocrocite and goethite) and carbonates (calcite and smithsonite), with minor occurrences of manganese oxides, pyrite, sphalerite, clay minerals, and micas, as well as minerals such as calcite-Pb, willemite, arseniosiderite and descloizite (Patinha, 2002). Online resources

Figure 1. Preguiça and Vila Ruiva mines located within mainland Portugal (left) and OMZ sectors with mining potential, extracted and modified from Mateus et al. (2013). The Preguiça and Vila Ruiva mines correspond to locations 32 and 33 respectively. Numbers in the figure, ranging from 1 to 51, show the locations of the mineral deposits and occurrences from OMZ.

Figura 1. Localização das minas da Preguiça e Vila Ruiva em Portugal continental (esquerda) e setores da Zona Ossa Morena (ZOM) com potencial mineiro, extraído e modificado de Mateus et al. (2013). Os números da figura, de 1 a 51, mostram as localizações dos depósitos e ocorrências minerais na ZOM. As minas da Preguiça e Vila Ruiva correspondem às localizações 32 e 33, respetivamente.

provide further descriptions of the mineralogy at Preguiça mine, including ankerite, aragonite, beudantite, cerussite, coronadite, hemimorphite, hydrozincite, mimetite, phosphohedyphane, plattnerite, quartz, and siderite (mindat.org).

Regarding the Vila Ruiva mine, Patinha (2002) describes the main mineralogy as comprising iron oxyhydroxides (hematite and goethite), carbonates (dolomite, calcite, and smithsonite), and quartz, with minor occurrences of zinc silicates, vanadates, manganese oxyhydroxides, and clay minerals (illite, kaolinite, and sericite-Fe). Minor minerals phases found include smithsonite, hydrozincite, descloizite, calcophanite and birnessite (Patinha 2002). Other available sources also mention arsendescloizite, calcite-Fe, chalcopyrite, coronadite, galena, hemimorphite, pyrite, siderite, and sphalerite (mindat.org).

3. Material and methods

To obtain the necessary data, two field surveys were conducted at the Preguiça-Vila Ruiva mining area during different periods. In December 2021, drone flights were used to delineate the current location of waste rock piles and open pits through orthophotography. Rock samples from the host rock and waste piles were collected for thin section preparation and X-ray diffraction (XRD) analysis.

The second field trip took place in the last week of April 2022 and focused on XRF-P analysis. Measurements were taken along six profiles (two in Preguiça, one between Preguiça and Vila Ruiva, and three in Vila Ruiva) with an approximate NE-SW orientation, spaced around 15 meters apart where terrain allowed. XRF-P measurements were also taken in the pits and waste piles of Preguiça and Vila Ruiva, totalling 132 measurements. The Skyray explorer 900 equipment was used in "environmental soil" mode, with a reading time of 100 seconds. Soil preparation involved removing vegetation, levelling, and compacting the surface. Each reading measured concentrations of Zn, Pb, V, Cr, Mn, Co, Ni, Cu, As, Cd, and Sb. During this trip, ten soil samples were collected—four from Preguiça and six from Vila Ruiva—prioritizing areas with higher concentrations of Zn, Pb, and Fe. Vegetation was removed, and the top 10-15 cm of soil was homogenized before collection.

Soil samples from the open pits and waste piles were dried at 50°C and sieved through a 2 mm mesh. The fraction smaller than 2 mm was reserved for XRD analysis.

The mineralogical composition of the powdered samples was determined through XRD analysis using a Philips X'Pert MPD instrument equipped with an automatic divergence slit and a Ni filter. Data interpretation was carried out using X'Pert HighScore Plus ©2006 PANalytical B.V. (v.2.2) software, supported by the

