

Using stable Fe isotopes to assess microbially-mediated Fe³⁺ reduction in a jet-fuel contaminated aquifer

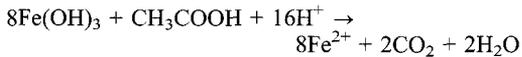
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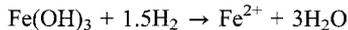
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Iron (Fe) is the fourth most abundant element in the earth's crust, and is an important constituent of a wide range of primary and secondary minerals. During degradation and metabolism of organic matter, a variety of microbes are able to use the abundant Fe³⁺ in minerals as an energy source, and Fe reduction is a common terminal electron accepting process. The oxidation of fermentation products proceeds according to reactions such as:



and



Fe reduction is clearly an important process during microbial degradation of organic contaminants such as fuel spills in aquifers, based on the considerable transport of Fe²⁺ to groundwater seeps at these sites. Although the above reactions suggest that in theory one could determine the amount of contaminant degradation that has occurred based on the amount of Fe²⁺ produced, there has been no simple way to estimate the extent of Fe³⁺-reduction in the total reactive system because much of the reduced Fe remains in the aquifer bound in secondary minerals. Here we propose that stable Fe isotope ratios of groundwaters and sediment leachates may provide a sensitive indicator of the extent of Fe³⁺-reduction that has occurred.

In a time-series experiment in which an amorphous Fe gel suspension was inoculated with Fe³⁺-reducing microbes, Bullen and McMahon (1997) demonstrated: (1) that ⁵⁷Fe/⁵⁶Fe of dissolved Fe produced by Fe³⁺-reduction is consistently 4‰ lower than that of Fe³⁺ in the reacted solid phase; and (2) that both dissolved and solid-phase Fe become heavier as Fe reduction proceeds. They used these experimental results to propose that microbially-mediated Fe³⁺-reduction was responsible for the Fe isotope variations observed in groundwaters and acid leachates of sediment from a JP-4 contaminated aquifer in South Carolina (USA). The isotope data

from this study are plotted in Fig. 1 in terms of δ⁵⁷Fe, the per mil deviation of ⁵⁷Fe/⁵⁶Fe from that in the U.S.G.S. rock standard BIR, an Icelandic basalt. Included in this diagram are values of Fe²⁺/Fe_{total} in 0.5 N and 6 N HCl leachates of aquifer sediment from both within and upgradient of the impacted zone.

The Fe²⁺/Fe_{total} data indicate that the 0.5 N HCl leach removed mostly Fe²⁺ from the sediments, whereas the subsequent 6 N HCl leach removed mostly Fe³⁺. Assuming that each leachate was a mixture of Fe²⁺ and Fe³⁺, pure 'end-member' values were calculated by simple mass balance. From Fig. 1 it can be seen that δ⁵⁷Fe of groundwater in both the shallow and deep impacted zone is about 3‰ higher than that of the accumulated Fe²⁺ on the surface of the reacted sediment in each zone, and about 3.5‰ lower than that of Fe³⁺ in the more tightly-bound sites of the reacted sediment of each zone. Furthermore, groundwater and sediment leachates from the deep impacted zone, where Fe-reduction has

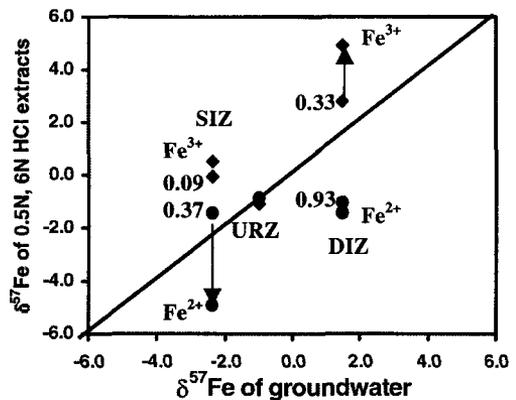


FIG. 1. Fe isotope variations in groundwaters and sediment leachates from the Hanahan, SC jet fuel spill site. SIZ = shallow impacted zone; DIZ = deep impacted zone; URZ = upgradient recharge zone. Circles are 0.5 N HCl leachate data; diamonds are 6 N HCl leachate data. Numbers are Fe²⁺/Fe_{total} of leachates. Points labeled 'Fe²⁺' and 'Fe³⁺' are calculated end-members.

progressed most, have systematically higher $\delta^{57}\text{Fe}$ than they do in the shallow impacted zone. In contrast, there is no isotopic difference between groundwater and sediment leachates from the upgradient recharge zone. We attribute these differences to the abundant Fe-reducing microbial activity in the organic-rich impacted zone, and the lack of such activity upgradient from the impacted zone.

