

Morphological changes during Fe atom exchange reactions between goethite and aqueous Fe(II)

PRACHI JOSHI AND CHRISTOPHER A. GORSKI^{1*}

¹Department of Civil & Environmental Engineering,
Pennsylvania State University, University Park, PA 16802,
USA (*correspondence: gorski@psu.edu)

Iron (Fe) (oxyhydr)oxides are found in virtually all natural environments, where they profoundly impact numerous biogeochemical cycles and serve as important proxies in the geological record. Recent experiments by our group and others have shown that when thermodynamically stable Fe oxides are exposed to dissolved ferrous iron (Fe(II)), rapid and extensive isotopic mixing occurs between the solid and aqueous phases, which can lead to trace element incorporation and release. Surprisingly, these studies did not observe any morphological changes over the course of the reaction, which has led to many questions regarding the thermodynamic driving force of exchange.

Here, we revisited Fe atom exchange between nanoparticulate goethite and aqueous Fe(II) over the course of 60 days using high resolution transmission electron microscopy (HR-TEM) and cryogenic TEM to evaluate if any morphological changes occurred. We also used radioactive ⁵⁵Fe isotope tracer experiments to quantify the extent of atom exchange. Over the first 30 days, we observed that the goethite nanorods uniformly shrank in all dimensions, with no indication of any particles growing. After 30 days, the particles regrew to their original dimensions. We also observed that the goethite nanoparticles underwent orientated aggregation during exchange, as evidenced from cryogenic TEM images. These observations suggest that Fe atom exchange reactions with goethite involve dissolution and precipitation reactions that likely change the particle morphology. Current investigations are underway to characterize these changes using spectroscopic techniques. Understanding the occurrence of this process in natural systems will lead to improved interpretation of the Fe oxide rock record by characterizing how Fe oxide isotopic signatures change over time and improve our ability to assess the roles that Fe oxides play in sequestering and releasing trace metals and radionuclides on modern Earth.