

# Transformation of Fe(III) oxides by the catalytic action of aqueous Fe(II) and the fate of associated arsenate

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Iron oxides may undergo structural transformations to new and more stable phases. These transformations were investigated under anoxic conditions using the isotopic exchange between aqueous Fe(II) and <sup>55</sup>Fe-labelled iron oxides. <sup>55</sup>Fe was incorporated congruently into a ferrihydrite, two lepidocrocites (#1 and #2), synthesised at 10°C and 25°C, respectively, a goethite and a hematite. The iron oxides were then submerged in Fe<sup>2+</sup> solutions (0-10 mM) buffered to a pH of 6.5 by HCO<sub>3</sub><sup>-</sup>.

In the presence of aqueous Fe<sup>2+</sup>, an immediate and very rapid release of <sup>55</sup>Fe was observed from ferrihydrite, the two lepidocrocites and goethite, whereas no release was observed in the absence of Fe<sup>2+</sup>. <sup>55</sup>Fe was not released from hematite at any Fe<sup>2+</sup> concentration. Ferrihydrite and 5 nm-sized lepidocrocite crystals attained complete isotopic equilibrium with aqueous Fe(II) within days. Within this timeframe ferrihydrite transformed completely into new and more stable phases such as lepidocrocite and goethite. Lepidocrocite #2 and goethite, having larger particles, did not reach isotopic equilibrium within the timeframe of the experiment; however, a continuous slow release of <sup>55</sup>Fe suggests that isotopic equilibrium will ultimately be attained.

The fate of trace amounts of arsenate coprecipitated with ferrihydrite and lepidocrocite was studied during the Fe<sup>2+</sup> catalyzed transformation of the iron oxides. Initially, all the arsenate was associated with the iron oxide surface, however, during the transformation of the iron oxides, the arsenate became bound more strongly to the product phases and was not released to the solution.

The results imply that the presence of aqueous Fe(II) may catalyse a recrystallization of solid Fe(III) phases. Accordingly, iron oxides should properly be considered as dynamic phases that change composition when exposed to variable redox conditions. A re-evaluation of current models for the release of trace metals under reducing conditions, the sequestration of heavy metals by iron oxides, and the significance of stable isotope signatures is therefore necessary. The experiments with arsenate show, that Fe(II) catalyzed transformation of iron oxides may be an important trapping mechanism in natural sediment. The results are of importance for the understanding of the behaviour of arsenic in aquifers and on sand filters in water works and for the disposal of arsenic containing chemical waste.