RARE ELEMENTS IN SULPHIDES FROM THE IBERIAN PYRITE BELT

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ABSTRACT

Volcanic-hosted massive sulphide deposits are among the most important producers of Indium in the world. The Iberian Pyrite belt hosts deposits with considerable concentrations over several hundreds of ppm of rare elements such as indium and germanium adding additional economic interest to the traditionally extracted ore. Research carried out using microprobe techniques, EPMA and PIXE confirmed that sulphides are the main In-bearing and Ge-bearing minerals. Sphalerite containing traces of indium was found in the Lagoa Salgada Deposit, in contrast with the Neves-Corvo Deposit where indium was mostly found in stannite and stannoidite. In the Barrigão Deposit, germanium was found to be contained in zoned areas of chalcopyrite.

INTRODUCTION

The Iberian Pyrite Belt (IPB) is one of three areas making up the South Portuguese Zone and is located in the SW of the Iberian Peninsula, comprising part of Portugal and of the provinces of Huelva and Seville in Spain. It forms an arch about 240 km long and 35 km wide between Seville and the proximities of Grândola in Portugal (Fig. 1).

The IPB, with more than 1600 Mt of massive sulphides originally in place and about 250 Mt of stockwork ore, is one of the most outstanding ore provinces in Europe and hosts one of the largest concentrations of volcanic-hosted massive sulphide deposits (VHMS) in the earth's crust [1]. Within the IPB there are more than 90 known deposits.

VHMS are a distinct type of mineralisation characterized by formation at or near the seafloor, in spatial relationship with volcanic rocks. They commonly include an underlying discordant epigenetic feeder zone with stockwork-like mineralisation [2] and can form in a variety of submarine volcanic environments [3].
Mining has taken place in this region for over 5,000 years [1]. Mining in the Iberian Pyrite Belt was very important in Tartessian and Roman times, working the oxidation and cementation zones of the deposits for gold, silver and copper. After centuries of almost complete inactivity, the mines were again worked during the 19th and 20th centuries, focusing on the production on copper and sulphuric acid. At the end of the 20th century and up to the present day, mining activity has intensively worked the base metals, gold and silver. Between 2005 and 2007 there was no mining in the Spanish IBP, although activities are being restarted in Las Cruces (Seville) and Aguas Teflidas (Huelva). In Portugal, mining continued in Neves-Corvo, while Aljustrel was reopened a few years ago and is currently in production.

The deposits within the IPB are in many cases, rich in other metals/elements that are not characteristic of the typical base metal suites that are ubiquitous in the IPB. Such examples are the Lagoa Salgada Deposit and the Neves-Corvo (rich in In) and the Barrigão Deposit (enriched in Ge).

In order to incentivise the European production of critical raw materials and facilitate the launching of new mining and recycling activities, the European Commission recently published a report on the critical raw materials for the EU [4] that considers these two elements among the list of the twenty critical raw materials and so fundamental to Europe's growth. Also according to the same report the forecast market balance predicts a small deficit for indium after 2015 making this element gain additional economic interest.

Whole-rock analysis results revealed considerable concentrations of indium and germanium in samples originated from several deposits. Research was carried out using microprobe techniques, which confirmed the existence of In- and Ge-bearing minerals in sulphides, in particular in the deposits at Lagoa Salgada, Neves-Corvo and Barrigão.
Indium was discovered in 1863 in Germany by Ferdinand Reich and Hieronymus T. Richter, is an element of subgroup IIIA, and it can be very incompatible during mantle melting. It can be found in association with zinc or copper, iron and tin. Indium minerals are quite rare. Native indium was first discovered quite recently in 1963 [5]. Amongst others, indium is used in the semiconductor industry and LCD, thin film applications and medical devices.

Germanium was discovered in 1886 in Germany by Clemens Winkler. It is an element of subgroup IVA, and it is a semiconductor. It can be found in association with zinc- and copper-rich sulphide ore deposits or in coal ashes. Pure germanium can be made in the laboratory. Amongst other applications, it is used in fibre-optic systems, thin film applications and electronic devices.

**STRATIGRAPHIC SEQUENCE**

The stratigraphic sequence of the IPB is relatively simple (Fig. 2). It begins with a basal unit [Phyllite-Quartzite Group or PQ Group - Frasnian (?) to Late Famennian (i.e., Late Devonian) age] with more than 2,000 m of slate and sandstone with siliciclastic shelf facies and of Late Devonian age.

