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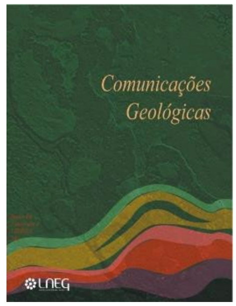
Mineral sustainability of the Portuguese sector of the Iberian Pyrite Belt



Sustentabilidade mineral no setor português da Faixa Piritosa Ibérica

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Abstract: The Iberian Pyrite Belt (IPB) is one of the most important volcanogenic massive sulphide districts in the world and has been mined during more than 5 000 years. Its early and rich mining history is known to have been very important in Tartessian and Roman times when working the oxidation and cementation zones of the deposits for gold, silver and copper preferentially took place in the outcropping deposits. Even after continuous metal extraction for more than 5000 years, the IPB retains exceptionally large metal reserves. The IPB remains a hub of continued research and exploration and as a consequence, sulphide reserves in the IPB are being continuously increased with new discoveries: Aguas Teñidas, Lagoa Salgada, Las Cruces, Migollas, Masa Valverde, Vallejin, Las Cruces, Semblana and Monte Branco, La Magdalena and Sesmarias. While today's mining activities are focused in massive and stockwork ores and confined to 7 Portuguese and Spanish districts: Aljustrel, Neves-Corvo, Sotiel-Migollas, Rio Tinto, Aznalcollar-Los Frailes, Tharsis and Las Cruces, the IPB retains a large potential for non-traditional (or accessory ores) products. In light of the critical raw materials and the concepts of the circular economy, the IPB has the potential to be an important source of accessory metals; sourced from both primary and secondary ores and mine waste, that fall both in the strategic and critical domains. Metals like indium, selenium, germanium, rhenium and the precious metals are targets to seek in future exploration scenarios within the IPB, particularly in the Portuguese sector and in key near mining areas.

Keywords: Iberian Pyrite Belt, mining, new discoveries, critical raw materials, strategic raw materials, circular economy.

Resumo: A Faixa Piritosa Ibérica (FPI) é uma das mais importantes províncias de sulfuretos maciços do mundo e tem sido explorada durante mais de 5 000 anos. A sua rica história de mineração é conhecida por ter sido muito importante nos tempos Tartessianos e Romanos, onde o trabalho ocorreu principalmente sobre os jazigos aflorantes, nomeadamente nas suas zonas de oxidação e cimentação dos depósitos de ouro, prata e cobre. Mesmo após a extração contínua de metais por mais de 5000 anos, a FPI mantém reservas de metal excecionalmente elevadas. A FPI contempla hoje todo o seu potencial favorável à prospeção mineral, observando-se uma intensa atividade extrativa e, consequentemente, um aumento das reservas, patente em novas descobertas como Águas Teñidas, Lagoa Salgada, Las Cruces, Migollas, Masa Valverde, Vallejin, Las Cruces, Semblana e Monte Branco, La Madalena, Sesmarias e Elvira. Embora a lavra ativa esteja atualmente limitada a 7 concelhos portugueses e espanhóis como Aljustrel, Neves-Corvo, Sotiel-Migollas, Rio Tinto, Aznalcollar-Los Frailes, Tharsis e Las Cruces, a FPI mantém um grande potencial para produtos minerais não tradicionais (ou acessórios). À luz das matérias-primas críticas e dos conceitos da economia circular, a FPI tem o potencial para ser uma importante fonte de metais acessórios, que se inserem nos domínios estratégicos e críticos, os quais são observados quer em minérios primários e secundários, quer em escombreiras mineiras. Metais como índio, selénio, germânio, rénio e elementos preciosos são alvos a serem procurados em cenários futuros de prospeção dentro da FPI, em particular no seu setor português e, sobretudo, em áreas de *near mining exploration*.

Palavras-chave: Faixa Piritosa Ibérica, mineração, novas descobertas, matérias-primas críticas, matérias-primas estratégicas, economia circular.

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1. Introduction

1.1. Mining overview

The Iberian Pyrite Belt (IPB) is in the SW portion of the Iberian Peninsula, comprising part of Portugal (Alentejo) and of the provinces of Huelva and Seville in Spain (Andalusia). It forms an arc about 240 km long and 35 km wide between Seville in Spain and the proximities of Alcácer do Sal in Portugal, near the Atlantic coast.

Geologically, it belongs to the South Portuguese Zone, the southernmost of the zones in which the Iberian Massif is divided (Lotze, 1945). The IPB is one of the most important volcanogenic massive sulphide districts in the world and has been mined for more than 5000 years. The province includes more than 90 Volcanogenic massive sulfide ore deposits (VHMS) deposits, some of them considered giants with >200 Mt (*e.g.* Neves-Corvo and Rio Tinto).

Its early and rich mining history is known to have been very important in Tartessian and Roman times (Pinedo Vara, 1963), where working the oxidation and cementation zones of the main outcropping deposits for gold, silver and copper preferentially took place. In the Portuguese IPB sector the Roman time mine wastes are present at Aljustrel (*Vipasca*), São Domingos, Caveira and Chança mines (Matos *et al.*, 2011). After centuries of almost complete inactivity, the mines were again worked during the XIX and XX centuries, focusing on the production of copper and sulphuric acid. From the end of the XX century and up to the present day, mining activity has intensively worked the base metals present in massive and stockwork ores and produced copper, zinc, zinc+lead and tin ore concentrates.

