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Germanium oxidation state and substitution mechanism in Ge-rich sphalerite from MVT deposits: Constraints from X-ray absorption fine structure (XAFS) and geometric optimization

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Abstract

Sphalerite is a crucial host mineral for germanium (Ge) resources worldwide. However, the oxidation state (+2 or +4) of Ge and its substitution mechanism in sphalerite remain a subject of ongoing debate. The Huize and Maoping deposits are the largest and second largest Pb-Zn-Ge deposits in the Mississippi Valley Type (MVT) metallogenic province in southwest China, respectively. Four types of Ge-rich sphalerite have been identified within these two deposits: C1-Huize, C3-Huize, C1-Maoping, and C5-Maoping. This study employs synchrotron-based microscale X-ray absorption fine structure (μ-XAFS) methods, including X-ray absorption near-edge structure (μ-XANES) and extended X-ray absorption fine structure (μ-EXAFS) analyses, to investigate the Ge distribution, oxidation state, and neighboring atomic environment within the Huize and Maoping Ge-rich sphalerites. The results suggest that the incorporation of Ge^{4+} and Cu^{+} into sphalerite occurs at varying Cu/Ge molar ratios, depending on the availability/concentration of Cu in the sphalerite (i.e., Cu/Ge ≥ 2). On the other hand, Ge^{2+} and Ge^{4+} coexist when Ge and one vacancy (□) substitute for Zn in sphalerite. These different types of Ge substitutions influence the position of Zn atoms in the second neighboring atomic shell in the structure, while they have minor effects on the location of S atoms in the first neighboring atomic shell. The presence of vacancies strongly affects Zn atoms in the second neighboring atomic shell when coupled with Ge substitution in sphalerite, resulting in smaller interatomic distances and significant structural disorder (Debye-Waller factor). Additionally, two Cd^{2+} ions are required to co-replace two Zn^{2+} ions to fill the structural defects caused by vacancies. In contrast, the substitution of Cu^{+} and Ge^{4+} for two Zn ions results in a more ordered spatial structure, which is not distinctly controlled by the Fe content of sphalerite. Based on the characterization of the Ge oxidation state and local structure, we redefined the Ge substitution mechanisms inferred from element correlations: (1) $Ge^{4+} + 2Cd^{2+} + \square \rightarrow 4Zn^{2+}$ and $Ge^{2+} \rightarrow Zn^{2+}$ in C1-Huize; (2) $Ge^{4+} + 2Cu^{+} \rightarrow 3Zn^{2+}$ in C3-Huize and C1-Maoping; and (3) $3Cu^{+} + As^{3+} + Ge^{4+} \rightarrow 5Zn^{2+}$ in C5-Maoping. This study not only elucidates the distribution of Ge in different valence states but also unveils its true spatial structure in sphalerite. These findings have significant implications for investigating Ge substitution and enrichment mechanisms in sphalerite.

Keywords: Germanium, HR-XAFS, Ge-rich sphalerite, MVT deposit