

Influence of Structural Defects on Biomineralized ZnS Nanoparticle Dissolution: An In-Situ Electron Microscopy Study

JEREMY R. ESKELSEN¹, JIE XU², MICHELLE CHIU¹, JI-WON MOON¹, BRANFORD WILKINS¹, DAVID E. GRAHAM¹, BAOHUA GU¹, AND ERIC M. PIERCE¹

¹Oak Ridge National Laboratory, P.O. Box 2008, MS 6038, Oak Ridge, TN 37831 pierceem@ornl.gov

²University of Texas at El Paso, 500 West University Ave, El Paso, TX 79968

Dissolution of metal sulfides, such as ZnS, is an important biogeochemical process affecting fate and transport of trace metals in the environment. Currently, studies of in-situ dissolution of metal sulfides and the effects of structural defects on dissolution are lacking. Here we examined the dissolution behaviour of ZnS nanoparticles synthesized by biotic and abiotic methods. Biogenic ZnS nanoparticles were produced by an anaerobic, metal-reducing bacterium *Thermoanaerobacter* sp. X513 in a Zn-amended solution, whereas mixing an aqueous Zn solution with either H₂S-rich gas or Na₂S solution produced the abiogenic ZnS nanoparticles. High-resolution transmission electron microscopy (TEM) images of the particles show that the characteristics of the sphalerite nanoparticles (i.e., size distribution, aggregation behaviour, and presence or absence of structural defects) vary with synthesis conditions.¹ For example, the biogenic ZnS nanoparticles are 2× larger (~10 nm) than the smaller quantum dot sized abiogenic nanoparticles (~3-5 nm).¹ In situ dissolution of the synthesized ZnS nanoparticles was examined with liquid-cell TEM methods. Analysis of the dissolution results suggests that the larger defect-bearing biogenic nanoparticles are more reactive than the smaller quantum-dot-sized abiogenic nanoparticles, evident by the higher surface free energy of the defect-bearing biogenic nanoparticles ($\gamma = 0.799 \text{ J/m}^2$).¹ These findings provide new insight into the factors that affect the dissolution of metal sulfide nanoparticles in relevant natural and engineered scenarios, and have important implications for fate of trace metals in the environment.

¹Eskelsen et al. (2018). *Environ. Sci. Technol.*, **52**(3):1139-1149