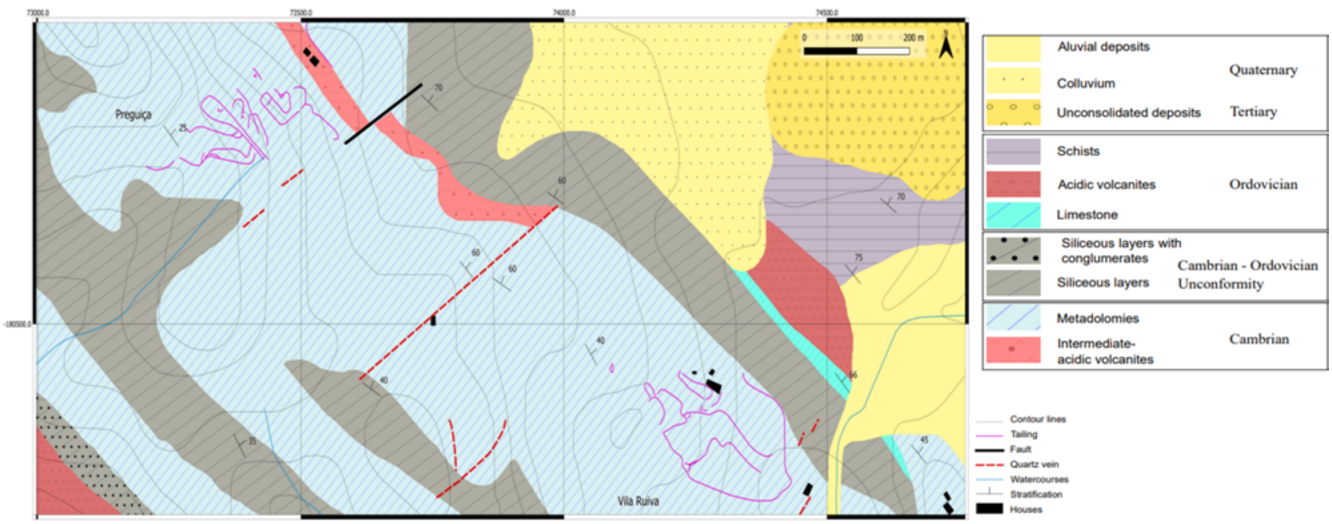

Figure 2. Geological map of the Preguiça-Vila Ruiva mining area adapted from Patinha (2002), representing the Preguiça - Vila Ruiva sector. The topographic information was based on the Carta Militar - 524 Sobral da Adiça (Moura) at a scale 1:25 000. Equidistance of the contour lines is 10 m.

Figura 2. Mapa geológico da zona mineira Preguiça-Vila Ruiva, adaptado de Patinha (2002). A informação topográfica foi baseada na Carta Militar – 524 Sobral da Adiça (Moura) à escala 1: 25 000. A equidistância das curvas de nível é de 10 m.

ICDD (International Center for Diffraction Data) database. The georeferenced information was organized within a GIS (Geographic Information System) project using the QGIS Desktop 3.22.7 software. Ordinary kriging was employed to interpolate elemental concentrations at unsampled locations. The theoretical models of spatial variability were obtained from the experimental omnidirectional variograms. The contour levels correspond to percentiles (0.25, 0.50, 0.75, 0.85, 0.90, 0.925, 0.95, 0.975 and 0.99) of the raw data. Due to the limited number of profiles and the heterogeneity of XRF-P sample locations, directional variograms were not feasible. A theoretical model of spatial continuity was fitted to the omnidirectional variogram. Variograms and maps generated through ordinary kriging were produced using Surfer 11 software by Golden Software.

4. Results

It was observed that the host rocks at the Preguiça mine exhibit a granoblastic texture and are primarily composed of carbonates and quartz. Large dolomite crystals are commonly observed in the samples. Clear deformation and metamorphic recrystallization evidence were observed in both the carbonates and quartz grains, along with enrichment in iron oxides responsible for the reddish colour of the matrix. Opaque minerals constitute a significant portion of these rocks, likely representing alteration products of carbonates and/or sulfides. Additionally, sodium amphibole, muscovite, and serpentine were identified as accessory minerals.

When analyzing samples of the host rocks from the Vila Ruiva mine, one predominantly observes rocks composed of carbonates and quartz. A granoblastic texture is noted in the Vila Ruiva host rocks as well as a blastomylonitic texture. Additionally, several rocks show evidence of crenulation and microfaults cutting through the carbonate matrix and veins filled with silica, sometimes amorphous, and carbonates.

