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Germanium and other trace element (Cd, Cu, Fe, Ga) substitution and speciation in sphalerites from MVT deposits in the United States: Implications for ore genesis and resource recovery

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Germanium (Ge) is a critical element mainly used in electronics, fiber and infrared optics, and photovoltaics. Sphalerite is enriched in Ge from Mississippi Valley Type deposits (MVT) where it is recovered as a byproduct. However, there is a lack of understanding as to why certain zinc (Zn) ores are enriched in Ge.

We explore the distribution, speciation, and substitution mechanisms of trace elements in sphalerites from four MVT districts in the U.S. to gain insight into ore enrichment processes. Districts include the following: Metaline (Josephine and Yellowhead ores, Washington), Central Tennessee (TN), East TN, and Tristate (Tar Creek Superfund Site, Oklahoma). Sphalerites contain 300 (Josephine), 170 (Yellowhead), 400 (Central TN), 20 (East TN), and 140 (Tar Creek) mg kg^{-1} Ge on average, and maximum concentrations reach over 1,000 mg kg^{-1} for all districts, except East TN [1, 2]. Copper (Cu) and Ge positively correlate in Metaline, Central TN and Tar Creek sphalerites, generally with a molar ratio of 2:1; the occurrence of mainly Cu^{+1} and Ge^{+4} is consistent with co-substitution of $2Cu^{+1} + Ge^{+4} = 3Zn^{+2}$. Additionally, Central TN sphalerites contain sub-grain domains enriched in gallium (Ga) compared to Ge, and exhibit a roughly 1:1 Cu:Ga molar ratio consistent with the co-substitution $Cu^{+1} + Ga^{+3} = 2Zn^{+2}$. In these latter domains, the Ge^{+2} observed suggests direct substitution of Ge^{+2} for Zn^{+2}. Commonly, the Ga-rich domains are optically anisotropic and have synchrotron-based XRD patterns consistent with hexagonal ZnS [3]. Additionally, iron (Fe) and cadmium (Cd) are also present in significant amounts in these sphalerites, but their molar ratio is commonly not close to 1:1 suggesting coupled substitution likely only partially explains their concentrations.

Overall, sphalerites display diverse geochemistry suggesting a range of mineralization conditions can lead to Ge enrichment at the deposit and grain scales. These geochemical insights can help focus exploration efforts and optimize recovery such as targeting Ge-enriched ores based on Cu-rich zones in certain MVT deposits.

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