![Stratigraphic Column](image)

**Figure 2.** Generalized stratigraphic column of the Iberian Pyrite Belt [1].
The PQ Group is overlain by the Volcano-Sedimentary Complex (Fig. 2) [VCS dated as Late Famennian to Early Late Visean [6]], reaching a thickness of 1300 m and deposited in an intracontinental basin during the oblique collision of the South Portuguese Zone (Avalonia?) against the Iberian Massif (Gondwana). The volcanism of the IPB shows compositions from basalt to rhyolite. The sequence has been traditionally grouped in three felsic volcanic cycles separated by two mafic ones [7]. The most felsic terms dominate, as domes and sills associated to volcanoclastic deposits with similar composition, as well as slate and chemical sediments [1]. The most felsic terms dominate, as domes and sills associated to volcanoclastic deposits with similar composition, as well as slate and chemical sediments.

The VS Complex is overlain by the Culm Group (Fig. 2), made up of shale, litharenite and rare conglomerate with turbiditic features. It has a thickness of up to 3,000 m and ranges in age from Late Visean to Middle-Upper Pennsylvanian. It represents the synorogenic foreland flysch related with the Variscan collision and tectonic inversion [8].

The whole series is affected by very low degree metamorphism and a fold and thrust tectonic ("epidermic belt") within the context of Variscan Orogeny [9, 10].

LAGOA SALGADA DEPOSIT

The Lagoa Salgada orebody/deposit is the most northerly of the IPB known so far. It occurs underneath approximately 130 m of sediments of the Sado Tertiary Basin, solely limiting interpretation to drill-hole data. Traditionally the ore body has been described as composed of a "central nucleus" and a "NW nucleus" [11] but it is better described as comprising two geographically distinct zones: a central stockwork and a massive sulphide lens in the NW [12] which together have an inferred mineral resource of 3.7 Mt [13].

The central stockwork zone comprises sulphide veins and semi-massive sulphide lenses and is mainly hosted by a thick; up to 250 m, and strongly chloritized quartz-phyric rhyodacite unit while the NW lens is made up of massive polymetallic sulphides and related chloritized stockwork are associated with the feldspar- and quartz-phyric rhyodacite [12].

The orebody is folded and faulted, and interpreted to occur mostly on the subvertical -overturned and intensely faulted limb of a SW verging anticline. It is clearly Cu-poor with local Cu concentrations in the region of 1 wt% but is clearly enriched in Pb in the paleo-gossan and in the supergene enrichment zones in its footwall. The massive sulphide lens is rich in Zn with values varying between 1 and 11 wt% Zn. These significant Zn concentrations result from sphalerite enriched zones, in what is generally an assemblage of pyrite with sphalerite, arsenopyrite, tetrahedrite-(tennantite), galena, löllingite, chalcopyrite, cassiterite, stannite, chalcocite, neodigenite, covellite, enargite, bornite, bournonite, meneghinite, bismuth sulphosalts and pyrrhotite.
Indium in the Lagoa Salgada deposit

Whole rock analysis performed on 6 samples collected from stored drill hole cores, showed indium content up to 90 ppm, which is significant as trace element. Microprobe analysis revealed that indium occurs in sphalerite and indium concentrations shows large variability. The maximum content of indium found in these samples was 0.8 wt%. Table 1 show EPMA averaged analysis performed in sphalerite grains.

Table 1. Average results (wt%) of sphalerite analysis performed on samples collected from the six drill holes in Lagoa Salgada orebody.

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<th>LS4 181.3</th>
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<td>100.86</td>
<td>99.84</td>
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In the same deposit but another drilling hole, recently collected, a 20 μm sphalerite included on recrystallized arsenopyrite was analysed and showed a concentration of 2.30 wt% indium (Fig. 3). This high value highlights the complexity of this deposit and strengthens the need to prospect new areas [14].
Figure 3. BSE image of a sample PX-08-20 sample with inclusion of sphalerite (Sp) (2.30 wt% indium) and one of chalcopyrite (Ccp), both included in recrystallized arsenopyrite (Apy). A small inclusion of cassiterite (Cst) is also visible.

NEVES-CORVO DEPOSIT

Neves-Corvo is a copper and zinc mine that is owned and operated by the Portuguese company Somincor, which is a subsidiary of Lundin Mining. It is situated approximately 220 km southeast of Lisbon and exploits a number orebodies from an underground mine.

Six massive sulphide lenses have been defined at Neves-Corvo comprising Neves (divided into North and South), Corvo, Graça, Zambujal, Lombador (divided North, South and East), and Sembiana. More recently a stockwork ore zone, Monte Branco, has been announced. The base metal grades are segregated by the strong metal zoning into copper, tin and zinc zones, as well as barren massive pyrite. The massive sulphide deposits are typically underlain by stockwork sulphide zones which form an important part of the copper orebodies [15].

