Spectroscopic study on the local structure of sulfate (SO$_4^{2-}$) incorporated in scorodite (FeAsO$_4$·2H$_2$O) lattice: Implications for understanding the Fe(III)-As(V)-SO$_4^{2-}$-bearing minerals formation

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**ABSTRACT**

The incorporation of sulfate (SO$_4^{2-}$) into the scorodite (FeAsO$_4$·2H$_2$O) lattice is an important mechanism during arsenic (As) fixation in natural and engineered settings. However, spectroscopic evidence of SO$_4^{2-}$ speciation and local structure in scorodite lattice is still lacking. In this study, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), sulfur K-edge X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) spectroscopic analyses in combination with density functional theory (DFT) calculations were used to determine the local coordination environment of SO$_4^{2-}$ in the naturally and hydrothermally synthesized scorodite. The SO$_4^{2-}$ retention in natural scorodite and the effect of pH value and initial Na$^+$ concentration on the incorporation of SO$_4^{2-}$ in synthetic scorodite were investigated. The results showed that trace amounts of SO$_4^{2-}$ were incorporated in natural scorodite samples. Scanning electron microscopy (SEM) results revealed that SO$_4^{2-}$ was homogeneously distributed inside the natural and synthetic scorodite particles, and its content in the synthetic scorodite increased slightly with the initial Na$^+$ concentration at pH of 1.2 and 1.8. The FTIR features and XANES results indicated that the coordination number (CN) of FeO$_6$ octahedra around SO$_4^{2-}$ in scorodite lattice is four. The DFT calculation optimized interatomic distances of S-O were 1.45, 1.46, 1.48, and 1.48 Å with an average of ~1.47 Å, and the interatomic distances of S-Fe were 3.29, 3.29, 3.33, and 3.41 Å with an average of ~3.33 Å. EXAFS analysis gave an average S-O bond length of 1.47(1) and S-Fe bond length of 3.33(1) Å with a CN$_{SO_4}$ = 4 for SO$_4^{2-}$ in the scorodite structure, in good agreement with the DFT optimized structure. The results conclusively showed that SO$_4^{2-}$ in the scorodite lattice may be in the form of a Fe$_2$(SO$_4$)$_3$-like local structure. The present study is significant for understanding the formation mechanism of scorodite in natural environments and hydrometallurgical unit operations for waste sulfuric acid treatment.

**Keywords:** Arsenic, scorodite, sulfate, incorporation, local environment

**INTRODUCTION**

Crystalline ferric arsenate (scorodite, FeAsO$_4$·2H$_2$O) is one of the least soluble As phases and a pivotal secondary As-bearing mineral controlling the fate and transport of As in acidic Fe(III)-As(V)-SO$_4^{2-}$-H$_2$O systems, such as arsenic-contaminated soil, hydrometallurgical tailings, and acid mine drainage (AMD) (Giere et al. 2003; Drahota and Filippi 2009; Murciego et al. 2011). Several studies have found that arsenopyrite (FeAsS) and arsenical-pyrite (As-FeS$_2$) solid wastes in abandoned mine tailings were enveloped by secondary scorodite and amorphous ferric arsenate under natural weathering conditions (Flemming et al. 2005; Langmuir et al. 2006; Paktunc and Bruggeman 2010). Furthermore, scorodite precipitation is a sink for As in metallurgical processing due to its high-As content (~32 wt%), low solubility, and good-settling properties (Debekauessen et al. 2001; Fujita et al. 2008b, 2008c, 2009b; Le Berre et al. 2008; Ma et al. 2019; Zhu et al. 2019).

It is well known that scorodite can be formed in natural and industrial settings, where the dissolved Fe and As appear simultaneously with sulfate (SO$_4^{2-}$). For example, the weathering of arsenide or sulfide minerals in natural settings (i.e., AMD) and the utilization of Fe$_2$(SO$_4$)$_3$ or FeSO$_4$ as an iron source for the conversion of arsenic into scorodite in metallurgical plant effluents (Giere et al. 2003; Drahota and Filippi 2009; Murciego et al. 2011). It has been reported that dissolved SO$_4^{2-}$ concentrations in such natural settings and industrial systems are a few orders of magnitude higher than those of toxic elements (e.g., As, Cu$^{2+}$, Zn$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$) at a wide pH range (~3.6 to circumneutral) (Nordstrom et al. 2000; López-Archilla et al. 2001; Casiot et al. 2003; Morin et al. 2003; Maillot et al. 2013). Due to the similar geometry and charge between HAsO$_4^{2-}$ and SO$_4^{2-}$, HAsO$_4^{2-}$ can be incorporated into SO$_4^{2-}$-bearing minerals via the isomorphic substitution for SO$_4^{2-}$ forming solid solutions. For example,