

Microstructural characterization and in-situ sulfur isotopic analysis of gold-bearing sphalerite from the Edmond hydrothermal field, Central Indian Ridge

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A close Zn-Au association has been noted recently in several polymetallic sulfide deposits from the Indian Ocean hydrothermal systems. However, the role of nanotextural controls on “invisible” gold distribution within sphalerite (the main Au carrier mineral) is still not well understood. In this study, typical Zn-sulfide samples from the Edmond vent field (Central Indian Ridge) can be generally classified into three different groups based on the preliminary results of electron microprobe analysis along with SEM and optical microscopic observations. Among them, sulfosalt-bearing colloform zinc sulfides in sulfate-dominated samples of outer chimney walls usually contain higher contents of precious metals than Fe-rich, massive and disseminated sphalerite in Zn-(Fe)-rich chimney fragments coated by silicified crusts. This later generation of sphalerite (enriched in gold and silver) is represented by coarse-grained botryoidal aggregates of optically anisotropic, porous sphalerite with a strongly disordered structure or hexagonal habit (6H-ZnS), which are actually formed by coalescence and agglomeration of colloidal nanocrystalline particles.

By using high-resolution transmission electron microscopy (HRTEM) and *in-situ* micro-XRD techniques, we carefully investigated the ultrastructure and crystal-chemistry of the {111} twin boundaries and wurtzite-type stacking faults that occur in colloform sphalerite. Submicroscopic electrum and Ag-bearing nanoparticles appear to nucleate on the micro-/nano-pore walls as cavity-fillings, or occur along grain boundaries between chalcopyrite-tennantite inclusions and the host sphalerite. The inhomogeneous distribution of precious metals and other chalcophile elements is generally concordant with the extent of lattice imperfectness as well as various degrees of disordering (i.e., defect density levels) in ZnS domains. Interfaces and defects at the nanoscale might play a key role in promoting the simultaneous introduction of exotic impurities into auriferous sphalerite samples during rapid growth. Even though certain aggregation-state and microstructural features seem to support a biogenic origin of these Fe-poor ZnS particles, the mineralogical and geochemical characteristics of highly-defective sphalerite crystals, in addition to their microscale sulfur-isotope signatures with relatively high $\delta^{34}\text{S}$ values ranging from +6.66‰ to +10.23‰ (N = 32), appear to exhibit signs of abiologically-mediated, rapid precipitation caused by extensive mixing (with seawater) and cooling during the late stage of low-temperature hydrothermal activity at Edmond. The physicochemical conditions and seafloor disequilibrium processes indicated by their ore-forming mechanisms might significantly facilitate the incorporation and mineralization of precious metal elements in sphalerite-bearing ores.

Moreover, Au-Ag redistribution can occur through a variety of pathways involving oxidation, leaching or coupled dissolution-precipitation reactions, probably via structural weaknesses, planar defects and vacancies. Noteworthy, intragrain microcracks/voids and permeable porosity generated in primary Zn-sulfides may also enhance fluid infiltration, thus promote nucleation, coarsening and secondary enrichment of precious metals as well as other impurities. From a

macroscopic view, pervasive hydrothermal alteration/reworking resulted from a long history of high-temperature venting in this field, together with post-depositional supergene replacement processes, are considered to be important for the remobilization and local reconcentration of early-formed precious metals, and may have been responsible for the formation of relatively coarse-grained native gold or silver within recrystallized massive sulfides and chimney debris.