

Article

A New Geochemistry Exploration Method to Identify Deep VMS-Type Deposits—Application to the Cu-Zn Neves-Corvo Deposit, Iberian Pyrite Belt

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Abstract

Mineral exploration in the Iberian Pyrite Belt follows increasingly deeper targets. The present study introduces an innovative methodology for the detection and identification of blind metallic mineral deposits, in particular volcanogenic massive sulfides based on surface rock coatings. This approach follows the identification pathways of upward metal escape routes and metal distribution in rock fractures located in different anisotropic or isotropic planes above the Neves-Corvo VMS deposit ore lenses, using VP-SEM-EDS and XRD. Coatings are dominated by poorly crystalline to amorphous phases, with goethite and birnessite as the main Fe- and Mn-bearing minerals. Copper, zinc and lead are systematically enriched in coatings developed above or near the ore bodies, reflecting chalcopyrite, sphalerite and galena acidic leaching. Tin shows a restricted and heterogeneous distribution, while Ni and Co display no systematic relationship with the ore bodies. Barium and late Ba–Pb–(Zn) mineralization along fault zones record VMS mineralization. Lead isotopic coating signatures overlap those of IPB massive sulfide deposits, confirming a dominant VMS-derived contribution. Fe–Mn coatings were formed by precipitation from ascending meteoric fluids that leached metals from massive sulfides, their alteration halos, and surrounding lithologies, preserving the geochemical footprint of buried mineralization. This approach constitutes a new patented exploration tool.

Keywords: Iberian Pyrite Belt; VMS mineralisation; rock coating geochemistry; mineral exploration



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1. Introduction

The Iberian Pyrite Belt (IPB) is one of the largest metallogenic provinces of volcanogenic hosted massive sulfides (VMSs) in the world, containing > 100 known deposits

formed by massive and/or stockwork mineralization and distributed along southern Portugal and Spain [1–4] with total tonnages of 2500 Mt of massive sulfides, thus representing the largest crustal anomaly of sulfur and iron [5,6]. Some deposits are considered giant-sized, e.g., Neves-Corvo and Aljustrel (in Portugal) and Rio Tinto (in Spain), with many medium-sized, such as Lousal, Lagoa Salgada, Montinho, São Domingos, Chança in Portugal and Tharsis, Sotiel and Aznalcóllar in Spain.

Mining in IPB by vertical twin shafts and galleries excavated sometimes to below 50 m dates to the Roman Empire, where the focus was the VMS deposit gossans (e.g., Riotinto, Tharsis, Aljustrel and São Domingos) that contained significant concentrations of Au, Ag, Cu and Pb [7–9]. With the evolution of exploration and exploitation methods and the increasing global demand for metal supply (e.g., Cu, Zn, and Pb) since the 19th century, a significant increase in the discovery of economically viable deposits at greater depths has been achieved, particularly through the use of geophysical exploration tools (e.g., IPB Portuguese sector, Refs. [10,11]). An emblematic example is the discovery, in 1977, of the Neves-Corvo VMS deposit, which, due to its unusually large tonnage [12–15] and high Cu, Zn, and Sn grades, revolutionized the exploration of massive sulfide deposits in the Portuguese sector of the Iberian Pyrite Belt. This modern mining operation demonstrates that massive sulfide mineralizations with exceptional reserves and high base-metal grades can occur at progressively greater depths, as illustrated by the Lombador deposit, located at depths exceeding 1000 m. Furthermore, the discovery of the Lagoa Salgada deposit in 1992 and the Sesmarias deposit in 2014 [10,16], both concealed beneath the sediments of the Alvalade-Sado Basin [17,18], as well as the discovery of the Las Cruces deposit between 1992 and 1994 beneath the Guadalquivir Basin sediments [19,20], substantially expanded the area of the Iberian Pyrite Belt considered prospective and significantly increased the expectations for new discoveries.

As a result of these discoveries, the development of new methodologies in geology, remote sensing, geophysics, and geochemistry, with enhanced capabilities to investigate greater depths, has become crucial for advancing the detection of potential blind deposits from surface data. Currently, several geophysical and geochemical techniques are applied in an integrated manner, supported by geological modeling and high-resolution stratigraphic frameworks. These include palynological studies and absolute age dating of sedimentary and volcanic units, which are essential for defining favorable horizons and selecting new targets prospective for hosting VMS mineralization [10,21–23].

For many years, gravity geophysics has been one of the most important and effective techniques for identifying blind ore bodies in the IPB, as it is based on density contrasts between different rock types [10]. Several significant deposits were identified using this method, including the Gavião, Feitais and the Neves-Corvo set of deposits [12,13,17,24–30]. Geochemistry and radiometric methods are also widely used exploration tools in the IPB, applied to different materials such as rocks, soils, stream sediments, and radiometric data [11,31–33]. The geochemical approach provides important information on the distribution of major and trace elements associated with mineralized zones in rocks and soils. However, conventional geochemistry has several limitations, particularly in its inability to provide indirect information on deep geological structures, in contrast to geophysical methods such as gravity and magnetics. Geochemistry has been widely applied as an exploration tool, mainly at the surface, but also through underground and subsurface sampling, including drill core analysis. However, in the Iberian Pyrite Belt, geochemical surveys are often constrained by the environmental impact of historical mining activities, particularly acid mine drainage, which can mask primary geochemical signatures. In addition, the complex multiphase deformation history of the region, including Variscan ductile deforma-

tion and late-Variscan brittle tectonics, contributes to the remobilization and dispersion of elements, further complicating the interpretation of geochemical anomalies [11].

The present study presents a new and innovative method for the identification, characterization, and evaluation of underground metallic mineral deposits, in particular VMS deposits based on present-day surface rock coatings.

The case study focuses on the Neves-Corvo Mine, where the ore lenses occur at depths ranging from approximately 230 m to about 1400 m below the surface (Somincor/Lundin Mining, 2017). This research was conducted by the Laboratório Nacional de Energia e Geologia in collaboration with the HERCULES Laboratory and involved both mine-proximal and regional study areas [31,32].

The aim of this publication is to describe the conditions and tests that led to the patent.

2. Geological Setting

The IPB is in the southwestern sector of the Iberian Peninsula, extending over 230 km long by 20–70 km wide. It stands as the foremost domain of the South Portuguese Zone (SPZ) [21,34–36], which was interpreted as a tectonostratigraphic terrane sutured to the Iberian Massif during the Variscan Orogeny [34,37–40]. The IPB is limited to the north by the Pulo do Lobo Antiform oceanic terrane, formed by the Ferreira–Ficalho Group (late Devonian), Chança Group (late Devonian) and Pulo do Lobo Fm. (late Devonian and older) and overlain by the synorogenic *Baixo Alentejo* Flysch Group (Mértola, Mira and Brejeira formations, Late Visean–Moscovian) (Figure 1).

The Neves-Corvo (NC) mine (Figure 2) is located in the Rosário–Neves-Corvo anticline structure in the Portuguese sector of IPB. The mine site includes, so far, seven massive sulfide ore bodies (Neves, Corvo, Graça, Lombador, Zambujal, Semblana and Monte Branco) at depths between 230 and 1400 m (Somincor/Lundin Mining). The NC stratigraphic sequence is one of the most studied and best defined in IPB, comprising from the bottom to the top: (1) Phyllite–Quartzite Group (PQ), a pre-orogenic siliciclastic succession composed by dark shales with siltstones and quartzite intercalations (Givetian to late Famennian age, and base unknown [41–43]). At the upper PQ sequence there are limestone rocks with crinoids (*Forno da Cal* limestones) usually associated with the first events of volcanism [21]; (2) Lower VSC sequence, comprising bimodal volcanic rocks (felsic rocks and minor basalts), Corvo Fm. sediments (Famennian age), black shales of the Neves Fm. (Late Famennian age, Strunian Miospore Biozone) and jaspers and carbonates at the top of this sequence (JC unit). Several rhyolite types have been identified within the sequence and classified according to their geochemical characteristics [44], defining two volcanic horizons: at ca. 351 Ma barren horizon and a ca. 360 Ma productive horizon [4,21,45,46]. Massive sulfides were genetically associated with the latest and are hosted by the Neves Fm. and related felsic volcanic rocks; (3) The Upper VSC sequence is represented by shales, siltstones and fine-grained volcanogenic rocks (Ribeira de Cobres Fm.), dark shales with siliceous-phosphatic nodules (Graça Fm.), grey shales with carbonate nodules, volcanogenic sediments and intrusive mafic rocks (Grandaços Fm.); also includes the Borra de Vinho Fm. purple and green shales key-horizon, siliceous shales and volcanogenic sediments (Godinho Fm.), and raised by the Brancanes Fm. black shales [21,41]. This CVS sequence in Neves-Corvo is covered by the (4) Mértola Fm., which is the *Baixo Alentejo* Flysch Group (BAFG) lower unit and includes intercalations of dark grey shales and greywackes.

Intense hydrothermal alteration is present [3,31,32] in the felsic volcanic rocks spatially associated with VMS. Concerning the metal distribution, one of the notorious characteristics of the NC deposit is the very well defined vertical and lateral metallic zonality [50]. The highest copper contents are generally located in the innermost areas of the stockwork ore type and at the footwall of the massive sulfide lenses. The zinc and lead are covariant

and concentrated on the most peripheral areas of the mineralizing system, laterally and vertically [14,50,51]. The tin occurs in association with areas of high content of copper, in the form of cassiterite and sulfosalts, and its depositions are tectonically controlled, such as the tin corridor in the Corvo ore lens [50]. The principal characteristics of each type of ore and the general geology of each mineralized orebody have been extensively studied and described in previous works [14,50,52–55]. The NC massive sulfide mineralization is composed mainly of pyrite associated with greater or lesser quantities of chalcopyrite, sphalerite, galena and cassiterite. Minor elements occur within these minerals internal structures or are associated with them as arsenic, mercury, indium, selenium, antimony, gold, silver and others.

Besides the different rock types and the corresponding stratigraphy and the metallic component of the massive sulfide occurrences, the structural control of the area plays an important role in the main purpose of this paper regarding fluid escape routes. The stratigraphy is affected by Variscan syntectonic deformation marked by low-angle, thin-skinned thrusts and folds and late/post-tectonic faulting and fracturing [22].