The mineral composition of the host rock samples analyzed by X-ray diffraction in the Preguiça mine shows some variability (Figura 3). Sample PR1 consists mainly of quartz (35%), sphalerite (31%), and dolomite (23%), with traces of hematite, ankerite, and cerussite. Sample PR4 is dominated by dolomite (37%) and hematite (35%), with smaller quantities of calcite, quartz, and anglesite. Preguiça waste pile samples are mainly quartz-rich, except for sample PR3, which has a significant presence of willemite (52%). Iron oxides, mainly goethite, hematite, and minor magnetite, range from 20-43%. Accessory minerals include calcophanite, anglesite, and cristobalite. Soil samples from Preguiça display substantial Zn-containing minerals, particularly willemite (7-52%), along with calcophanite and hemimorphite. Quartz content varies from 9-28%. Iron oxides, mainly hematite and goethite, dolomite and calcite are also present. Pb minerals like cerussite and anglesite were detected in minor amounts, along with birnessite and phyllosilicates.

As for Vila Ruiva host rock XRD analysis (Figura 3), dolomite is the predominant mineral phase (c.a. 80%), quartz shows and abundance of 10%, with occasional occurrences of magnetite (1%).

The Vila Ruiva gossan sample mainly comprises quartz (38%) and iron oxides, including magnetite (33%), hematite (17%), and goethite (12%). In the soil samples, Zn minerals are represented by smithsonite (2-19%), willemite (3-7%), and hemimorphite (5%), while the only lead mineral identified was anglesite (1-4%). The Vila Ruiva soils are notably rich in iron oxides, mainly hematite (53-86%), with lesser amounts of goethite (2-8%) and magnetite (1%). Silicates in the soils are mainly composed of quartz (5-56%) and phyllosilicates (1-28%), with cristobalite occurring in **VRO63** (1%).

Figure 4 presents the geochemical maps obtained by ordinary kriging. Analyzing the geochemical maps of Zn, Pb, and Fe (Figura

