



Experiment title: The binding state of In and Sn in sulphides: a XANES study at the L₃-edge

Experiment number:
EC-450

Beamline: ID-21	Date of experiment: from: 26 June 2009 to: 30 June 2009	Date of report: 2009.08.27
Shifts: 12	Local contact(s): Dr. Vincent de Andrade	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

*T.P. Silva, *M.O. Figueiredo, J.P. Veiga, INET/IGM, Geological Data Centre, 2721-866 Alfragide & CENIMAT / I3N, Mater. Sci. Dept., Fac. Sci. Technology, New University of Lisbon, 2829-516 Caparica, Portugal

* D. De Oliveira, D. Rosa, INET/IGM, Geological Survey, Estrada da Portela, 2721-866 Alfragide

Report:

Indium and tin are scarce metals that have lately gained increasing relevance in the production of “high-tech” devices based on new materials (e.g., ITO, CIS, CIGS) and innovative technologies (LCDs, OLEDs, etc). While Sn has a dominant lithophile behaviour, occurring locally concentrated as an oxide (cassiterite, SnO₂), In is typically chalcophile and occurs mainly dispersed within polymetallic sulphides, seldom forming specific minerals. Accessory minerals from Neves-Corvo polymetallic sulphide ores (Iberian Pyrite Belt, IPB) are known to carry interesting bulk contents of both In and Sn [1,2]. On the other hand, synthetic indium chalcogenides are recognized to enclose polycations [3], either dimmers [(In₂)⁴⁺ in In₆Se₇] or trimmers [(In₃)⁵⁺ in In₄Se₃]. Once the closest packing anionic array configured by sulphur anions in massive copper sulphides (not seldom carrying In) displays unfilled interstices, tetrahedral and octahedral, a tendency towards metal-metal interactions to form mixed-valent indium could be achieved by filling closely located interstitial sites [4].

During a previous experiment (EC-290, report dated July 23, 2008) polished surfaces which mineralogical constitution was studied under the optical microscope (reflected light) have disclosed difficulties in attaining the required vacuum level and in clearly identifying indium in the energy dispersive XRF spectrum due to the overlapping of In L α and K K α lines (from mounting resin). Nevertheless, challenging results were obtained for a few In L₃-edge XANES spectra when irradiating a fragment of sulphide ore (bulk sample).

The aim of the present experiment was to perform a micro-mapping of In and Sn in selected fragments of polymetallic sulphide samples from IPB deposits, using scanning X-ray microscopy (SXM) and thereafter to investigate the electronic state of these elements using X-ray absorption spectroscopy at the L₃-edge. A significant improvement in SXM analysis was attained by fitting of the XRF spectrum with PYMCA; due to the low concentration of indium in the ore samples, spectra deconvolution (including escape peaks) was crucial, making possible to collect In and Sn XANES spectra at the same irradiated point. Once model compounds of indium had already been studied (thin films of indium-tin-oxide, indium metal and synthetics containing In⁺ and In³⁺ - namely, InF₃ in which XANES spectrum a “white line” was assigned), only a few additional spectra were collected for comparison, including In-metal for energy calibration.

Model phases for different electronic states and coordination environments of tin were irradiated: the metal (a ESRF standard foil of “white tin”), oxide minerals - cassiterite, SnO₂ (Sn⁴⁺ in octahedral coordination) and romarchite, SnO (with a litharge-type crystal structure), sulphide minerals - herzenbergite, SnS (with

distorted NaCl structure) and stannite, $\text{Cu}_2\text{FeSnS}_4$ (a sphalerite-derivative), plus a commercial compound, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$.

In L_3 -edge was scanned from 3.71 to 3.80 keV in fluorescence yield (FY) mode and Sn L_3 -edge from 3.91 to 4.02 keV in the same mode. Fragments of a In-containing ore sample (LS5-180.6, pyrite-rich with ~90 ppm In according to Actlabs analysis) were irradiated at different points and various scans were performed per point. From a total of about 1230 registered scans (526 for In and 665 for Sn), 78 good XANES sum-spectra were obtained (30 and 42 respectively).

In two irradiated model mineral sulphides - bornite and chalcopyrite - silver was detected in the XRF spectra along with tin and Ag L_3 -edge XANES spectra (3.33 to 3.50 keV) were also collected.

