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Examination of germanium in sphalerites using multiple complementary approaches

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Understanding the mineral hosts and speciation of byproduct critical elements in ore-forming environments provides insight into the conditions controlling their enrichment in ore deposits, which can aid in exploration, quantification of future resources, and development of extraction methods. We applied a suite of traditional and synchrotron-based techniques to examine the speciation of germanium (Ge) in sphalerite (ZnS) from four mineral districts where Ge is or has been recovered within the United States. Examination of Ge in ZnS by traditional methods is complicated by spatially variable and low Ge concentrations in ores (typically 1-10 mg kg^{-1}), and overlap between the Zn Kβ and Ge Kα X-ray fluorescence signals in energy dispersive detectors. Synchrotron-based techniques are necessary to examine oxidation state, which is critical in understanding the substitution of Ge within the ZnS crystal lattice. We examined the distribution and speciation of Ge and potential co-substituent elements, such as Cu, in sphalerite using micro-focused X-ray fluorescence (XRF) mapping, bulk and micro-focused X-ray absorption spectroscopy (XAS), and micro-focused X-ray diffraction (XRD). A new high energy resolution fluorescence detector (HERFD) was used to collect micro-focused XAS to reduce the contribution from the Zn Kβ to the measured Ge Kα signal, which significantly improved signal to noise and spectral resolution. Multiple energy XRF maps enabled us to map the distribution of Ge between sphalerite and oxidized weathering products in historical mine waste. Both Ge oxidation states (Ge^{2+} and Ge^{4+}) were observed in ZnS, but their abundances varied with the presence and abundance of co-substituent elements (especially Cu, Ga, Sb, and Ag, depending on the deposit). In some cases, the combination of Ge speciation and trace element content measured by electron microprobe indicated specific substitution mechanisms, including: $Ge^{4+} + 2Cu^{+} \Leftrightarrow 3Zn^{2+}$ and $Ge^{2+} \Leftrightarrow Zn^{2+}$. Locally compositional variability correlates with optically anisotropic domains within sphalerite where synchrotron-based XRD mapping suggests hexagonal wurtzite (ZnS) is present. The analytical tools employed here can be extended to other byproduct critical elements in complex matrices in order to more fully understand ore enrichment processes, which have important applications in exploration, resource quantification, and extraction.