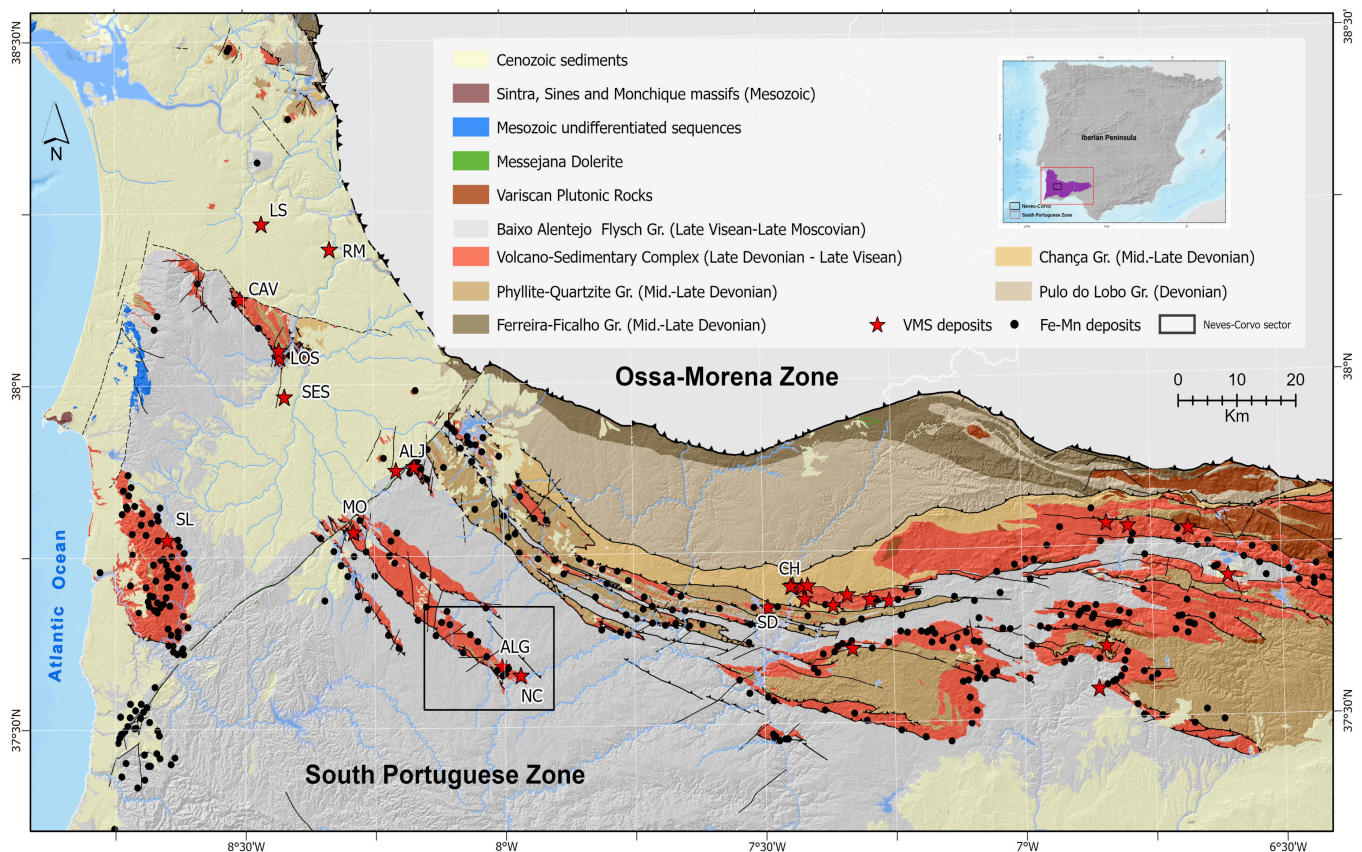


Figure 1. Simplified geological map of the Iberian Pyrite Belt, illustrating the location and reference of major sulfide deposits and occurrences, as well as the main Fe-Mn occurrences. Legend: LS—Lagoa Salgada; RM—Rio de Moinhos; CAV—Caveira; LOS—Lousal; SES—Sesmaria; SL—Salgadinho; MO—Montinho; ALJ—Aljustrel; ALG—Algaré; NC—Neves-Corvo; CH—Chança; SD—São Domingos. Modified after [1,12,35,47,48].

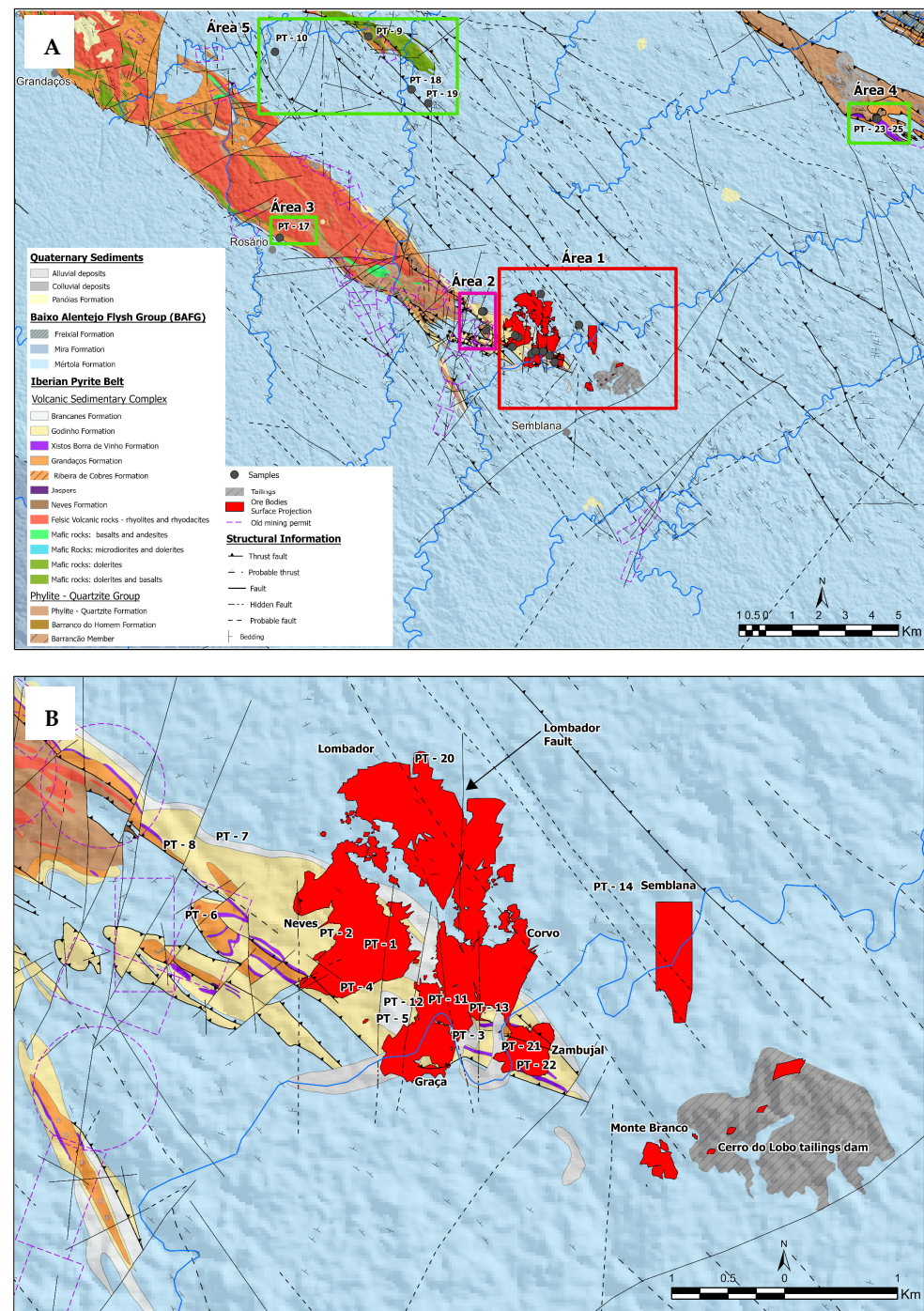


Figure 2. (A) Geological map of the study area in the Rosário–Neves–Corvo antiform (adapted from [10,49]. Grey dots: studied samples. Proximal areas to VMS deposits: Red rectangle—Area 1/Neves–Corvo mine (enlarged in (B)); Purple rectangle—Area 2/Algaré and Monte dos Mestres. Background areas (VMS deposits not identified): Green rectangles—Area 3/Rosário village; Area 4/Alvares structure and Area 5/Castro Verde—São Pedro das Cabeças structure). **(B)** Detailed geological map of the Neves–Corvo mine area (Area 1). Red polygons—vertical projections of the massive sulfides (MSs) ore bodies.

NW–SE-oriented folds plunging to SE and verging SW with NE-dipping axial planes are the main recognized structures of Portuguese IPB in general and Neves–Corvo in particular, at regional mapping scale. Before this folding event, the Variscan compressive regime had generated low-angle, thin-skinned thrusts [56,57] affecting mainly the upper lithologies of the VSC, which are syn-tectonic [36]. A major Neves–Corvo Main Thrust has

been identified in the upper-lower VSC interface, sometimes resting directly above the massive sulfide lenses (e.g., Neves and Corvo deposit). This tectonic marker plan has been mapped underground and surface interpreted, being identified in most massive sulfide lenses [22,46]. These low-angle thrust faults sometimes create multiple stratigraphic section stacks, affecting mainly the upper VSC units, resulting in an overestimated width. Further Variscan tectonics has favored the folding style of major structures, also affected by frequent, imbricated thrust faults locally with strong shear deformation. The root detachment plans of some of these imbricated faults have been associated with the above-mentioned NC Main Thrust [4,51].

The late post-Variscan faulting is identified by strike-slip, oblique to subvertical, block-defined brittle deformation faults affecting all the Rosário–Neves–Corvo Anticline. Major fault directions are N-S to NNW-SSE and NNE-SSW and ENE-WSW [27,49]. One of those N-S faults drives across the Lombador deposit, being interpreted at the surface but well documented and mapped underground.

All lithologies are affected by a variable penetrative S1 S2 cleavage that is present at VSC and PQ rocks, with the same NW-SE orientation of the major anticline structure, dipping 50–70° to NE. In the second case, the most ductile volcanic rocks and the quartzite PQ layers are to be mentioned. These last evolved to a fracture cleavage and can show different orientations due to the late faulting [36].

Having these geology and tectonic settings in mind, there are subhorizontal to low-angle faults, subvertical to high-angle imbricated faults, and late subvertical block faults, besides later decompression fracturing and subsurface fracturing effects, all designed as a fracture-fill network directly above a massive sulfide lens. These are the identified pathways of metals being transported upwards to the surface. This approach is valid for Flysch, VSC and PQ rocks.

3. Rock Coats and Their Formation

Surface rock coatings are an innovative approach to geochemical sampling based on the principle that these materials transport information from the ore deposits located at depth. These coatings are small, thin (from about 1 µm to several hundreds of µm), black-brown surfaces exposed in the rock surface [58]. It is mainly composed of clay minerals and amorphous silica (about 70%) and Mn and Fe oxides/hydroxides (about 30%) [59–61]. These minerals can be deposited in anisotropic planes like bedding, cleavage and diaclasses, commonly in late/very late brittle stages. Black Mn-rich coatings have been described for a wide variety of environments, including alpine, arctic and antarctic settings [62–64], and also in cold and hot springs [65–68].

Conceptual Models to Coating Formation

Rock coatings are a small, thin, black-colored film (Figure 3) found most prominently on rock surfaces in arid environments, where it is called “desert varnish”, and it has been long studied in these climates [59,60,69–74]. However, rock coatings can be found in a variety of climates and locations worldwide, including tropical and polar environments [63,75,76].