Even after almost continuous metal extraction for more than 5000 years, the IPB retains exceptionally large metal reserves. It has been continuously explored and studied and, as a consequence, sulphide reserves in the IPB are continuously being increased with new discoveries, such as Aguas Teñidas (NAVAN, 1996), Lagoa Salgada (Oliveira *et al.*, 1993, 1998; Matos *et al.*, 2000; de Oliveira *et al.*, 2011b), Migollas (Santos *et al.*, 1993), Masa Valverde (Ramirez *et al.*, 1988), Vallejin (Bonnemaison *et al.*, 1993) and Las Cruces (RTZ, 1996). Additionally, mines consisting of more than one mineral mass, such as Neves-Corvo, have announced further mineralized bodies, namely Semblana (Lundin Mining, 2010) and Monte Branco (Lundin Mining, 2012). Elsewhere, in other sectors of the IPB, the La Magdalena (Sáenz de Sicilia, 2013) and Sesmarias (Avrupa Mining, 2014), Lagoa Salgada Central (Redcorp, 2017) and Elvira (Matsa, 2018; Gisbert *et al*., 2019) discoveries have also been made known. Today's mining activities are confined to 7 districts: Aljustrel, Neves-Corvo, Sotiel-Migollas, Rio Tinto, Aznalcollar-Los Frailes, Tharsis and Las Cruces (Sáez *et al.*, 1999).

About 80 mines have operated during the last hundred years in the IPB, with a total production of about 300 million tons of polymetallic ores, although sulphur and copper have been the main elements processed in most cases (Strauss and Madel, 1974). The recovery of other elements (including Pb and Zn) is often hindered due to the abundance of fine-grained ores and intergrowths. Nevertheless, these elements are extracted in some localities, *e.g.* at Aznalcollar, Sotiel and Neves-Corvo. The latter mine was also a primary source for Sn.

Apart from the massive sulphide deposits, some hundreds of smaller manganese deposits have been mined throughout its history. These are related to chert and jasper horizons and occur at a stratigraphic position roughly like that of massive sulphide lenses (Sáez *et al.*, 1999) and Upper Volcano-Sedimentary Complex sequences (Matos *et al.*, 2008; Oliveira *et al.*, 2013). Size and metal content make them uneconomic nowadays, although they were important in the past (Pinedo Vara, 1963). In Portugal, the last manganese mine to be closed in 2001 was the Cercal mine, located in the IPB NW sector, where large late discordant dykes, rich in Fe-Mn oxides, baryte and quartz, were exploited both at surface and underground (Matos *et al.*, 2013. Along the IPB arc dozens of veins associated with fault breccias, were exploited in the XIX century for copper, lead, zinc, barium and antimony: 1- region of Odeleite-Alcoutim, located between the Neves-Corvo and the Guadiana river, 2- Barrigão, 3- Brancanes, 4- Porteirinhos, 5- Cova dos Mouros, 6- Alcaria Queimada, 7- Furnazinhas and, 8- Fortes (Matos *et al.*, 2003, 2008; Inverno *et al.*, 2015; Carvalho *et al.*, 2016).

In the Portuguese sector of the IPB there are two mines that are actively extracting ore: Aljustrel (copper and zinc producer) and Neves-Corvo (copper and zinc producer). The former exploits massive and stockwork ores, in the Feitais and Moinho ore lenses (Aljustrel mine, Almina Company) and the latter exploits the Neves, Corvo, Graça, Zambujal and Lombador orebodies (Neves-Corvo mine, Somincor/Lundin Mining Companies).

1.2. Mineral demand for critical elements in Europe

Europe is strongly dependent on mineral imports to satisfy its high demand for raw materials. This is partly due to the exploration and exploitation rules and to differences in environmental regulations between Europe and other producing regions. This situation led to the forming of the Raw Materials Initiative (EU, 2008). In addition, a working group was formed in which critical raw materials (CRM) were defined as scarce materials with high demand and low market supply to raise awareness to the problem of European demand versus producing countries. A map was produced with the critical raw materials reported by the Ad-Hoc Working Group created at European level (Fig. 1).

Critical raw materials include metallic minerals, industrial minerals, construction materials, wood and natural rubber with a global market. The focus of the present review study is the metallic minerals, namely aluminum, copper, lead, nickel, tin and zinc. Cobalt, gallium, indium and rare earths have much lower volumes than the base metals therefore their trade rules are mostly related with the demand of the new technologies and their increasing demand from developing countries. Consequently, their scarce supply sources reflect very much in their price. Furthermore, their sources lie mostly outside Europe. Therefore, there was a necessity to create this CRM list with a periodic review. The first list was implemented in 2010 and composed of 14 raw materials, revised to 20 in 2014 (SWD (2014) 171 final) and to 27 in 2017 (COM (2017) 490 final). The current 2017 list contains antimony, beryllium, borates, cobalt, coking coal, fluorspar, gallium, germanium, indium, magnesium, natural graphite, niobium, phosphate rock, silicon metal, tungsten, platinum group metals, light and heavy rare earths, baryte, bismuth, hafnium, helium, natural rubber, phosphorus, scandium, tantalum, and vanadium.

This initiative's next step was to go from european to national initiatives that in the portuguese policy resulted in the National Strategy for Geological Resources - Mineral Resource (Resolution of the Council of Ministers N.º 78/2012).

In addition, the European Commission is strongly pushing the concept of the "Circular Economy", an approach to environmental sustainability characterised by the creation of economic models where no negative environmental impact is generated.

2. Sustainability and accessibility of the commodities in the Portuguese Iberian Pyrite Belt

The Brundtland Commission report (1987) states that "sustainability is a development that meets the needs of the present without compromising the ability of future generations to meet their own needs". With this in mind, mineral provinces need to develop tools to use the exploited mineral resources until most of the useful commodities are extracted and the environmental footprint is reduced to a minimum.

The concept of sustainability includes three dimensions: Economic, Environmental and Social. Considering the geoscientific approach, those dimensions are observed in figure 2.

