Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.4616

Size-dependent thermodynamics of mackinawite and greigite

SANGBO SON AND KIDEOK KWON

Kangwon National University

Presenting Author: s3247@kangwon.ac.kr

Iron sulfides play an important role in the geochemical cycles of major elements and trace metals in anoxic sediments. Pyrite (FeS_2), the dominant authigenic iron sulfide mineral, typically forms via the precipitation of non-equilibrium phases such as metastable nanocrystalline mackinawite (FeS), greigite (Fe_3S_4) or both. Because the observed metastable phase is highly sensitive to experimental conditions, the non-equilibrium crystallization pathway is perplexing to rationalize with conventional thermodynamics alone. Previous metal-oxide studies have shown that a metastable phase with its low surface energy can be stabilized at the nanoscale compared to the bulk stable phase [1]. In this study, we investigate size-dependent stabilities of FeS, Fe_3S_4, and FeS_2 by application of the *ab-initio* size-dependent thermodynamics based on density functional theory [2]. We present for the first time the calculated nanoscale Pourbaix diagrams of the Fe-S system, and propose the possible crystallization pathways at different environmental conditions (pH, redox potential, and aH_2S/pH_2). Our nanoscale thermodynamic results can rationalize crystallization pathways of iron sulfides and the precursor role of nanocrystalline metastable iron sulfides.

[1] Birkner N. and Navrotsky A. (2012) *American Mineral.* **97**, 1291-1298.

[2] Sun W., Kitchaev D. A., Kramer D. and Ceder G. (2019) *Nat. Commun.* **10**, 1–9.