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PhD Thesis abstract

Selected trace and minor elements in sulfides from the Cu-Ag Kupferschiefer deposit in Poland - implications for silver, rhenium and germanium enrichment

Trace elements in sulfides are a reflection of hydrothermal fluids from which they crystallized and are considered as a proxy for both metal source and mineralizing processes. Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) has emerged recently as a solution to the problem of measuring low-concentrations of trace elements in situ in minerals at the micron-scale and its utilization in ore geology has grown exponentially in recent years. Application of LA-ICP-MS method, paired with electron microprobe and micro-beam X-ray fluorescence (microXRF), to sulphides from the Kupferschiefer deposit in Poland, allows studying hydrothermal ore systems where redox conditions play a dominant role and can overshadow factors such as temperature, salinity and pH in controlling trace element partitioning.

A clear pattern in silver concentration is observed and an almost linear decrease (on a logaritmic scale) from chalcocite/djurleite > bornite > chalcopyrite > sphalerite. It suggests that on a scale of the whole ore district, silver distribution in the deposits of the Fore-Sudetic Monocline could be controlled by the redox conditions and linked to general zonation of Fe^{3+}-Cu-Pb-Zn-Fe^{2+} as well as mineral zonation sequence of hematite-chalcocite-bornite-chalcopyrite-galena-sphalerite-pyrite. Similar pattern is observed for Pb but not for any other trace or minor element.

The majority of analysed sulfides do not contain rhenium above detection limits (0.1 ppm Re), but measurable quantities were found in two types of djurleite. The first one (up to 0.9 ppm Re) is adjacent to “red spots” while carbonate-hosted djurleite constitutes the second group (up to 3.9 ppm Re). This suggests that djurleite could be a preferential host for rhenium in the deposit.

Trace element signatures are linked to a specific mineralization style, for example sulfides adjacent to or surrounded by hematitic “red spot” zones are particularly enriched in some of the redox-sensitive elements: djurleite in V, Se, Re, Au, Hg and Tl, chalcopyrite in V, Se, Hg and Tl, while pyrite in Tl.

A group of sulfide-calcite epigenetic veins crosscutting lithologies and associated with local faults and tectonic zones contains chalcopyrite exceptionally enriched in germanium (up to 5016 ppm of Ge). Results suggest that these veins were formed in processes involving hydraulic fracturing and cracking due to high-pressure fluids. Micro-XRF maps show that the distribution of germanium in chalcopyrite

is heterogeneous and visually resembles dendrite/spherulite-like features suggesting that the dispersal of this element preserves the morphological history of the crystal and indicate fast crystallization. Observed patterns in germanium distribution can be explained by switching between different growth mechanisms (adhesive, 2D nucleation and spiral) manifesting variations between different levels of supersaturation in the mineralizing fluid during chalcopyrite precipitation. It is suggested that besides high salinity and low temperature (80-150°C), fluid overpressure might be one of the crucial factors responsible for germanium enrichment, not only in Kupferschiefer ores but applicable to a wide range of seemingly unrelated deposits worldwide.

Comparison between samples from the Fore-Sudetic Monocline and Nchanga deposit (Central African Copperbelt) indicate that some of the trace element signatures might be basin specific and could be an important additional proxy for metal sources, as chalcopyrite from the Zambian Copperbelt has much lower contents of Mo, Ag, Sb, Tl, Pb but higher contents of In and Sn.