



	Experiment title: Germanium crystal chemistry in Ge-rich zoned Cu-sulphides: combined μ -XRF mappings and <i>in situ</i> Ge K-edge μ -XAFS	Experiment number: ES-305
Beamline: BM23	Date of experiment: from: 02/09/2015 to: 08/09/2015	Date of report: 12/02/16
Shifts: 17	Local contact(s): Olivier MATHON	<i>Received at ESRF:</i>
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Report:

Scientific stakes and aim of the study

The increasing demand in germanium (Ge) for the high-tech industry is driving renewed research for refining our knowledge of its geological cycle and the factors controlling its concentration in minerals. It averages 1.3 ppm in the Earth's crust and is mostly partitioned into silicates. However, Ge can occur as a significant trace element in oxide and sulphide minerals, and represents a highly valuable by-product in Pb-Cu-Zn ores¹. Among Ge-rich sulphides minerals, sphalerite (ZnS), one major and most studied economic source of Ge, can host up to 3000 ppm Ge. Ge enrichments may also occur in Cu-sulphides up to thousands ppm, e.g., up to 6000 ppm Ge were reported in chalcopyrite (CuFeS₂) from Barrigão, Iberian Pyrite Belt, Portugal², or rarely occur as Ge-sulphides grading 6–18 wt.% Ge, e.g., renierite from Kipushi, Central African Copperbelt, D. R. Congo³. Constraining the oxidation state of Ge in Cu-sulphides is crucial for its incorporation mechanism in Cu-sulphides to be understood. Thus, combining *in situ* XRF to XAFS at the microscale is privileged to succeed in this investigation. Synchrotron-based techniques will be coupled to trace element (LA-ICP-MS) and Ge isotope (MC-ICP-MS) analyses in order to better understand the mechanisms involved in Ge enrichment, partitioning, and isotopic fractionation in Cu-sulphides.

Material and experimental techniques

The Ge K-edges were recorded at the BM23 beamline for three thin sections of the Cu-sulphides from Barrigão and Kipushi ore with different Ge grades. Other sulphides were analysed for a calibration purpose: renierite, germanite (Ge⁴⁺) and synthetic GeS (Ge²⁺). The following methodology was applied: (1) μ -XRF mappings, and (2) collection of Ge K-edges μ -XAFS spectra. 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. XRF maps were recorded at 12 keV prior to the collection of μ -XAFS at the K-edges with less than 1 μ m drift of the incident $\sim 3 \times 3 \mu$ m X-ray beam. The raw XRF signal was converted into element maps (Ge, Cu, Fe, Sb, As) using ROI imaging or batch curve-fitting if necessary. Edges positions were determined using the centroid of the corresponding peak on the first derivative. Ge K-edge XAFS spectra were collected at room temperature by scanning the monochromator over the energy range of 11000–11600 eV with the smallest energy increments around the absorption edge (11070–11110 eV), above which the energy increment was progressively increased, to about 2.5 eV at the upper end of the scan (11600 eV). XAFS spectra were cut at 11600 eV because in

samples having low Ge contents, the Pt L_3 -edge absorption (at 11564 eV), which constitutes the KB mirrors, was visible. The drift in the incident X-ray beam positioning is generally lower than 3 μm . For optimal fluorescence counting, deadtime was adjusted to 10%.

Results and discussion

X-ray fluorescence intensity maps in Cu-sulphides from Kipushi showed homogeneous Ge distributions. In contrast, chalcopyrite from Barrigão showed significant variations in Ge contents due to zoning patterns. XRF-intensity maps suggest that Ge-rich zones, either coating grain borders or in vein-like networks (**Fig. 1**), are superimposed to a primary, Ge-poor chalcopyrite. The broad correlation of Ge with As and the proximity of Ge-rich zones with tennantite grains appear to involve a late-stage hydrothermal overprint that deposited both Ge-rich chalcopyrite and, maybe afterwards, tennantite.

