HTMET

FKZ 033R131

Innovative Technologien für Ressourceneffizienz

Bereitstellung wirtschaftsstrategischer Rohstoffe

Germany´s base metal ore deposits and their potential for HT elements: trace element distribution in sulfides from the Ruhr district

Henning, S.[1]*, Krassmann, T.[2], Graupner, T.[1], Haas, A.[3], Birkenfeld, S.[4], Gäbler, H.-E.[1], Goldmann, S.[1], Pursche, K.[1]

[1]Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, D-30655 Hannover
[2]Mineral & Exploration Dr. Krassmann, Blumenstraße 21, D-91438 Bad Windsheim
[3]TU Clausthal – IFAD, Walther-Nernst-Straße 9, D-38678 Clausthal-Zellerfeld
[4]Clausthaler Umwelttechnik-Institut GmbH (CUTEC), Leibnizstraße 21+23, D-38678 Clausthal-Zellerfeld
*Corresponding author email: soeren.henning@bgr.de

Introduction

- Hydrothermal ore deposits in the Ruhr district are related to the intersection of normal faults and anticlinal axis in Carboniferous mud- and sandstones and preserve several million tonnes of inaccessible Pb-Zn resources [1]
- Within this study, the raw material potential of eleven Pb-Zn-Cu deposits was investigated with focus on concentration and distribution characteristics of high tech (HT) elements and the data compared with ten deposits from the nearby “Bergisches Land” district (Fig. 1)
- Therefore, 54 Westphalian sulfidic ore samples, taken from collections, were investigated

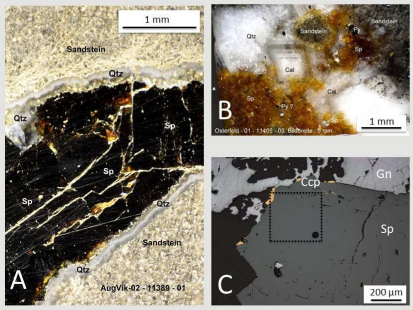

Figure 2: *Optical microscopy images showing: (A) Silification of sandstone as indicated by quartz rims (Qtz); (B) Zoned, idiomorphic calcite crystals (Cal), pyrite crystals (Py) and replacement of calcite and sandstone by sphalerite (Sp); (C) Chalcopyrite (Ccp) at the contact between sphalerite and galena (Gn); 40 µm laser spot (black hole) indicates an In enriched area, which was subsequently mapped by EMPA (square see Fig. 6 A,B).*

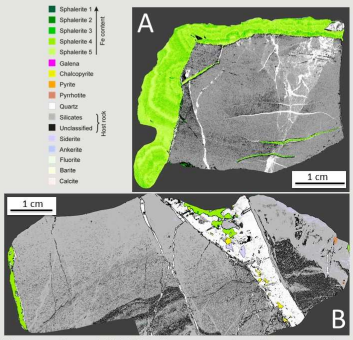

Figure 3: *µ-EDXRF images showing samples with hydrothermal sulfides (Sp, Ccp) and gangue (Qtz, Ank, Sd) in sandstone from the Ruhr district; Growth zoning of sphalerite is indicated in a few samples by varying Fe contents (A); commonly Fe is low.*

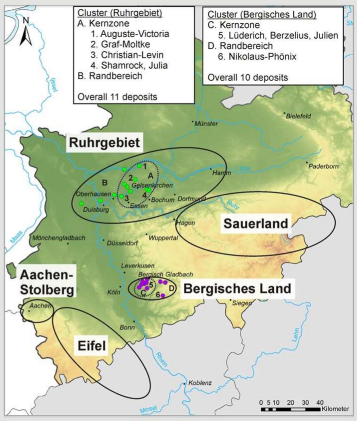

Figure 1: *Sample locations in the Ruhr (green) and “Bergisches Land“ (purple) districts divided into two clusters. Further shown areas are currently under investigation.*

Methods

- Mineralogical analyses using µ-EDXRF and optical microscopy
- Quantitative trace element analysis of sphalerite was conducted using a PlasmaQuant MS Elite quadrupole ICP-MS coupled with a 213 nm laser ablation unit
- Up to 50 spots per sample (40 µm spot size); quantified by using an in-house sulfide reference material [2]
- Studies on HT element distribution in sphalerite were conducted by a Jeol JXA-8530F Hyperprobe (FEG-EMPA)

