



	Experiment title: Selenium in wastes from the old mine of São Domingos in southern Portugal (IPB): retained in relics of former ore chalcogenide minerals or already attached to oxygen?	Experiment number: EV-13
Beamline: BM-25A	Date of experiment: from: 14 June 2013 to: 18 June 2013	Date of report: 2013.08.27
Shifts: 12	Local contact(s): Dr. Eduardo Salas	<i>Received at ESRF:</i>
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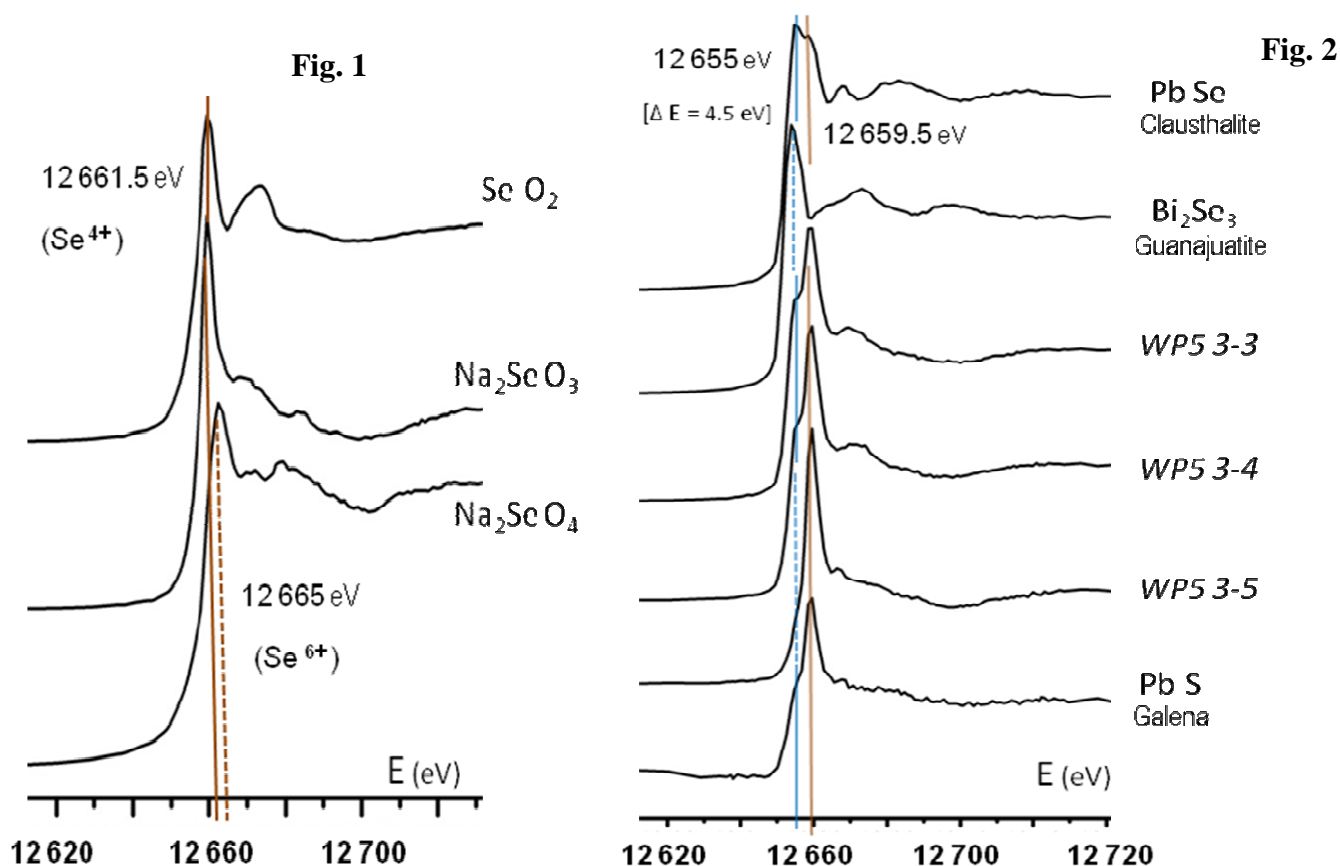
Report:

