	Experiment title: Determination of the oxidation state of Ge, Cu and Fe in zoned Ge-rich sphalerite from the Saint-Salvy Zn-Ge deposit (Tarn, France)	**Experiment number**: ES-64
Beamline: BM23	**Date of experiment**: from: 03/10/2013 to: 09/10/2013	**Date of report**: 27/02/2014
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Report:

Scientific stakes and aim of the study

The increasing worldwide demand in germanium (Ge) is driving renewed research for understanding its geological cycle and the factors controlling its concentration in minerals. Ge is a critical metalloid of high importance in high-tech devices and optoelectronic devices. It averages 1.4 ppm in the Earth's crust and is mostly diluted in silicates. However, Ge can reach several thousands ppm in oxides and sulphides, particularly in sphalerite (ZnS) of low-*T* Zn-rich ore deposits in which it represents the most valuable by-product[1]. Several studies suggest that coupled substitutions in Zn tetrahedal sites by mono-, tri-, or tetravalents trace elements (e.g., Ge^{4+}) should be responsible for their enrichments in sphalerite, though their oxidation states remain mostly unconstrained[2-4]. Our recent study on sphalerite from the Saint-Salvy deposit (France) points out that Ge and related trace elements can be anthetically distributed among different types of compositional zonings in sphalerite due to crystallographic controls[5]. Accordingly, we report an *in situ* μ-XANES investigation of Ge, Cu and Fe oxidation states in sphalerite compositional zonings at the K-edges.

Material and experimental techniques

The Ge, Cu and Fe K-edges were recorded at the BM23 beamline for three thin sections of the Saint-Salvy sphalerite ore with different Ge grades, together with sphalerite from the Kipushi deposit (R.D. Congo) for comparison. Other sulphides were analysed for a calibration purpose: renierite, germanite, a Ge-rich chalcopyrite (for Ge, Cu and Fe K-edges), bornite, covellite (Cu K-edge), pyrite, arsenopyrite (Fe K-edge), and synthetic GeS (Ge K-edge). The following methodology was applied: (1) μ-XRF mapping of Ge, Cu and Fe to select the richest spots in both zoning types, and (2) collection of K-edges μ-XANES spectra for these elements. XRF maps were recorded at 11.2 keV prior to the collection of μ-XANES at the K-edges with less than 1 μm drift of the incident ~3×3 μm X-ray beam. Excitation energy were selected using a Si(111) double-crystal monochromator, the BM23 beamline includes a micro-XAS setup using an optical microscope and a Vortex silicon-drift detector.

The raw XRF signal was converted into element maps using batch curve-fitting of Ge Kα (convoluted with Zn Kβ) and Cu Kα and ROI imaging for Fe. Edges positions were determined using the centroid of the corresponding peak on the first derivative. Intermediate mixture spectra were assessed using linear combinaison fits between GeS (Ge^{2+}) and renierite (Ge^{4+}) for Ge, and two extreme sphalerites for Cu and Fe.