Mine life cycles depend of the following parameters: exploration, exploitation, closure and remediation. Exploration is undertaken to increase the mine life with the increase in the ore deposit knowledge or with the possible discovery of new ore deposits.

Exploitation cut-off (grades) must be sustainable to deliver profit but balance against the maximum extension of possible the mine life.

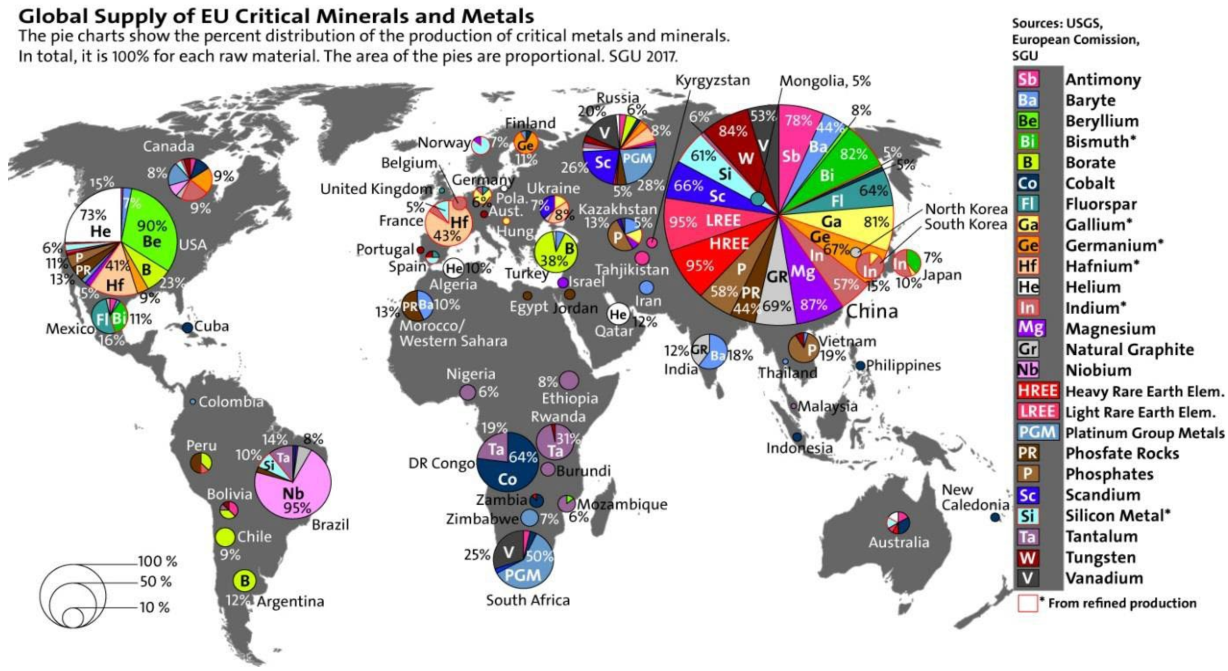

Figure 1. Production of the critical raw materials by source country (MEMO/10/263).

Figura 1. Produção de matérias-primas críticas por país de origem (MEMO/10/263).

The current low cut off values (≤ 1.5% Cu) permit the exploitation of new reserves of massive and stockwork ores, the latest characterized by a simpler mineralisation and, in consequence, a more economic processing treatment in the mine plants. The exploitation potential of stockwork ores promoted new exploration campaigns that allowed the discovery of new reserves in mine areas like Aljustrel and Neves-Corvo. In these near mining scenarios, the study of stockwork zones and related hydrothermal systems and improvement of the knowledge of the local stratigraphy become new exploration models (*e.g.* LNEG-Évora University EXPLORA Neves-Corvo mine research project, Matos *et al.*, 2017). Mine closure must be planned to minimize the social and economic impacts in the local communities by increasing education of the mining workers to create new qualifications (Meixedo *et al.*, 2008). Remediation should prioritize preservation of the remaining ore body, if it is still present, and the safety of the mine works for future operations, in addition to the normal environmental and landscape improvement concerns. Apart from that, waste potential should be addressed.

Research was undertaken in the mines of São Domingos (abandoned), Aljustrel (presently working but with historic periods of care and maintenance, *e.g.* at Algares and São João mine sectors) and Neves-Corvo (working uninterruptedly) to meet the primary objectives of the sustainability of mining industry such as 1) saving primary resources, 2) decreasing the waste volume of mining and 3) reducing the energy consumption.

2.1. Economic dimension – Profit from waste materials

Metals such as selenium, tantalum, tin and rhenium are considered important worldwide and an added value in the IPB. In many cases, these are available as secondary resources in mining waste piles scattered throughout Europe as a result of lengthy mining histories.

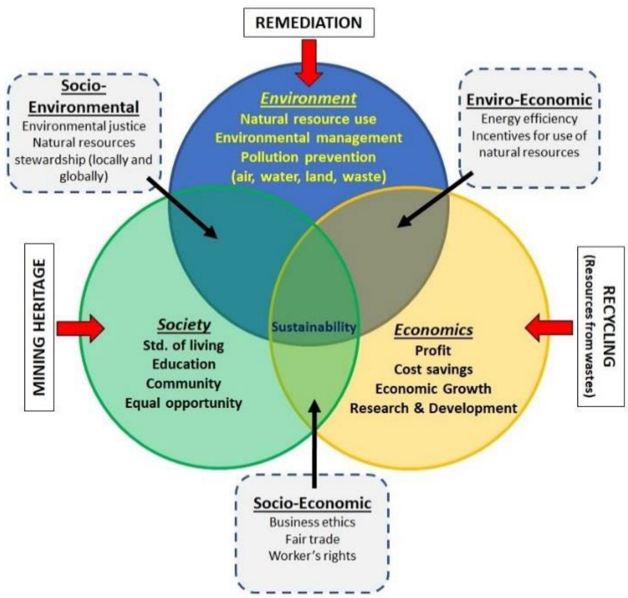

Figure 2. Illustration of the concept of sustainable development adapted to the mineral industry (adapted after Rodriguez *et al.*, 2002).

