Online Resource 1: Additional information about the analytical procedures

Article title: Processes of enrichment of trace metals for high tech applications in hydrothermal veins of the Ruhr Basin and the Rhenish Massif, Germany

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3.2. Analytical methods

3.2.1. Textural analysis

Energy dispersive X-ray fluorescence spectrometry maps (µ-EDXRF): An endmember database developed for base metal sulfides and associated minerals was used for the creation of mineral distribution maps by use of the "Spectral Angle Mapper" algorithm (Nikonow & Rammlmair 2017). Mixed analysis, boundary, and diffraction effects were considered during manual spectrum interpretation and endmember definition (Nikonow & Rammlmair 2016).

3.2.2. Element composition

Quadrupole laser ablation-ICP-MS: Raw data were exported and processed with a data-handling software tool (Gäbler *et al.* 2011). The need for additional element analysis at each spot for internal standardization by an independent method (*e.g.*, EMPA) was eliminated by using a calibration strategy based on ablation yield correction factors (Liu *et al.* 2008, Danyushevsky *et al.* 2011), where the sum of all cations was normalized to the stoichiometric content of Zn in sphalerite (67 wt.%) and Cu + Fe in chalcopyrite (65 wt.%). A typical analytical uncertainty for laser ablation of less than 20–30 % is expected for the analyzed element concentrations (Cook *et al.* 2009, Danyushevsky *et al.* 2011). Single spots with clear indications of mixed mineral analyses involving underlying minerals or larger mineral inclusions (ragged spectrum) were excluded.

3.2.6. Host rock composition analysis

X-ray fluorescence (XRF), X-ray diffraction (XRD), and inductively coupled plasma-mass spectrometry (ICP-MS) analyses: For XRF analysis, the sample material was melted to homogeneous glasses in a platinum crucible (1200°C, 20 minutes) after adding lithium borate and lithium bromide. The determination of the loss on ignition (LOI) was conducted by a two step heating and holding phase (700°C and 1030°C, 80 minutes in total) in a Pt(95 %)-Au(5%) crucible. The final temperature was held constant for 20 minutes in the melting furnace (HAG-12-1500, Fa. Herzog).

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