Investigating isotopic exchange between dissolved aqueous and precipitated iron species in natural and synthetic systems

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Investigating Fe isotope exchange between amorphous iron oxyhydroxides (ferrihydrite) and dissolved aqueous Fe species is critical to unraveling the complexities of Fe geochemical cycling. Understanding the extent and rate of isotopic exchange between solid and aqueous Fe components will increase our understanding of abiological Fe isotope fractionations, and ultimately further our ability to recognize Fe isotope fractionations induced solely by biological processes.

The kinetics of isotope exchange between solid and aqueous Fe phases has been studied using an aqueous Fe(III) ^{57}Fe tracer and a manufactured nanoparticulate ferrihydrite (3 nm particle size), where approximately 1/3 of the Fe atoms are considered to be surface atoms. Experiments were run at 25ºC at pH 4.7, where the solubility of Fe(III) is 0.1 ppm, and no net mass transfer between solution and solid occurred. Based on changes in the measured ^{57}Fe/^{56}Fe ratio of the liquid component over time, we observe an initial rapid exchange (as much as 20% exchange in the first 100 hours) followed by continued, slower exchange. Presumably this corresponds to an initial period of rapid surficial exchange, coupled with subsequent slower diffusional exchange.

Though the rates of exchange observed in laboratory experiments may not be directly correlated to natural systems, we have demonstrated that significant isotopic exchange between the two Fe components does in fact occur on surface sites of the nanometer-sized particles. In natural systems, however, individual ferrihydrite crystals are much larger and commonly form aggregates, which should markedly decrease the surface isotopic exchange relative to total mass. It is still unclear what, if any, measurable isotopic effect this exchange mechanism has in natural settings. Given the numerous natural situations in which solid and aqueous Fe phases could potentially exchange isotopically, our findings illustrate the necessity for further understanding the kinetics of such exchange in natural systems, and the impact it may have on global Fe cycling.

Carbon isotope fractionation of monoaromatic hydrocarbons and chlorinated ethylenes during oxidation by Fenton's reagent

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Introduction

Chlorinated ethylenes and monoaromatic hydrocarbons are frequently detected as groundwater contaminants in many locations around the world. Oxidation of these compounds using Fenton's reagent, a mixture of ferrous iron and hydrogen peroxide, has been shown to be a rapid and effective remediation technique. Stable isotope analysis has potential applicability as a technique to monitor the extent of remediation by Fenton's reagent.

Experimental

Eight compounds were investigated: trichloroethylene (TCE), tetrachloroethylene (PCE), cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, 1,1-dichloroethylene, monochlorobenzene, benzene, and toluene. All experiments used Fenton's reagent with Fe^{2+} = 30 mg/l and H_2O_2 = 1000 mg/l, and an initial organic compound concentration of 50 mg/l.

Results

The oxidation reaction is first-order with respect to organic compound concentration. Degradation rates for the monoaromatic hydrocarbons ($k = 8.5$ to $24.2 \times 10^{-4} s^{-1}$) are faster than for the chlorinated ethylenes ($k = 2.1$ to $3.9 \times 10^{-4} s^{-1}$). Carbon isotope enrichment factors, ε, for the monoaromatic hydrocarbons are very small (ε = -0.3 to -0.6‰), somewhat larger for the dichloroethylenes and TCE (ε = -2.1 to -2.8‰), and largest for PCE (ε = -3.7‰).

Conclusions

Enrichment factors are significantly smaller than other chemical degradation processes, such as permanganate oxidation, and reductive dechlorination by Fe^0. However, the results indicate that carbon isotope analysis may have utility as a technique to monitor the extent of oxidation of chlorinated ethylenes by Fenton's reagent, but not of monoaromatic compounds. For example, 90% oxidation shifts $\delta^{13}C$ by +4.8 to +8.6‰ for chlorinated ethylenes, but only +0.7 to +1.4‰ for monoaromatic hydrocarbons.