Mine wastes represent two quite opposite interests since they configure simultaneously an environmental concern due to the presence of hazardous metals and other toxic elements and a potential mineral resource. Indeed, the demand of some scarce metals, increased in the last decade, has intensified the search for a sustainable recovery of economically valuable metals from residual mine exploitation materials and wastes, thus enhancing the need for a full comprehension of the way these metals are incorporated. Selenium is recognized as an essential nutrient for animals, humans and microorganisms but its toxicity – developed along a complex cycle involving adsorption by soil components (clays and other particulate minerals) and subsequent accumulation by plants [1,2] – is well known; simultaneously, it configures a serious concern as a component of radioactive wastes through its isotope ^{79}Se [3]. Selenium was recently quantified in mining products and waste materials from the sulphur factory at the S. Domingos mine (Iberian Pyrite Belt) exploited until 1966, and contents above 900 ppm were occasionally obtained [4]. The Se-carrier phase(s) could be either oxygen-rich compounds resulting from the sulphide ore processing at the old sulphur factory or relics of a former Se-containing chalcogenide ore mineral – namely, galena (PbS) or bismuthinite (Bi_2S_3). To clarify this uncertainty, a speciation study of selenium was carried out by X-ray absorption spectroscopy (XAS), with the characterization of irradiated materials by high-resolution powder diffraction (HRPD) using the instrumental facilities available at beamline BM-25A (SpLine).

HRPD patterns were collected with a fixed wavelength of 0.82 Å at room temperature. Powdered samples were placed inside a 0.8 mm diameter capillary, which was rotated during exposure. XRD spectra (a total of 10) were collected in a continuous 2θ -scanning mode from 2° to 33° . XANES spectra at the Se *K*-edge (nominally at 12658 eV for elemental selenium) were collected in fluorescence yield (FY) mode using a 13-element Si(Li) solid-state detector and a Si(111) monochromator, by irradiating either powdered samples or mineral fragments placed between two Kapton foils. Clausthalite (PbSe) and guanajuatite (Bi_2Se_3), plus isostructural Se-bearing sulphide minerals - galena and bismuthinite - and the synthetics SeO_2 , Na_2SeO_3 , Na_2SeO_4 were used as model compounds. XANES spectra of Zr and Zn metal foils (transmission mode) and gray Se (FY mode) were collected for energy calibration. Whenever convenient, X-ray fluorescence (XRF) spectra were registered using *PyMca* program. From a total of more than one hundred scans, thirty good Se *K*-edge XANES spectra were obtained by averaging about 5 scans per irradiated sample.

Profiting from the energy proximity of W and Re *L*₃-edges relatively to Se *K*-edge, a preliminary search for tungsten and rhenium state in the studied mine waste materials was also carried out.

Se K-edge XANES spectra obtained for the oxide reference compounds are reproduced in Fig. 1, showing that the white-line maximum energy responds to the formal valence of selenium cationic species (selenite, Se^{4+} , and selenate, Se^{6+}). Fig. 2 compares the spectra collected from selenide model minerals and from the studied mine waste samples; for a quick comparison, the energies of white-line maxima are indicated.



Obtained spectroscopic data conform to the presence of various oxidation states in the irradiated mine waste samples [5,6], including selenide [Se^-] and possibly diselenide [$(\text{Se}=\text{Se})^-$] species. Indeed, the energy corresponding to the white-line maximum in the spectrum collected from guanajuatite (isostructural with bismuthinite, Bi_2S_3 and stibnite, Sb_2S_3) reflects the expected occurrence of Se–Se interaction/binding. The studied galena sample (with a minor replacement of sulphide [S^-] by selenide [Se^-]) is oxidized at least in surface, and the layout of Se K-edge XANES spectrum collected from clausthalite (isostructural with galena) suggests the presence of multiple oxidation states, also anticipated for the complex mine waste materials which dominant mineral phase is either anglesite, PbSO_4 (WP5 3-3 & 3-4) or jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ (WP5 3-5).

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