Fig. 1 illustrates the Sn L_3 -edge XANES spectra collected from model compounds and fig. 2 reproduces XANES spectra obtained for Sn and In L_3 -edges at the same points in one ore fragment. These spectra display similar trends (including two white lines) and are at present under study. Preliminary results concerning In were presented at the recent XVIIIth Internat. Materials Research Congress, IMRC2009 [5].

Further work is nevertheless necessary to fully interpret the spectra collected from polymetallic sulphides.

Fig.1- Tin model compounds

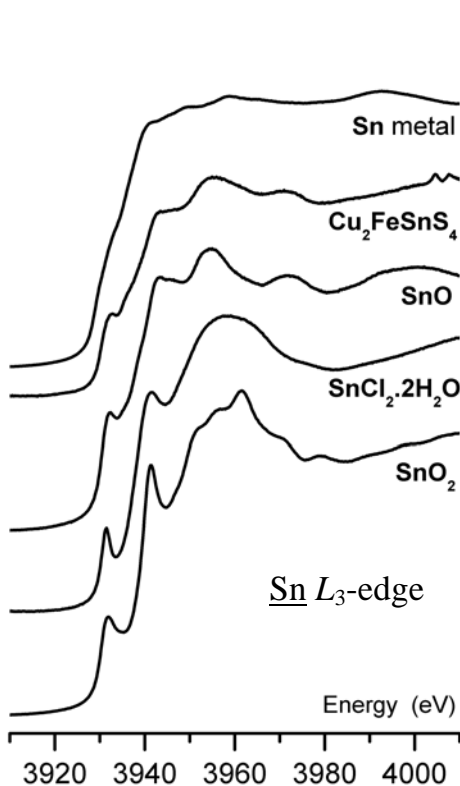
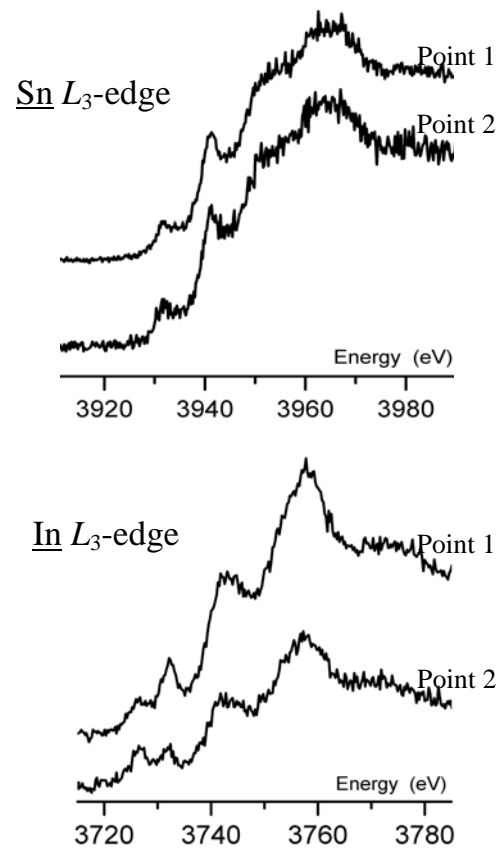


Fig.2- Sample LS 5 – 180.6m, fragment



- [1] Gaspar, O.C. (2002) Mineralogy and sulphide mineral chemistry of the Neves-Corvo ores, Portugal: Insight into their genesis. *Canad. Miner.* **40**, 611.
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- [3] Epple, M., *et al.* (2000) Crystal-chemical characterization of mixed-valence In-chalcogenides by X-ray absorption spectroscopy (EXAFS). *Zeit. Krist.* **215**, 445.
- [4] Figueiredo, M.O., Silva, T.P., *et al.* (2007) Searching for In-carrier minerals in polymetallic sulphide deposits: digging deeper into the crystal chemistry of In chalcogenides. *Proc. 9th Biennial SGA Mtg.*, Dublin, 1355.
- [5] Figueiredo, M.O. & Silva, T.P. (2009) The binding state of indium in natural chalcogenides: A XANES approach through the L_3 absorption edge. *XVIII Internat. Mater. Research Congress*, Cancún/Mexico, August 16-20. Poster.