

Sulfur K-edge EXAFS Analysis of Synthetic Schwertmannites and Natural Schwertmannite from the Chinkuashih Acid Mine Drainage Area, Northern Taiwan

Wei-Teh Jiang (江威德) and Chun-Jung Chen (陳君榮)

Department of Earth Sciences, National Cheng Kung University, Tainan, Taiwan

Sulfur K-edge EXAFS analyses of a naturally occurring As-bearing schwertmannite specimen collected from the Chinkuashih acid mine drainage area and three synthetic schwertmannite specimens prepared by different methods and starting materials (mixing of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 solutions, mixing of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Na_2SO_4 solutions, and hydrothermal bath of $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$) was carried out at the NSRRC 16A1 BM beam line in order to investigate the fundamental sorption/incorporation mechanisms of sulfate anions in schwertmannite. An understanding the sorption mechanism of SO_4^{2-} tetrahedra in schwertmannite will help us to resolve the behavior of $\text{As}(\text{O},\text{OH})_4$ tetrahedra as $\text{As}(\text{O},\text{OH})_4$ is substituting for SO_4^{2-} in the schwertmannite structure.

The S K-edge EXAFS spectra (k-space) and Fourier transform patterns of the four studied specimens are shown in Figure 1 and Figure 2, respectively. The spectral quality was poor due to unusual high background and low amplitude of fine structures at the high energy end of the edge, and in part was affected by the presence of Cl in one synthetic sample (Sch-SC). The result of spectral fitting suggests that the bonding lengths of the first sphere coordination are in the range of 0.133-0.143 nm, consistent with a tetrahedrally coordinated S-O bonding distance. However, the calculated coordination numbers are not compatible with the ideal number of 4. The bonding lengths of the second sphere coordination are in the vicinity of 0.190-0.200 nm, comparable with the S-Fe distance in iron sulfides or the S-S distance between corner-sharing sulfate tetrahedra. It might be possible that iron sulfide precipitation occurred during the preparation processes of synthetic schwertmannite. A S-Fe distance of ~ 0.300 nm in the ideal schwertmannite structure (Figure 3) cannot be positively identified.

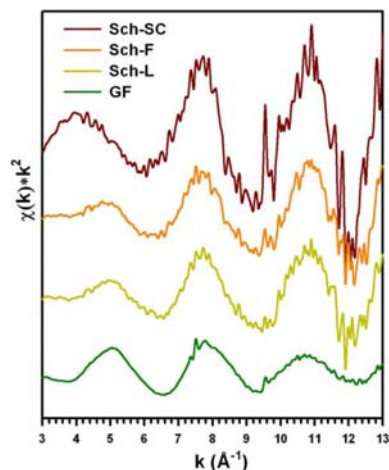


Figure 1. Sulfur K-edge EXAFS spectra (acquired with

the fluorescence mode) of Chinkuashih schwertmannite (GF) and synthetic schwertmannite specimens prepared by mixing of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and Na_2SO_4 solutions (Sch-SC), mixing of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and Na_2SO_4 solutions (Sch-F), and hydrothermal bath of $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (Sch-L).

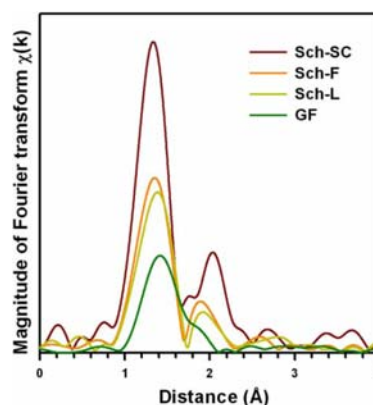


Figure 2. Sulfur K-edge EXAFS Fourier transform patterns of schwertmannite specimens. Symbol notations can be seen in Figure 1.

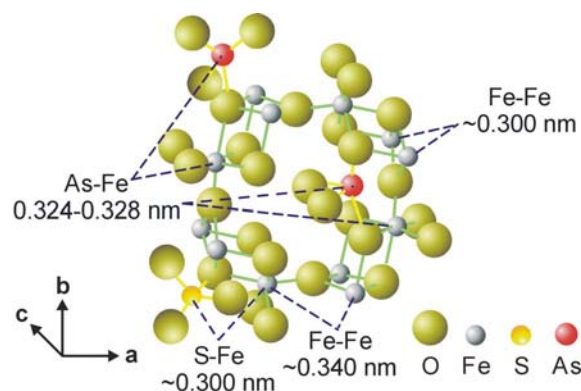


Figure 3. A structural model of schwertmannite with surface bonding of arsenate and sulfate tetrahedra and coordination of an arsenate tetrahedron in the structural tunnel. Note that the ideal S-Fe distance is ~ 0.300 nm.

The aforementioned result suggests that the specimen preparation methods need to be improved and the techniques of datum acquisition and spectral analysis need to be verified with well crystallized sulfate minerals.