Figura 2. Ilustração do conceito de desenvolvimento sustentável, adaptado à indústria mineral (adaptado de Rodriguez *et al.*, 2002).

In the Portuguese sector of the IPB, three case studies are considered – the São Domingos mine, located near Mértola and close to the Portuguese/Spanish border, the Aljustrel mine, located SW of Beja and the Neves-Corvo mine, located near Almodôvar. The São Domingos VHMS deposit was exploited from Roman times until it ceased operating in 1966. It is the most studied and relevant case study related with the large volume (14 Mt) of diverse mining wastes, produced between 1857 and 1966 and distributed along the São Domingos stream valley (Matos *et al.*, 2008; Álvarez-Valero *et al.*, 2008; Batista *et al.*, 2011). This old and abandoned mine shows a long history of open pit and underground mining and development in mining strategies considering changing commodity requirements according to the price of metals and demand from external markets and afterward from the internal market. The Aljustrel mine was exploited during Roman times with the name of *Vipasca* (Erdkamp *et al.,* 2015). The modern exploitation period started in the 1850's and was developed up to the 1980´s, mainly for pyrite. Between 1990-1993 and 2004-2008 copper and zinc mine projects were developed at Aljustrel. Presently the mine is being exploited by the Almina Company that produces >1.8 Mt of copper concentrates from the underground works of the Feitais and Moinho ore lenses. From the 1980s, large areas of mining waste are present in the Algares and São João mine sectors, currently rehabilitated by the EDM Public mine company. The IPB Neves-Corvo mine, discovered in 1977 and exploited since 1987, is considered as a European example of modern green mining, exploited presently by the Somincor/Lundin mining company. Consisting of 7 ore lenses/bodies (5 in current production) Neves-Corvo is classified as an IPB giant massive sulphide deposit (>200 Mt) with annual production of >2 Mt of Cu and >0.5 Mt Zn concentrates. The mine is known as an important supplier of indium as by product of the concentrates (pers. com. A. Franco, 2017). In the Neves-Corvo case, the mine wastes are concentrated in the modern Cerro do Lobo dam, where a current dry waste landfill disposal project is being developed by Somincor.

Research carried out in the ores of these two contrasting mine scenarios shows the potential for extraction of critical and/or strategic/valuable metals from mining wastes. These case studies can also be correlated with other areas located in Portugal and Spain.

2.1.1. São Domingos and Aljustrel mining areas

The São Domingos mining area is formed from north to south by the mine open pit, located near the village, by the Moitinha ore mills and by the Achada do Gamo sulphur factories, located in the downstream sector of the São Domingos stream. Different waste materials are located along this valley (>14 Mt) and intense acid mine drainage is observed. The exact volume of the waste located near the sulphur plants in Achada do Gamo is unknown because dissolution inside the pile generated holes that make the access difficult. Vertical variation in colours, observed in marginal profiles, occur due to chemical alterations during the storage period. The chemical characterization of a profile shows high concentrations of Au, Pb, Sn, Sb, Bi and Re in different layers. Out of these metals, Sb is a critical element (COM (2017) 490 final) whereas some of the others are high-value materials used in development of high-tech uses as is the case of Re. The mineralogical constitution of the profile shows that lead sulphate, anglesite ($PbSO_4$), is a dominant mineral phase in these materials, accompanied by jarosite [$(K,Pb)Fe_3(OH)_6[(S,As)O_4]_2$], hematite ($Fe_2O_3$), quartz ($SiO_2$), anhydrite ($CaSO_4$); and gypsum ($CaSO_4.2H_2O$). An XRF qualitative assay was conducted to complement the chemical characterisation of some elements exceeding the upper detection limit of the laboratory ICP-MS method. The observed decrease of Sb and concomitant increase of Sn with depth is an evidence for the need of properly homogenizing the samples in case of a rigorous reserve calculation.

A gossanous dump located near the open pit in the southern São Domingos area and another dump of the same type of material located near the facilities of the former mine operations show very interesting results for Au and Sb. In addition, very high Pb concentrations were found.

The São Domingos mine waste CONASA evaluation program performed in 1990-1991 by representative sampling obtained by drilling and homogenizing by splitting large scale samples accounting for different grain sizes and evaluated the same wastes with high Au content (Vieira *et al*., 2020).

Roman slags with high concentrations of Cu and some Au and Ag, show the low recovery of the ores in ancient times. The modern slags were the result of ore processing, in order to recover the sulphur for the production of sulphuric acid to be used in chemical industry and for producing fertilisers. This process resulted in a metal-rich waste (Fe 36%, Zn 1%, Cu 0.3%) with a residual sulphur concentration of 2.2% in an interesting volume near the open pit.

The Aljustrel mine was sampled in materials that were already confined in an existing environmental project. The analysed dark red colour materials located in Pedras Brancas are linked to the XIX century pyrite ore roasting process, performed at open air, in *Teleiras* structures (a metric dimension cone shape structure, where the pyrite ore was burnt using coal and/or wood). This hematite rich mine wastes have high concentrations of Au (930 and 822 ppb) and Ag (14.3 and 13.2 ppm). Lower concentrations were obtained in milled pyrite located in the Algares tailings compared to the similar milled pyrite ore waste located in the São Domingos mine. These discrepancies are attributed to the different ore treatment and different mined ores (Batista *et al.*, 2011; Batista *et al.*, 2016).