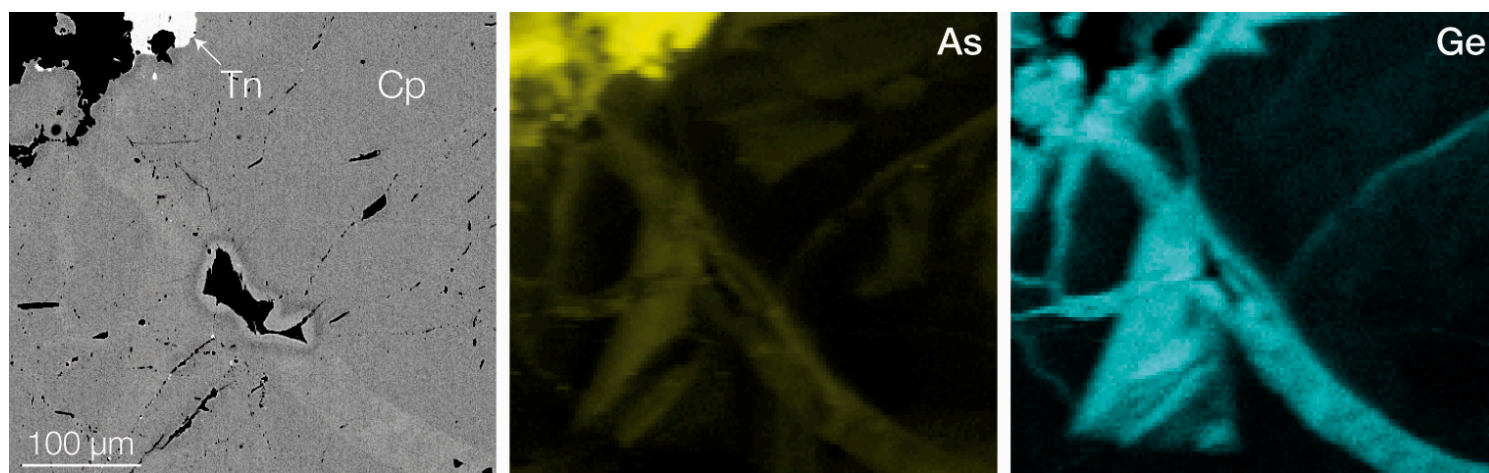


Fig. 1 – XRF-intensity maps of As (log-scaled) and Ge in sample Barr8 ($400 \times 400 \mu\text{m}^2$, step size 3 μm) (Barrigao deposit, Portugal) showing vein-like Ge-rich zones in chalcopyrite (Cp). Tn stands for tennantite.

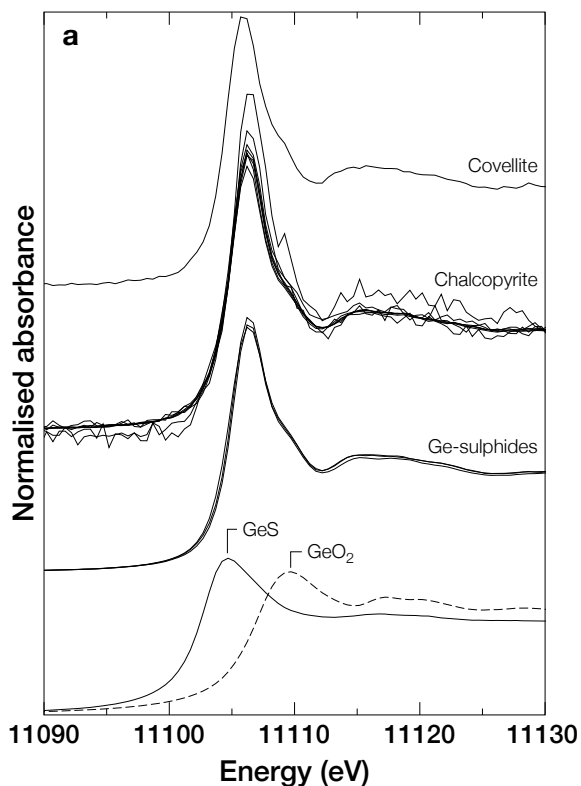


Fig. 2 – Germanium K-edge XANES normalised spectra. Model compounds include GeS (Ge^{2+}), GeO_2 (Ge^{4+} bonded to O), and Ge^{4+} -bearing sulphides. Studied samples include chalcopyrite from Barrigão and Kipushi, and covellite from Kipushi.

These XRF maps, combined with previous SEM maps and multivariate statistical treatment of *in situ* trace elements analyses (LA-ICP-MS), show that Ge and related trace elements (e.g., As, Sb) are anticorrelated to Fe. In addition, XANES data suggest the presence of only Ge^{4+} in chalcopyrite, substituting for Fe^{3+} in tetrahedral sites, most likely through coupled substitution such as $3\text{Fe}^{3+} \leftrightarrow 2\text{Ge}^{4+} + \text{Cu}^+$. These results are consistent with our preceding Ge K-edge μ -XANES study in sphalerite⁴.

References

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