American Mineralogist, Volume 97, pages 1469–1482, 2012

The enigmatic iron oxyhydroxysulfate nanomineral schwertmannite: Morphology, structure, and composition

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Abstract

Two sets of precipitates collected from stream sediments in the Monte Romero (MR) and Tinto Santa Rosa (TSR) abandoned mine sites—located in the Iberian Pyrite Belt (IPB) of Spain—were identified as the iron oxyhydroxysulfate nanomineral schwertmannite using X-ray diffraction (XRD) and bulk digestion and were further studied in great detail using analytical high-resolution transmission electron microscopy (HRTEM). Extensive HRTEM observations suggest that schwertmannite should not be described as a single-phase mineral with a repeating unit cell, but as a polyphasic nanomineral with crystalline areas spanning less than a few nanometers within an amorphous matrix. The *d*-spacings measured from lattice fringes within schwertmannite's needles match with *d*-spacings of the known transformation products of schwertmannite (goethite and jarosite). This finding implies that the initial stages of schwertmannite transformation occur as a gradual structural reordering at the nanoscale. Energy-dispersive X-ray analysis applied across individual schwertmannite needles with ~3 nm spot size resolution reveal a decreasing ratio of sulfur to iron and silicon to iron from the surface of the needle to the core with the silicon to iron ratio consistently higher than the sulfur to iron ratio. Amorphous silicon-rich precipitates were identified on the surface of the TSR schwertmannite. All of these observations explain why the measured solubility product of schwertmannite is variable, resulting in calculated stability fields that differ greatly from sample to sample. Arsenic is the most abundant trace element in these samples [MR: 0.218(1) wt% and TSR: 0.53(2) wt%], keeping in mind that schwertmannite has been shown to be a key player in the cycling of this element on a global basis, particularly from the IPB. Furthermore, arsenic in the TSR schwertmannite is associated with crystalline areas within its needle matrix, implying that schwertmannite-derived goethite nanocrystals may be an important host of arsenic.

Keywords: Nanomineral, schwertmannite, goethite, jarosite, iron oxide, arsenic, silicon, sulfate