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Structure of Amorphous Ferric Arsenate from EXAFS Spectroscopy and Total X-ray Scattering

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Short-range ordered ferric arsenate ($FeAsO_4 \times n H_2O$) is a secondary As mineral frequently encountered in acid mine-waste environments. Its structure has been proposed to resemble that of scorodite ($FeAsO_4 \times 2H_2O$) in which isolated FeO_6 octahedra share corners with four adjacent arsenate (AsO_4) tetrahedra in a three-dimensional network (scorodite model). Conversely, short-range ordered ferric arsenate was postulated to consist of single chains of corner-sharing FeO_6 octahedra being bridged by arsenate bound in a monodentate binuclear ^{2}C complex (butlerite/fibroferrite model). In order to test the accuracy of both structural models, we synthesized ferric arsenates and analyzed their structure by As and Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy and total X-ray scattering. We found that both As and Fe K-edge EXAFS spectra were most compatible with isolated FeO_6 octahedra being bridged by AsO_4 tetrahedra (R_{Fe-As}= 3.33 ± 0.01 Å). EXAFS shell-fits and reduced pair distribution functions, $G(r)$, indicated a lack of evidence for single corner-sharing FeO_6 linkages in ferric arsenate. Wavelet-transform analyses of the Fe K-edge EXAFS spectra of ferric arsenates complemented by shell fitting confirmed Fe atoms at an average distance of 5.3 Å, consistent with crystallographic data of scorodite and in disagreement with the butlerite/fibroferrite model. A scorodite-type local structure of short-range ordered ferric arsenates provides a plausible explanation for their rapid transformation into scorodite in acid mining environments.