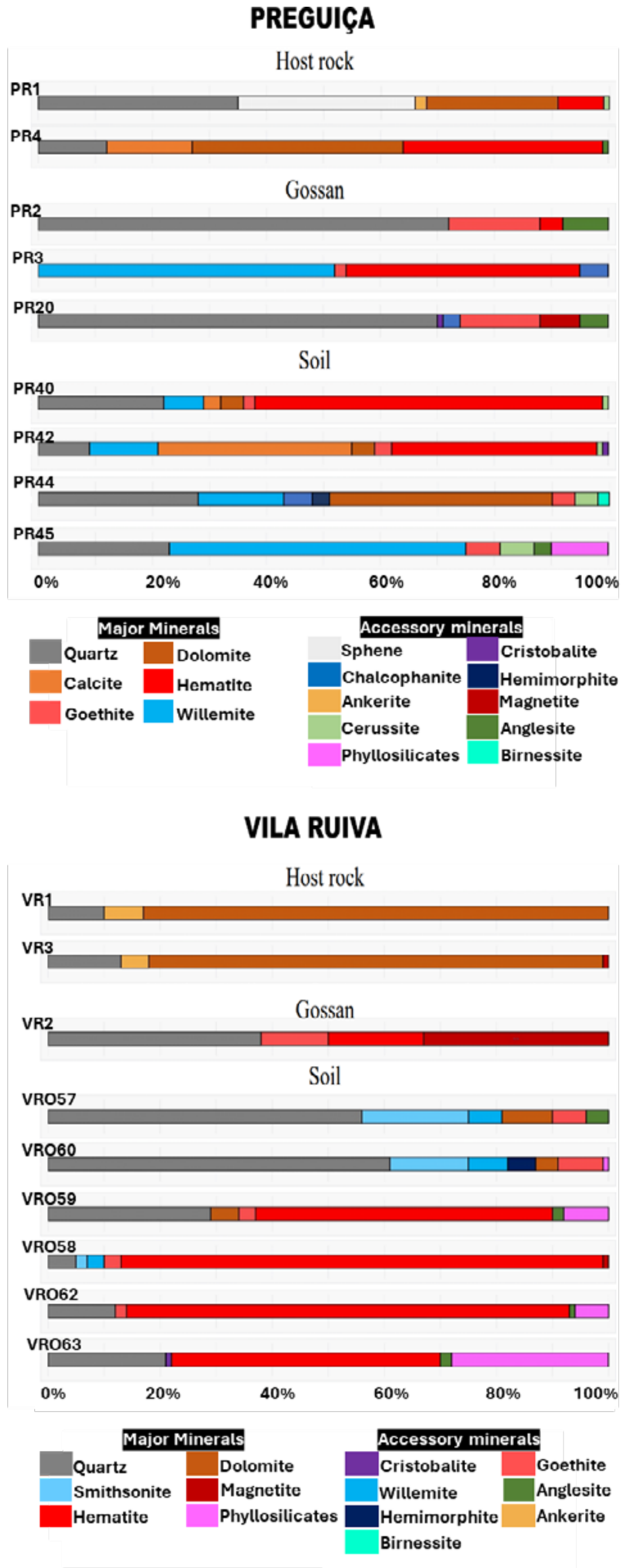

Figure 3. Representation of the total mineralogical composition in the samples collected at Preguiça (top) and Vila Ruiva (bottom) by XRD analysis.

Figura 3. Representação da composição mineralógica total das amostras recolhidas na Preguiça (topo) e em Vila Ruiva (baixo) por análise de difração de raio-X.

4) it is evident that Zn exhibits a notable concentration (anomaly) in the vicinity of the Preguiça waste piles and the Vila Ruiva open pit. In Vila Ruiva, the waste piles have lower concentrations compared to the open pit. For Pb (Figura 4b), there is less dispersion of this element in the study area, primarily concentrating in the soils of the open pits and waste piles. Regarding Fe (Figura 4c), two anomalies (areas of high concentrations) are identified to the north (A) and northeast (B) of the Preguiça open pit, which are not evident in the geochemical maps for Zn and Pb. Further examination of the geochemical maps for the remaining chemical elements (Cr, Mn, V, Co, Ni, Cu, As, Cd, Sb) shows the following:

- Cr and Co, similar to Fe, exhibit a spatial variation pattern with anomalies A and B, north and northeast of the Preguiça open pit, respectively.
- V (Figura 4d) also shows anomalies A and B, as well as one to the north-northeast of the intermediate profile (anomaly C) and to the north of the Vila Ruiva open pit (anomaly D), suggesting a potential alignment of these anomalies in the northwest-southeast direction across the entire area.
- Mn (Figura 4e) displays a spatial pattern similar to Fe, with anomalies A and B observed, along with lateral dispersion in Vila Ruiva.
- Ni exhibits anomaly B and lateral dispersion, especially to the west of the open pit, similar to Zn.
- Cu displays anomalies A and B, with a spatial pattern in Vila Ruiva closely resembling Ni and Zn. Additionally, it is observed an anomaly in the middle profile.
- As exhibits patterns similar to Pb in the soil of the study area, primarily concentrating on the waste pile and open pit areas.
- Cd and Sb show distinct behaviour compared to the other chemical elements, with spatial patterns unrelated to the open pits and waste piles.

5. Discussion

The petrographic study of thin sections of the Preguiça mine supports the classification of the host rock as metadolomites. The textural characteristics of the Vila Ruiva samples suggest that they may have undergone more intense deformation compared to those from Preguiça. However, further analysis of additional samples is required to confirm this hypothesis.

In the context of host rock characterization, samples PR1 and PR4 can be considered metadolomites, with varying proportions of ankerite and calcite. The reddish-brown coloration observed in the samples, attributed to iron-magnesian minerals, and the high hematite content contribute to high density of the rock, which is particularly noticeable in PR4. While previous literature (Piçarra *et al*., 2007) has mentioned magnetite in these carbonated rocks, our study predominantly identified hematite. The occurrences of anglesite and cerussite in the rocks likely result from the alteration of primary lead sulfides. The occurrence of a high concentration of sphene in sample PR1 is anomalous for this type of lithology, although Franz *et al*. (1985) identified the occurrence of sphene, especially aluminous sphene, in siliceous dolomites. The petrography observation also identified the possibility of sphene in the metadolomites.

The mineralogical analysis of the samples collected from the Preguiça waste pile shows an assemblage of minerals indicative of significant Zn enrichment, especially in sample PR3, which is believed to represent the deeper gossan, in contrast to PR2 and PR20, which are inferred to correspond to the superficial gossan due to their iron concentration and quartz content.