2.1.2. Neves-Corvo

Monthly composite samples of the ore that enter in the Neves-Corvo ore plant, the concentrate that leaves the plant and the reject that goes to the tailings pond show interesting concentrations of critical elements. Cobalt, In, Mg and Sb whereas, Co and Sb are not concentrated with the Cu ore concentrate and Mg is not retained in the concentrate but goes to the tailings pond. Indium is concentrated along with the Cu concentrate. However, 39% of the in present in the ore that enters the plant still goes to the tailings. Other interesting elements of high economic importance although low supply risk are Fe, Zn and Al. Out of these, Fe and Al are going to the tailings pond while the about 0.8% Zn, out of which 33% is in the Cu concentrate, goes to the tailings. Other interesting elements that predominantly go to the tailings are Se and Sn (Batista *et al.*, 2011; Batista *et al.*, 2016).

2.2. Possible change in the footprint of the waste materials

After consulting the Best Available Techniques Reference (BREF) documents published by the EU (2004) it was realised that those measures although very important only mention the environmental aspect of the footprint by advising the mining companies to backfill the waste material. In the context of the IPB, it was decided to focus attention to draft documents being produced by the European Economic and Social Committee CCI/087 – R/CESE 412/2011 "The processing and exploitation, for economic and environmental purposes, of industrial and mining waste deposits in the European Union" where the exploitation of the wastes as secondary materials is addressed. With this argument, backfilling potentially valuable materials or tailings storage, will be discussed in the light of the findings of the former mine wastes of Aljustrel, in São Domingos mine and in Neves Corvo where characterisation of specific materials was done in the context of the ProMine project (Deliverable 5.2 report, 2011).

Market conditions dictate whether both ore and waste can be profitable. Therefore, an attempt was made, based on subjective arguments, to choose a change to economic profit whereas others increased the importance of environmental aspects, especially when intense acid mine drainage is observed related with dispersion of mining wastes.

In order to evaluate the potential footprint changes from these secondary resources, rigorous volumes need to be determined not only based in estimated depth but also sampling needs to be representative, *e.g.* high resolution digital terrain models, complemented by a narrow grid of mine waste drills and detail control of waste vertical thickness and variation. These evaluation programs must be supported by detail geological and mining mapping, like the LNEG surveys performed at 1:2 500 scale at São Domingos (Matos, 2004), Aljustrel (Matos, 2005a), Lousal (Matos, 2005b) and Caveira (Matos, 2006). Tables 1, 2 and 3 indicate the potential change in footprint at the studied São Domingos waste materials, Aljustrel in the abandoned mine wastes and in Neves-Corvo.

Table 1. Potential change in footprint from different waste materials in São Domingos mine.
Tabela 1. Potencial alteração de uso para os diversos tipos de resíduos mineiros da área mineira de São Domingos.

Mining waste	Area (m^2)	Volume (m^3)	Potential change in footprint	General evaluation
Modern slag	109,138	802,212	Zn and Fe	Economic potential
Roman slag	28,179	91,000	Cu potential resource. Protected for industrial tourism	Cultural interest. Identified below modern tailings and also economical interest
Ore processing ash	27,968	90,793	Environmental confinement	Sparse location. Strong erosion in the main stream, environmental penalty
Pyrite ore + milled ore	10,345	50,088	Sb, Sn, Au, Bi, Pb, Re in Achada similar material	Milled ore located at the open pit, similar is deposited in Achada do Gamo with economical potential
Gossan ore + volcanics	104,913	700,366	Au	Gossan material bellow landfills not considered

Table 2. Potential change in footprint from different waste materials from the Aljustrel mining area.
Tabela 2. Potencial alteração de uso para os diversos tipos de resíduos mineiros da área mineira de Aljustrel.

Mining waste	Area (m^2)	Volume (m^3)	Potential change in footprint	General evaluation
Roman slag	79,809	239,427	Heritage	Cultural interest. Used in dam construction
Roasting products	414	414	Au (accessibility is restricted)	Sparse location with economical interest. Probable mine product. Main material in remediated area
Pyrite ore + milled ore	231,096	3,466,440	Environmental interest	In rehabilitation process

2.3. Accessibility of the areas

Primary resources could be safe guarded by utilizing the waste from the extraction of the ore body. In the case of Neves-Corvo, there is potential for extraction of CRM (primarily Mg, In, Sb) in addition to the elements such as Se, Sn, Zn, Cu, Pb that are sent to the tailings pond. However, extraction of metals from the secondary materials requires the development of extraction technologies. It is not possible today to evaluate if such methods will be economically viable.

Table 3. Potential change in footprint from different waste materials in Neves Corvo mine.
Tabela 3. Potencial alteração de uso para os diversos tipos de resíduos mineiros da área mineira de Neves Corvo.

Mining waste	Area (m^2)	Volume (m^3) (dumps in tonnes)	Potential change in footprint	General evaluation
Tailings	1.8 km^2	20.4x10^6 m^3 (22 Mtonnes)	Cu, Pb, Zn, Sn, Se, In, Ag	Exploitation potential in the future
Pyrite rich dump (Escombreira 1)		2,713,030 tonnes	Py	Currently used for backfill to avoid AMD
Waste-rock dump (Escombreira 2)		5,536,000 tonnes	Aggregates	To use in backfill

It should also be noted that most of the potential of the mine in the operating company perspective is still (the rich) primary resources. Therefore, accessibility is very much incentivised on market prices, especially during primary ore extraction. Investments need to be made with this objective in the closure periodic revision, which depends also on the company policy to increase the mine life.