The genesis of rock coatings is controversial and a topic of discussion by several authors. Currently three main hypotheses are suggested: (1) the enrichment in Mn occurs abiotically through local physical–chemical changes in the rock surface by oxidation of Mn^{2+} to Mn^{4+} [69,74]; (2) enrichment occurs through biological mediation, where microbes produce minerals of the birnessite family on the rock surface [64,77,78]; and (3) a mixed model that combines aspects of biotic and abiotic origin [59,79]. None of these mentioned models correspond to what the coatings are described as in this study.



Figure 3. Examples of rock coatings collected on the Neves-Corvo mine area rock outcrops. Black colors represent zones enriched in iron (Fe) and manganese (Mn). (a) Rock Fe-Mn coating in the diacalse zone of Grandaços Fm. (Volcano–Sedimentary Complex). (b) Rock Fe-Mn coating in the greywacke cleavage (Mértola Fm.). (c) Fe-Mn outcropping-rich zones of the Grandaços Formation shales. (d) Rock coating cross-section (Grandaços Formation shale).

The proposed models do not take into account the fluid circulation at great depth, whether they are mostly hydrothermal fluids, i.e., high-temperature fluids that heat up thanks to the geothermal gradient of a particular region and/or the presence of active volcanism in the vicinity, or whether these fluids result from meteoric fluids that infiltrate through fractures and faults to great depths.

In the IPB context, this fluid circulation is probably at the origin of most coatings that are observed on the surface of the rocks. Any of those fluids, with hydrothermal or meteoric origin, due to its characteristics like pH and Eh, for example, promote the leaching of metals and other components from geological formations crossed by them. The metalliferous content of hosted rocks and associated mineralizations are gradually transferred to these fluids, which ascend to the surface through faults and fractures and are deposited along planes of discontinuity. The tectonic forces, including rock folding, stretch and faulting, do affect geological structures, generating anisotropic planes, i.e., “weakness planes” along which secondary fluids with metals can be transported to reach the surface and be concentrated in some specific mineral phases (Figure 4).

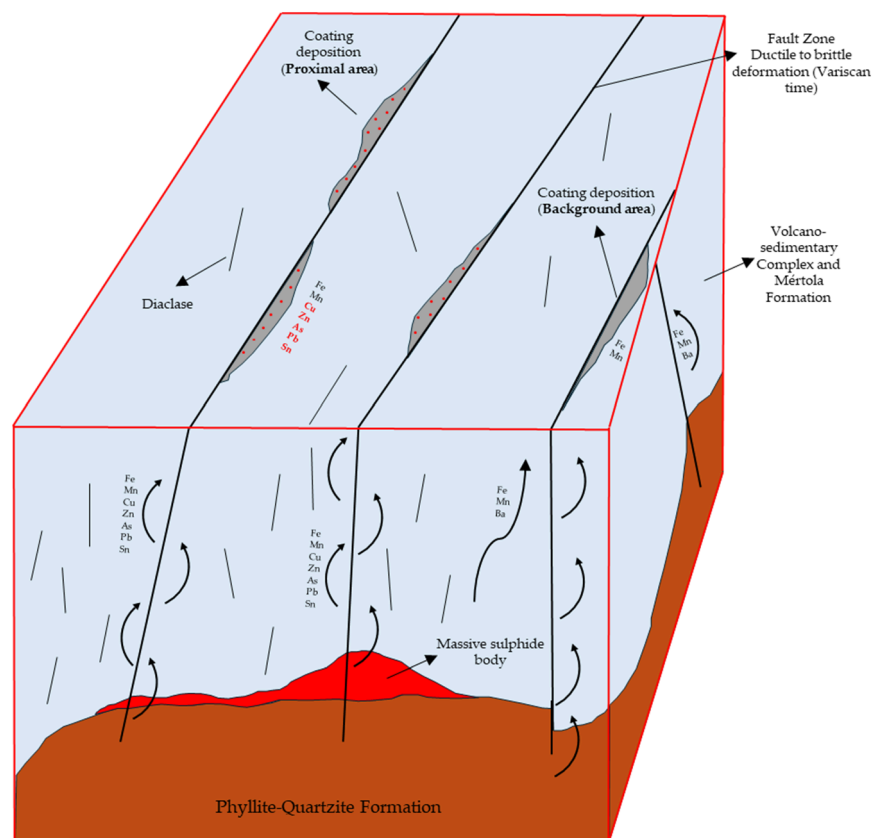


Figure 4. The conceptual model illustrates the formation of the coating surfaces associated with VMS deposits.

The coating chemical composition is intrinsically linked to the mobility of each element but also to the chemical composition and metal content likely to be leached from each geological formation. The IPB is one of the major regional iron anomalies at the world level [18,80] and one of the biggest concentrations of massive sulfide mineralizations with appreciable contents of copper, zinc, lead and tin in massive and stockwork ores [1,18,81]. Important manganese mineralizations are typically found on top of VMS deposits and associated with upper VSC geological formations (Gradaços and Xistos Borra de Vinho Formations) characterized by sediments and volcanoclastic sediments formed in an erosion setting after the main volcanic events. Cherts and jaspers that occur on top of the VMS deposits (e.g., Aljustrel, Neves-Corvo and Lagoa Salgada, Refs. [1,17,21]) also present intense Fe-Mn deposition in rock fractures. In volcanogenic massive sulfide systems, sulfides (pyrite, copper, lead, zinc) are deposited near vent sources, while manganese, being more soluble and mobile, precipitates farther away at lower temperatures or later in the seafloor depositional cycle. Within the geological context, the Mn mineralizations can be related to the fragmentation of the Upper Devonian basin, where smaller anoxic basins favorable for the deposition of manganese-rich sediments [82]. Epigenetic Mn remobilized from primary sources deposited in faults [83] is also often observed and again not related to the study presented here. Therefore, in principle, the source of the manganese and iron from the coatings is different from the one in these referred Mn mineralizations.

For the present study, the rock coatings and fracture fills materials can be classified in five types in function of their chemical compositions and internal organization: coating type 1—composed by iron (predominant) and manganese and another metals associated with iron and manganese phases; coating type 2—rock coating composed by manganese (predominant) and iron and another metals associated with manganese and iron phases; coating type 3—coating composed by manganese and another metals associated with

manganese phase; coating type 4—rock coating composed by iron and another metals associated with iron phase and coating type 5—iron and manganese veins linked with superficial coating.

This work is based on the premise that the coating chemical composition directly reflects the geochemical signature of the rocks where the fluids are driven through and may be enriched in elements such as Zn, Pb, Cu and Sn if these fluids cross the massive sulfide mineralization. In this scenario, the methodology can be applied on a large scale throughout the IPB or other similar provinces around the world and can be an important tool for mineral exploration of these types of deposits (Figure 4).

4. Materials and Methods

Fifteen samples were collected above and in the vicinity of Neves-Corvo VMS ore bodies and were considered proximal near-deposit samples (Area 1 and 2, Figure 2). Nine samples were collected in places where previous studies, such as detailed geological mapping, geophysics and geochemistry, did not reveal the presence of massive sulfide deposits and were considered as background samples (Area 3, 4, 5 and sample PT-15) (Figure 2A,B). These areas are characterized by limited hydrothermal alteration related to the regional deformation setting. The location and description of each sample are presented in Table 1. Three types of samples are considered: (1) proximal samples—collected above or surrounding the VMS vertical projection of the Neves-Corvo mine site (Area 1); (2) near-deposit samples—collected in the vicinity of VMS mineralization (Area 2) and (3) background samples—collected in sectors where mineralization is not known (Area 3, 4 and 5).

The samples were collected from different anisotropic structures, including faults (with visible displacement), cleavage planes (metamorphic reorientation), fractures (without displacement), and diaclasses (small-scale fractures without movement), as well as from isotropic planes such as sedimentary bedding and volcanic layering (Figure 3a–c).

Table 1. Rock coating samples with sampling location, sector, host rock and number of analyses in spot points (# of analysis represent the number of spot analysis in each sample) and profile (e.g., +26).

Sample ID	GPS Coordinates (Coordinates in D73/HG)		Location	Sector	Host Rock	Anisotropic Surfaces	# of Analysis
PT-1	13,684.059	−232,272.826	Proximal—Area 1	above Neves orebody	shales of Godinho Fm.	diaclasses	6
PT-2	13,571.337	−232,203.853		above Neves orebody	shales of Godinho Fm.	diaclasses	4
PT-3	14,861.461	−232,961.593		Corvo—Zambujal bridge	siliceous shales of Grandaços Fm.	diaclasses	3
PT-4	13,473.798	−232,628.270		above Neves orebody	shales of Godinho Fm.	diaclasses	4
PT-5	14,179.038	−232,906.903		above Graça orebody	shales of Godinho Fm.	diaclasses	3
PT-11	14,331.799	−232,794.709		above Graça—Corvo orebody	shales of Godinho Fm.	diaclasses N43E	3 (+26)
PT-12	14,331.799	−232,794.709		above Graça orebody	shales of Godinho Fm.	diaclasses N68E	4
PT-13	14,622.169	−232,803.641		Graça—Neves bridge	shales of Godinho Fm.	diaclasses	3
PT-14	15,968.960	−231,810.981		Corvo—Semblana bridge	shales of Mértola Fm.	diaclasses	3
PT-20	14,535.363	−230,643.569		N Lombador	shales of Mértola Fm.	diaclasses	3
PT-21	15,051.367	−233,206.126		above Zambujal orebody	shales of Grandaços Fm.	fault	2
PT-22	15,051.367	−233,206.126		above Zambujal orebody	shales of Grandaços Fm.	diaclasses	1
PT-6	12,476.068	−232,015.244	Distal—Area 2	W of Neves orebody	shales and quartz of Grandaços Fm.	fault	2
PT-7	12,385.633	−231,300.162		W of Neves orebody	shales of Godinho Fm.	bedding (S0)	2
PT-8	12,324.534	−231,308.601		W of Neves orebody	shales of Godinho Fm.	fault	1
PT-15	5675.679	−243,564.522	Background	Almodôvar	shales of Mértola Fm.	diaclasses	3
PT-16	5675.600	−243,564.420			shales of Mértola Fm.	diaclasses	2
PT-17	4710.010	−228,526.554	Background—Area 3	Rosário area	shales of Borra de Vinho Fm.	diaclasses N80W	3

Table 1. *Cont.*

Sample ID	GPS Coordinates (Coordinates in D73/HG)		Location	Sector	Host Rock	Anisotropic Surfaces	# of Analysis
PT-23	27,169.476	−223,998.797	Background—Area 4	Alvares area	quartzites of Phyllite–Quartzite Group	diacalse	2
PT-24	27,167.309	−224,023.583		Alvares area	shales of Phyllite–Quartzite Group	diacalse	2
PT-25	27,189.929	−224,055.035		Alvares area	siliceous scales of Grandaços Fm.	diacalse	1
PT-9	8040.979	−220,955.619	Background—Area 5	S. Pedro das Cabeças area	shales of Godinho Fm.	diacalse E-W	3 (+13)
PT-10	4530.626	−221,541.343		S. Pedro das Cabeças area	shales of Mértola Fm.	bedding (S0) layering; N30W	4
PT-18	9663.992	−222,956.136		S. Pedro das Cabeças area	greywackes of Mértola Fm.	bedding (S0)	3
PT-19	10,298.027	−223,476.287		S. Pedro das Cabeças area	greywackes of Mértola Fm.	diacalse	3

In the lab the rock fragments were cut perpendicularly to the fracture plane with a cutting machine to produce a cross-section of the rock coating or fracture fill (Figure 3d).

