Goldschmidt 2025 Abstract
https://doi.org/10.7185/gold2025.27557

Enrichment conditions of critical raw materials in sphalerite from VMS-type ore deposits – opportunities for more cost-effective and sustainable metal extraction

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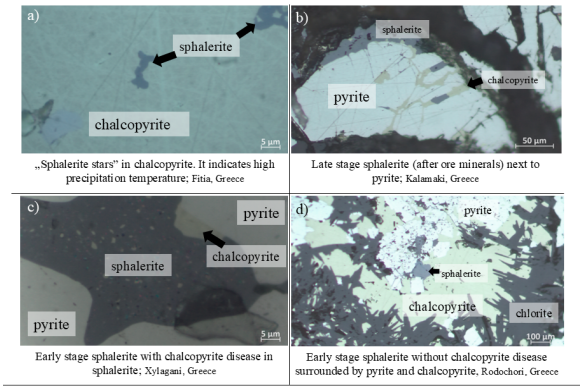
Sphalerite is the most important host mineral for several economically mineable elements, e.g., Zn, Cd, Co, Ga, Ge, In, Tl. However, details on their enrichment conditions are not available in several deposit types, including the volcanogenic massive sulphide (VMS) deposits. Therefore, sphalerite might bear with more economic significance, than previously thought.

Altogether seven VMS deposits were analysed from the Neotethyan realm, including Fitia, Kalamaki, Rodochori, Xylagani *(Greece)*, Gjegjan *(Albania)*, Lasail, Aarja *(Oman)* with SEM-EDS, EPMA, and LA-ICP-MS. Most of them were studied several decades ago. Therefore, detailed modern mineralogical investigations were performed, including identifying new minerals (e.g., sperrylite, electrum from Fitia; clausthalite, molybdenite from Kalamaki) and determination of the mineral precipitation series. Early precipitated sphalerite (Fig.1.) usually contains chalcopyrite disease that sometimes hindered the measurement of pure sphalerite. Mathematically, the presence of chalcopyrite is certain above 0.6-0.7m% Cu limit, based on SEM-EDS and EPMA measurements and Cu-Fe correlation analyses. After removing the suspicious datasets, sphalerite formation temperatures were calculated with different geothermometers, depending on the usability of the methods, yielding results between <138-610°C. Proximal or distal sample location within the deposit, formation during the upbuild or waning of the hydrothermal system and metamorphic overprint could both have effect on temperature conditions. However, the up to 610°C in Fitia might points to its erroneous classification as VMS deposit and thus needs further studies. Formation temperature and Fe-content allows to determine an intermediate sulphidation state for most ore-forming processes, except for Fitia, where low sulphidation state was found.

Iron, Cd, Mn and Ge contents are generally within typical VMS range, though anomalously low Fe and Mn values are characterising Kalamaki, pointing to possible role of regional metamorphic overprint. Copper, Co, Ga, In, and Ag contents are often higher than expected in VMS, that could be caused by local variations of formation conditions (e.g., sudden fO_2 and/or fS_2 change could cause up to 1720 ppm Co content or sudden temperature drop could cause up to 2260 ppm Ga content) (Fig.2.). Data analysis reveals a new Ag-Pb-Bi-(Tl) and Cu-Ag correlation in VMS sphalerite, as the effects of possible micro/nano inclusions can be most likely excluded.

Fig. 1. Petrography



„Sphalerite stars" in chalcopyrite. It indicates high precipitation temperature; Fitia, Greece

Late stage sphalerite (after ore minerals) next to pyrite; Kalamaki, Greece

Early stage sphalerite with chalcopyrite disease in sphalerite; Xylagani, Greece

Early stage sphalerite without chalcopyrite disease surrounded by pyrite and chalcopyrite, Rodochori, Greece

Sphalerite appearance in different textures. On the a) cut, sphalerite stars appeared surrounded by chalcopyrite. On the b) cut, sphalerite precipitated later than other ore minerals, while on the c) and d) cuts, early-stage sphalerite crystals are presented with different inner structures.

Fig. 2. Trace elements composition in sphalerite from every location, using LA-ICP-MS and EPMA measurement data, and the typical amount of each element regarding VMS-type ore deposit according to Frenzel et al. (2016) (see in black)