

Article

## Indium-Carrier Minerals in Polymetallic Sulphide Ore Deposits: A Crystal Chemical Insight into an Indium Binding State Supported by X-ray Absorption Spectroscopy Data

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Received: 28 August 2012; in revised form: 17 October 2012 / Accepted: 18 October 2012 /

Published: 6 November 2012

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**Abstract:** Indium is a typical chalcophile element of the Earth's crust, with a very low average content that seldom forms specific minerals, occurring mainly as dispersed in polymetallic sulphides. Indium recovery is based primarily on zinc extraction from sphalerite, the prototype of so-called tetrahedral sulphides, wherein metal ions fill half of the available tetrahedral sites within the cubic closest packing of sulphur anions, leaving interstices accessible for further in-filling. Ascertaining the tendency towards the establishment of In-In interactions through an x-ray absorption spectroscopy approach would efficiently contribute to understanding the behavior of indium in the carrier mineral. The successful results of applying such a near-edge absorption (XANES) study at In  $L_3$ -edge to samples collected at the Lagoa Salgada polymetallic orebody in the Iberian Pyrite Belt (IPB) are described and the crystal chemistry of indium is re-evaluated, disclosing a potential clue for the metal binding state in polymetallic sulphides.

**Keywords:** indium; carrier minerals; polymetallic sulphide deposits; Iberian Pyrite Belt; crystal chemistry; XANES

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## 1. Introduction

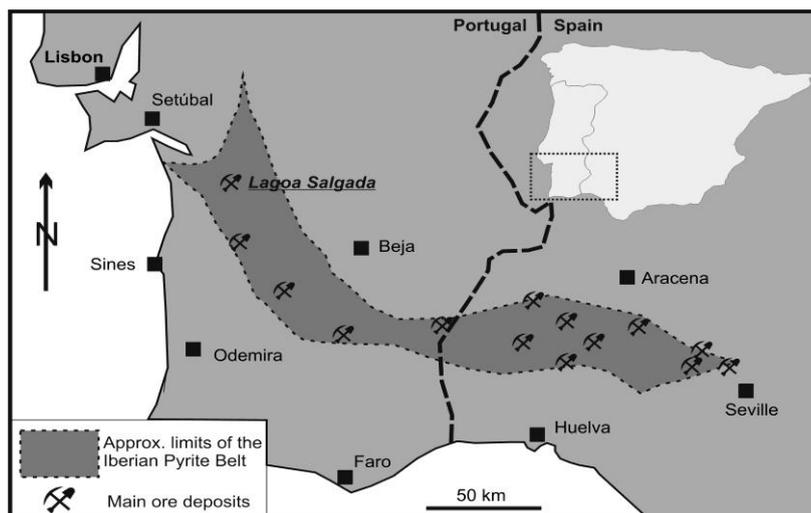
Indium is a very scarce metallic element discovered quite accidentally in 1863 and isolated four years later. This chalcophile element seldom forms specific minerals, occurring mainly as dispersed in polymetallic sulphides [1]. The first In-mineral to be described was roquesite—ideally  $\text{CuInS}_2$  [2], followed by indite, a thiospinel with the ideal formula  $\text{FeIn}_2\text{S}_4$ —and dzhalindite, the hydroxide  $\text{In}(\text{OH})_3$  [3]. Curiously, native indium metal was assigned about fifty years ago to granites from East Transbaikalia, in close association with lead [4].

Nowadays, indium is a strategic metal used in both classic technological fields (e.g., low melting-temperature alloys and solders) and innovative nanotechnologies, used particularly to produce “high-tech devices” and in the application of new advanced materials—liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and ionic amorphous oxide semiconductors (IAOS) used in transparent flexible thin-films. Indium consumption is therefore expected to increase in the following years, keeping the trend registered in the nineties and focusing a special interest simultaneously on its exploitation from promising polymetallic sulphide ores—such as those found within the Iberian Pyrite Belt [5], an important metallogenic province crossing the south of Portugal and extending into Spain, and on the improvement of primary recovery and recycling technologies. To improve the search for this scarce metal and to enhance its exploitation, experts are overwhelmed [6,7], and therefore a reappraisal of the crystal and mineral chemistry of indium, focused on excess-metal chalcogenides, appears to be a decisive and helpful step.

