

## Critical metals in zinc ores: distribution and oxidation state of germanium in hydrothermally- synthesized and natural sphalerite

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Germanium (Ge) is listed as one of the critical minerals by major countries and is recovered as a by-product of mining other commodities, such as Zn and thermal coal. One of the scientific challenges to enabling better exploration and beneficiation of critical minerals as a by-product of major commodities is understanding the geochemical processes that lead to the incorporation of trace elements into the principal host minerals.

We investigated the Ge incorporation mechanism in sphalerite (ZnS) synthesized under hydrothermal conditions which mimic the formation of sediment-hosted Zn-Pb deposits. Sphalerite  $\pm$  galena  $\pm$  barite formed via reactions of Ge  $\pm$  Fe  $\pm$  Cu-bearing brine with calcite and reduced sulfur at 200 °C and water vapor-saturated pressure<sup>[1]</sup> (Fig. 1). The products were examined using multiple microanalytical techniques including synchrotron micro-X-ray absorption near-edge structure (m-XANES). We show that Ge(IV) is incorporated into sphalerite and bonded with reduced sulfur, both in the experimental sphalerite and in natural zinc ore samples from the MacArthur River Zn-Pb-Ag deposits, Australia. Copper K-edge XANES spectra show that copper occurs as Cu(I) in the experimental sphalerite, consistent with previous studies on Cu in natural sphalerite. The experiments reveal that Ge(IV) substitution in sphalerite occurs with and without the presence of other metal ions (e.g., Cu(I)), indicating that Ge(IV) substitution can be accommodated via charge balance by vacancies as well as by coupled substitution in the synthesized sphalerite. *Ab initio* quantum chemical simulations confirm that sphalerite can readily accommodate Ge within the crystal structure and average Zn-S, Zn-Zn, S-S distances are retained when replacing >3 mole% of the Zn sites with Ge(IV), Ge(II), Cu(I) or Fe(II), indicating the resilience and flexibility of the sphalerite crystal structure. These Ge incorporation mechanisms explain the previous observations showing multiple ways of Ge incorporation in natural sphalerite. This study provides experimental and molecular simulation insights for understanding the processes related to the formation and extraction of Ge in zinc ores.

Reference:

[1] Liu, W. et al. (2023) *Geochimica et Cosmochimica Acta* 342, 198-214. <https://doi.org/10.1016/j.gca.2022.11.031>

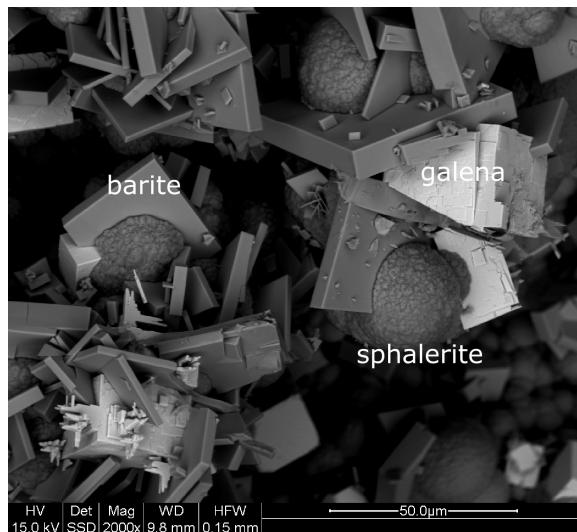


Fig. 1 A backscattered electron image of hydrothermally synthesized sphalerite, galena and barite.