



	<b>Experiment title:</b> Searching deeper to interpret the details in $L_3$ -edge XANES spectra of <u>In</u> and <u>Sn</u> carried by tetrahedral sulphides in polymetallic ore samples	<b>Experiment number:</b> EC-806
<b>Beamline:</b> ID-21	<b>Date of experiment:</b> from: 15 June 2011 to: 19 June 2011	<b>Date of report:</b> 2011.12.15
Shifts: 12	Local contact(s): Dr. Giulia Veronesi	<i>Received at ESRF:</i>
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## Report:

The recovery of indium from polymetallic sulphide ores stands mainly on the zinc extraction from sphalerite, ZnS – prototype of the so-called “*tetrahedral sulphides*” where the metal ions fill half of the available tetrahedral sites in a cubic closest packing of sulphide anions. In solid solution, and not seldom along with tin, indium is carried also by excess-metal copper-rich tetrahedral sulphides. Once the anionic closest packing displays unfilled tetrahedral and octahedral interstices, an eventual tendency towards the settlement of metal-metal interactions between additional ions could be satisfied by filling closely located interstitial sites.

Previous XANES experiments to study the binding state of indium and tin in polymetallic sulphide ores (EC-450 & EC-628, reports dated August 27, 2009 and August 23, 2010, respectively) have provided challenging results – namely, a similar general trend was observed for the In and Sn  $L_3$ -edge XANES spectra, with two shoulders close to the edge and an extra “white line” preceding the edge in the case of indium [1].

With the aim of clarifying those spectral details, a polymetallic ore sample (LS 1 - 428) from the still unexploited deposit of Lagoa Salgada in the Portuguese sector of the Iberian Pyrite Belt (IPB) – a large, if not the largest, complex ore body in Europe and a potential supplier of indium in years to come [2] – was studied in this experiment, along with additional model compounds:  $\text{In}_2\text{S}_3$  (a poorly crystalline spinel-type sulphide),  $\text{In}_2\text{Se}_3$  (a commercial multiphase selenide) and SnS, with sodium chloride type-structure. Electron microprobe (EPMA) results showed that the studied sample contains In-rich small sphalerite domains, along with stannite, within large tetrahedrite grains (fig. 1).

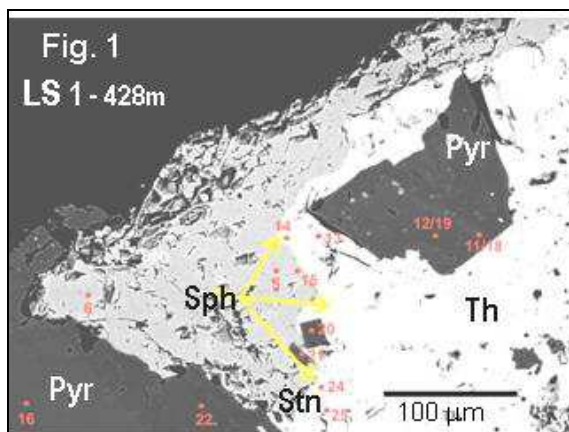
As an attempt to locate In-rich nanophases, preliminary topochemical mappings of selected fragments collected from this ore sample were performed with the scanning X-ray microscope (SXM) at 3.7 and at 3.8 keV (before and after In  $L_3$ -edge). Once the results were not conclusive, the sample section studied by EPMA (fig. 1), previously rough-hewed with a diamond paste in the laboratory, was also irradiated to trace the presence of indium; the optical difficulties in clearly distinguishing distinct domains within the very reflective ore mineral grains under the visible light video-microscope were in part overcome with the collaboration of beamline Scientists to accomplish detailed topochemical mappings.

The analysis of XRF spectra using PYMCA enabled to infer the possible host mineral of In-carrier nanodomains. Various points were irradiated to collect XANES spectra in fluorescence yield mode by scanning from 3.71 to 3.80 keV for In  $L_3$ -edge, from 3.91 to 4.02 keV for Sn  $L_3$ -edge and from 2.45 to 2.55 keV for S  $K$ -edge. Occasionally, XANES spectra from 3.33 to 3.50 keV for Ag  $L_3$ -edge and from 3.60 to 3.64