The Fe^{2+} produced by microbial Fe-reduction is either transported by groundwater to seeps or bound into secondary minerals that are essentially inert in the groundwater. Thus to a first approximation the Fe isotope budget of this system can be viewed in terms of a simple Rayleigh distillation process in which the relatively light Fe^{2+} product is continuously removed from the reactive system, leaving a progressively heavier Fe^{3+} reactant (Fig. 2).

Assuming that $\delta^{57}\text{Fe}$ of groundwater is equal to that of the instantaneous Fe^{2+} produced by Fe-reduction at the point where the water is sampled, Fig. 2 can be used to predict $\delta^{57}\text{Fe}$ of both the instantaneous reactant (i.e. the 6 N HCl leach) and the accumulated Fe^{2+} that has been removed from the reactive system (i.e. the 0.5 N HCl leach). For example, $\delta^{57}\text{Fe}$ of groundwater in the shallow impacted zone is 1.5‰ lower than that of groundwater from the unreacted upgradient recharge zone. The vertical line SIZ on Fig. 2 that intersects the Fe_i^{2+} curve at -1.5‰ predicts that Fe_i^{3+} should have $\delta^{57}\text{Fe}$ of $+2\text{‰}$; for comparison, $\delta^{57}\text{Fe}$ of Fe^{3+} in the shallow impacted zone is 1.5‰ higher than that in the upgradient material. The line likewise predicts Fe_A^{2+} of -3‰ ; for comparison, $\delta^{57}\text{Fe}$ of leachable Fe^{2+} in the shallow impacted zone is 3.5‰ lower than that in the unreacted upgradient material. Predicted values for the deep impacted zone (line DIZ in Fig. 2) are likewise in good agreement with measured values, suggesting that the Rayleigh approximation is valid.

$\delta^{57}\text{Fe}$ of groundwater discharge at a seep zone downgradient from the impacted zone is 1.5‰ higher than that of groundwater from the upgradient recharge zone. Based on line SZ in Fig. 2, and

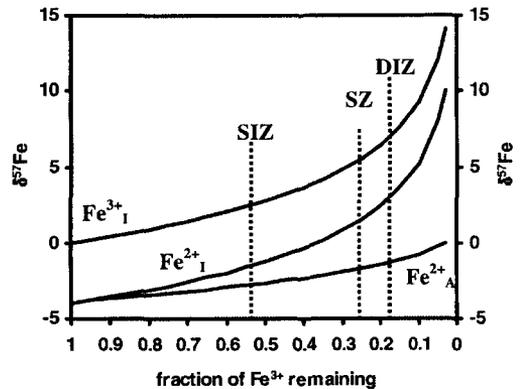


Fig. 2. Simple Rayleigh distillation model for Fe isotope evolution in the microbial reduction system. The fractionation factor is assumed to be 1.004, based on the experimental data of Bullen and McMahon (1997). Fe_i^{3+} = instantaneous Fe^{3+} reactant; Fe_i^{2+} = instantaneous Fe^{2+} product; Fe_A^{2+} = accumulated Fe^{2+} removed from the reactive system. Lines labeled SIZ, DIZ, and SZ represent conditions in the Shallow Impacted Zone, the Deep Impacted Zone, and a downgradient Seep Zone, respectively, based on $\delta^{57}\text{Fe}$ of water in each zone. $\delta^{57}\text{Fe}$ of starting material is assumed to be 0.

assuming that the groundwater seeps effectively integrate groundwater flow through the impacted zone, we predict that approximately 75% of the original available Fe^{3+} in the impacted zone has been reduced to Fe^{2+} . Providing this sort of estimate of the amount of Fe-reduction that has occurred in contaminated aquifers may prove to be an especially powerful application of stable Fe isotopes. Clearly, however, additional field and laboratory studies of Fe isotope systematics must be conducted to confirm fractionation factors used to calibrate plots such as Fig. 2.

References

- Bullen, T.D. and McMahon, P.M. (1997) *EOS*, **78**, S173.