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Understanding incorporation of trace elements in sphalerite from the Ge-bearing Zn-Pb-Ag Prairie Creek deposit, NWT, Canada

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Sphalerite is the main Zn ore mineral, and commonly hosts a variety of trace elements, including Ge, Ga, Cd, and In, which are typical by-products of Zn production. Among these, Ge is particularly significant because sediment-hosted Zn–Pb deposits represent its primary global source. However, the incorporation mechanism of Ge into sphalerite remains debated. Here, we investigate the trace-element geochemistry of sphalerite from the Ge-bearing Zn-Pb-Ag Prairie Creek deposit at both micro- and nano-scale to constrain the mechanisms of its incorporation.

The Prairie Creek deposit exhibits two styles of mineralization: 1) stratabound massive sulfides (SMS) and 2) quartz-carbonate veins (MQV), hosted in sedimentary rocks. Two generations of sphalerite (Sp I and Sp II) occur in both styles and are distinguished by texture, color, and grain size. LA-ICP-MS spot analyses reveal contrasting trace-element behavior. In SMS, Sp I shows enrichment in Ge and Cu (up to 2600 ppm and 4275 ppm, respectively), whereas Sp II exhibits much lower concentrations (<50 ppm Ge; <200 ppm Cu). In MQV, sphalerite displays low Ge content. However, Sp II shows a relative enrichment in Ge, As, Sb, Cu and Ga compared to Sp I. Trace-element mapping reveals distinct spatial associations. In SMS Sp I, Ge locally occurs with Cu, Ag, and Tl, whereas in MQV Sp II, it spatially associates with Cu, Ag, Sb, As, and Ga. Nevertheless, quantitative spot analyses show that, in SMS Sp I, only Cu displays a consistent positive correlation with Ge, suggesting a potentially coupled substitution involving Cu, Ge, and Zn.

In contrast, APT and TEM analyses reveal that Ge and Cu in SMS Sp I predominantly occur as discrete nano Cu–Zn–Fe–Ge sulfides, rather than being lattice-bound. Ge enrichment in SMS is therefore controlled by nano-mineral inclusions rather than Zn substitution. Conversely, in MQV Sp II, Ge is homogeneously distributed within the sphalerite matrix, consistent with incorporation at the sphalerite crystal lattice. These nanoscale contrasted distributions demonstrate that Ge incorporation varies across sphalerite generations, explaining the distinct elemental behaviors observed in the micro-scale data. These results underscore the importance of nanoscale characterization in critical metal research.