The new sample sections have a size of approximately 25 mm in diameter and 10–15 mm in thickness, oriented perpendicular to the fracture plane, preserving the stratigraphy of the coating layer.

The sampled rock coatings or fracture fill fragments are impregnated with an epoxy resin at room conditions (temperature of 20–25 °C and pressure of 1 bar). Afterwards, a gridding and polishing procedure is applied to each sample using a polishing tool with an integral abrasive automatic feeding system. In the stratigraphic sections of interest, image acquisition is performed under the stereoscopic and metallographic microscope to observe the surface layer, namely aspects such as its color and texture.

The chemical analysis of the coating layer is evaluated on the polished surface using VP-SEM-EDS (Variable Pressure Scanning Electron Microscope with Energy Dispersive Spectroscopy) at low vacuum (40 Pa) and with an accelerating voltage of 20 keV. The VP-SEM-EDS tool generates a 2D image of the sample (Figure 5) and through an X-ray system, elemental analysis or chemical characterization is obtained (Figure 6). The variable pressure mode in the SEM-EDS allows imaging and chemical analysis without the need for coating.

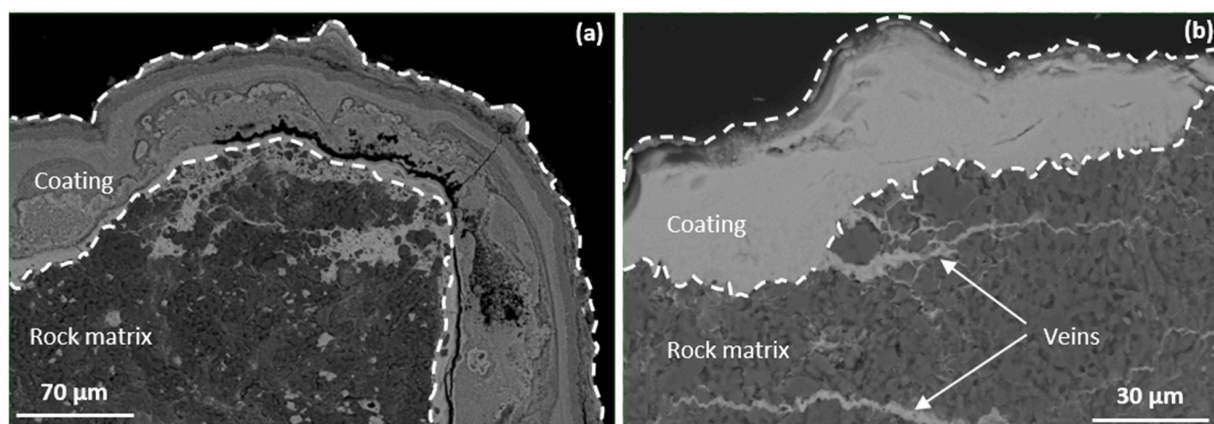


Figure 5. Images of rock coatings acquired by VP-SEM-EDS. (a) Irregular rock Fe-Mn coating deposition above the rock matrix. (b) Irregular Fe-Mn coating and veins resulting from the filling of fractures in the rock surface. Some veins are connected to each other, being at the origin of metals ascent to the rock surface. Dashed lines are drawn to guide the eye to the boundaries of the Fe-Mn coating.

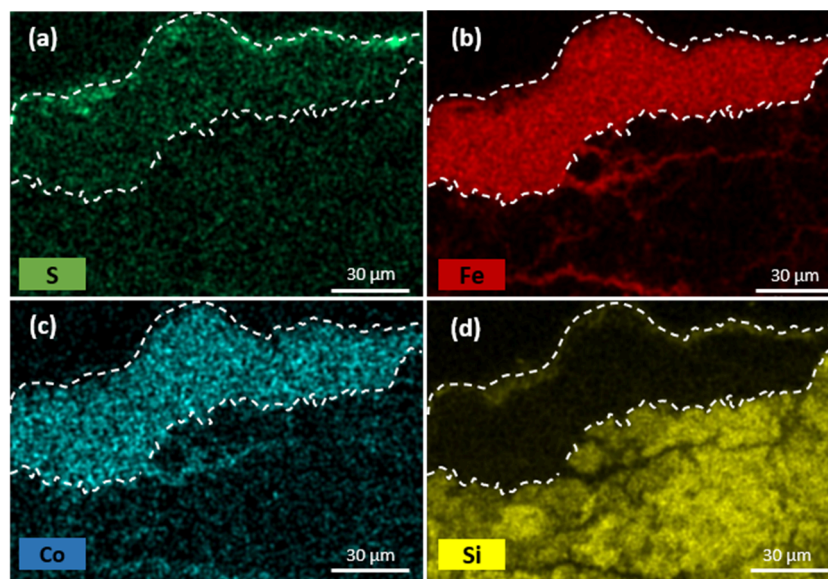


Figure 6. Single-element EDX maps of the same area showing the locations where each element is concentrated. Dashed lines are drawn to guide the eye to the boundaries of the Fe-Mn coating. (a) S-rich particles in the surface of the rock coating and inside Fe-rich layers and associated with sulfide particles like pyrite, sphalerite and chalcopyrite. (b) The Fe-rich layer is the principal compound of rock coating; Fe veins are observed penetrating the rock matrix. (c) Co enrichment associated with the Fe layer and (d) Si concentration present in the rock matrix.

X-ray diffraction (XRD) was performed at the LNEG Lumiar laboratory on polished surfaces for phase identification, using a D8 Advance Bruker AXS diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) with Cu K α radiation, operating at 40 kV and 40 mA. The diffractograms (5–70° 2 θ) were obtained using a step size of 0.015° and a step time of 0.3 s with a LYNXEYE XE-T detector. The XRD data treatment was performed using DIFFRAC.EVA v5 software.

5. Results and Discussion

5.1. Textural Features

The collected rock sample fragments are diverse in nature, depending on the geological setting of each sampling location (see the host rock in Table 1). From the 24 samples collected for this study, 16 samples were gathered from black and siliceous shales of Upper VSC formations, 6 from the shales and greywackes of the Mértola Fm. (Baixo Alentejo Flysch Group) and 2 samples from shales and quartzites of the lower Phyllite–Quartzite Group.

Polished cross-sections and polished surfaces show that coatings are composed of a thin surface deposit of dark-brown fine material locally with dendrite facies (Figure 7a). The coating thickness varies from a few microns to a maximum of 25–30 microns, and sometimes the coating is absent. In more fractured areas associated with diaclasses and/or fault zones, black to dark gray impregnations may occur in the rock matrix (Figure 7b). Veinlets are also common, with a clear relationship between the coating deposition on the rock surface and the impregnation and the rock-filling phenomena (Figure 7e,f). Macroscopically, the coating surface is not homogeneous, exhibiting a variable heterogeneity that depends directly on the chemical and mineralogical composition. In some cases, a first black coating immediately above the rock matrix (essentially with iron composition) is observed, and then a second stage of black-bluish color coating (essentially with manganese composition) (Figure 7c,d).

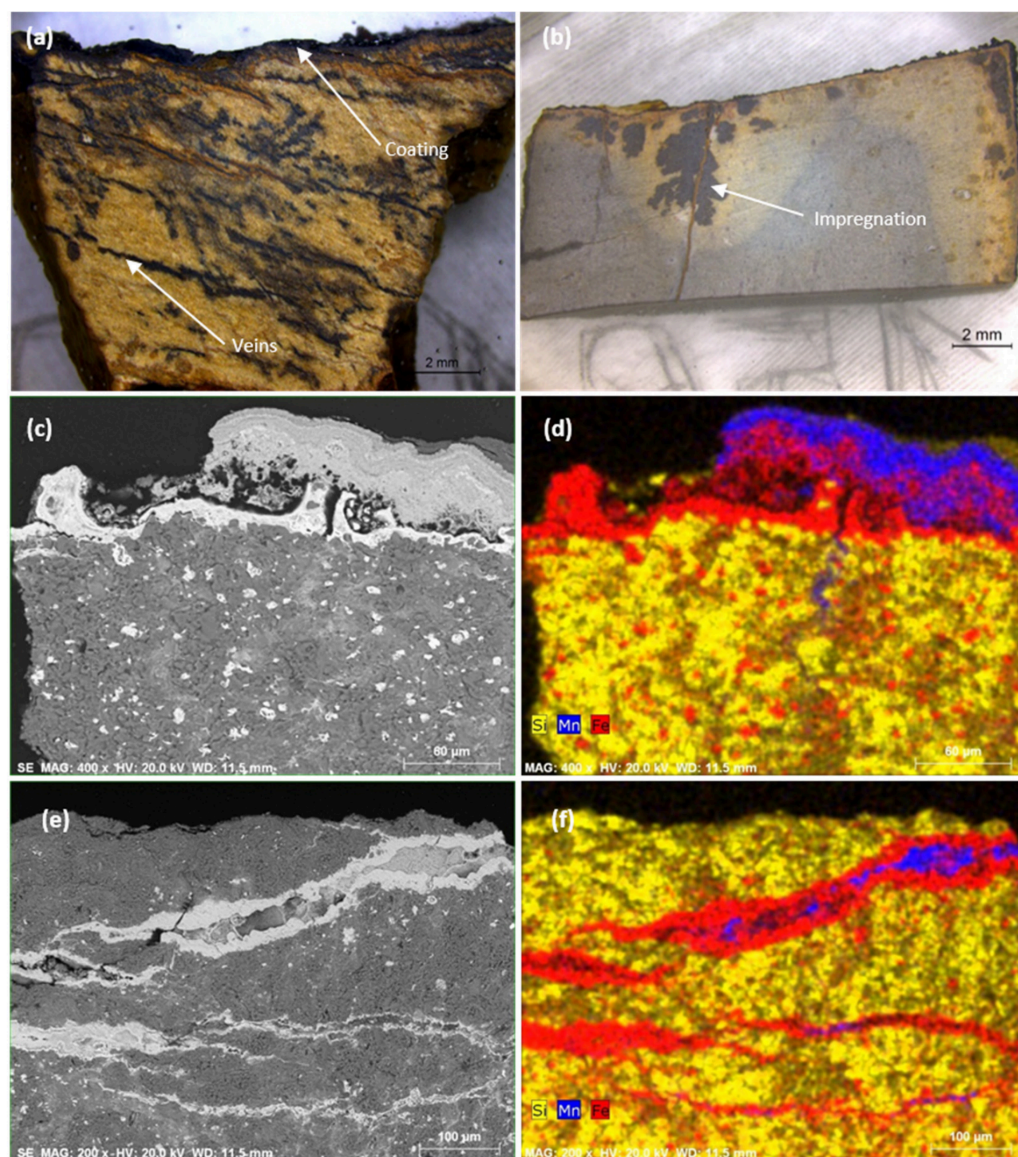


Figure 7. Images of some aspects of rock coating samples. (a) Rock sample with the representation of coating surface and associated veins; (b) impregnation area in the rock matrix of greywackes of Mértola Formation; (c,e) SEM-EDS and SEM-EDX (d,f) images of the coating surface. Chemical zonation is observed. Zones with high iron content (Fe) are deposited immediately above the rock matrix, and zones with high manganese content (Mn) are deposited closer to the surface of the sample; SEM-EDS (e) and SEM-EDX (f) images of veinlets with an iron and manganese filling.