A strong tendency towards the establishment of In-In interactions leading to the formation of metallic polycations was already identified in synthetic In-chalcogenides [8]. X-ray absorption spectroscopy is the appropriate technique to address this binding question [9], the results of which would efficiently contribute to the understanding of indium crystal chemistry and the bonding state in excess metal chalcogenide minerals. Accordingly, the results of applying x-ray absorption near-edge spectroscopy (XANES) in the study of the  $L_3$  absorption edge of indium in carrier phases from samples collected at the Lagoa Salgada polymetallic orebody are described and the crystal chemistry of indium in natural chalcogenides is accordingly reappraised.

### 1.1. The Lagoa Salgada Orebody

This polymetallic orebody is the most northerly VHMS-type (volcanic-hosted massive sulphide) deposit of the Iberian Pyrite Belt (IPB) known so far (Figure 1). It occurs underneath approximately 130 m of sediment from the Sado Tertiary basin, limiting interpretation to drillhole data. The orebody is folded, faulted, and interpreted to occur mostly on the sub vertical overturned and intensely faulted limb of a southwest-verging anticline. Lagoa Salgada is further offset by an east-west-trending Alpine-age fault in the north, with a 50 m down throw of the northern block, but whose horizontal amount and sense of displacement remain unknown [10].

**Figure 1.** Location of the Lagoa Salgada orebody in the Iberian Pyrite Belt (IPB).

The deposit comprises a Central Stockwork Zone and a Northwestern Massive Sulfide Lens. The Central Stockwork zone is 700 m thick and comprises sulfide veins and semi massive sulfide lenses and is mainly hosted by an Upper Devonian (Fammenian) age, is thick (up to 250 m) and a strongly chloritized quartz-phyric rhyodacite unit. Additionally, there is a feldspar- and quartz-phyric rhyodacite that dominates the sequence hosting the massive sulfide lens in the northwest. These two rhyodacites are clearly distinguished by their phenocryst content; geochemically, the former corresponds to a more evolved series than the latter. The Central Stockwork is characterized by minor Pb, Zn and Sn, and Cu values can reach 1.4 wt % [11].

The known part of the Northwestern Massive Sulfide Lens averages 20 to 25 m in thickness and displays a large variation in metal contents, including significant concentrations of Zn (maximum 20 wt %) and Pb (maximum 23 wt %) associated with the feldspar- and quartz-phyric rhyodacite. Lesser quantities of Sn, Cu, Hg, As, Sb, Au, Ag and In were also detected [12]. Average grades of 0.35% Cu, 3.22% Pb, 4.43% Zn, 0.40% Sn, 72.52 g/t Ag, and 0.95 g/t Au have been estimated [13].

The deposit has an inferred mineral resource of 3.7 Mt from both the Central Stockwork and the Northwestern Massive Sulfide Lens. Setting Lagoa Salgada aside from other nearby VHMS deposits is the presence of indium as a trace element within the base metal element suite. This very scarce metal is preferentially hosted by sphalerite (see Figure 10 from [11]), with contents attaining an average maximum of 0.62% In. The fact that until now discrete inclusions of In-bearing minerals have not been observed reinforces the idea that indium occurs possibly within nanophases [12] as postulated before [1]. The preponderance of sphalerite-associated indium in the Lagoa Salgada deposit suggests that it was formed at relatively low temperatures with intermittent pulses of higher temperatures that have originated the Cu-bearing ores.