Results and discussion

Some μ-XANES spectra showed regular drifts in energy (~0.5 eV) after going from one element to another that is probably caused by thermal destabilisation of the monochromator after changing the selected X-ray energy. Drifted spectra have been removed from the dataset. Element distribution on XRF maps are consistent with previous observations by SEM maps and LA-ICP-MS analyses (Fig.1a). Ge and Cu are enriched in sector zonings whereas Fe is enriched in rhythmic bands. Ge K-edge spectra have been measured only in spots richer than ~700 ppm Ge due to interferences between Ge Kα and Zn Kβ (in sectors zonings for Ge). Ge is correlated to Cu in zoning types due to coupled substitutions of Zn, thus, Cu should be a good proxy to measure if redox variations occurs between zoning types. Moreover, Fe could record redox variations independently from coupled substitution mechanisms as it directly substitutes Zn.
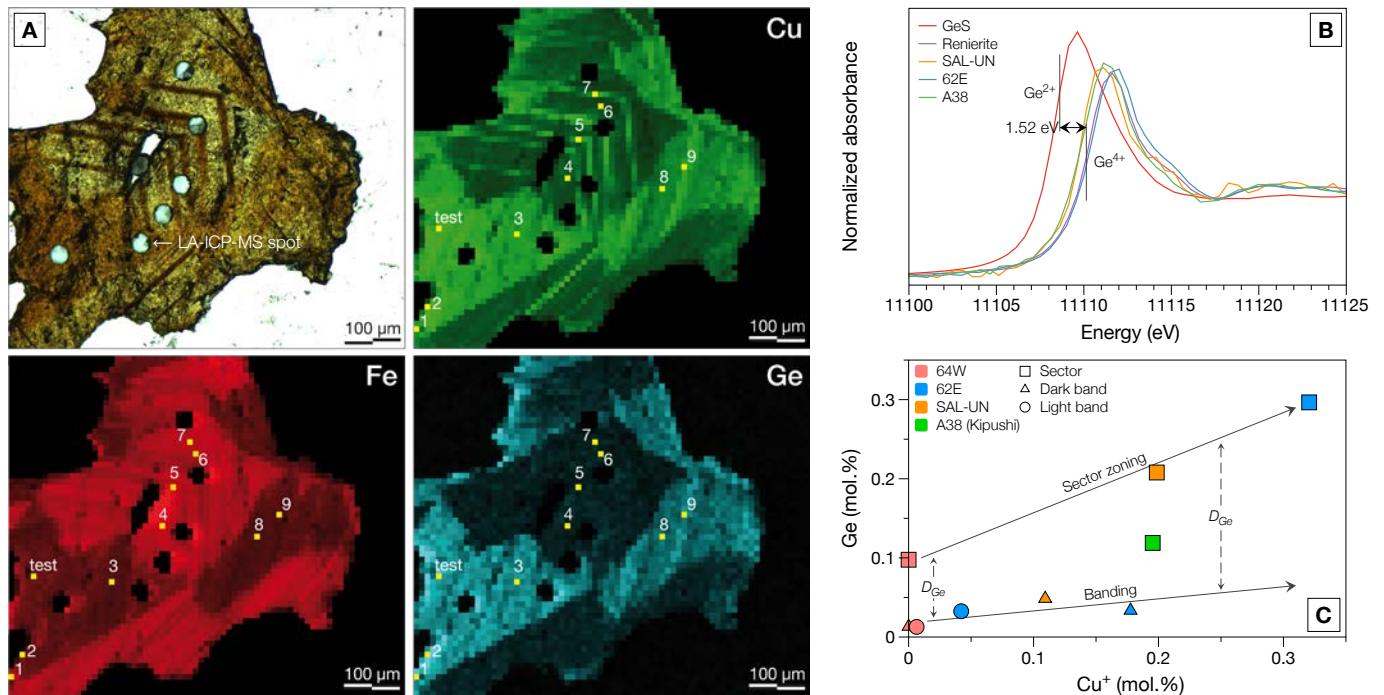

Fig.1: A. μ-XRF maps of a Ge-rich sphalerite (Saint-Salvy) and μ-XANES spots. Spots 'test'-1-2-3-8-9 in sectors, spots 4-5-6-7 in rhythmic bands. B. Ge K-edge spectra in sphalerite, renierite and GeS. C. Ge (mol.%) *vs* Cu^+ (mol.%), D_{Ge}=[Ge]$_{sect}$/[Ge]$_{band.}$

No significant variation in the edge position has been observed among and between zoning types. However, a consistent separation of the Cu and Fe edges positions of ~1.5 eV have been observed beween extreme samples: sample 64W (St-Salvy) stands as the most 'oxidised' and A38 (Kipushi) as the most 'reduced'. Despite no Ge K-edge spectrum for 64W (Ge-poor) we note that the difference of ~0.4 eV between 62E and A38 (Fig.2b) is smaller than those of ~0.8 eV and ~0.7 eV for Cu and Fe, respectively, which suggests that all Ge is present in a formal Ge^{4+} oxidation state. Concerns raised for calibrating Cu and Fe oxidation states with sulphides other than sphalerite in view of their very different edge features. For a first-order assessement, we assumed that the 'reduced' sample (A38) represents Cu^+ and Fe^{2+} and the 'oxidised' one (64W), Cu^{2+} (despite no characteristic $1s{\rightarrow}3d$ transitions pre-edge) and Fe^{3+}, and used them as standards. There is a good correlation between Cu^+ and Ge (Fig. 2c) which strongly support that incorporation of Ge is enhanced with increasing Cu^+. Moreover, two trends are observable between the zoning types (Fig.2c), suggesting an increase of the partionning coefficient with Cu^+ content and thus with the 'reduced' degree of the sample. This innovative work fully supports and completes the current knowledge on the incorporation mechanisms of economic trace metals in sphalerite drawn by previous works[2,5,6]

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