5.2. Mineralogical Analysis

To obtain additional information about the mineralogy of iron–manganese-rich coatings, the X-ray diffraction (XRD) methodology was performed at the LNEG Alfragide laboratory. The 3 samples selected for mineralogical characterization—one sample from background zones (PT-10) and two samples from proximal zones (PT-4 and PT-14)—show a similar mineralogical assemblage (Table 2). The presence of quartz, albite and muscovite is typical of the coating rock matrix (Figure 6d) and is consistent with the mineralogical composition of the sedimentary rock types of the IPB geological formations (essentially black shales, siliceous shales and greywackes). However, it should be noted that minerals such as albite, quartz, and clinochlore are interpreted, at least in part, as microfragments derived from the surrounding host rock, mechanically incorporated into the Fe–Mn oxide matrix during coating formation, rather than representing *in situ* crystallization.

Despite the high Fe and Mn content in the coating samples (SEM-EDX analysis), the XRD analysis shows that the Fe/Mn compounds are mostly amorphous or, at least, poorly crystalline. The birnessite ($((\text{Na,Ca})_{0.5}(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O})$) is the manganese mineral common to all samples, which, together with ganophyllite ($((\text{K,Na,Ca})_2\text{Mn}_8(\text{Si,Al})_{12}(\text{O,OH})_{32} \cdot 8\text{H}_2\text{O})$), forms the predominant Mn mineralogical assemblage in the studied samples. The presence of Cu, Zn and Pb in the coating surface is associated with the mineralogical phases of birnessite and ganophyllite, since these metals are not found in the coatings of the background area rock samples. Several studies have shown that birnessite has a high adsorption capacity for these elements in aqueous and acidic solutions [86]. Sample PT-10 reveals some impregnation in the rock matrix (Figure 7b) characterized by the presence of goethite, which is the predominant iron mineral in the samples (Figure 8A).

5.3. Elemental Distribution and Chemical Composition

The chemical composition of the coatings was analyzed using SEM-EDX of the sample cross-sections. For a better interpretation of the results, the samples were grouped in three categories: a first group including the samples located over the Neves-Corvo ore bodies (Table 3), a second group, the samples located in the vicinity of the Neves-Corvo mineralization and a third group regarding the background area (Table 4). In each sample, several point analyses were performed using SEM-EDX.

The coating layer is generally composed of a large fraction of Mn and Fe, and no significant differences in these elements were observed between samples collected from proximal, near-deposit, and background areas. In the samples from the proximal sector, the Fe atomic percentages range between 1.52 and 56.37 and the Mn content between 0.62 and 67.72, whereas in the near-deposit and background sectors, Fe content ranges from 1.14 to 87.22 and Mn from 0.68 to 80.43. No correlation was observed between Fe and Mn concentrations in the samples, indicating that these elements exhibit distinct geochemical behaviors and likely precipitate in different mineralogical phases. This interpretation is partially supported by X-ray diffraction (XRD) results. Some analyses reveal local concentrations of Cu, Ba and Sn exceeding those of Fe and Mn, explained by the relative accumulation of these elements in Mn and Fe mineral phases; however, this topic will be discussed in greater detail later.

The coating geochemistry signature is intrinsically related to the geochemical signature of the rocks that are crossed by the fluids during the coating formation process, and the geological formations act as metal-bearing reservoirs that are leached during the fluid ascension process. In the study area, the main source of base metals (Cu, Pb, Zn and Sn) that we will find in the coating samples is related to the metal remobilizations during the leaching progression from the VMS deposits or, secondarily, from vein deposits associated with late-Variscan faults (e.g., Barrigão and Brancaneves old copper mine). There is also a contribution of metals contained in the geological formations or units (Phyllite–Quartzitic Group; Volcano–Sedimentary Complex and Mértola Formation). Samples on the vertical projection of the massive sulfide deposits, in this case the Graça, Neves, Corvo, Zambujal, Lombador, Semblana and Monte Branco ore bodies, show interesting concentrations of Cu, Zn, Ba, Sn, whereas samples from the background do not. The massive sulfides are predominantly composed of pyrite (FeS_2), which constitutes the main mineral phase. However, they also exhibit variable but significant relative enrichments in other sulfide minerals, namely chalcopyrite (CuFeS_2), sphalerite (ZnS), galena (PbS) and arsenopyrite (FeAsS), as well as subordinate amounts of cassiterite (SnO_2). The seven massive sulfide ore bodies are characterized by distinct tectonic settings and mineralogical assemblages. These

differences are critical and must be carefully considered when interpreting the analytical and geological results.

Table 3. SEM-EDS analyses of Fe-Mn coatings of proximal samples. The site analyses represent the spot analyses of each sample (e.g., 1a, 1f, ...). Values are reported as atomic percentages (%). The O, Na, Mg, Al, Si, K, Ti, F, Ca, P and Cl are not represented.

Sample	Site Analyses	Fe	Mn	Cu	Pb	Zn	Ba	Sn	As	Ni	Co	S
PT-1	1a	2.98	3.64	0.42	-	-	-	-	-	-	-	0.60
	1b	-	1.01	2.64	-	-	-	14.36	-	-	-	0.28
	1c	-	1.31	2.63	-	-	-	12.57	-	-	-	0.49
	1d	7.80	5.64	0.68	-	-	-	-	-	-	-	-
	1e	4.04	7.80	0.90	0.47	-	-	-	-	-	-	-
	1f	12.69	7.77	0.81	0.74	-	-	-	-	-	-	-
PT-2	2b	4.72	2.38	-	-	-	8.26	-	-	-	-	10.98
	2c	6.50	1.70	0.58	-	-	-	-	-	-	-	1.35
	2e	2.52	12.85	0.42	-	0.34	-	-	-	0.37	-	0.20
	2f	2.88	12.85	0.40	-	0.26	-	-	-	0.55	0.22	0.13
PT-3	3b	-	21.89	1.48	-	-	-	-	0.59	-	-	0.17
	3c	2.75	14.71	0.92	-	0.63	-	-	-	-	-	0.37
	3d	1.52	12.84	0.72	-	0.47	-	-	-	-	-	0.23
	4b	-	16.25	-	-	0.26	-	-	-	0.59	-	-
PT-4	4d	34.55	2.37	-	-	-	-	-	1.25	-	-	56.51
	4e	6.19	3.28	14.64	-	-	-	0.71	-	-	4.48	0.70
	4f	3.54	2.79	2.58	-	-	-	-	-	-	1.07	0.36
PT-5	5a	12.87	21.70	-	-	2.48	-	-	-	-	-	2.95
	5c	19.98	21.95	1.06	-	1.90	-	-	-	-	-	1.48
	5e	12.37	17.09	-	-	1.94	-	-	-	-	-	0.87
PT-11	11b	10.14	34.57	3.11	-	2.04	-	14.69	-	-	-	1.97
	11c	7.83	31.85	3.03	-	1.84	-	-	-	-	-	2.40
	11e	9.44	33.07	2.62	-	1.72	-	-	-	-	-	2.13
PT-12	12a	8.12	17.70	1.79	-	1.45	-	-	-	-	-	3.11
	12b	56.37	6.43	1.76	-	1.23	-	-	-	-	-	0.89
	12c	42.53	24.21	2.44	-	1.32	-	-	-	-	-	1.64
	12d	10.43	19.37	2.49	-	5.78	-	-	-	-	-	10.95
PT-13	13a	24.01	43.13	1.10	-	2.66	-	-	-	-	-	1.35
	13b	23.00	37.79	1.14	-	1.59	-	-	-	-	-	2.24
	13c	24.74	41.39	1.21	-	2.17	-	-	-	-	-	1.71
PT-14	14a	11.60	15.25	-	-	1.10	0.62	-	-	0.50	-	1.90
	14b	4.67	36.07	0.63	-	1.13	0.46	-	-	2.14	-	1.05
	14c	6.06	22.53	-	-	-	1.06	-	-	-	-	-
PT-20	20b	6.51	43.16	-	5.09	-	0.75	-	-	-	3.97	2.80
	20c	6.66	35.14	-	-	-	0.56	-	-	3.15	-	-
	20d	6.15	42.17	-	-	-	0.39	-	3.20	-	7.31	8.67
PT-21	21b	-	67.72	4.08	-	-	-	-	-	-	-	0.56
	21c	6.05	61.19	1.35	-	-	-	-	-	-	-	1.09
PT-22	22c	27.43	0.62	22.97	-	-	-	-	-	-	-	39.49

The tin (Sn) is found in three analyzed samples (PT-1, PT-4 and PT-11) (Table 3; Figure 9A) corresponding to coatings above the Neves and Graça orebodies. Unlike the other elements, tin is not found uniformly in the analyzed samples, indicating that its deposition is likely due to factors not yet understood or the tin sources are not uniformly

distributed throughout the massive sulfide deposits. The last hypothesis appears to be the most plausible, given the Neves-Corvo deposit tin zonation [14] and the sample's location in relation to the projection of the massive sulfide mineralization (see the localization in Figure 2B). Samples PT-1 and PT-4 (located above the Neves orebody) and sample PT-11 (located above the Corvo–Graça orebody) indicate Sn atomic proportions between 0.71% and 14.69% (Figure 9A; Table 3). This location is not a mere coincidence but is intrinsically related to the Neves-Corvo ore bodies, which are richer in tin and were exploited during the early stages of the mining (tin content of Corvo > Graça > Neves). Sample PT-11 is located near the tin corridor reported by several authors [1,14,87], indicating remobilization of the primary tin from the tin-rich massive sulfides of the Corvo, Graça and Neves ore bodies to the surface.

Table 4. SEM-EDS analyses of Fe-Mn coatings of near-deposit (6, 7 and 8) and background samples. The site analyses represent the spot analyses of each sample (e.g., 6a, 6b, ...). Values are reported as atomic percentages (%). The O, Na, Mg, Al, Si, K, Ti, F, Ca, P and Cl are not represented.