Results

- Mineralogical analyses confirmed the influence of earlier silification and fracturing on metal precipitation (Figs. 2,3)
- Sphalerite in the Ruhr district commonly has low Fe (< 2.5 wt.%) and a large variability for all trace elements (e.g. Cu 200 - 3100 ppm, max. 0.9 wt.% Cu (mineral inclusions?))
- The HT elements Ga and Ge were measured in elevated amounts in most samples of the Ruhr district (30 - 150 ppm in average) (Fig. 4)
- Elevated In contents occur only in a few samples with values up to 0.2 wt.% in single laser spots
- Compared to the Ruhr district, Cu and HT element concentrations are generally lower in the “Bergisches Land“ district (Fig. 4)
- A high variability of all trace elements is not only restricted to different sphalerite grains, but also present in domains within single grains
- To illustrate this variability, sphalerite was mapped by EMPA
- Within the sphalerite grains, Ga, In and Cu are enriched in < 50 µm wide bands (Figs. 5,6)
- Although laser ablation data indicate a correlation of Ge/Ga/In with Cu, EMPA mapping only partially confirms this correlation within the zoning/domains

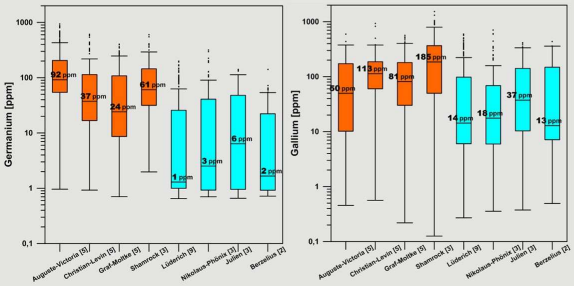

Figure 4: *Boxplot diagrams showing Ge and Ga concentration in sphalerite. Median values of Ruhr district deposits (orange) show generally higher values for Ge and Ga than those from the “Bergisches Land“ district (blue). The number of samples is added in brackets.*

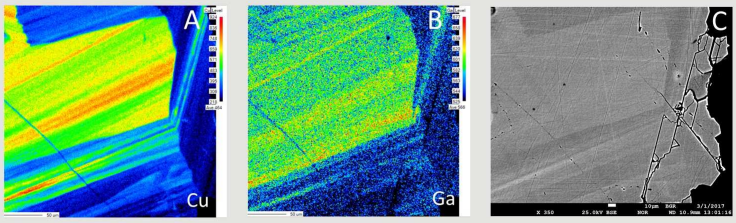

Figure 5: *EMPA mapping of Cu (A) and Ga (B) (25 kV, 40 nA) indicating the presence of Ga in a Cu enriched sphalerite domain (see BSE image C). False colour scaling indicating low (blue) and high (red) concentration levels.*

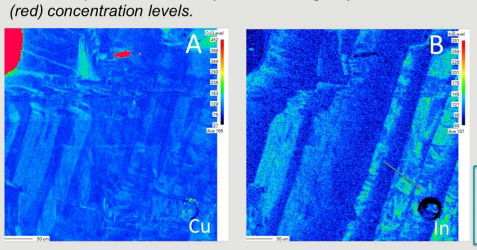

Figure 6: *EMPA mapping of Cu (A) and In (B) (15 kV, 40 nA) in sphalerite (see Fig. 2C). A 40 µm laser spot cuts through In zoning which is partly related to Cu zoning; high Cu values (red) represent chalcopyrite inclusions.*

Conclusions

- 40 µm laser spots are suitable for determination of the HT element content in a given sample, but characterisation of distribution and substitution mechanisms requires smaller spot sizes
- High variability of all trace elements are related to different domains within the sphalerite grains
- Although both districts have similar host rocks and similar Fe contents of sphalerite, the Ruhr district is characterised by elevated HT element concentrations compared to the „Bergisches Land“
- We suppose an influence of the high amount of organic material (coal layers) in the Ruhr district on the metal precipitation

This study contributes to the project RoStraMet of the BGR and the project HTMET (FKZ 033R131) funded by the German Government (BMBF).

[1] Pilger, A. (1961): Die Blei-Zink-Erzvorkommen des Ruhrgebietes und seiner Umrandung – E1. Das Südliche Mittel des Blei-Zink-Erzganges und die sonstigen mineralisierten Klüfte auf der Zeche Auguste Victoria – Monographien der Deutschen Blei-Zink-Erzlagerstätten, Band 1, Lieferung 3, Beihefte Geologisches Jahrbuch, Bd. 40, S.59-81, Hannover 1961

[2] Onuk, P., Melcher, F., Mertz-Kraus, R., Gäbler, H.-E. and Goldmann, S. (2016): Development of a Matrix-Matched Sphalerite Reference Material (MUL-ZnS-1) for Calibration of *In Situ* Element Measurment by Laser Ablation Inductively Coupled Plasma-Mass Spectrometry. Geostandards and Geoanalytical Research, in press, DOI:10.1111/ggr.12154

GEFÖRDERT VOM Bundesministerium für Bildung und Forschung | FONA Ressourceneffizienz BMBF | BGR Bundesanstalt für Geowissenschaften und Rohstoffe GEOZENTRUM HANNOVER | CUTEC Informationen Ressourcen Energie | TU Clausthal | RECYLEX | MONTAN UNIVERSITÄT | Mineral & Exploration Dr. Krassmann