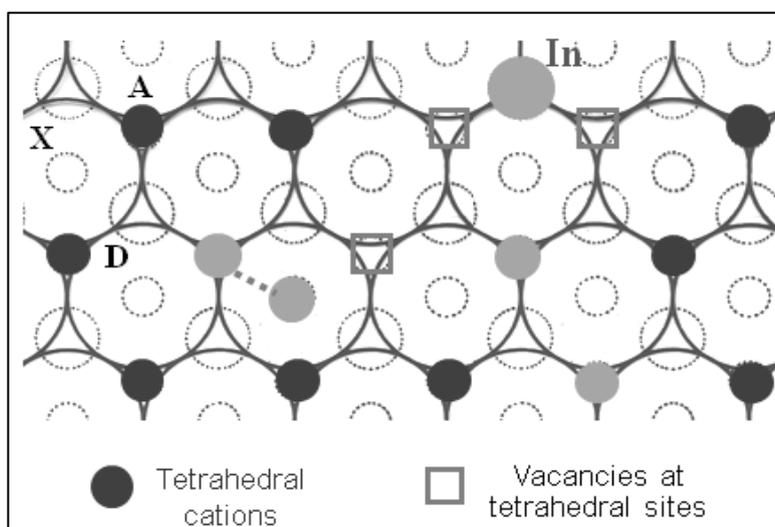
### 1.2. A Brief Survey of Indium Crystal Chemistry

Indium is the element with atomic number 49, having the electronic structure  $[\text{Kr}] 4d^{10} 5s^2 5p^1$ . Accordingly, a trivalent state is frequently assumed by indium ions, suggesting an inertness of the  $5s^2$  electron-pair. In Nature indium is mainly carried by zinc sulphide - the mineral sphalerite [14].

Stable In-compounds are diversified, ranging from the hydride (InH) and the nitride (InN) that configure the two stable formal valences (1+) and (3+), to the phosphide (InP) and the arsenide (InAs) that have been extensively applied in semiconductor technologies and where indium behaves formally as a trivalent cation. Other synthetic In-compounds include halides, oxides and chalcogenides, the latter being worthy of a particular interest for the understanding of indium geochemical behavior.

The recovery of indium stands mostly on zinc extraction from sphalerite, the common cubic form of zinc sulphide which is the prototype of the so-called “tetrahedral sulphides” where the metal ions fill half of the available tetrahedral sites within the cubic closest packing (*ccp*) of sulphur anions, leaving interstices still accessible for further in-filling (Figure 2).

**Figure 2.** Condensed model sheet [15] figuring out the closest-packed layers of sulphur anions (X) in the crystal structure of “tetrahedral sulfides” where the cations fill half of the available tetrahedral sites (A) in the cubic closest packing of sulfur anions (X), leaving unoccupied the octahedral interstices (D). Insertion situations of indium are exemplified.



The crystal-chemical formula of sphalerite can then be written  $Zn^{\underline{t}} [S]_{\underline{c}}$  where  $\underline{t}$  specifies the tetrahedral coordination of cations and  $\underline{c}$  quotes the *ccp* of anions. Indium is also carried in trace (but noteworthy) contents by excess-metal copper-rich sulphides [16] like the mineral bornite, with structural formula  $Cu_5^{\underline{t}} Fe^{\underline{t}} [S_4]_{\underline{c}}$ . Very seldom does indium form specific minerals; beyond the already mentioned natural sulphides (roquesite and indite), another example is sakuraiite [17,18], also a “tetrahedral sulphide” with approximate formula  $(Cu,Zn,Fe)_3(In,Sn)S_4$ . However, it is still not clear if sphalerite carries indium mainly in solid solution through a diadochic replacement of zinc or if indium concentrates alternatively (or simultaneously) in nanodomains by filling interstitial sites available in the structural array of sphalerite. The fact that discrete inclusions of In-bearing sulphides—such as sakuraiite and roquesite—could not yet be observed in sphalerite from Lagoa Salgada ore samples reinforces the idea that indium occurs mainly within nanophases [1,19].

Excess-metal indium chalcogenides—namely  $In_2Se$ —were first quoted fifty years ago [20]. Pure In-chalcogenides have been synthesized since then –  $In_6Se_7$ ,  $In_7Te_{10}$ ,  $InTe$  and  $In_4Se_3$  plus  $In_4Te_3$ , most of them with excess metal – and their structural characterization has revealed the occurrence of polymetallic cations:  $[In_2]^{4+}$  dimers and/or  $[In_3]^{5+}$  trimers [8,21].