The potential of São Domingos lies all in the waste as the mine is no longer in operation. Because mining in the past was performed with higher cut-offs, and methods with less efficiency in metal recovery, some of the waste material is comparatively rich in valuable metals. The accessibility is very good. Other metal resource of the São Domingos mine is the acid mine water, with high metal content, which is present in the flooded open pit and underground mine galleries. As performed between 1966 and 1972, where native copper was obtained by cementation process, new water treatment process can be studied and planned, considering the leaching process of the underground non-mined sulphide ore and consequent metal enrichment. The use of this methodology is however limited, related with the complexity of the engineering and necessity of respect of the environmental legislation.

In the Aljustrel mine the waste materials in abandoned state have less potential due to the different methods of ore treatment, therefore, although the access is good the potential is lower. The Algares mine sector presents the highest value compared with the São João sector, showing brittle pyrite ore wastes and roasted pyrite ore wastes, the latter transported from Pedras Brancas to Algares, by the EDM Public company. The wastes already in confinement have difficult access due to the cost of the environmental remediation already spent (>13 M€ spent in the Algares sector rehabilitation). In this sense, the balance between high grades and the access is site dependent.

3. Future scenarios

At the onset of the XXI century the IPB has lots still to offer even in the light of ever-changing technologies and metal recuperation by recycling and even substitution. Boosting electricity consumption, increasing costs of fossil fuel use and the need to reduce CO_2 emissions (UNFCCC, 2008), will inevitably lead to a radical transformation of the energy system in the current century and will require a large-scale diffusion of a range of renewable energy technologies, which will necessarily include photovoltaic technologies. Thin-film solar photovoltaics (PV) have been suggested as possible major components of a more sustainable energy system. However, as with other renewable energy technologies, the energy source may indeed be renewable but the equipment to collect it is not. Therefore, considering eventual massive diffusion of renewable energy technologies occurring as a response to increasing fossil fuel prices and/or environmental restrictions on their use makes Europe hungry for specific and rare high-tech metals. Other industrial sector in change is the automotive industry with the increase of use of more technology (*e.g.* led panels and driving support sensors and cameras) and electrical motors.

3.1. Indium

Discovered quite accidentally in 1863 and isolated four years later as a metallic element, indium has been widely used since the middle of the past century in various technological fields, namely, in low melting-temperature alloys, solders and electronics. In the last decades, it became one of the most relevant scarce metals used in the production of new high-tech devices based on innovative nanotechnologies. Suggestive examples of indium incorporation – along with other rare metals like gallium and tin – are nowadays used in liquid crystal displays (LCDs), and organic light emitting diodes (OLEDs), as well as transparent flexible thin-films (Figueiredo *et al.*, 2007) and the manufacture of supermagnets. The recovery of the metal stands mostly on the zinc extraction from sphalerite, present in the IPB massive and stockwork ores.

Also, a global shift in power generation from fossil fuels and nuclear fission to various forms of renewable energy will be accompanied by a strong demand for non-fuel raw materials required for the generation, storage, transmission and utilisation of these energy forms. The importance of alternative energy sources and the proposed objectives of the EU's Green Deal outlined as a key strategic point by the EU Commission (COM, 2019) has led experts to predict that the consumption of raw materials needed to manufacture wind turbines and PV panels is expected to increase drastically in the coming decades (Carrara *et al*., 2020). Some of the raw materials are potentially exhaustible and some are already regarded, rightly or wrongly, as geochemically "scarce" and many have been characterised, generally, by price hikes in recent years. Examples are neodymium, praseodymium and dysprosium for rare earth-based permanent magnets in wind turbines; indium, gallium, selenium and tellurium for thin film solar cells (Bradshaw *et al.,* 2013). Therefore, serious supply problems for at least some of the considered elements will arise. This is especially the case for indium, with a current static depletion time of 22 years (Reiser *et al.*, 2009) that is well documented at the Neves-Corvo IPB deposit (Benzaazoua *et al.*, 2003).

The Lagoa Salgada deposit, discovered in 1992 after detection of a Bouguer and a magnetic anomaly (Oliveira *et al.*, 1998), located 80 km northwest of Neves Corvo is another IPB orebody that contains anomalous concentrations of In (de Oliveira *et al.*, 2011b). The Lagoa Salgada orebody, the most northerly of the Iberian Pyrite Belt known so far, occurs underneath approximately 130 m of sediments of the Sado-Alvalade Cenozoic basin and comprises two geographically distinct zones: a central stockwork and a massive sulphide lens in the northwest, which together have an inferred mineral resource of 12.8 Mt (Murahwi and Gowans, 2019). Analytical results for Lagoa Salgada samples show maximum concentrations of 3.74, 20.70, and 7.23 percent for Cu, Pb, and Zn, respectively. Also, significant amounts of In were identified in a few samples with a maximum value of 93.4 ppm. Indium metal is extremely rare (the average In-content of the Earth's crust is estimated at 0.1 ppm, similar to silver) and is mainly found as a trace element in a few sulphide minerals, particularly in sphalerite (de Oliveira *et al.*, 2011b). This cubic mineral is the prototype of "tetrahedral sulphides" where cations fill half of the available tetrahedral sites in the cubic closest packing (*ccp*) of sulphur anions, leaving interstices still accessible for further in-filling. The crystal-chemical formula of sphalerite can then be written Zn^t $[S^t]^c$, where t stands for tetrahedral coordination of metal cations and c quotes the *ccp* of anions (Figueiredo *et al.*, 2007). Such packing array is particularly suitable for accommodating polymetallic cations by filling closely located interstitial sites as happens in excess-metal tetrahedral sulphides – *e.g.* bornite, ideally Cu_5FeS_4, recognized as an In-carrying mineral (Figueiredo *et al.*, 2010). Aiming at a sustainable recovery of indium, an X-ray absorption near-edge spectroscopy (XANES) study at In L_3-edge was undertaken at the ESRF (European Synchrotron Radiation Facility, in Grenoble/France) and the results suggested the possible occurrence of In-In bonding in polymetallic sulphides (Figueiredo *et al.*, 2012).

