

## Stealth excursions from equilibrium provide the rules for nanomineral geochemistry

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A quote from the Basic Energy Sciences Advisory Committee of the US Department of Energy probably says it all: “One of the fundamental challenges facing science in the 21<sup>st</sup> century is understanding systems away from equilibrium.” This is not to say that important advances have not been made, particularly in the last century, in understanding systems that wonder from equilibrium. Great progress in both quantum and classical kinetics and dynamics is well known. Yet understanding and predicting behavior in non-equilibrium systems, especially systems far from equilibrium, is especially perplexing. And in the Earth sciences, systems far from equilibrium, and systems that never reach equilibrium, abound. In the world that can only be described and understood by delving into the field of nanogeoscience, we “see” that non-equilibrium situations are common, yet we have not figured out a convenient way to parameterize, quantify, and predict them on the macroscale.

This talk will present several key examples from our laboratories of what is described above, including, but not limited to: 1) the discovery of the growth of Mn<sub>3</sub>O<sub>4</sub> nanowires from nanohematite catalysts [1]; 2) Mn<sup>2+</sup>(aq) oxidation promoted at various rates by different sizes and shapes of nanohematite particles, emphasizing the distortion of surface binding environments [2,3]; 3) the polyphasic nature of the mineral schwertmannite, and its transformation to goethite [4]; 4) the varying non-oxidative dissolution rates of nanogalenite from crystal faces that are adjacent to both bulk and confined solution [5,6]; and 5) the influence of size, morphology, surface structure, and aggregation state on the reductive dissolution of nanohematite, including the influence of newly discovered “deep” penetrating nanopores within the nanohematite [7,8].

[1] Veeramani *et al* (2013) *ACS Sustain. Chem. Eng* **1**, 1070-1074. [2] Madden & Hochella (2005) *Geochim. Cosmochim. Acta* **69**, 389-398. [3] Madden *et al* (2006) *Geochim. Cosmochim. Acta* **70**, 4095-4104. [4] French *et al* (2013) *Amer. Mineral.* **97**, 1469-1482. [5] Liu *et al* (2008) *Geochim. Cosmochim. Acta* **72**, 5984-5996. [6] Liu *et al* (2009) *Env. Sci. Technol* **43**, 8178-8183. [7] Echigo *et al* (2012) *Geochim. Cosmo. Acta* **90**, 149-162. [8] Echigo *et al* (2013) *Amer. Mineral* **98**, 154-162.