



Experiment title: Micro mapping of indium in polymetallic sulphides and assessment of its binding state

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Report:

Indium is widely used in various technological fields (e.g. low melting-temperature alloys, solders, electronics) and lately it became relevant for the production of “high-tech devices” based on innovative nanotechnologies, therefore its consumption is expected to increase in the next years.

The recovery of indium (a chalcophile element that occurs dispersed within polymetallic sulphides instead of forming specific In-minerals) stands mainly on the zinc extraction from blende (ZnS); however it is known that In is also carried by excess-metal copper sulphides, like bornite, Cu_5FeS_4 , and by specific sulphides - e.g. sakuraiite, $(\text{Cu,Ag})_2(\text{Zn,Fe})(\text{In,Sn})\text{S}_4$. Accessory minerals from Iberian Pyrite Belt (IPB) massive copper sulphide ores (south of Portugal) – bornite itself, tetrahedrite, mawsonite (ideally $\text{Cu}_6\text{Fe}_2\text{SnS}_8$), Se-rich galena, $\text{Pb}(\text{S,Se})$ – are known to carry interesting bulk contents of both In pontually concentrated [1,2].

The aim of the experiment was to perform a micro-mapping of In in selected polymetallic sulphide samples from IPB, using scanning X-ray microscopy (SXM) and thereafter to probe the electronic state of indium by X-ray absorption spectroscopy at the L_3 -edge.

The bulk indium content and the main mineral phases present on these samples were previously ascertained by X-ray fluorescence spectrometry with a laboratorial wavelength dispersive system (XRF-WDS) and X-ray powder diffraction. Optical microscopy was also performed on polished surfaces embedded in resin to select possible areas of interest.

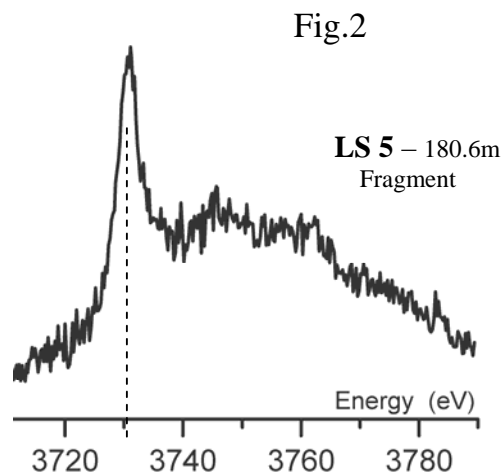
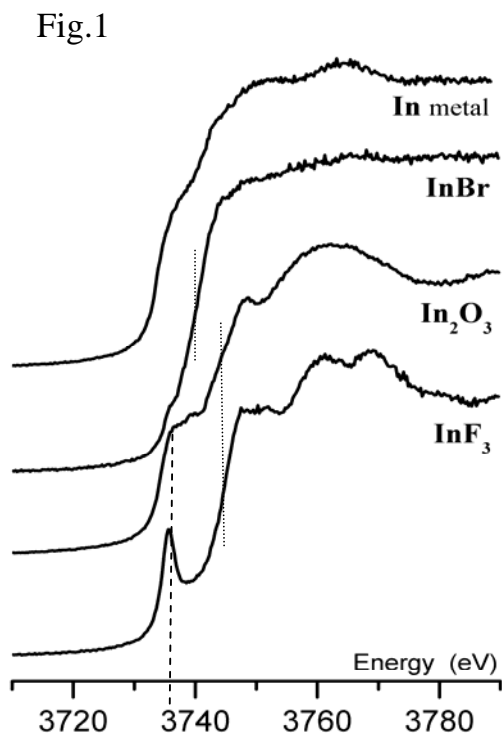
Two types of polymetallic sulphide samples were therefore irradiated: polished surfaces and fragments. The first ones have disclosed difficulties in attaining the required vacuum level and in clearly identifying indium due to the overlapping of K $K\alpha$ and In $L\alpha$ peaks in the energy dispersive XRF spectrum.

An improvement on SXM analysis was attained with fresh surfaces of polymetallic sulphide fragments although the minor content of K present in most mineral samples makes difficult the micro-mapping of indium, also in low concentration. Despite this difficulty, some useful XANES spectra could be collected from bornite-rich sulphide fragments from Lagoa Salgada (LS). The In L_3 absorption edge was scanned from 3.71 to 3.79 keV in fluorescence yield (FY) mode and the energy calibration was performed using a gypsum standard.

As model phases for different coordination environments of indium (and electronic states), the metal (with a *bcc* structure) and the following commercial powder compounds were used: the halides InBr (In⁺ in square coordination with one close extra-neighbour) and InF₃ (In³⁺ in octahedral coordination) plus the oxide In₂O₃ - cubic bisbyite-type structure with In³⁺ ions occupying two different coordination environments: six equidistant oxygen anions at the vertices of a cube with two body-diagonally opposite corners unoccupied and a less regular coordination geometry for the same coordination number [3].

Sulphide fragments were irradiated at various points and five scans were performed per point. From a total of about 300 registered scans (50 from model compounds), 15 good XANES sum spectra were selected.

Fig. 1 illustrates the In L₃-edge XANES spectra collected from model compounds and fig. 2 reproduces one of the few useful spectra collected from sulphide fragments. A remarkable feature is the “white line” [4] in the XANES spectrum from InF₃, not perceptible for the oxide where In has the same formal valence; a similar effect was observed in the spectra collected from a sample (LS-5) where the laboratory characterization has assigned the occurrence of minute grains of bornite, Cu₅FeS₄.



According to the actual results and despite the few good spectra collected so far, it is expected that a further analysis of carefully selected polysulphide mineral grains could provide an insight into the electronic state of In, particularly when hosted by excess-metal sulphide minerals [5].

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