Isotopic Signatures of Calcium and Sulfur Partitioning During Biostimulation: Experiments and Simulations

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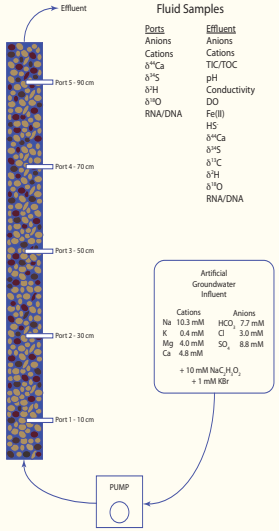
OVERVIEW

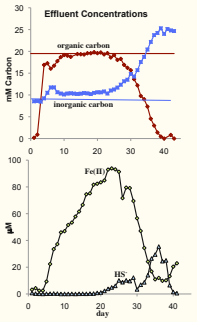
Motivation

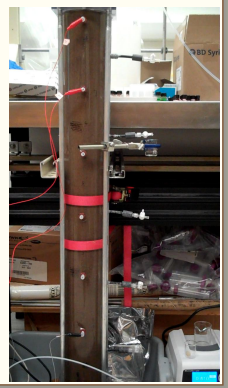
Bio-induced stabilization of metals in subsurface systems involves a complex and concurrent series of dissimilatory reduction reactions, each with a unique metabolism and contaminant affinity. Stable isotope fractionations of key species in the bioreduction process provide information complementary to but distinct from traditional concentration measurements. Detection and modeling of such enrichments therefore provide novel constraints on the rates, progress and secondary mineralization associated with *in situ* biogeochemical processes.

Approach

Meso-scale flow-through columns serve to bridge the gap between field-scale and small-scale column studies by circumventing the need for scaling relationships. Here we present such a meso-scale approach to measure stable isotope fractionations associated with acetate stimulated uranium bioreduction in sediments recovered from the Rifle IFRC site. $\delta^{13}C$-labeled acetate was added to artificial groundwater influent in a 10cm diameter, 1m long packed sediment column for 43 consecutive days. Biogenic sulfate reduction produced characteristic fractionation in $\delta^{34}S$ while increased alkalinity induced carbonate precipitation and associated enrichment in fluid $\delta^{44}Ca$. Reactive transport modeling of these isotopic datasets provides new insight into the processes governing solute chemistry during enhanced bioreduction.





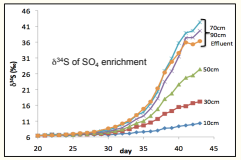


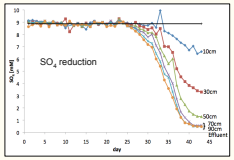
SULFUR ISOTOPES

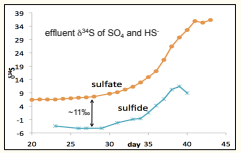
Background

Bacterially-mediated sulfate reduction favors sulfate molecules containing the lighter isotope of sulfur (^{32}S) causing the residual sulfate pool to become enriched in the heavier isotope (^{34}S)[1]. The characteristic enrichment in $\delta^{34}S$ of sulfate is commonly used to detect SRB activity in subsurface systems. During acetate amendment at the Rifle site, enrichment of 10-20‰ in $\delta^{34}S$ has previously been measured in association with SRB activity[2,3].

Column Sulfur Dataset







- SO_4 and $\delta^{34}S$ profiles indicates SRB activity occurs predominantly over the first 70cm.

Sulfate reduction:

$$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$$

$\delta^{34}S$ notation:

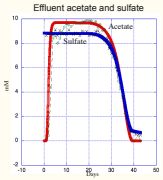
$$\delta^{34}S = \left[\frac{\left(\frac{^{34}S}{^{32}S}\right)_A}{\left(\frac{^{34}S}{^{32}S}\right)_B} - 1\right] * 1000\ ‰$$

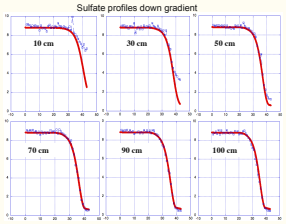
Fractionation:

