ESRF	**Experiment title:** Binding state of fifth-period metals in natural polymetallic sulphides: SXM mapping and XANES at the L_3-edge of Sn, In, Ag, and at the S *K*-edge	**Experiment number**: EC-628
Beamline: ID-21	**Date of experiment**: from: 9 April 2010 to: 13 April 2010	**Date of report**: 2010.08.23
Shifts: 12	Local contact(s)**: Dr. Jakub Szlachetko**	*Received at ESRF:*

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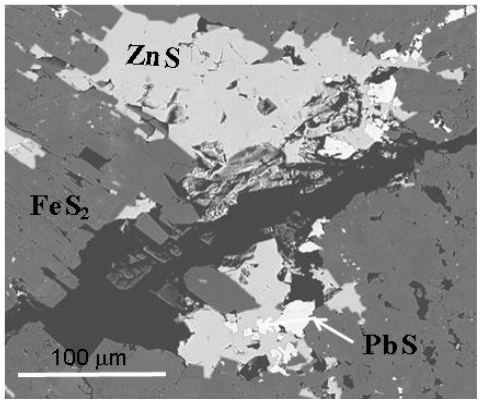
Report:

Natural polymetallic sulphide samples of ore deposits from the Portuguese sector of the Iberian Pyrite Belt (IPB) with interesting In, Sn, Ag bulk contents were studied in the experiment – an orebody at present under exploitation, Neves-Corvo [1], and another still unexploited but promising ore deposit, Lagoa Salgada [2,3].

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. Accordingly, the main aim of EC-628 experiment was to assess the binding state of indium and tin, along with silver, in sphalerite-rich polymetallic sulphide ores (fig. 1) and to contribute for unveilling the conditions that drive the hosting of these fifth-period metals in those ores. Simultaneously, the electronic state of sulphur was also studied for natural Ag_2S and for both natural and synthetic tetrahedrites.

Fig. 1- Photomicrograph of a polished section from ore sample LS 5-180.6; in black, a fissure.



Previous experiments (EC-290 & EC-450, reports dated July 23, 2008 and August 27, 2009, respectively) have provided challenging results – namely, two shoulders close to the L_3-edge of In and Sn spaced by about 10 eV and an extra "white line" preceeding the edge in the case of indium [4] – but simultaneously rised some difficulties quoted in the reports that were partially overcome through the present experiment [5].

Sample fragments were irradiated in different points and various spectral scans were performed per irradiated point. L_3-edge XANES spectra were collected in fluorescence yield (FY) mode by scanning from 3.71 to 3.80 keV for In, from 3.91 to 4.02 keV for Sn , from 3.33 to 3.50 keV for Ag , and from 2.45 to 2.55 keV for sulphur. Spectra collected from metal foils were used for energy calibration. For comparison purposes, the spectrum of tetrahedral tin in stannite, Cu_2FeSnS_4, and of octahedral indium in InF_3 were also collected. Preliminary topochemical mappings were performed with the scanning X-ray microscope (SXM) at 3.7 and

3.8 keV (before and after the L_3-edge of indium) in selected areas of sample fragments. The analysis of XRF spectra using PYMCA enabled to collect In and Sn XANES spectra at the same irradiated point.

Ag L_3-edge spectra were collected from natural Ag_2S - acanthite & argentite, both with tetrahedral [Ag^+] in a body-centred packing of [$S^=$] anions - and from synthetic Ag-tetrahedrite (fig. 2), along with S K-edge spectra (fig. 3), collected also from natural tetrahedrite.

The possible interference of K K–edge and of Cd L_2-edge on In L_3-edge XANES spectra (fig. 4) was checked. A full spectrum of In L-edges (3.7 to 4.4 keV) was collected from InF_3 in order to analyse a possible constrain induced by In L_2-edge over Sn L_3-edge when the tin content is low at the irradiated point (fig. 5).

From the fourteen hundred registered scans, the following XANES spectra were collected: 12 for the S K-edge and 111 for the L_3-edges of In (60), Sn (45) and Ag (6). The first approach to the assignement of edge shoulders observed for In and Sn L_3-edge XANES spectra from Lagoa Salgada samples [5] requires further experimental work on other In-rich ore samples and on Sn model compounds so that a full interpretation of the spectra collected from natural polymetallic tetrahedral sulphides can be attained.