Sample	Site Analyses	Fe	Mn	Cu	Pb	Zn	Ba	Sn	As	Ni	Co	S
PT-6	6a	4.08	10.87	0.48	-	-	-	-	-	-	-	-
	6b	1.14	13.65	0.82	-	-	-	-	-	-	-	-
PT-7	7a	26.65	-	-	-	-	-	-	-	-	-	0.33
	7b	34.18	-	-	-	-	-	-	-	-	-	0.25
PT-8	8a	27.79	-	-	-	-	-	-	-	-	-	0.43
PT-9	9a	5.24	14.33	-	-	-	-	-	-	-	-	0.15
	9b	10.19	12.19	-	-	-	-	-	-	-	-	-
	9c	5.50	22.06	-	-	-	-	-	-	-	-	0.41
PT-10	10a	4.80	32.23	-	-	-	2.01	-	-	1.73	-	0.68
	10b	2.76	29.27	-	-	-	2.30	-	-	2.17	-	-
	10c	-	45.51	-	-	4.76	6.77	-	-	-	1.41	-
	10d	-	38.53	-	-	-	2.06	-	-	1.18	1.21	0.21
PT-23	23a	87.22	-	-	-	-	-	-	-	-	-	-
	23b	73.23	-	-	-	-	-	-	-	-	-	-
PT-24	24a	76.49	-	-	-	-	-	-	-	-	-	-
	24b	13.1	-	-	-	-	-	-	-	-	-	-
PT-25	25a	48.84	-	-	-	-	-	-	-	-	-	-
PT-15	15a	33.28	19.56	-	-	-	-	-	-	-	-	0.68
	15b	8.73	26.99	-	-	-	-	-	-	-	-	-
	15c	30.01	23.78	-	-	-	-	-	-	-	-	-
PT-17	17a	-	15.47	-	-	-	-	-	-	-	-	0.02
	17b	1.48	4.44	-	-	-	-	-	-	-	-	-
	17c	2.23	3.73	-	-	-	-	-	-	-	-	0.2
PT-18	18a	-	57.24	-	-	-	7.66	-	-	-	-	-
	18b	-	80.43	-	-	-	11.25	-	-	-	-	-
	18c	3	5.1	-	-	-	0.92	-	-	-	-	-
PT-19	19a	-	57.92	-	-	-	2.3	-	-	2.38	-	-
	19b	-	62.47	-	-	-	2.15	-	-	1.83	-	-
	19c	-	43.12	-	-	-	0.89	-	-	1.61	-	1.11
PT-16	16a	26.96	0.68	-	-	-	-	-	-	-	-	-
	16b	21.27	17.51	-	-	-	-	-	-	-	-	1.12

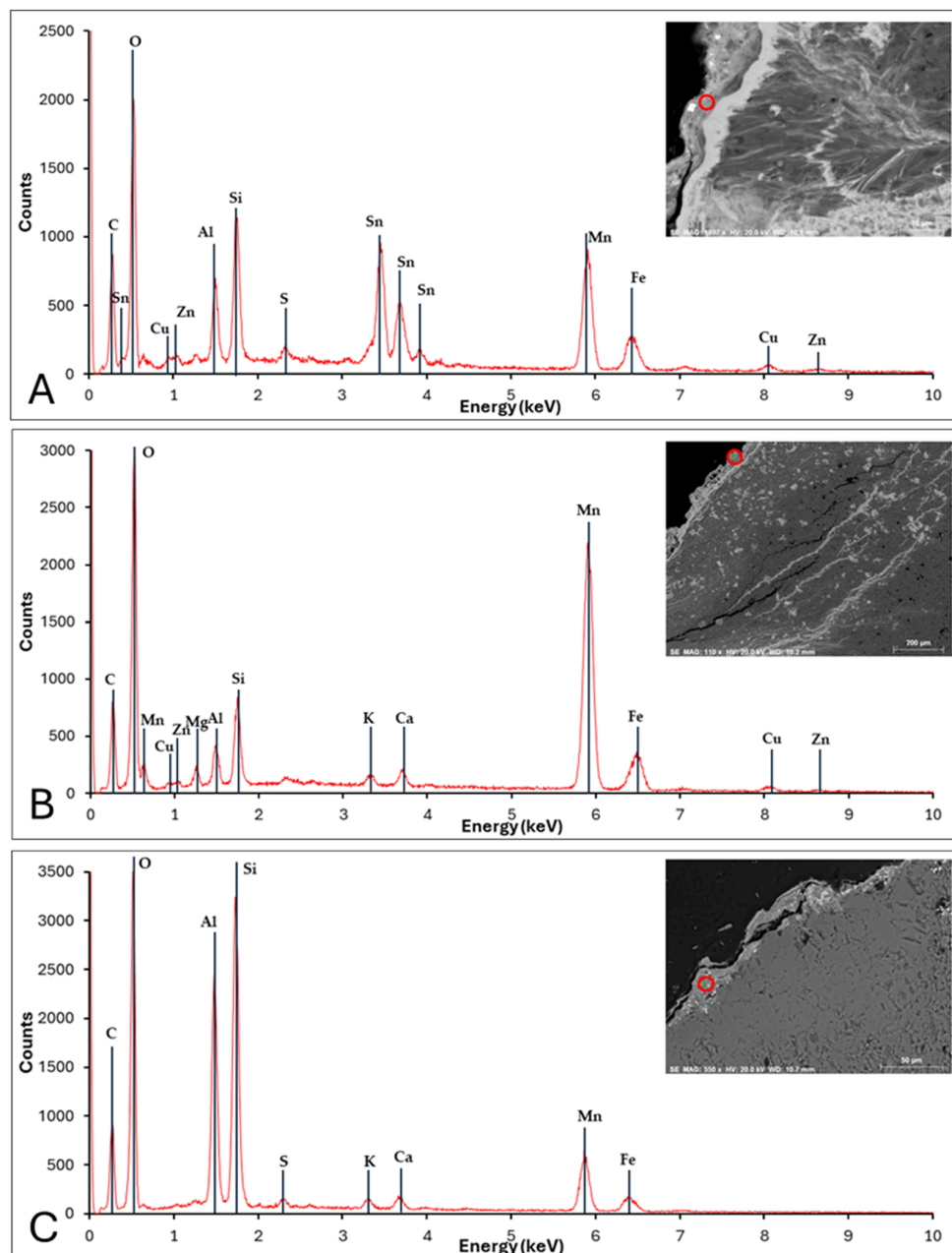


Figure 9. EDS spectra showing the chemical coating variations. The red circles show the area of analysis. Panel (A,B) shows the spectrum of sample PT-11 (proximal sector); panel (C) shows the spectrum of sample PT-9 (background sector). Abbreviations: C—carbon; O—oxygen; Al—aluminum; Si—silicon; K—potassium; Ca—calcium; Mg—magnesium; Sn—tin; Cu—copper; Zn—zinc; S—sulfur; Fe—iron; Mn—manganese.

Copper and zinc are found in all samples collected in proximal sectors, with atomic proportions between 0.40 and 22.97 for Cu and 0.26 and 5.78 for Zn. The lead is found in two samples (PT-1 above the Neves orebody and PT-20 near the N-S fault zone of the Lombador orebody). The mobility of the metals (Cu, Zn and Pb) is directly related to the pH of the meteoric fluids (in this case, they must necessarily be acidic), the presence of organic matter (for example, the black shales of the Neves, Graça and Grandaços Formations), mineralogical compositions and the redox conditions tending to show a greater mobility for Zn and less for Pb (Zn > Cu > Pb) [88]. The metal source is directly related to the massive sulfide mineralization (VMS deposit): Cu (chalcopyrite), Zn (sphalerite), and Pb (galena), which, like Sn, will be leached from primary mineralization during fluid ascent

processes. No relationship is found between the content of these metals in the coating samples and the Cu-Zn-Pb-rich zones of the massive sulfide ores, probably indicating a greater geochemical dispersion phenomenon from the primary source to the deposition spot. However, secondary metal sources (essentially copper and zinc) are one important hypothesis to be considered in the coating's genesis and are observed in one sample from the distal sector (sample PT-6) and one sample from the background sector (sample PT-10). Sample PT-6, located near the Monte dos Mestres–Algaré sector, shows a Cu content between 0.48% and 0.82%. This sample clearly indicates the Cu remobilization associated with the Neves-Corvo main thrust, which defines the hanging wall zone of the mineralization in the mine sector and extends towards the Monte dos Mestres–Algaré–Malhão do Touro sector (Figure 2). This structural alignment is characterized by a relatively strong Cu, Zn soil anomaly reported in the beginning of the geological exploration of the Neves-Corvo–Rosário sector [12,89]. Sample PT-10 is located in a background zone where no massive sulfide mineralization occurrences have been identified to the moment; however, this sample exhibits an unusually high Zn content (4.76%), which can be explained by the presence of Ba-Pb-(Zn) vein mineralization in the area (Horta do Surdo small old mine and mineral occurrence) (SIORMINP—LNEG database and [90]). This footprint is supported by the high barium content in the sample and is typical of these types of mineralization.

The barium (Ba) deposition in VMS deposits is associated with distal sectors and cold environments of the hydrothermal plume; however, the Ba genesis may be (1) syn-mineralization, precipitating as barite intercalated or disseminated in the massive sulfides, or (2) post-mineralization, essentially filling fractures or fault zones [91,92]. For the studied samples, the two barium sources are present. Sample PT-2, for example (located above the Neves orebody), indicates that the primary barium source is the massive sulfides (Ba-Pb veins are not known in this area); however, for the remaining samples (PT-14 and PT-20 near fault zones of the proximal sector and PT-10, PT-18 and PT-19 in background sectors), the barium sources are associated with fractures and/or fault zones with possible late-stage Ba infillings related to Pb and Zn enrichments.

The nickel (Ni) and cobalt (Co) appear to be related in the samples; however, the origin is not directly related to the massive sulfide deposits, and no significant differences between samples from proximal, distal and background sectors are observed. The atomic percentage ranges from 0.37 to 3.15% for Ni and 0.22% to 7.31% for Co (Tables 3 and 4). These two elements are typically found associated with mafic rocks (e.g., basalts and spilites) integrated in the IPB Volcano–Sedimentary Complex, with reported contents of 500 mg/kg of Ni and 150.9 mg/kg of Co [32], and some felsic volcanic rocks in the Neves-Corvo region are relatively enriched in Ni and Co, with contents of 131 mg/kg and 100.7 mg/kg, respectively. High Co contents have been reported in the mafic rocks of the Cercal region [32]. The goethite (FeO(OH)) shows a high Co and lower Ni adsorption capacity, whereas the manganese oxides (e.g., birnessite) could absorb Ni and Co into their structure (the two minerals are found in the coating samples) (Figure 8) [93,94].

Further, the chemical homogeneity degree of the coating layers is verified, and two samples are selected to perform three geochemistry profiles with SEM-EDX (PT-11 and PT-9) (Table 5). The SEM-EDS images and the chemical distribution by SEM-EDX show a great heterogeneity in the composition of the coating layer. Typically, the first layer is enriched in Fe (layer in contact between the coating and rock matrix), and the second layer (external layer) is enriched in Mn (Figure 10B); however, small internal variations are observed in all layers, probably related to different deposition phases and/or variations in deposition conditions (Figure 10D). The variations observed in the chemical compositions of the profiles clearly show this heterogeneity (Figure 11). The red and blue and the yellow bar indicate the contact between the coating and the rock matrix of samples PT-11 and PT-9,

respectively. In both samples, the contact between the coating and rock matrix is marked by a generalized Si increase caused by the presence of silicate minerals of the rock matrix and a decrease from the outer layer in Fe, Mn, Cu, Zn and S (Figure 11). The Si content is directly related to the rock nature (Si content quartzite > greywackes > shales), and the metallic elements are found essentially in the coating layer.