3.2. Germanium

Germanium is also an element increasingly used for a range of high-tech applications, *e.g.* as a polymerization catalyst, for infrared optics, fiber-optic systems, thin-film applications and electronic SiGe devices (USGS, 2008). There is a strong growth potential for Ge uses, and current global reserves are limited to 10000 metric tons (Feltrin and Freundlich, 2008). Germanium does not form specific ore deposits but occurs in minor and trace amounts in a variety of ore types; the crustal average is estimated to be of about 1.4 ppm. Grades of a few tens to several hundred ppm of Ge are known from sulphide ore deposits (Höll *et al.*, 2007), including volcanic-hosted massive sulphides, porphyry and vein-stockwork deposits, sediment-hosted massive sulphides, carbonate hosted Zn-Pb and polymetallic Kipushi-type deposits.

Germanium is mainly recovered as a by-product of zinc production from sphalerite-rich ores. The estimated annual refinery amount of 100 metric tons in 2007 (USGS, 2008) is about to increase because of growing Ge demand (International Mining, 2008) and it has been reported that in recent years consumption exceeded primary production (USGS, 2013).

The Barrigão copper vein deposit, located SE of the Neves-Corvo mine, consists of two converging meter-thick vein structures, extending approximately 1 800 m along strike (Matos *et al.*, 2003) with several small secondary vein structures branching off the main structures. Copper ore extraction was carried out in the second half of the nineteenth century. From 1965 to 1973, the state-owned *Serviço de Fomento Mineiro* (SFM) executed extensive pilot exploitation for copper reserves in the pre-existing mine galleries (Ferreira *et al.* 1995), which resulted in several dumps from which sulphide±sulphossalts±quartz±carbonates samples have been collected (Reiser *et al.*, 2011).

Anomalous trace element contents of Ge (up to 280 ppm) and Sn in chalcopyrite of the copper ore in Barrigão are most likely the result of a late re-mobilization process which locally affected chalcopyrite and tennantite-tetrahedrite along ‘vein-like’ zones of different sizes (micron to millimetre width) (Reiser *et al.*, 2011).

3.3. Selenium

The Lousal mine located in the village of Lousal near Grândola labored between 1900 and 1988. The ore horizons are generally lenticular in shape and the massive sulphide deposits are aligned along the fold axes, dipping approximately 80° to the SW (Strauss, 1970). Considering a folded massive sulphide horizon in the sub-vertical Lousal antiform structure, two groups of massive sulphide lenses are considered the “western limb group” formed by the Extreme South, South and West lenses and the “eastern limb group” formed by the Central, Miguel, José, Fernando, North, Northeast and António lenses, (Matos and Oliveira, 2003). The western group is suboutcropping and represented by narrow gossans in the open pit. The eastern group is less eroded and shows a large extension both in depth and northwards (Matos and Relvas, 2006). The massive and semi-massive pyrite ores of the Lousal mine were processed since the 1950s in the chemical factory of Companhia União Fabril (CUF), located at Barreiro, near the Tagus river, south of Lisbon (Silva, 1996; Leal da Silva Pers. Com.). Ore from other IPB mines were also processed at CUF (*e.g.* Aljustel and São Domingos). In 1956, a small selenium extraction pilot plant was built at CUF (operated between 1963 and 1969), to permit chemical extraction from massive and semi-massive IPB ores. This plant recovered Se with concentrates averaging 95.5% Se. Se contents of 30 to 100 ppm are reported by Pinedo Vara (1963) in the Spanish IPB ores produced in the 1960s in the mines of Rio Tinto, San Telmo and Torerera. Recent preliminary, unpublished, in-house studies carried out in the Lousal ores indicate the presence of slightly anomalous concentrations of Se (Tab. 4). The Neves-Corvo orebodies also contain Se in much higher concentrations (Pinto *et al.*, 2013) than the other IPB deposits.

The Lousal mine has also recently been the target of gold studies as there are appreciable localized concentrations of Au. Grades of up to 66 g/t have been reported (de Oliveira *et al.*, 2011a, 2013).

The increased demand of some scarce metals observed in the last decade has intensified the search for their recuperation from mine wastes and residual exploitation materials, thus enhancing the need for a full comprehension of the way these metals are incorporated. Selenium contents above 900 ppm (Batista *et al.*, 2011) were measured in mine waste from the Achada do Gamo sulphur factory at the São Domingos (pyrite) mine.

The São Domingos massive sulphide orebody is dominated by pyrite and located at the top of the IPB Volcano Sedimentary Complex (VSC) sequence. The weathering of the São Domingos deposit (Matos *et al.*, 2006) resulted in extensive gossan horizons that were intensely mined during the Roman occupation of Iberia, particularly in southern Lusitania, and fully exploited during the XIX century. The recovery of sulphur for the production of sulphuric acid – largely used in the chemical industry – remained significant until the fifties of the XX century.

Aiming at a sustainable remediation of this mining site, an X-ray absorption spectroscopy study at Se *K*-edge using synchrotron radiation, combined with X-ray diffraction, was undertaken to clarify the speciation state of selenium and the nature of Se-carrier phase(s). In fact, Se-carrier phase(s) could be either oxygen-rich compounds resulting from the ore processing at the old sulphur factory or remains of former chalcogenide ore minerals. The results showed that selenium does not significantly replace sulphur under the form of selenate in the dominant sulphate phases and occasionally remains as a substituting selenide anion in debris of the original sulphides present in the mine waste materials (Figueiredo *et al.*, 2014a).