The soil samples from the Preguiça area exhibit varying mineral distributions. They contain quartz and willemite in all samples and goethite and anglesite in smaller proportions. Samples with lower silicate content, such as PR40 and PR42, display higher iron

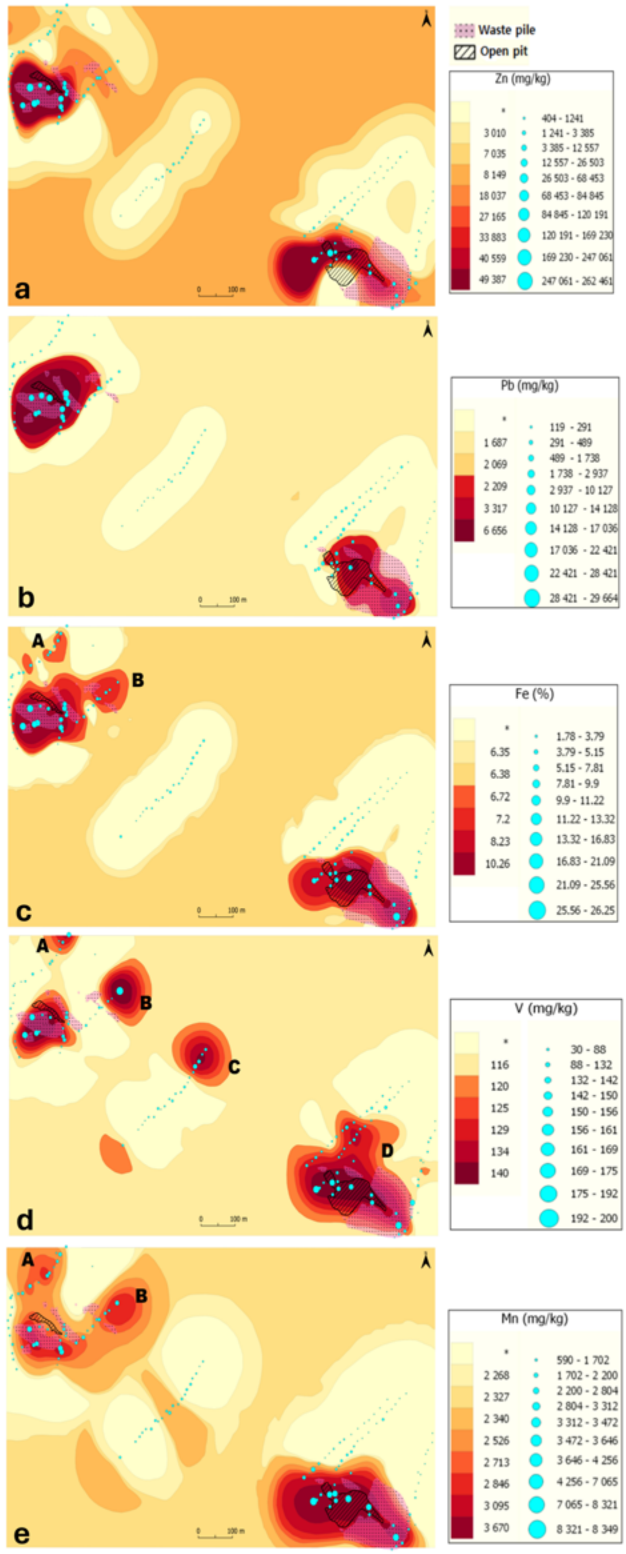

Figure 4. Surface geochemical maps of the total data obtained by XRF-P for the elements Zn (a), Pb (b), Fe (c), V (d) and Mn (e) with the representation of all the 132 XRF-P measurements points (blue dots). Labels A to D locate anomalies that are common to different chemical elements.

Figura 4. Mapas geoquímicos de superfície dos dados totais obtidos por fluorescência de raio-X portátil (FRX-P) para os elementos Zn (a), Pb (b), Fe (c), V (d) e Mn (e) com a representação de todos os 132 pontos de medição FRX-P (pontos azuis). A a D localizam as anomalias comuns aos diferentes elementos químicos.

oxide concentrations. Other minerals like birnessite, cristobalite, and cerussite are also present in some samples. XRD analysis indicates a heterogeneous distribution of major mineral groups in the Preguiça soils. While some samples are iron oxide-dominated, others show enrichment in silicates and carbonates.