Therefore, the occurrence of In-In interactions capable of leading to the formation of metallic polycations in nanodomains within the sphalerite host mineral is a possibility to be considered, thus contributing to improve the understanding of indium crystal chemistry in natural chalcogenides.

## 2. Experimental Section

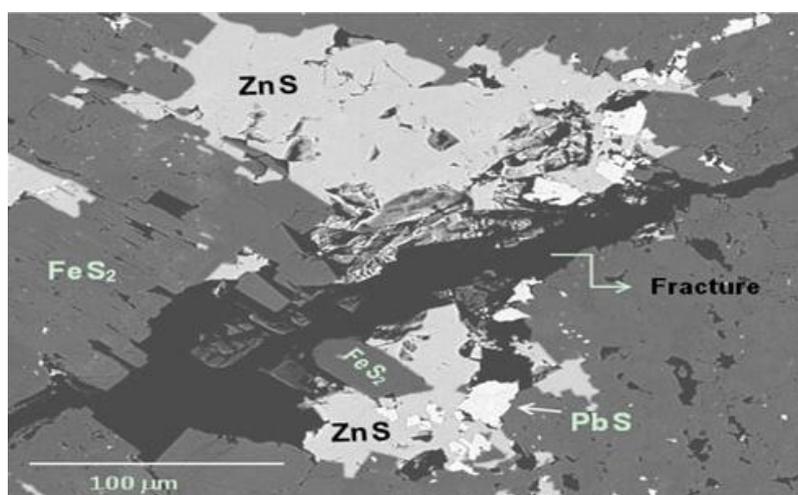
With the purpose of addressing the question still pending about the binding state of indium in natural chalcogenides, X-ray absorption near-edge spectroscopy (XANES) experiments were carried out at the *ESRF* (European Synchrotron Radiation Facility, Grenoble/France) using beamline ID21 [22] to perform micro-fluorescence and micro-XANES measurements.

### 2.1. Studied Samples

Irradiated materials were samples of polymetallic chalcogenide ores from the Lagoa Salgada deposit with an indium bulk content of about 90 ppm and which phase constitution plus chemical composition were previously characterized using laboratory methodologies, respectively X-ray diffraction and EPMA (as described in [11]). Figure 3 reproduces the micrograph of the studied sample surface where sphalerite is well represented.

Metallic indium was used for energy calibration (In  $L_3$ -edge at 3730.1 eV). Commercial products were used as model compounds displaying distinct bonding situations of indium in the formal valence state 3+:  $\text{InF}_3$ ,  $\text{In}_2\text{O}_3$  and  $\text{In}_2\text{S}_3$ . These synthetics were also previously checked by X-ray diffraction in the laboratory and the sulphide demonstrated as poorly crystallized.

**Figure 3.** Photomicrograph of a polished section from ore sample LS 5-180.6 displaying the major constituting minerals: sphalerite ( $\text{ZnS}$ ), pyrite ( $\text{FeS}_2$ ), galena ( $\text{PbS}$ ).