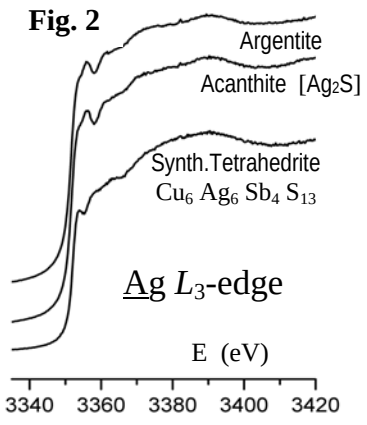


Fig. 2

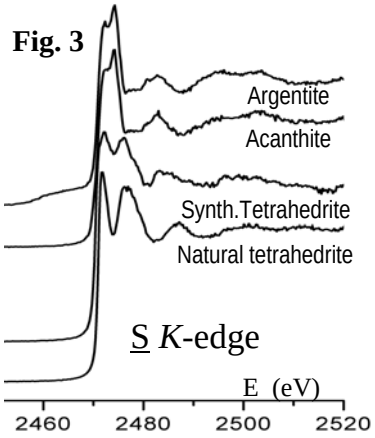


Fig. 3

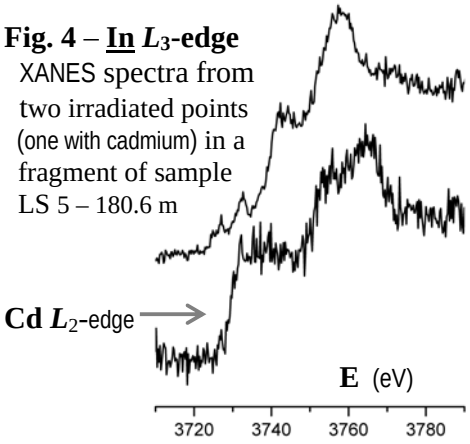


Fig. 4 – In L_3-edge XANES spectra from two irradiated points (one with cadmium) in a fragment of sample LS 5 – 180.6 m

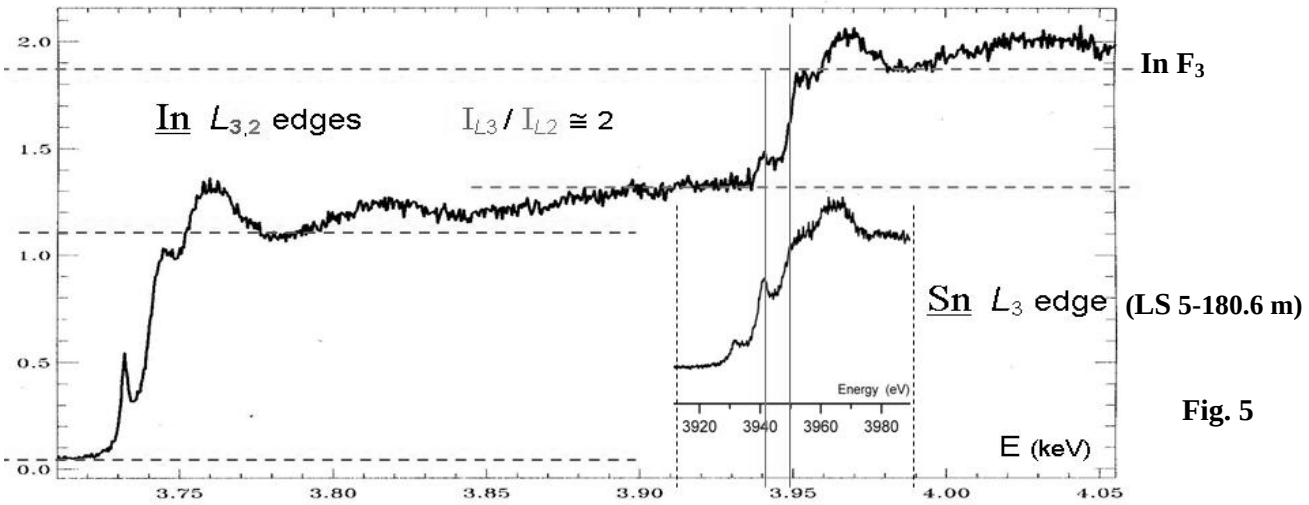


Fig. 5

[1] Benzazoua, M., *et al.* (2003) Tin and Indium mineralogy within selected samples from Neves Corvo ore deposit (Portugal): a multidisciplinary study. *Minerals Engineering* 16, 1291.

[2] Oliveira, V., *et al.* (1998) Geology and geophysics as successful tools in the discovery of the Lagoa Salgada Orebody (Sado Tertiary Basin, IPB), Grândola, Portugal. *Mineralium Deposita*, 33, 170.

[3] De Oliveira, D., *et al.* (2009) Indium in the ore body of Lagoa Salgada, Iberian Pyrite Belt, Portugal. *Procd. 10th Biennial Mtg. Soc. Geoogy Applied to Mineral Deposits*, edt. P.J. Williams *et al.*, vol. 1, 424.

[4] Figueiredo, M.O., *et al.* (2010) How metallic is the binding state of indium hosted by excess-metal chalcogenides in ore deposits? *Geophysical Research Abstracts*, vol. 12, EGU 2010-10673.

[5] 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. To be presented as a poster at *IMA 2010-Bonds & Bridges: Min. Sci. & Applications, Symp.* MA-92, Budapest/Hungary, August 21-27.