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### Title

Reanalysis of the Schwertmannite structure and the incorporation of SO<sub>4</sub><sup>2-</sup> groups: An IR, XAS, WAXS and simulation study

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**REANALYSIS OF THE SCHWERTMANNITE STRUCTURE AND THE INCORPORATION OF  $\text{SO}_4^{2-}$  GROUPS: AN IR, XAS, WAXS AND SIMULATION STUDY.** G. A. Waychunas<sup>1</sup>, S. C. B. Myneni<sup>2</sup>, S. J. Traina<sup>3</sup>, J. M. Bigham<sup>3</sup>, C. C. Fuller<sup>4</sup> and J. A. Davis<sup>4</sup>, <sup>1</sup>E.O. Lawrence Berkeley National Laboratory, Earth Sciences Division, Geochemistry Department ([gawaychunas@lbl.gov](mailto:gawaychunas@lbl.gov)), <sup>2</sup>Princeton University, Department of Geosciences ([smyneni@princeton.edu](mailto:smyneni@princeton.edu)), <sup>3</sup>Ohio State University, School of Natural Resources ([traina.1@osu.edu](mailto:traina.1@osu.edu), [bigham.1@osu.edu](mailto:bigham.1@osu.edu)), <sup>4</sup>U. S. Geological Survey, Menlo Park, CA ([ccfuller@usgs.gov](mailto:ccfuller@usgs.gov), [jadavis@usgs.gov](mailto:jadavis@usgs.gov)).

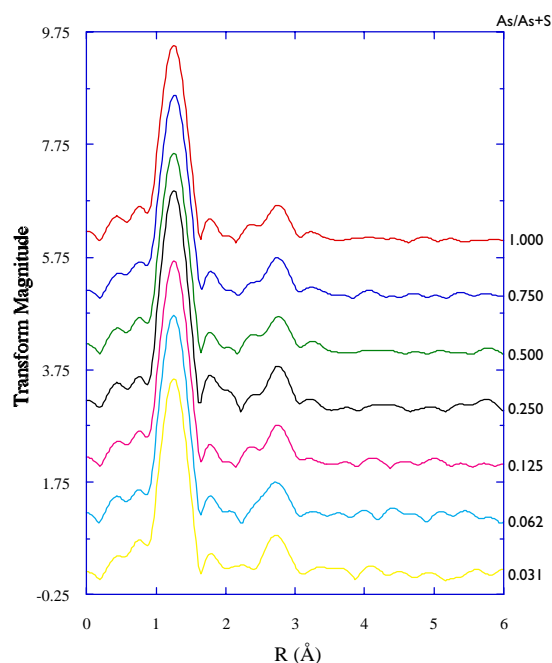
Schwertmannite is a poorly crystallized iron oxyhydroxide with essential structural sulfate that can be a major component in acid mine drainage environments. Original characterization work concluded that the sulfate was largely contained within tunnels of an ordered akaganeite-like structure based on powder XRD, analysis of IR spectra, and sulfate extraction procedures [1]. Since the original description, problems have emerged with the nature of the tunnel sulfate, and with the interpretation of the IR spectra. Other related work has shown that it is now possible to determine sulfate-iron oxide inner sphere binding unambiguously from the S K-edge XANES spectrum. Hence a reassessment of the evidence for the original schwertmannite structure was deemed necessary and timely.

We have carried out detailed characterization of synthetic schwertmannites prepared with sulfate, selenate and arsenate in various proportions using IR spectroscopy, EXAFS and XANES spectroscopy on the S, As, Se and Fe K-edges [2], wide angle x-ray scattering (WAXS) with calculation of pair-correlation functions [3], and simulations of the structure using distance least squares (DLS) methods [4]. This work substantiates the structure as being akin to akaganeite, but with a large portion of structural defects proportional to the sulfate (or other anion) content. The evidence for tunnel occupation by sulfate in the usual sense appears poor. Instead sulfate appears to occupy both inner and outer sphere positions on the surface of schwertmannite crystallites, and probably on the internal surfaces of defect regions within the structure. We suggest that it is the growth of schwertmannite around the surface sorbed sulfate that results in structural disorder correlated with sulfate content.

Selenate behaves essentially identically to sulfate, but the substitution of arsenate even at low concentrations for sulfate disrupts the structure resulting in poorly crystalline ferrihydrite or other highly disordered iron oxyhydroxides. Only inner sphere binding is observed for the arsenate at all concentrations (Figure 1), suggesting that it is the outer sphere surface complexation of sulfate and selenate that stabilizes the tunnel structure.

We suggest a number of possible nanocrystalline structural motifs that can explain the observed powder diffraction patterns qualitatively and the stabilization of the structure without tunnel occupation. Should these structures be shown realistic, they may represent a more widely existing set of defect structures that incorporate "sorbed species" via an "entrapment" mecha-

nism. Possibilities for designing analogous structures for the intentional collection or dispersal of particular complexes will be discussed.



**Figure 1.**  $\text{AsO}_4\text{-SO}_4$  substituted schwertmannites. As K-edge radial structure functions. All As is inner sphere mainly with a bidentate sorption complex.

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