LBNL Sustainable Systems SFA: Evolution of Pore Structures and Flowpath Challenge

Isotopic Signatures for Key Mineralogical Reactions Accompanying Biostimulated Uranium Reduction

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ABSTRACT

Stable isotopes provide a valuable means of distinguishing between microbially mediated and abiotic processes during subsurface bioremediation through characteristic fractionations. The isotopic signature associated with a fractionating reaction is preserved in both the residual reactants and products, providing a means of detecting principal contaminant sequestration processes as well as monitoring the long-term stability of precipitates. This project focuses on identification of isotopic systems useful in studying stimulated subsurface bioremediation processes, and incorporation of these isotopes into reactive transport modeling. A reactive transport model that treats isotopes as individual species and includes fractionations associated with microbial reactions will provide valuable insights into the formation and stability of key mineralogical reactions contributing to permeability and flowpath evolution during *in situ* amendment. This research is part of the LBNL SFA challenge addressing the evolution of hydrologic flow patterns at the Rifle IFRC site. Previous analysis of sulfur isotopes show enrichment of up to 7‰ in $\delta^{34}S$ of sulfate and a corresponding sulfide $\delta^{34}S$ of -20‰ in down-gradient monitoring wells, followed by a transition to smaller fractionation factors as sulfate became less available. Preservation of the $\delta^{34}S$ of sulfide signature within iron sulfide precipitates further suggested a means of monitoring iron sulfide reoxidation through the isotopic composition of sulfate. An extensive dataset of $\delta^{34}S$ of sulfate and sulfide, as well as $\delta^{18}O$ of sulfate using samples from the 2008 Rifle amendment is currently being developed. Preliminary data indicate a correlation between decreasing sulfate concentrations and increasing $\delta^{34}S$ values similar to previous results, despite a more complex electron donor injection scheme. $\delta^{18}O$ of sulfate in the same samples averages roughly 2‰ and correlates with both $\delta^{34}S$ and sulfate concentrations, though the magnitude of variation is less pronounced. Preliminary $\delta^{44}Ca$ data analysis shows no variation due to ion exchange, while column samples obtained during high rates of calcite precipitation show detectable shifts of roughly 2‰.

BACKGROUND, HYPOTHESIS & APPROACH

Sulfur Isotopes

- Sulfate reducing bacteria (SRB) preferentially use sulfate containing the lighter ^{32}S over the heavier ^{34}S isotope.
- The degree to which the residual sulfate pool is enriched in the heavy isotope is principally dependant on two factors:
  - The magnitude of the SRB preference for the lighter isotope (the fractionation factor)
  - The extent of sulfate depletion that has already occurred
- Under most conditions this difference is 10‰ or greater, though when the sulfate pool becomes limited this value reduces
- Biogenic sulfide precipitated as iron sulfides preserves the depleted ^{34}S signature.

$$\delta^{34}S = \left[\left(\frac{\left(\frac{^{34}S}{^{32}S}\right)_s}{\left(\frac{^{34}S}{^{32}S}\right)_R}\right) - 1\right] * 1000 \%$$

isotope	abundance	mass (amu)
^{32}S	95.03957	31.97207
^{33}S	0.74865	32.97146
^{34}S	4.19719	33.96789
^{36}S	0.01459	35.96708

Hypothesis

- Sulfur isotopes provide valuable information on

1) the onset of sulfate reduction

2) sulfate vs. electron donor limited conditions

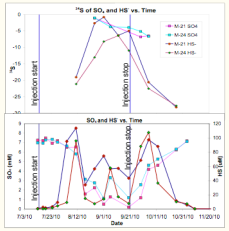
3) the stability of sulfide precipitates

4) biogenic vs. transport limited sulfate reduction processes

BACKGROUND, HYPOTHESIS & APPROACH

Preliminary Study

- Samples collected during the 2006 Rifle acetate amendment study were analyzed for $\delta^{34}S$ of sulfate and sulfide (Druhan et al., 2008).



- Results indicated enrichment of up to 7‰ in $\delta^{34}S$ of sulfate and variation in sulfide $\delta^{34}S$ between -27‰ and -1‰.
- These data show:
  - sulfur isotopes indicate the transition between sulfate and acetate limited conditions through changes in the fractionation factor between sulfate and sulfide
  - sulfide $\delta^{34}S$ appears to be a sensitive indicator of the onset of sulfate reduction
  - sulfur isotopes may be used to explain complex aqueous sulfur species concentration data

Approach

- Samples collected during the 2008 Big Rusty amendment are being used to generate a more complete timeline of sulfate and sulfide sulfur isotope data to expand upon results obtained in the preliminary study.

day	date	Acetate / Bromide (mM)	Tank #
0	7/20/08	50 / 13	1
15	8/04/08	0 / 0	2
24	8/13/08	50 / 13	3
38	8/27/08	150 / 13	4
57	9/15/08	150 / 13	5
73	10/01/08	150 / 13	6
90	10/17/08	150 / 13	7
110	11/06/08	stop	