3.4. Rhenium

Rhenium is a very scarce element (average concentration in the Earth’s crust estimated to be lower than 1 ppb), occurring mainly in ores of porphyry copper-molybdenum deposits and carried by molybdenite (MoS_2). It has been extracted mainly as a by-product of the copper mining and recovered in the refinement of molybdenum concentrates. Due to its unique properties – high melting point (3180 ^{0}C, only exceeded by tungsten and by carbon in diamond), high density, high modulus of elasticity and electrical resistivity, low friction, no ductile-to-brittle transition and high resistance to creep—rhenium applications cover distinctive areas that range from the biological and nuclear fields to the electrical and aero-spatial industries, particularly for the production of nickel-based super alloys applied in jet engines. Due to a very low availability comparative to the actual industrial demand, rhenium is nowadays one of the most expensive mineral commodities and an increased interest is focused on exploring residues resulting from a long-term mining, particularly of sulphide ore deposits. It is therefore noteworthy to assign the presence of rhenium, in a concentration up to 3 ppm (Batista *et al.*, 2011), in the waste materials from the old Achada do Gamo sulphur factory at the abandoned mine of São Domingos.

Aiming at a potential sustainable recovery of rhenium as a by-product, X-ray near-edge absorption spectroscopy (XANES) was applied to clarify the Re-binding and mode of occurrence by comparing Re L_3-edge XANES spectra obtained from mine waste samples with similar spectra collected from Re-rich molybdenites ($Mo_{1-x}Re_xS_2$) and from Re-O model compounds configuring various valences and coordination environments of rhenium ions.

Table 4. Selected analyses of samples collected in the Lousal mine.

Tabela 4. Análises químicas de elementos selecionados, em amostras recolhidas na mina do Lousal.

Element unit	As (ppm)	Au (ppm)	Bi (ppm)	Cu (ppm)	Pb (ppm)	Re (ppm)	Sb (ppm)	Sn (ppm)	Se (ppm)	Zn (ppm)	Ge (ppm)	In (ppm)
L2	1610	362	38.3	6510	834	0.017	161	25	47	2950	0.5	6.4
L4	2650	261	95.9	6790	2050	0.013	249	10	37	112	0.6	11.4
L5	8930	466	194	9060	>5000	0.007	303	18	46	49600	1.4	17.1
L6	775	1190	165	3690	1020	0.005	115	>200	119	2830	0.9	10.7
L7	1890	322	47.9	3310	>5000	0.036	518	16	19	3550	0.5	5.4

The results obtained conform with the binding of rhenium to oxygen in the analysed mine waste materials (Figueiredo *et al.*, 2014b; Silva *et al.*, 2017).

4. Discussion and conclusion

The study of mineral deposits and ores hosting high-tech elements is essential in establishing what kind of supply exists to fulfill the expected increasing demand. It is likely that demand may outstrip supply. In this case, the consequential resource scarcity constitutes a unique opportunity for mining companies and local communities, who could benefit from the discovery of new deposits that are rich in the required high-tech elements or from the reevaluation of known base metal deposits for their (trace) high-tech elements content, eventually turning sub-economic base metal deposits into profitable mines if high-tech elements can be produced as a co- or by-product. This favorable scenario can also be observed in old mines, where current resources can be reevaluated, allowing for the development of new mining projects and also to improve the environmental impact of the current waste pits and dams.

The identification and characterisation of IPB massive and stockwork ores anomalous in high-tech elements is essential in the Portuguese and Spanish IPB sectors. Dozens of known IPB deposits can be considered, including giant deposits (>200 Mt) like Neves-Corvo and Aljustrel in Portugal and Rio Tinto in Spain. This improvement will contribute to promote near mining exploration projects that can promote the identification of new resources, both in deep orebodies, both at surface in gossans and mine wastes. The IPB, a metallogenic province long known for its massive sulphide base metal resources can be a strong candidate as a European supplier of high-tech elements. In the Portuguese IPB sector the following VMS deposits present high potential for high tech elements: Neves-Corvo, Aljustrel, Lousal, Lagoa Salgada, Salgadinho and Caveira. The remobilized vein deposits include examples like Barrigão and Ferrarias. The identification and characterisation of ores anomalous in high-tech elements would allow for the reassessment of what are presently considered sub economic deposits, potentially kick-starting a new stage in the long mining history of this province. Indium has already been identified and recovered from one of the producing mines of the IPB, *e.g.*, the Neves-Corvo mine. However, other high-tech elements which are commonly associated with indium in massive sulphide deposits were also studied, namely selenium and tellurium. These studies will encompass the distribution and content of the high-tech elements taking into consideration the crystal chemistry of different ore minerals, thus leading to the identification of carrier minerals. The studies of the distribution of high-tech elements are fundamental to assess the potential for their recovery. Additionally, the position of the carrier minerals in the paragenetic sequence needs to be determined, thus allowing to disclose possible mechanisms leading to the deposition of high-tech elements within the framework of the volcanogenic massive sulphide metallogenic model and subsequent remobilization processes. Such model can contribute towards the establishment of exploration strategies leading to further discoveries.

Furthermore, waste materials from Neves Corvo, São Domingos and Aljustrel already demonstrated to have that potential, although with different accessibility. The same knowledge needs to be applied in the processes of long term storage of these wastes and the physical-chemical characteristics of the carrier minerals of those high-tech elements in natural P-T conditions. The changes along time such as mobilisation, alteration and erosion need to be addressed in the studied materials in comparison with the primary ores. Therefore, the potential for this type of secondary ores is still much unknown.

The availability of a range of high-tech elements (In, Ge and Se, in particular) and the presence of precious metals, many of which are common accessory mineral phases makes the IPB a much sought-after target for continued exploration.

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