### 2.2. Experimental Methodology

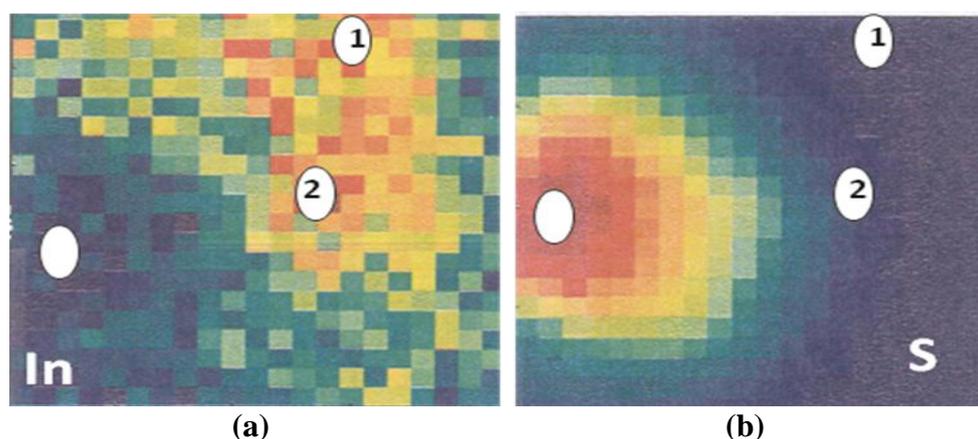
The instrumental set-up of ID21 beamline at the ESRF is equipped with a Scanning X-ray Microscope that can be operated in the energy range 2.1–9.2 keV, thus enabling the analysis of both relevant absorption edges when studying indium chalcogenides: the In  $L_3$ -edge (ideally at 3730.1 eV for the metal) and the S  $K$ -edge (at 2472 eV for elemental sulphur).

In  $L_3$ -edge XANES spectra were collected in fluorescence yield (FY) mode using a photodiode detector mounted in the horizontal plane perpendicular to the X-ray beam and performing the energy scanning between 3.71 and 3.80 keV. A fixed-exit Si(111) monochromator was used, assuring a good energy resolution (0.4 eV) at the edge.

Small sample fragments were directly irradiated with a beam-size of  $1 \times 0.3 \mu\text{m}^2$  and the fluorescence yield was detected using a high-purity germanium solid state detector.

Access to the user-friendly program PyMCA 4.3.0 (Python multichannel analyzer, [23]) is assured at the beamline, thus enabling the selection of most suitable points to irradiate in the ore samples. A preliminary tracing of topochemical maps was a further significant aid in this selection (Figure 4).

**Figure 4.** Topochemical map of a small area from a fragment of ore sample LS 5-180.6. Concentration of the selected element (a) In or (b) S: Red, maximum; blue, minimum. Points irradiated to collect In  $L_3$ -edge XANES spectra are marked by ellipses.



### 3. Results and Discussion

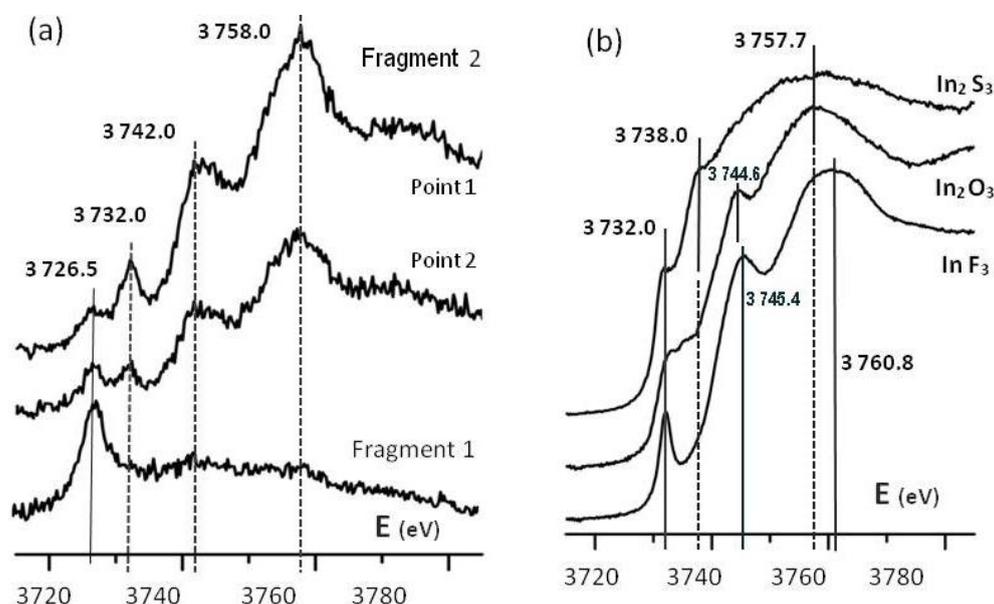
Collected In  $L_3$ -edge XANES spectra are reproduced in Figure 5. A similar general trend is displayed by the spectra obtained from points irradiated in the ore sample (Figure 5a) and by the ionic model compounds  $\text{InF}_3$  and  $\text{In}_2\text{O}_3$  (Figure 5b), both containing  $\text{In}^{3+}$  ions, respectively in a quite regular octahedral coordination by fluorine anions forming an hexagonal closest packing and in a less regular coordination by six surrounding oxygen anions in a cubic bixbyite-type crystal structure. Remarkably, the spectrum collected from indium fluoride has an intense “white line” [24] at 3732 eV (Figure 5b), not perceptible in the spectra obtained from the other model compounds.