Table 5. SEM-EDS analyses of Fe-Mn coating samples. Profile analysis of samples PT-11 (profiles 1 and 2) and PT-9 (profile 3) (Figure 10). Values are reported as atomic percentages (%). O, Na, Ti, F, Ca, P and Cl are not represented. - not detected.

Sample	Site	Si	Al	Mg	Fe	Mn	Cu	Zn	Ni	S
PT-11	1	10.70	5.05	0.52	10.92	20.76	2.10	2.54	-	2.42
	2	5.28	3.53	1.20	4.41	39.45	2.62	1.31	-	1.37
	3	4.52	1.95	0.93	5.69	46.65	2.06	0.91	-	0.91
	4	4.83	2.72	1.26	6.48	39.75	1.83	1.19	-	0.50
	5	2.52	1.16	1.65	-	47.81	2.02	0.76	-	0.21
	6	2.28	0.99	2.07	-	45.06	1.82	-	-	-
	7	2.60	1.15	1.88	-	46.47	1.92	-	-	-
	8	3.50	1.16	1.68	8.59	40.63	2.03	-	-	-
	9	5.98	1.85	0.96	39.50	7.01	0.81	0.96	-	0.33
	10	11.37	2.86	0.88	37.34	2.19	-	-	-	-
	11	24.99	3.52	0.58	18.49	1.62	-	-	-	-
	12	26.50	4.61	0.63	15.91	1.50	-	-	-	-
	13	31.26	6.24	0.50	6.37	1.10	-	-	-	-
	14	11.37	5.06	0.36	8.60	17.87	3.75	-	-	2.38
	15	8.29	6.31	1.16	4.21	32.62	2.13	1.15	-	0.66
	16	7.12	5.43	1.37	3.86	28.77	1.85	1.19	-	0.56
	17	4.63	2.99	0.80	24.99	11.66	1.44	1.05	-	17.73
	18	15.67	3.91	0.87	3.50	23.72	2.28	1.19	-	1.26
	19	2.96	1.33	1.37	2.51	41.35	2.15	0.87	-	1.76
	20	2.16	1.05	1.83	2.35	42.30	2.16	0.85	-	0.88
	21	10.42	4.29	1.09	7.79	26.82	2.95	-	0.40	2.65
	22	2.46	1.31	1.97	-	44.05	1.70	0.70	-	0.27
	23	2.83	1.11	1.76	3.77	44.73	1.73	-	-	-
	24	4.90	1.52	0.86	10.56	45.82	1.97	-	-	-
	25	29.02	7.98	0.94	8.27	2.26	-	-	-	-
	26	33.97	4.95	0.37	6.15	1.45	-	-	-	-
PT-9	27	10.17	7.89	1.08	20.63	11.62	-	-	-	0.10
	28	13.69	8.35	0.70	33.40	2.54	-	-	-	-
	29	9.94	7.63	0.95	28.61	7.96	-	-	-	0.16
	30	11.27	8.48	0.93	31.94	1.72	-	-	-	0.10
	31	12.29	9.38	0.94	27.29	2.30	-	-	-	-
	32	12.72	9.30	0.90	21.30	8.17	-	-	-	-
	33	12.30	9.45	0.95	29.61	1.81	-	-	-	-
	34	12.62	9.71	1.03	26.76	1.88	-	-	-	-
	35	9.68	5.90	0.34	31.46	8.70	-	-	-	0.34
	36	19.07	13.52	1.86	13.62	1.45	-	-	-	0.78
	37	38.67	2.29	0.19	3.73	0.92	-	-	-	-
	38	24.28	16.85	1.20	5.21	1.19	-	-	-	0.16
	39	20.94	17.04	1.39	5.23	0.76	-	-	-	-

Sample PT-11 shows peaks of Fe and Mn enrichment and depletion (Figure 11), with a strong Fe enrichment in profile 2 between the contact coating rock matrix; however, in profile 1, this enrichment is observed inside the coating layer. This fact is justified by the relative abundance of Fe-rich mineralogical phases identified by XRD (goethite).

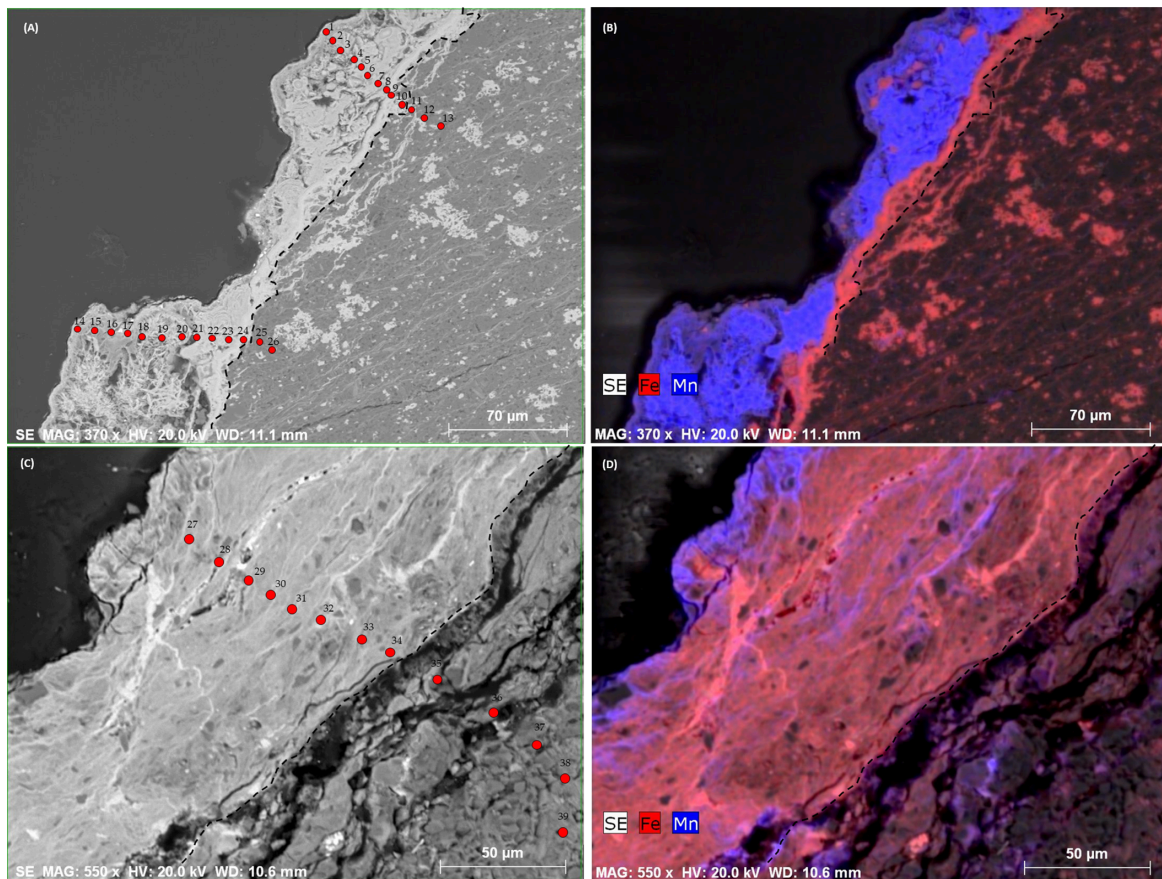


Figure 10. SEM-EDS and SEM-EDX images of the coating samples. Panel (A,B) shows the images of sample PT-11 with the location of the analytical points (profile 1 analysis 1 to 13 and profile 2 analysis 14 to 26). Panel (C,D) shows the images of sample PT-9 with the location of the analytical points (profile 3 analysis 27 to 39). In panel (B,D), it is possible to see the Fe and Mn zonation of the coating layer.

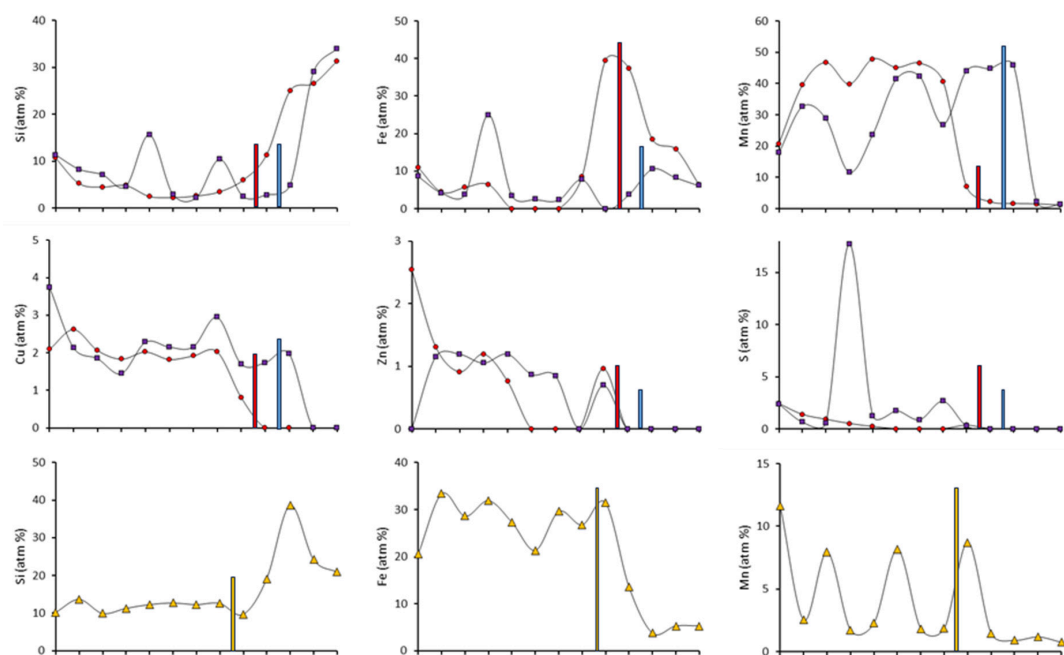


Figure 11. Chemical distribution along the analyzed profiles. The red, blue and yellow bars represent the contact between the coating and rock matrix in profiles 1, 2 and 3, respectively. Legend: red dots—distribution along profile 1 (sample PT-11); purple squares—distribution along profile 2 (sample PT-11); yellow triangles—distribution along profile 3 (sample PT-9).

