

Evidence for a dissolution-reprecipitation mechanism for Fe(II)-driven ferrihydrite recrystallization

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Under reducing conditions, electron transfer between aqueous Fe(II) and ferrihydrite rapidly accelerates ferrihydrite transformation to more stable Fe(III) oxides. Although the major steps of Fe(II)-catalyzed ferrihydrite transformation are known, processes in the initial phase that lead to nucleation and growth of product minerals remain unclear. To track ferrihydrite - Fe(II) interactions during the initial phase of transformation we used Fe isotope tracers, acid extractions, X-ray diffraction, and isotope-specific ⁵⁷Fe Mössbauer spectroscopy to simultaneously track Fh recrystallization and Fe atom exchange. We also observed rapid isotope mixing between aqueous Fe(II) and ferrihydrite during this initial lag phase. Using Mössbauer spectroscopy we found that a more magnetically-ordered Fe(III) phase initially forms that is distinct from ferrihydrite and bulk crystalline transformation products. The initially-forming phase is consistent with the emergence of lepidocrocite-like lamellae observed in previous transmission electron microscopy studies. The Mössbauer-spectral signature of this phase is removed using xylenol orange extractions, the same approach used to identify a chemically labile form of Fe(III) resulting from Fe(II) and was ultimately correlated with the emergence of crystalline Fe(III) minerals. At longer times (> 2h) ferrihydrite transformed to lepidocrocite and goethite as expected. Isotope ratios of sequential extractions of the recrystallizing Fh further suggest that a fraction of the Fe undergoing exchange may be “buried” and no longer participating in further exchange consistent with previously proposed heterogeneous isotope exchange models for Fe(II)-catalyzed recrystallization of Fe oxides. Our study provides additional evidence that dissolution and reprecipitation is the main transformation mechanism during Fe(II)-catalyzed ferrihydrite transformation due to facile electron transfer and atom exchange at the Fe(II)-Fh interface.