



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

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ABSTRACT

A close Zn-Ag association has been noted recently in several polymetallic sulfide ore deposits from the Indian Ocean. However, the role of nanotextural controls on “invisible” silver distribution within sphalerite (a significant Ag-carrier) is still not well understood. In this study, typical Zn-sulfide samples from the Edmond vent field (Central Indian Ridge) can be roughly classified into three different groups based on their chemical compositions and mineral textures. Among them, sulfosalt-bearing, Fe-poor zinc sulfides in sulfate-dominant outer chimney walls usually contain higher contents of Ag, Cu and Pb (up to wt% levels) than Fe-rich, massive to disseminated sphalerite in Zn-(Fe)-rich chimney fragments coated by silicified crusts. Such sphalerite is represented by colloform/botryoidal aggregates of optically anisotropic ZnS with a strongly disordered structure or hexagonal habit, which are actually formed by coalescence and agglomeration of colloidal nanocrystalline particles. Using high-resolution transmission electron microscopy (HRTEM) and *in-situ* micro-XRD techniques, we have investigated the ultrastructure and crystal-chemistry of the {1 1 1} twin boundaries and wurtzite-type stacking faults that occur in Ag-rich, colloform or porous dendritic sphalerite. Submicroscopic electrum and Ag 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. Interestingly, the inhomogeneous distribution of precious metals and other chalcophile elements is generally concordant with the extent of recrystallization, intragranular porosity as well as various degrees of structural disordering/imperfectness (i.e., bulk defect density) in ZnS domains. Lattice defects and interfaces may play a limited role in promoting the simultaneous introduction of exotic impurities into colloform sphalerite during rapid growth. Even though certain morphological traits and aggregation state at the nanoscale seem to support a biogenic origin of these ZnS particles characterized by admixed polytypic intergrowth structures, the mineralogical and geochemical features of highly-defective sphalerite crystals, in addition to their microscale S-isotope signatures with relatively high $\delta^{34}\text{S}$ values, exhibit signs of abiologically-mediated, rapid precipitation caused by extensive mixing and cooling at Edmond. The physicochemical conditions and seafloor disequilibrium processes indicated by ZnS formation mechanism might facilitate the incorporation and enrichment of Ag or other trace elements in hydrothermal sphalerite.

1. Introduction

Sphalerite is one of the most common sulfide phases as well as an important host mineral for a broad range of minor and trace elements in

ancient/modern volcanogenic massive sulfide (VMS) deposits (Hannington and Scott, 1989; Cook et al., 2009; Ye et al., 2011; Lockington et al., 2014). Wurtzite, a high-temperature hexagonal polymorph of sphalerite, is also the major ore mineral in a number of

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active and inactive chimneys. Over the past three decades, the potential economic importance of precious-metal mineralization in zinc sulfide ores from submarine hydrothermal vent systems has aroused great attention and interest. Zn-rich sulfide assemblages have been found to contain high concentrations of both Ag and Au, especially in many VMS deposits located at mid-ocean ridges (MORs) and back-arc spreading centers (Fouquet et al., 1993; Herzig et al., 1993; Herzig and Hannington, 1995; Moss and Scott, 2001). Typically, Ag-Au enrichment in seafloor hydrothermal precipitates is consistently related to a phase of low-temperature (< 300 °C) venting, commonly within sulfide chimneys associated with Fe-poor sphalerite and late-stage Pb-Sb-As sulfosalts (Hannington et al., 1986, 1991, 1995; Herzig et al., 1993).

Recently, the occurrence of “invisible” precious metals has been reported in a suite of sphalerite-bearing ores from the Edmond chimney samples that contain up to 18.7 ppm Au and 1450 ppm Ag (Wu et al., 2016). Similarly, a close Zn-Ag-(Au) association has also been noted in several sulfide deposits located along the Southwest Indian Ridge (Ye et al., 2012; Nayak et al., 2014; Wang et al., 2014). These findings provide a unique opportunity to examine in greater detail some of the geological factors controlling Au-Ag mineralization in the Indian Ocean hydrothermal systems. However, the microstructural features of these zinc sulfides and their roles in facilitating silver or gold enrichment remain poorly understood. The physicochemical properties of ZnS (especially at the nanoscale) are strongly affected by its formation processes, and thus may indicate its depositional mechanism and ore-forming environment (e.g., Šrot et al., 2003; Moreau et al., 2004; Ciobanu et al., 2011; Xu et al., 2016). Hence, typomorphic characteristics (such as textural and compositional fingerprints) of Ag-rich sphalerite samples may serve as important indicators of their crystallization conditions.