Another feature with a similar layout—a peak or shoulder—occurs in the spectra of the fluoride and oxide at 3745.4 eV and 3744.6 eV, respectively (Figure 5b). Conversely, the compound  $\text{In}_2\text{S}_3$  offers a different spectral trend, as would be expected from a poorly defined lacunar spinel-type sulphide [25] with an ordered (high temperature  $\beta$ -form) or a random (low temperature  $\alpha$ -form) distribution of cations and vacancies in the tetrahedral sites.

Beyond the presence of a “white line” at 3732 eV (most prominent in the spectrum obtained from  $\text{InF}_3$ ), all the In  $L_3$ -edge XANES spectra obtained from the studied Lagoa Salgada ore sample fragments display an additional similar feature at lower energy (3726.5 eV), which was disclosed from the time of the first X-ray absorption spectroscopy experiment.

Compared with the details observed for the studied model compounds, all the spectra collected so far from chalcogenide ore samples display such detail at an energy that precedes the  $L_3$  absorption edge of indium metal (3730.1 eV). Curiously, in the In  $L_3$ -edge XANES spectra collected from one ore fragment (Figure 5a, Fragment 1) only the pre-edge feature at 3726.5 eV could be clearly observed.

**Figure 5.** In  $L_3$ -edge XANES spectra collected from (a) two fragments of sample LS 5-180.6 (points 1 & 2 in Figure 4) and (b) from selected model compounds.



#### 4. Comments and Conclusions

X-ray absorption spectroscopy at the  $L$ -edge (arising from  $s,p \rightarrow d$  transitions) is a suitable methodology for probing unoccupied density of states and orbital hybridization, capable of accounting for the details of XANES spectra collected from studied ore samples.

As pointed out in a recent study [26] on indium oxy-nitride (wurtzite-type structure), the presence of a “white line” in In  $L_3$ -edge XANES spectrum denotes the occurrence of non-occupied electronic states in indium atoms. The two shoulders observed in the spectra collected from the ore sample, separated by 10 eV (at 3732 eV and at 3742 eV), possibly indicate electronic transitions to unoccupied  $d$  states above the Fermi level and may be formally assigned to  $2p \rightarrow 5s$  electronic transitions, enhanced by an  $s-d$  hybridization [27,28].

A preliminary account on the binding state of indium in natural sulphides, stemming from the results of X-ray absorption spectroscopy studies at the  $L$ -edge, suggests the possible occurrence of metal-metal bonding [29]. Further study is in progress to explore this hypothesis, once the nanoscale phase hosting indium in the irradiated ore fragments could not yet be clearly identified, thus hindering a full interpretation of X-ray absorption data, particularly in what concerns the pre-edge feature.

#### Acknowledgments

EU financial support to perform the X-ray absorption experiments at the *ESRF* is acknowledged (Reports available at <http://www.esrf.fr>). Part of this research was developed under the Project INCA

(PTDC/CTE-GIN/67027/2006, Characterization of Crucial Mineral Resources for the Development of Renewable Energy Technologies: The Iberian Pyrite Belt Ores as a Source of Indium and Other High-Technology Elements), financed by the Portuguese Foundation for Science & Technology.

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