

## **Distribution of Ge-enriched sphalerites in the Pb-Zn deposits of the Drau Range (Eastern Alps, Austria/Slovenia)**

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Sphalerite (ZnS) is known to be a host of a wide range of trace elements and is regarded as a major primary sink for the elements In, Ge, and Ga, classified as critical by the ad-hoc working group on defining critical raw material of European Commission (2010).

We investigated the distribution of Ge-enriched ZnS in the carbonate-hosted Pb-Zn deposits of the Drau Range (Eastern Alps, Austria/Slovenia). Historically, Ge was an economically important byproduct during processing of sphalerites. During the period of active mining, 172 t of Ge were extracted from the Bleiberg mine (Austria)(Schroll, 2008). However, not all sphalerites from the Pb-Zn district of the Drau Range are enriched in Ge.

This study aims to decipher the relation between Ge and other minor/trace elements within the sphalerites. For this purpose, sphalerites originating from the Eastern Alpine Pb-Zn deposits are investigated for their Ge, As, Fe, Pb, Cd, Tl and Cu contents. Furthermore, the trace element patterns are compared to the sulfur isotopic composition of the sphalerites, to test if there is any fluid/reservoir-controlled dependency of Ge-enrichment in sphalerites.

The investigated sphalerites can be characterized by specific trace/minor element enrichment/depletion patterns. Differences in the mineral geochemistry occur on both regional and local scales. The most obvious enrichment/depletion patterns concern the elements Fe (up to ~10 mass%) and Cd (up to ~3 mass%), which act partly as a substitute for Zn. Sphalerites tend to be either enriched in Fe/depleted in Cd or vice versa. High Ge abundances occur in samples that contain more Fe with respect to Cd. The highest Ge concentrations (up to 2800 ppm) have, however, been analyzed in sphalerites showing a maximum Fe concentration of 0.2 mass%. Therefore, Ge enrichment does not correlate positively with further Fe enrichment.

$\delta^{34}\text{S}$  of the sphalerites ranges between +1.8‰ and -30.4‰ indicating a mineralization process triggered by at least two different fluids: one of hydrothermal origin transporting relatively isotopically heavy sulfur. Furthermore, light S-isotopes indicating a fluid of bacteriogen origin. S-isotopic composition seems to correlate with Fe-Cd ratios of the sphalerites. Typically, more Fe-rich ZnS is characterized by light S-isotopes ( $\delta^{34}\text{S} < -22\text{‰}$ ) whereas Cd-rich ZnS often contains intermediate to heavy isotopes ( $> -20\text{‰}$ ). The most Ge-rich sphalerites (1000 – 2700 ppm) from the Jauken deposit (Austria) are also enriched in Fe with respect to Cd, and yet display the heaviest S-isotopic composition we have measured (+1.8 ‰).

Differences in geochemistry (and also in Ge-enrichment) are present on a local and regional scale. Ge-enriched sphalerites occur in certain parts of the large deposits Bleiberg and Mezica and in two smaller deposits (Jauken and Radnig) in the western Drau Range.

At present, we found no evidence for a consistent correlation between the S-isotopic composition and Ge-concentration in the sphalerites, which indicates that Ge-enrichment/-depletion cannot be predicted from the dominance of the involved fluid (e.g. more or less hydrothermally influenced). Ge-enrichment might instead be controlled by the source rock from which the metals for the sphalerites were leached on a regional scale.

### References

Schroll, E. (2008). Die Blei-Zink Lagerstätte Bleiberg die Geschichte ihrer Erforschung. Klagenfurt: Naturwiss. Verein für Kärnten.

Critical raw materials for the EU: report of the Ad-Hoc Working Group on defining critical raw materials.  
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