Associated with the copper-rich massive lenses found in Neves-Corvo, unusual sphalerite + tetrahedrite–tennantite and bornite-rich discrete ore horizons have been found. Within the Neves-Corvo deposit a large variety of Cu, As, Sn, Co, Bi, Te (Se) and Ag sulphosalts has been observed in stringer ores. Cassiterite occurs as large metre-sized discrete massive lenses cross-cut by chalcopyrite veins, centimetric lenses in the rubané ores, stringer ores at the base of massive sulphides, and centimetric clasts of cassiterite in the middle of the tin-bearing copper-rich massive sulphides. In the copper-rich and polymetallic massive ores with low contents of tin, cassiterite mainly occurs as clusters formed by fine-grained cassiterite intergrown with sphalerite and phyllosilicates [16].

Tin (the main ore mineral is cassiterite) occurs in the deposit. Other tin sulphides such as stannite and different forms of chalcostannate) also occur in various amounts depending on ore types [17].

Current ore grades (first quarter results 2014) at the mine are reported as being 2.3 % Cu/t and 7 % Zn/t [13].
Indium and selenium in the Neves-Corvo deposits

It has been reported that Neves-Corvo mineralisation contains remarkable indium trace concentrations (150 to 300 ppm) with its highest level in the Cu-Sn and massive copper ores. Microprobe analysis reported indium in cassiterites in the range 50 - 150 ppm. Furthermore, it occurs also as a trace in sphalerite (0.09 - 0.28 wt%), chalcopyrite (0.06 - 0.21 wt%), tennantite (0.06 - 0.20 wt%), stannite (0.22 - 3.01 wt%), and stannoidite (0.29 - 0.5 wt%) [17].

In 2002 a large number of samples from the four main types of ore, RC (Rubané with copper rich content), RT (Rubané with tin rich content), MC (massive copper ore) and MS (massive copper tin ore) were analysed by PIXE and electron microprobes [18]. In this study, PIXE data revealed that stannite is the main In-bearing phase with concentrations of 675 ppm (MS ore) and 1077 (MC ore). Cassiterite also contains traces of indium with 284 ppm (MS ore) and 309 ppm (RT ore). Tetrahedrite-tennantite showed considerable concentration of selenium with 1201 ppm (MS ore) and indium with 178 ppm (MS ore). EPMA data shows an indium concentration of 0.1 wt% in sphalerite from MS ore.

Another study used a combination of EPMA and SIMS techniques [19] and investigated 3 types of ore: MC (massive copper ore), MS (massive copper-tin ore) and MT (massive tin ore). It was found that tin-bearing minerals contain significant amounts of indium. In particular, EPMA analysis of 5 minerals of ore types MC (massive copper ore) and MS (massive copper-tin ore) showed that stannite and stannoidite are the main In-bearing phases, with stannite exhibiting the highest level of 7030 ppm. In quantitative analysis the interference between In Lα and Sn Lν was corrected. Indium concentration analysed in chalcopyrite can reach 50 ppm.

A 2013 study showed that among all deposits, Graça, Lombador and Zambujal orebodies have the higher average grades of indium, 215, 152 and 150 ppm respectively. These higher indium grades were observed within zinc-rich ores (MZ) at the Graça and Lombador orebodies, and in the copper-zinc-rich ores (MCZ) of the Zambujal orebody. Indium is present as a minor element in the structure of major minerals and analysis showed concentrations up to 345 ppm in minerals such as chalcopyrite, 664 ppm in sphalerite, 5701 ppm in stannite and 215 ppm in fahlores [20]. The same study analysed Se and reported concentrations between 10 to 3220 ppm, the highest grades of this element having been found at lead-zinc rich ores from Zambujal and copper-zinc rich from Lombador respectively. Galena containing claushtalite and the first reported junoite in this area were the main Se-bearing minerals found [20].

Roquesite, although rare was found in another systematic sampling campaign at Lombador. Preliminary EPMA data show high concentrations (0.01 - 2.47 wt%) of In in stannite [21]. More recently, another study focussed on the geology of Lombador orebody (massive and stockwork) reported concentrations (0.01 - 4.3 wt%) of In in sphalerite and (0.01 - 7.41 wt%) in stannite[22].
BARRIGÃO DEPOSIT

The Barrigão deposit consists of two converging metric thick vein structures, extending approximately 1800 m along strike [23, 24]. Several small secondary vein structures branch off the main structures. The age of the Barrigão vein deposit and other similar copper vein structures in the region (Brancanes, Ferrarias/Cova dos Mouros, etc.) is considered to be late Variscan with possibly an Eo-Alpine overprint [25]. Copper ore extraction was carried out in the second half of the 19th 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 [26], which resulted in several dumps from which the study samples have been collected. Their supergene enrichment zones, represented by copper (Cu) and iron (Fe) minerals, e.g., malachite, hematite, azurite, and tenorite [25] have been mined during Roman and possibly even earlier, in Chalcolithic, times.