5.4. Isotopic Compositions and Metal Source

Thirty-four spot coating samples were analyzed for their lead isotopic compositions (Table 6). The first observation when plotting the results on a $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram is that the overall isotopic compositions are heterogeneous, with $^{206}\text{Pb}/^{204}\text{Pb}$ from 18.0873 to 18.5015, $^{207}\text{Pb}/^{204}\text{Pb}$ from 15.0477 to 15.6504 and $^{208}\text{Pb}/^{204}\text{Pb}$ from 37.2677 to 38.9815, suggesting that the metal sources may have originated from multiple distinct sources. To better understand the potential metal sources involved in coating formation, the obtained data was compared with lead isotopic signatures from additional possible reservoirs. Clustering analysis was performed to define Cluster 1 (ore deposits cluster) using the Neves-Corvo massive sulfide data (polymetallic complex ore, massive pyrite ore and Cu-Sn-rich ores) [95] and the Rio Tinto massive pyrite data [82] compiled data. For the host rocks, Cluster 2 was defined with IPB felsic volcanic rocks [96], while Cluster 3 was defined according to the Mértola Formation (Flysch Group) [97]. The isotopic data of the Phyllite–Quartzite Group [97] is identical to Cluster 1; therefore, it was not defined (Figure 12).

Table 6. Pb isotope ratios of coating samples from coating samples PT-14 and PT-4.

Sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$
PT-4	18.2486	15.2348	38.0284	0.8349	2.0839
	18.2234	15.2152	38.1172	0.8349	2.0916
	18.2836	15.2439	38.3922	0.8338	2.0998
	18.1761	15.4053	38.0799	0.8476	2.0950
	18.2730	15.3895	38.4122	0.8422	2.1021
	18.2669	15.2948	38.4834	0.8373	2.1067
	18.2057	15.3031	38.1447	0.8406	2.0952
	18.3016	15.4180	38.3752	0.8424	2.0968
	18.2568	15.2182	38.2717	0.8336	2.0963
	18.2508	15.3378	38.3229	0.8404	2.0998
	18.3162	15.2931	38.3369	0.8350	2.0930
	18.2631	15.2620	38.0231	0.8357	2.0819
	18.2345	15.2204	37.7446	0.8347	2.0699
PT-14	18.3689	15.4030	38.4347	0.8385	2.0924
	18.3547	15.5744	38.5601	0.8485	2.1008
	18.4051	15.6504	38.9815	0.8503	2.1180
	18.1024	15.0963	37.8675	0.8339	2.0918
	18.2858	15.0477	37.2677	0.8229	2.0380
	18.2681	15.0531	37.4565	0.8240	2.0504
	18.1781	15.2033	37.6883	0.8364	2.0733
	18.4865	15.6058	38.3282	0.8442	2.0733
	18.3161	15.5805	38.6800	0.8507	2.1118
	18.3421	15.4614	38.4715	0.8429	2.0974
	18.3866	15.4377	38.2981	0.8396	2.0829
	18.1422	15.2477	37.4215	0.8405	2.0627
	18.1492	15.1282	37.9481	0.8336	2.0909
	18.4565	15.3942	38.5122	0.8341	2.0866
	18.0873	15.2512	37.6792	0.8432	2.0832
	18.3351	15.3326	38.3293	0.8363	2.0905
	18.5015	15.4890	38.1404	0.8372	2.0615
	18.3513	15.4907	38.6991	0.8441	2.1088
	18.4140	15.3661	38.4369	0.8345	2.0874
	18.3635	15.5434	38.3850	0.8464	2.0903
	18.4205	15.2359	37.9097	0.8271	2.0580

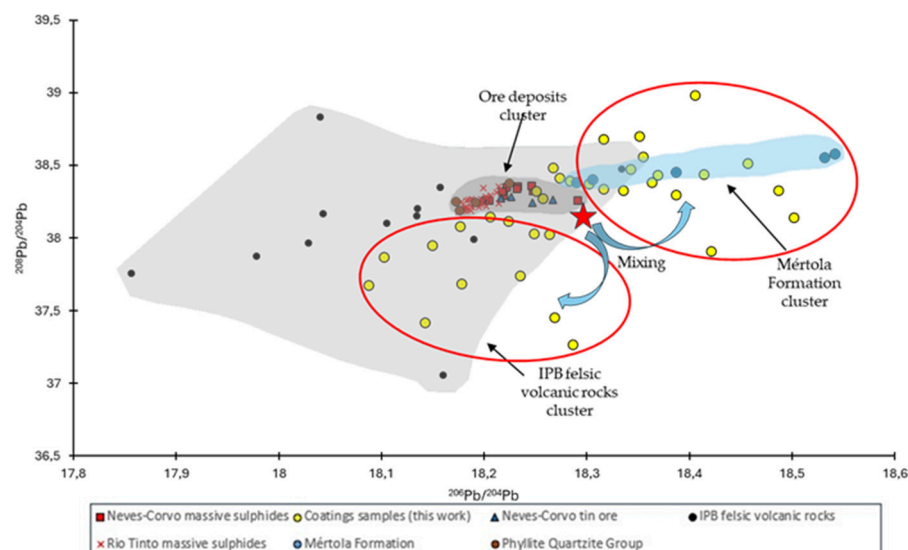


Figure 12. $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ diagram with the projection of the coating samples. The clusters are defined from previous data: IPB felsic volcanic rocks cluster (Cluster 2) [96]; ore deposits cluster (Cluster 1) [82,95]; Mértola Formation cluster (Cluster 3) [97]; Phyllite–Quartzite Group [97]. Samples showing mixed isotopic signatures are represented by red circles. The red star indicates the average value of all samples.

When considering the average $^{206}\text{Pb}/^{204}\text{Pb}$ versus $^{208}\text{Pb}/^{204}\text{Pb}$ values projection of the coating samples (Figure 12), it is observed that they plot very close to the field defined for the IPB ore deposits cluster (Cluster 1); however, the overall dispersion of the data supports the hypothesis of the involvement of multiple reservoirs as metal sources for the coatings, as previously proposed for the metal sources of the massive sulfide deposits [82,98,99]. The hypothesis of the unknown reservoir's contribution is further supported by the high $^{206}\text{Pb}/^{204}\text{Pb}$ (>22.391) and $^{208}\text{Pb}/^{204}\text{Pb}$ (>38.466) ratios found in cassiterites from Neves-Corvo [100] (data not projected in Figure 12); however, the absence of high isotopic ratios in the coating samples indicates that this reservoir (probably of magmatic origin for tin mineralization) cannot be considered the source of the metals in the coating.

The isotopic data corroborate the proposed model for the coating formation process, indicating the contribution of a primary metalliferous source, where the lead and other metals were mainly mobilized through the interaction of meteoric fluids that leached chemical elements present in the massive sulfides and their alteration zones (direct origin). These fluids were subject to several degrees of contamination or contribution from other reservoirs (volcanic rocks of the IPB and the shales and greywackes (flysch turbidites) of the Mértola Formation) during the ascent and interaction process (mixing process). The fact that the weighted average isotopic compositions of the coatings and the massive sulfides are very similar (18.29 and 18.23, respectively, for the $^{206}\text{Pb}/^{204}\text{Pb}$ ratio) tends to indicate that meteoric fluids played a fundamental role in the homogenization process of the different reservoir's contribution (geological sequences or units) during the fluid ascent processes. The deviation observed in some samples does not rule out the involvement of reservoirs with unknown isotopic ratios, as suggested for the genesis of massive cassiterite ores [98], or the lead loss during leaching and metal ascent processes.

6. Conclusions

Fe–Mn-rich rock coatings from the Neves-Corvo mining district contain a robust geochemical and isotopic record of subsurface fluid circulation linked to volcanic-sediment-hosted massive sulfide (VMS) mineralization. Integrated textural, mineralogical, geochemi-

cal and Pb-isotopic data demonstrate that surface rock coatings are not simple weathering products but represent low-temperature mineral precipitates formed from metalliferous meteoric fluids ascending through permeable fracture and fault networks. This model is compatible with syn-to-late-Variscan deformation (from semiductile to brittle stages) and basement uplift during the late Carboniferous, Mesozoic and Cenozoic ages. Fissural-type aquifers are a key reference promoting interaction between syn-to-late-tectonic fluids with massive sulfide and stockwork mineralization.

The coatings occur as thin ($<30\ \mu\text{m}$), discontinuous layers commonly associated with impregnation halos and secondary vein fillings. Internally, they show strong chemical and textural heterogeneity, typically expressed by basal Fe-rich zones in contact with the host rock and outer Mn-rich layers. This systematic in/out zonation indicates multi-stage precipitation controlled by evolving redox conditions and variable fluid chemistry during episodic fluid flow.

XRD analyses reveal that the coatings are dominated by poorly crystalline to amorphous phases, with goethite and birnessite as the main Fe- and Mn-bearing minerals, respectively. Minor Mn-silicates occur locally, while silicate phases derived from the host rocks reflect passive substrate inheritance. The predominance of poorly ordered Fe–Mn oxides is consistent with rapid precipitation from low-temperature fluids under near-surface conditions.

SEM-EDX data show that Fe and Mn contents are relatively uniform across proximal, near-deposit and background sectors, indicating that their accumulation is governed mainly by precipitation kinetics and redox gradients rather than by distance to the ore bodies. In contrast, trace metals (Cu, Zn, Pb, Sn and Ba) exhibit strong spatial variability. Copper, zinc and lead are systematically enriched in coatings developed above or near the Neves-Corvo massive sulfide ore bodies, reflecting acidic meteoric fluids leaching chalcopyrite, sphalerite and galena from massive sulfides and associated alteration zones. The observed mobility sequence ($\text{Zn} > \text{Cu} > \text{Pb}$) matches established geochemical behavior under oxidizing conditions.

Tin shows a restricted and heterogeneous distribution, limited to coatings spatially related to the Corvo, Graça and Neves Sn-rich ore bodies. This pattern directly links Sn in the coatings to remobilization from Sn-enriched massive sulfides and provides surface-scale evidence of metallogenic zoning at depth.

Barium records both primary and secondary sources, reflecting barite associated with VMS mineralization as well as late Ba–Pb–(Zn) mineralization along late Variscan fault zones. Nickel and cobalt display no systematic relationship with the ore bodies and are interpreted to derive mainly from mafic and felsic volcanic rocks of the IPB, with their distribution controlled by adsorption onto Fe–Mn oxyhydroxides.

$^{206}\text{Pb}/^{204}\text{Pb}$ isotopic compositions further constrain the metal sources. Although individual analyses show dispersion, the average Pb isotopic signature of the coatings closely overlaps that of IPB massive sulfide deposits, confirming a dominant VMS-derived contribution. Minor deviations indicate limited mixing with additional reservoirs, including IPB VSC volcanic rocks and turbidite sediments of the Mértola Formation. The absence of highly radiogenic Pb signatures excludes a significant contribution from deep magmatic Sn reservoirs.

Overall, Fe–Mn coatings in the Neves-Corvo district were formed by precipitation from ascending meteoric fluids that leached metals from massive sulfides, their alteration halos and surrounding lithologies. These coatings faithfully preserve the geochemical footprint of concealed mineralization and represent a powerful mineral exploration tool for vectoring towards buried VMS systems in the Iberian Pyrite Belt and comparable metallogenic provinces.

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