NAME: Jennifer Druhan
ORGANIZATION: LBNL / Stanford University
PROGRAM AFFILIATION: SBR
ABSTRACT TITLE: Sulfur cycling and isotopic fractionation in biostimulated Rifle sediments

ABSTRACT: Biologically catalyzed redox reactions often produce large stable isotope fractionations between reactant and product species. The isotope ratios of these species contain information complementary but distinct from traditional concentration measurements, and therefore provide novel constraints on the rates, progression and secondary mineralization processes associated with *in situ* biostimulation. Stable isotope ratios of sulfur have been measured over three consecutive years of acetate-enabled biostimulation at the US Department of Energy's Rifle Integrated Field Research Challenge (IFRC) site. The data show a previously undocumented trend towards an earlier onset of sulfate reducing conditions over subsequent amendments, from 20 days in the 2007 experiment to 4 days in the 2009 experiment (Druhan et al., 2012). Such novel insights into the cycling of metals and radionuclides in the near surface environment through the lens of stable isotope distributions motivates a quantitative, mechanistic treatment of stable isotope distributions in a process based reactive transport model. This study demonstrates a mechanistic incorporation of the stable isotopes of sulfur into the CrunchFlow reactive transport code to model the range of microbially-mediated redox processes affecting kinetic isotope fractionation. Previous numerical models of microbially mediated sulfate reduction have suggested that $\delta^{34}S$ fractionation is not accurately simulated when substrate concentrations become limiting because the fractionation factor decreases under these conditions. However, we suggest a single kinetic fractionation factor can be used to accurately simulate $\delta^{34}S$ variation over a wide range of substrate concentrations when the effect of the half saturation constant on the behavior of individual isotopes within Monod or Michaelis-Menten-type rate expressions are appropriately considered. This new model capability is tested through simulation a large-scale column study designed to replicate field scale conditions of an organic carbon (acetate) amended biostimulation experiment in Old Rifle sediments (Druhan et al., 2013). The reactive transport model accurately reproduced the measured enrichment in $\delta^{34}S$ of both the reactant (sulfate) and product (sulfide) species of the reduction reaction using a single fractionation factor of 0.987 obtained independently from field-scale measurements. The model also accurately simulated the accumulation and $\delta^{34}S$ signature of solid phase elemental sulfur over the duration of the experiment, providing a new tool to predict the isotopic signatures associated with reduced mineral pools formed during redox transitions. Extension of the model to the $\delta^{34}S$ data collected during biostimulation experiments at the field site demonstrates that the trend towards an earlier onset of sulfate reduction is a result of shifts in the population size and spatial distribution of sulfate reducing bacteria in response to multiple stimulation events.

Druhan et al. (2012) Timing the onset of sulfate reduction over multiple subsurface acetate amendments by measurement and modeling of sulfur isotope fractionation. ES&T, 46(16), 8895 – 8902.
Druhan et al. (2013) A large column analog experiment of stable isotope variations during reactive transport: I. A comprehensive model of sulfur cycling and $\delta^{34}S$ fractionation. GCA (in review)