Ferrihydrite transformation by Fe(II): Nucleation, growth, and phase stability at neutral pH

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At low termperature ferrihydrite, the poorly ordered Fe hydroxide, gradually transforms over a period of months to years into thermodynamically stable Fe(oxy)hydroxide phases like lepidocrocite γ-FeOOH and/or goethite α-FeOOH. However, exposure to aqueous Fe(II) accelerates this transformation into just a matter of hours. In addition, Fe(II) complexing counteranions appear to control crystallization pathways and in turn, the products formed and their size, shape, and relative phase proportions.

At the molecular level, the acceleration mechanism induced by Fe(II) is unresolved. The kinetics of transformation however, are thought to be triggered and controlled by the rate of electron injection and transport through the bulk of ferrihydrite. To begin to develop a fundamental understanding of redox-catalyzed mass and charge transfer pathways in this system, we investigated the nucleation and growth of Fe oxides with a combined diffraction and microscopy study. *In situ* μX-ray diffraction complemented with scanning electron microscopy allowed identification of the nucleating phases and their spatial relationships with respect to precursor ferrihydrite particles. Cryo-transmission electron microscopy was also used to investigate the early stages of nucleation, to elucidate aspects of Fe(II) induced transformation in a quasi-*in situ* manner.

Our data shows that lepidocrocite is the first phase to nucleate in chloride-rich solution, at earlier induction time than previously thought (30 min.). Incipient lepidocrocite sheets one unit cell thick but ~300-450 nm long are found to contour the ferrihydrite aggregate surface at this induction time. At five days, lepidocrocite develops in place by layer growth into ~20 nm thick crystallites. In CO_3-rich solution, both lepidocrocite and goethite form at this induction time, but in contrast to lepidocrocite incipient goethite needles appear to nucleate and grow outwards from ferrihydrite aggregates. The observations suggest that the mass transfer pathways sustaining lepiocrocite and goethite growth at the expense of ferrihydrite are different, providing an important clue for unraveling the acceleration mechanism.