As for Vila Ruiva, the host rocks can be classified as metadolomites with smaller amounts of calcite (c.a.81%), when compared to Preguiça. These metadolomites are poorer in silicates and iron oxides, although minerals such as quartz, ankerite, and magnetite are present in accessory proportions.

The Vila Ruiva gossan is likely to be more enriched in iron oxides than that of Preguiça, although only one sample was analysed. The sample is primarily composed of quartz and iron oxides (62%), whereas samples from the Preguiça gossan contain <50% iron oxides, with significant proportions of quartz and zinc minerals. Sample VR2 possibly represents a sample from the shallower gossan layer where iron oxides and quartz mainly accumulate.

The Vila Ruiva soil samples allow for their categorization into two groups of samples: soils VRO57 and VRO60, characterized by a high quartz fraction and significant levels of smithsonite, and soils VRO59, VRO58, VRO62, and VRO63, characterized by high concentrations of hematite and substantial proportions of phyllosilicates. In comparison with the soils from Preguiça, it can be suggested that the soils in Vila Ruiva are potentially less silicate-rich, contain lower concentrations of Zn and Pb minerals, and have a reduced content of carbonates. However, they appear to be significantly enriched in iron oxides.

The geochemical maps of Figure 4, indicate that the high concentration of Zn (>49 387 mg/kg) observed in the mining areas of Preguiça and Vila Ruiva (Figura 4a) is attributed to the presence of Zn-bearing minerals in the soils of the open pits and waste piles (Figura 3). The dispersion of this element is likely due to its high mobility in acidic oxidative environments, which are typical conditions for supergene alteration processes of sulfides (McQueen, 2008). Erosion from the waste piles promotes the mechanical dispersion of Zn-containing minerals. The concentration of Pb (Figura 4b), mainly in the waste piles and open pits (>6 656 mg/kg), can be explained by the presence of Pb-bearing minerals, such as cerussite and anglesite (Figura 3). In contrast to Zn, which is easily adsorbed by clay minerals, carbonates, and hydroxide oxides (McLean and Bledsoe, 1992), facilitating its dispersion in the soil, Pb exhibits low mobility (McQueen, 2008), resulting in anomalies confined to the open pits and waste piles. As for the anomalies identified, the presence of intermediate-acidic volcanites with hematite, occurring in the area may explain anomalies A, B, C and D. The spatial distribution pattern of V (Figura 4d) suggests a northwest-southeast alignment, possibly corresponding to the outcrop of these volcanites (Figura 2). These volcanites may have more intermediate compositions, potentially explaining the similar spatial distribution of Fe, Co, Cr, and V to the north and northeast of Preguiça, as they are elements with stronger calcophilic and siderophilic affinities. The high Mn content (>3 670 mg/kg) in the waste piles of Preguiça and Vila Ruiva (Figura 4e) may be explained by Mn-bearing minerals in the soil, such as birnessite and calcophanite (Figura 3). The concentration observed in the intermediate profile may have been influenced by erosion from the waste piles in Preguiça.

6. Conclusions

The petrographic study of the host rocks of Preguiça and Vila Ruiva mines indicates metadolimites composed of carbonates and quartz with predominant granoblastic textures. Vila Ruiva's rocks also exhibit blastomylonitic texture with prominent deformation features, such as crenulation and microfaults. However, Vila Ruiva has a larger dolomitic fraction (≥81%) and contains fewer silicates and iron oxides than Preguiça. The Vila Ruiva gossan shows a higher iron while that of Preguiça is characterized by larger amounts of Zn minerals, quartz, and Pb sulfates. Soil analysis indicates that Vila Ruiva's soils are poorer in Zn and enriched in iron oxides relative to Preguiça.

The geochemical mapping shows that Zn, Pb, and Fe predominate in the waste piles and open pits, each exhibiting distinct patterns of spatial variation. Zn shows some dispersion around the waste piles of Preguiça and the open pit of Vila Ruiva, demonstrating higher mobility compared to Pb. Anomalies of Fe, Co, Cr, and V identified near the Preguiça open pit may be attributed to the occurrence of intermediate-acid volcanites in that location.

Future research should include more petrographic analysis of thin sections, expanded XRD studies with more samples, and broader soil sampling to better understand geochemical processes. More measurement points in geochemical mapping, especially between the mines, would clarify spatial patterns of element dispersion.

Acknowledgements

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