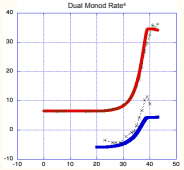
$$\alpha^{34}_{HS^- - SO_4^{2-}} = \frac{R_{HS^-}}{R_{SO_4^{2-}}} \qquad R = \frac{^{34}S}{^{32}S}$$

Reactive Transport Modeling of $\delta^{34}S$

$$r^{Ac}_{SRB} = \mu^{Ac}_{SRB} B_{SRB} \left(\frac{[SO_4^{2-}]}{K^{SO_4^{2-}}_{S-SRB} + [SO_4^{2-}]}\right)\left(\frac{[Ac]}{K^{Ac}_{S-SRB} + [Ac]}\right)$$







$$r^{Ac}_{SRB} = \mu^{Ac}_{SRB} B_{SRB} \left(\frac{[^{34}SO_4^{2-}]}{K^{^{34}SO_4^{2-}}_{S-SRB}\left(1 + \frac{[^{32}SO_4^{2-}]}{K^{^{32}SO_4^{2-}}_{S-SRB}}\right) + [^{34}SO_4^{2-}]}\right)\left(\frac{[Ac]}{K^{Ac}_{S-SRB} + [Ac]}\right)$$

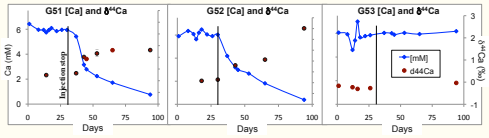
Accurate modeling of $\delta^{34}S$ fractionation due to SRB activity cannot be accomplished by requiring the reduction to behave as either strictly zero or first order, but rather requires adjustment of the dual Monod equation to facilitate reactivity of both isotopologues throughout.

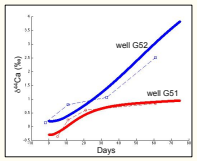
CALCIUM ISOTOPES

Background

Mid-mass stable isotope systems typically exhibit kinetically driven fractionations leading to enrichment of the heavy isotope in solution (^{44}Ca) and preferential incorporation of the light isotope (^{40}Ca) into the solid phase[5]. At the Rifle field site, reduced permeability in injection wells has resulted an an observed enrichment of >2‰ $\delta^{44}Ca$ of the borehole fluid, however no observable fractionation has been detected in down-gradient monitoring wells.

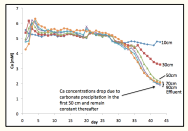
Field Calcium Dataset and Modeling

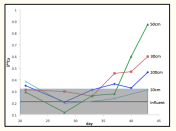




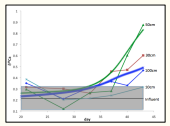
- G53 exhibited no fractionation because the well remained hydrologicaly connected to the aquifer.
- Difference in clogged well G51 and G52 fractionation is attributed to relatively more clogging in G52, leading to more CO_3^{2-} buildup and lower Ca:CO_3 ratio[6].

Column Calcium Dataset and Modeling





Balance between carbonate precipitation in the first 50 cm of the column and ion exchange as Ca becomes depleted.



The signal of calcium isotope fractionation associated with carbonate precipitation is buffered by exchange with available surface Ca of background $\delta^{44}Ca$ composition. This means that the fractionation signal of carbonate precipitation only persists over ~50 cm of transport before it is lost.

SUMMARY

In order to facilitate the development of stable isotope fractionation in the RTM, we have designed and executed a large scale flow-through column experiment specifically created to provide sub 20 cm sampling resolution at field-scale flow rates of sufficient volume to conduct stable isotope measurements. This experiment has generated an unprecedented stable isotope reactive transport dataset that serves as a basis for developing stable isotope RTM modeling of biogeochemically dynamic systems.

REFERENCES

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4)Maggi & Riley, J. Contam. Hydrol. 2009
5)DePaolo, D.J. GCA 2011
6)Nielsen et al., GCA in review

Funding for this study was provided by the U.S. Department of Energy, BER Program Contract DE-AC020SCH11231 to the LBNL Sustainable Systems Scientific Focus Area