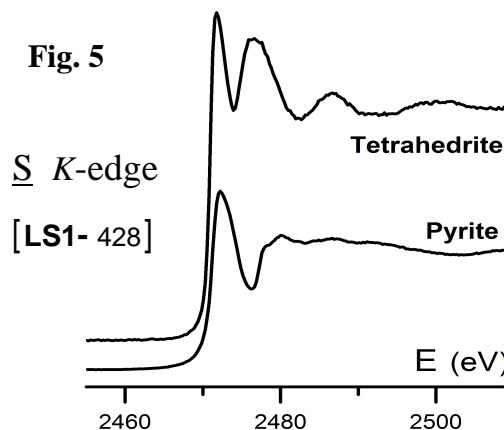
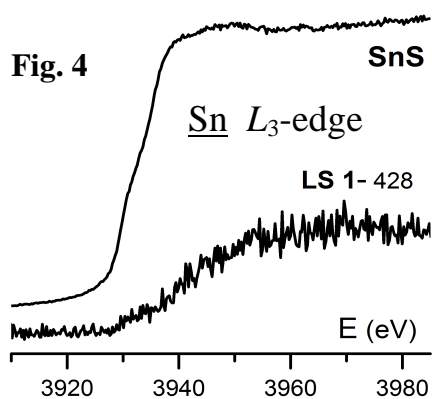
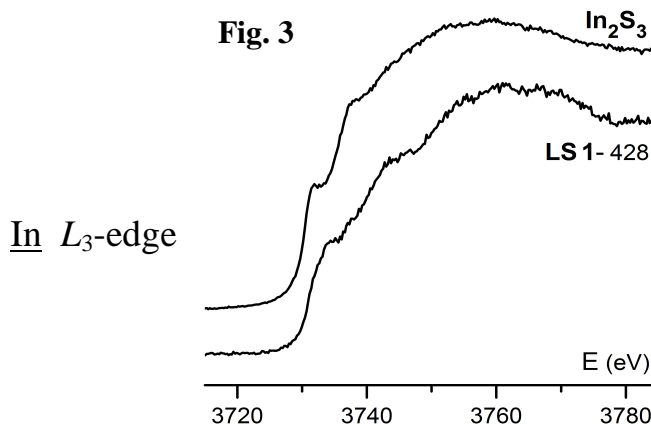
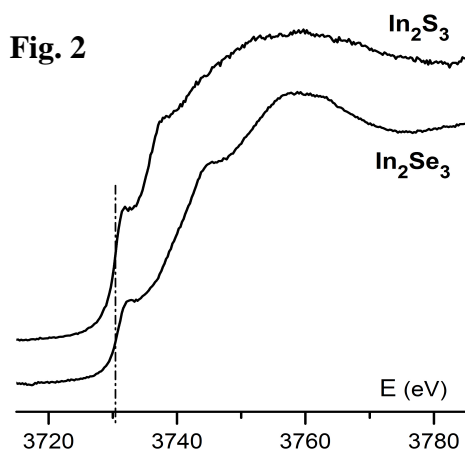
keV for K *K*-edge were also collected. An indium metal foil and anhydrite (CaSO<sub>4</sub>) were used for energy calibration.

**Fig. 1** – Polished section used for EPMA (analyzed points assigned in red; yellow arrows assign sphalerite grains).

Pyr, pyrite (FeS<sub>2</sub>); Sph, sphalerite (ZnS); Th, tetrahedrite [(Cu,Fe)<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>]; Stn, stannite (Cu<sub>2</sub>FeSnS<sub>4</sub>).



From a total of about 750 registered scans, good XANES sum-spectra were collected: 31 for the In *L*<sub>3</sub>-edge, 4 for the Sn *L*<sub>3</sub>-edge and 15 for the S *K*-edge.



XANES spectrum collected from the spinel compound In<sub>2</sub>S<sub>3</sub> (fig. 2) agrees with published data [3] and compares quite well with the spectrum collected from an irradiated point in LS1-428 sample (fig. 3). Conversely, data collected for Sn are fairly poor (fig. 4) and no sphalerite grains could be identified through the collected S *K*-edge spectra (fig. 5), despite having been located in the sample by EPMA (fig. 1).

[1] Figueiredo, M.O. & Silva, T.P. (2010) The binding state of indium and tin in natural sulphides: first results of a comparative study by X-ray absorption spectroscopy at the *L*-edge. *IMA 2010-Bonds & Bridges: Min. Sci. & Applications, Symp.* MA-92, Budapest/Hungary, August 21-27. *Acta Mineralogica-Petrographica Abst. Ser.*, **6**, 662.

[2] De Oliveira, D., Rosa, D.R.N., Matos, J.X., Guimarães, F., Figueiredo, M.O. & Silva, T.P. (2009) Indium in the ore body of Lagoa Salgada, Iberian Pyrite Belt, Portugal. *Procd. 10th Biennial Mtg. Soc. Geogy Applied to Mineral Deposits*, ed. P.J. Williams *et al.*, vol. **1**, 424.

[3] Womes, M., Jumas, J.C. & Olivier-Fourcade, J. (2004) X-ray absorption spectra and conduction band structure of In<sub>2</sub>S<sub>3</sub>. *Solid State Comm.* **131**, 257.