Germanium in the Barrigão deposit

Whole-rock analysis for trace elements of 10 ore samples, collected from the local mine dump, revealed an average of 61 ppm of Ge and 320 ppm of Sn. Macroscopic and microscopic studies revealed that ore formation took place in several phases: stage I (primary), II (replacement), III (overprint), and IV (supergene) [25]. The ore suite is dominated by chalcopyrite+ tennantite-tetrahedrite.

Microprobe analysis on samples representative of all ore formation stages were performed to investigate the possible Ge-bearing phases (Table 2). As an immediate conclusion, tennantite and tetrahedrite did not show any content in Ge. On the contrary, Ge was detected locally in chalcopyrite but not always.

The BSE electron image of Fig. 4 shows two different types of chalcopyrite; the upper chalcopyrite is from replacement assemblage (stage II) and contains some inclusions and is slightly zoned. Below, in the image, chalcopyrite from the hydrothermal overprint assemblage shows patchy zoned phase that corresponds with a considerable increase in Ge and Sn concentrations. Analysis revealed up to 0.64 wt% of Ge and 1.88 wt% of Sn. The occurrence of tin in chalcopyrite is coevally associated with arsenide as shown also on Fig. 5. These Ge and Sn-bearing zones are exclusive for the replacement chalcopyrite affected by element re-mobilisation occurred during hydrothermal overprint [25].

μ-PIXE analysis confirmed that chalcopyrite is the main Ge-bearing mineral and in particular in the patchy area, where values ranged from (0.07 wt% up to 0.62 wt%) [25].

The BSE image and maps shown in Fig. 5 suggest that hydrothermal re-mobilisation affect both tennantite and chalcopyrite at the same time and along vein like zones possibly opened by previous fractures. Maps also suggest the Se and Ge previously contained in tennantite or in inclusions have somehow been incorporated into chalcopyrite stage II.
Table 2. Microprobe analysis of chalcopyrite representative of all ore formation stages. Sample \textit{barr10} belongs to primary ore assemblage. Sample \textit{barr1a} is a representative of the replacement assemblage (stage II) with some overprint texture (stage III). Sample \textit{barr3-1} comes from a typical hydrothermal overprint assemblage (stage III). Samples \textit{barr8b} and \textit{2barr8} suffered additional supergene overprint (stage IV) [25] (\textit{bdl} = below detection limit).

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Total 98.95 100.24 99.58 99.50 100.21 99.77 100.05 98.77 99.18 98.59

The origin of germanium and tin in these patchy phases of chalcopyrite along remobilized veins may be attributed to the fault related genesis of the Barrigão deposit and it’s possibly to its-geographic proximity the Neves-Corvo deposits (10 km), which were mined for tin.

\textbf{CONCLUSIONS}

Our heavy dependence on mineral resources presents humanity with some difficult changes related to sustainability, including how to cope with finite supplies and how to mitigate the enormous environmental impacts of mining and processing of ore. As global population growth continues to grow-and perhaps more importantly, as standards of living rise around the world,-demand for mineral-based products made from minerals will increase.
Figure 4. BSE images of vein like patchy areas with typical replacement textures rich in Ge and Sn. The image on the right is a close up, where it seems that the chemical process that formed these veins affected equally both tennantite and chalcopyrite.

Mineral resources are essential to our modern industrial society and they are used everywhere. However, as technology leaps and bounds forward, our necessity for rare and technologically important elements may be compounded by low substitutability and low recycling rates. It is this deficit that drives research into "technological elements" so that knowledge gaps and ultimately production gaps can be filled.

The complexity of the deposits within the IPB is reflected in the mineralogy and range of concentrations found for the investigated elements. The traditional products of the IPB can now also be enhanced and improved and made more economically viable with the addition of significant trace element concentrations of rare elements as is the case of In and Ge. With maintained perspectives of a deficit of Indium in the forecast market Balance for the next years, it is imperative that research continues and extraction of these elements highlights the need of prospecting new target areas.
**Figure 5.** BSE image (upper image) of area affected by hydrothermal overprint element re-mobilisation. Element maps of Ge, Sn, Ab and As is presented. Note the sharp transition area in tennantite, also evidenced in As and Sb map (below). Elemental maps show a correlation between Ge, Sn, and As in patchy chalcopyrite. Sn in chalcopyrite is also coeavally associated with As [25].
REFERENCES

[2] Large R R 1992 *Econ. Geol.* **87** 471-510