Furthermore, the relationship between impurity incorporation and defects in crystal structure of sphalerite has not been well established yet. Although the solubility limits of trace elements in sphalerite are still not clearly known, previous LA-ICP-MS studies have suggested that the clustering of precious metals into nanoparticles is favored over their incorporation into the ZnS structure as solid solution (e.g., Cook et al., 2009). To some extent, the partitioning of Au and Ag into nanoparticles (during sphalerite precipitation from hydrothermal fluids) may be affected by non-equilibrium factors, especially the defect density and chemical changes/compositional zoning of the host sphalerite. Likewise, extensive incorporation of arsenic and gold nanoparticles in pyrite is commonly accompanied by formation of vacancies and defects (Vikentyev, 2015). Thus, we propose that impurities and nanotextures may have the same catalyzing effects stimulating the incorporation of precious metals in the sphalerite structure. Similar mineralogical/crystallographic controls on trace-element uptake have also been reported for auriferous sphalerite from some ancient and modern massive sulfide deposits (Wohlgemuth-Ueberwasser et al., 2015; Maslennikov et al., 2017). Until now, however, little convincing microanalytical evidence has been presented for the precipitation-remobilization of “invisible” silver/gold enhanced by the effects of impurities, intrinsic defects or interface during ZnS crystal growth.

In this article, we present an integrated mineralogical and geochemical study on typical sphalerite samples from the Edmond hydrothermal system. This field was among the first two confirmed active vent sites discovered on the Central Indian Ridge (CIR) in the early 2000s, which represents a typical basaltic-hosted VMS deposit located on intermediate-spreading, sediment-starved oceanic ridges (Van Dover et al., 2001). By using *in-situ* micro-XRD technique and HRTEM, careful characterization of distinct textures and micro-environments in Ag-rich zinc sulfides enable us to relate chemical measurements, phase identification, and ultrastructural investigation specifically to the occurrences of discrete Ag-Au nanoparticles. The aim of this work is to obtain further insight into the role of lattice defects in non-equilibrium impurity incorporation, as well as the enrichment mechanism of precious metal elements in hydrothermal sphalerite. Combining the abundance of

certain trace elements and *in-situ* sulfur isotope signatures with TEM observations of microstructural features can provide us with abundant useful information on the influence of deep-sea (extreme) environmental factors and mechanisms of the formation of polymetallic sulfide deposits.

2. Geological setting

The Central Indian Ridge is classified as an intermediate-spreading ridge, with a full opening rate of ~47.5 mm/yr (DeMets et al., 1994), whose rift valley trends NNW and is 5–8 km wide (Briais, 1995). The Edmond vent field (23°52.68'S, 69°35.80'E; at a depth range of 3290–3320 m), approximately 160 km NNW away from the Kairei vent field near the Rodriguez Triple Junction (RTJ), is located at the northern end of CIR segment S3 on the eastern rift-valley wall about 6 km from the adjacent ridge axis (Fig. 1A). It is constructed on a small protrusion that extends south from the eastern rift-valley wall and forms the northeast corner of a ~60-m deep basin (Humphris and Fornari, 2001; Van Dover et al., 2001).

The Edmond vent field (~100 m long by 90 m wide) is dominated by old, disaggregated sulfide structures, peripheral relict black-smoker chimneys, and massive sulfide talus, indicating that hydrothermal activity has been focused at this site over a long period of time (Humphris and Fornari, 2001). Orange-brown, Fe-oxyhydroxide sediments covered by extensive microbial mats are common at this field, accumulating to thicknesses of several cm within depressions and coating many of the sulfide structures and much of the talus. Hydrothermal venting (likely fault-controlled) exhibits a wide range of styles and chimney morphologies. High-temperature venting is manifest as discrete clusters of large chimneys (up to 20 m in height and 2 m in diameter) with vigorous black-smoker fluids emanating from multiple orifices and “beehive” structures. Within and between these chimney clusters, smaller (up to 5 m high), branched, candelabra-like structures with orifice diameters of ~2–20 cm ornament the seafloor and discharge black-smoker fluids at slower flow rates (Van Dover et al., 2001). Like many other MOR vent fields, widespread diffuse flow and blocks of anhydrite suggest that sub-surface seawater entrainment and mixing processes occur over a broad area. It has also been inferred that significant albitization appears to occur below the Edmond field (Gallant and Von Damm, 2006).

The Edmond hydrothermal fluids are extremely hot, with a maximum temperature of 382 °C (Humphris and Fornari, 2001). All of the fluids collected from various vent sites at Edmond (Table 1) are characterized by low pH (~3), high iron content (~14 mmol/kg), and several mmol/kg of H₂S (Gallant and Von Damm, 2006; Kumagai et al., 2008). Most notably, the Edmond end-member vent fluids have chlorinities about 70% greater than local ambient seawater due to phase separation of seawater at supercritical conditions, making them by far some of the hottest brines yet observed venting from the Indian Ocean hydrothermal systems (Van Dover et al., 2001), and thus resulting in unusually high concentrations of several dissolved transition metals.

3. Materials and methods

3.1. Sampling information

The Edmond hydrothermal precipitates were recovered from the surface of active mounds and relict sulfide deposits during the Chinese research cruises DY105-17A and DY115-19 (2005–2007) on board the R/V Dayang Yihao. The locations of active vent sites, relict chimneys and three sampling stations are shown in a detailed bathymetric map (Fig. 1B). Basic information about selected sampling sites and typical ore types is listed in Table 2. As described in a previously published article (Wu et al., 2011), hydrothermal precipitates collected by a TV-guided grab sampler represent various types of hydrothermal products

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