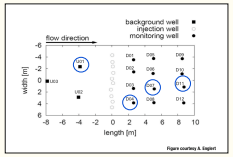


Figure courtesy A. Englert

Calcium Isotopes

- Previous studies suggest under kinetically controlled conditions secondary calcite precipitation results in preferential incorporation of the lighter ^{40}Ca isotope into the solid phase. This fractionation has been observed in portions of the Madison aquifer (Jacobson and Holmden, 2008)

$$\delta^{44}Ca = \left[\left(\frac{\left(\frac{^{44}Ca}{^{40}Ca}\right)_s}{\left(\frac{^{44}Ca}{^{40}Ca}\right)_R}\right) - 1\right] * 1000$$

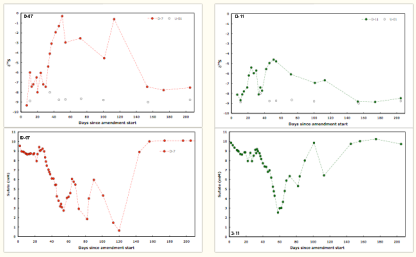
Hypothesis and Approach

- Calcium isotope fractionation should be observable during rapid calcite precipitation associated with bioreduction at Rifle, and may provide information on the amount of precipitation and flowpath evolution.
- A preliminary dataset of $\delta^{44}Ca$ was generated using samples from a through-flow column of Rifle sediment to determine if fractionations could be observed under these conditions.

isotope	abundance	mass (amu)
^{40}Ca	96.941	39.62591
^{42}Ca	0.00647	41.95862
^{43}Ca	0.00135	42.95877
^{44}Ca	0.02086	43.95548
^{46}Ca	0.00004	45.95369
^{48}Ca	0.00187	47.95253

RESULTS

Sulfur Isotopes



- A dataset of $\delta^{34}S$ for sulfate and sulfide throughout the Big Rusty amendment is currently being generated.
- Sulfate $\delta^{34}S$ from monitoring wells D07 and D11 show enrichment from a background value of -9‰ to -0.3‰ and -4.6 ‰, respectively.
- Reduction in the magnitude of enrichment at the height of sulfate reduction suggests transition to a sulfate limited condition similar to that observed in the 2006 amendment.

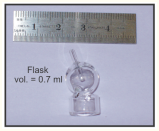
Sulfate Diffusion

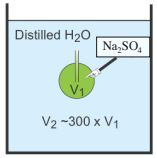
- The sulfur isotope dataset provides an opportunity to distinguish between two fractionation processes:

1) biogenic fractionation associated with preferential utilization of sulfate containing the lighter ^{32}S isotope

2) In the situation where SRB are reducing all available sulfate, the limitation becomes the ability of the system to deliver more sulfate to the depleted zone, leading to a diffusion based transport fractionation

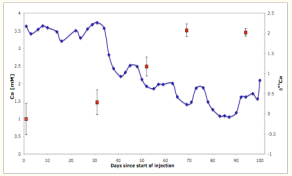
- Distinguishing between these processes will yield valuable insight into the relationship between microbial activity and solute transport.
- In order to do so the diffusion coefficients of the isotopologues of sulfate must be determined. These measurements will be made under conditions similar to Rifle and will be used in future reactive transport models.





RESULTS (CON'T)

Calcium Isotopes



- Samples collected from a through-flow column of Rifle sediment designed to replicate the bioremediation process showed a 3-fold decrease in aqueous calcium concentrations associated with calcite precipitation.
- Five samples spaced throughout the timeline of the column experiment were chosen for $\delta^{44}Ca$ analysis.
- Results show enrichment of 2‰ in $\delta^{44}Ca$, from a starting value of -0.133‰ to 2.075‰ during calcite precipitation. This value coincides with the range of fractionations observed during rapid calcite precipitation observed elsewhere and confirms that this shift is detectable under conditions of subsurface bioremediation.
- These findings suggest a potential means of quantifying the extent of calcite precipitation in situ using calcium isotopes. Future work will include analysis of a subset of samples from the Big Rusty experiment to determine if this shift can be detected in the field, and further column experiments designed specifically for isotopic measurements.

SUMMARY

- Sulfur isotopes of sulfate from the Big Rusty field experiment show enrichment during sulfate reduction associated with SRB activity. These data provide a direct means of monitoring sulfate vs. electron donor limited conditions through changes in the associated fractionation.
- Sulfide data for the Big Rusty experiment are currently being generated and are expected to show sensitivity to the onset of sulfate reduction prior to observable declines in sulfate concentration.
- The fractionation observed between sulfate and sulfide may result from biogenic or transport processes. Discerning between these effects will provide information on the relationship between microbial and hydrologic conditions.
- Calcium isotope data from a Rifle column experiment show fractionation associated with calcite precipitation, suggesting a promising means of quantifying in situ secondary calcite formation.
- Future work will include a new Rifle column experiment designed specifically for isotopic measurements, including isotopes of sulfur, calcium, oxygen, hydrogen, carbon and iron.

REFERENCES

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•Jacobson, A.D. and Holmden, C. (2008) δ44Ca evolution in a carbonate aquifer and its bearing on the equilibrium isotope fractionation factor for calcite. EPSL, v. 270(3-4) 349-353.

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