The fleeting (bio)availability of ferrihydrite

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Within non-sulfidogenic, anaerobic sediments, the majority of Fe reduction is thought to occur via bacterial Fe(III) respiration. Due to its high solubility and intrinsic reactivity, ferrihydrite ($Fe(OH)_3 \cdot nH_2O$) is considered the most bioavailable Fe (hydr)oxide for dissimilatory iron-reducing bacteria, allegedly resulting in the preservation of more crystalline phases within mature sediments. Here we illustrate that ferrihydrite may have a less significant role in both early and long-term microbial reduction and Fe phase transformations than currently deemed.

Reduction of ferrihydrite-coated sand under advective flow by *Shewanella putrefaciens* results in the secondary mineralization of ferrihydrite to goethite (α-FeOOH) and magnetite (Fe_3O_4). The mineralization of ferrihydrite occurs via a coupled biotic-abiotic reaction pathway such that bacterial-generated ferrous Fe reacts abiotically with the ferrihydrite surface. Conversion of ferrihydrite upon abiotic reaction with aqueous Fe(II), however, proceeds through a lepidocrocite (γ-FeOOH) precursor, ultimately resulting in the formation of goethite and magnetite. The residence time and extent of lepidocrocite precipitation, being a function of Fe(II) concentration and complexing ligand, dictates the ensuing secondary mineralization pathways.

Upon the onset of ferrihydrite reduction, a rapid pulse of Fe(II) generation and ferrihydrite conversion occurs followed by slower sustained rates consistent with those of more crystalline phases (*e.g.* goethite). Moreover, reduction of natural Fe(III)-coated sands by *S. putrefaciens* within minimal media under advective flow results in the preferential consumption of more recalcitrant Fe (hydr)oxide phases relative to ferrihydrite. Instead, ferrihydrite is converted to hematite (α-Fe_2O_3), most likely a consequence of sorbed and/or coprecipitated ions decreasing the solubility of ferrihydrite therefore favoring internal ordering to hematite rather than dissolution/ reprecipitation to lepidocrocite. Thus, the reactivity and reducibility of ferrihydrite is transient (*i.e.*, conversion to lepidocrocite) and/or compromised (*e.g.* ion substitution) suggesting that the generation of Fe(II), ensuing secondary mineralization pathways, and subsequent reducing capacity of sediments will be controlled by more crystalline phases ultimately imposing limitations on the rates of microbial respiration.

Coupling biogeochemical Fe(III) oxide reduction and contaminant transformation

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In anoxic environments, dissimilatory Fe(III) mineral reduction may generate reactive, surface bound Fe(II) species, which are capable of reducing organic and inorganic contaminants. Despite extensive studies on microbial strategies of Fe(III) mineral transformation and on abiotic contaminant reduction, respectively, only few studies addressed the environmentally relevant, coupled process. Current knowledge suggests that the bioavailability of Fe(III) minerals is inversely correlated with the reactivity of adsorbed Fe(II) species towards contaminant transformation. To this end, we examined the environmental conditions that favor the occurrence of the coupled process, e.g., the influence Fe(III) mineral type and Fe(II) surface concentration on the rates of nitroaromatic compound (NAC) reduction in suspensions of pure cultures of *G. metallireducens*.

We observed the highest rates of contaminant reduction in batch assays where two iron oxides were present simultaneously, i.e., amorphous ferrihydrite as microbial electron acceptor and lepidocrocite as sorbent for reactive Fe(II). Pseudo-first order rate constants of NAC reduction were almost identical to those obtained in abiotic reference experiments in the absence of microorganisms confirming that surface bound Fe(II) was the predominant reductant. In contrast, NAC reduction was up to two orders of magnitude slower when only ferrihydrite was present in the assays. Over the entire pH-range investigated (6.8 - 7.5) increasing reduction rate constants correlated well with the higher concentrations of adsorbed Fe(II). We found that in the presence of *G. metallireducens*, non-reactive Fe(II) species exist. Despite significant amounts of adsorbed Fe(II), no contaminant reduction was observed in the absence of dissolved Fe(II) suggesting that dissolved Fe(II) is essential for the regeneration of reactive Fe(II). Our results highlight that contaminant reduction in anoxic environments by Fe(II) species strongly depends on the phase distribution and bioavailability of Fe(III) minerals.