

Multiple Sulfur Isotope Effects During Sulfite and Bisulfite Oxidation in Aqueous Solution

DANIEL L. ELDRIDGE^{1*}, SANG-TAE KIM², AND J. FARQUHAR¹

¹Dept. of Geology and ESSIC, University of Maryland, College Park, MD 20742 USA (*correspondence: eldridge@umd.edu)

²School of Geography and Earth Sciences, McMaster University, Hamilton Ontario, Canada, L8S 4K1.

The multiple sulfur isotope fractionations accompanying the oxidation of sulfite (SO_3^{2-}) and bisulfite (HSO_3^-) to sulfate via oxygen (O_2) have been investigated, revealing both normal (-) and inverse (+) fractionations depending on pH. These compounds are important reaction intermediates in the oxidation of biogenic and volcanogenic hydrogen sulfide (e.g., [1]) and can be used by a variety of prokaryotes for dissimilatory metabolism, including the processes of oxidation, reduction, and disproportionation (e.g., [2]). Reactions involving these compounds are also relevant to the sulfur cycle in a variety of environments, including hydrothermal hot springs (e.g., Yellowstone NP), the chemocline in euxinic water bodies, marine sediments, and the atmosphere (forming acid rain).

Buffered sulfite and bisulfite solutions were prepared in batch reaction vessels from sulfur dioxide (99.9+%, Sigma Aldrich) at a pH of 12.5 (corresponding to ~99.9% SO_3^{2-}) and 4.6 (corresponding to ~99.5% HSO_3^-) using a custom built glass vacuum line. Oxidation of sulfite/bisulfite was initiated after placing vessels in a temperature controlled water bath (stability of 0.01 °C) and introducing ultrapure oxygen (Airgas), enough to oxidize a fraction of the bisulfite/sulfite in solution. Residual sulfite/bisulfite was separated from product sulfate via acidification and cryogenic trapping of evolved SO_2 , and both product and residual reactant were processed for isotopic analysis using standard techniques.

Table 1 shows the preliminary results of sulfite and bisulfite oxidation experiments conducted at 5.00 ± 0.01 °C. At relatively low pH where bisulfite is dominant, product sulfate is isotopically *light* relative to reactant bisulfite by about 5.32 ‰ based on $^{34}\text{S}/^{32}\text{S}$. In contrast, at high pH where sulfite is dominant, product sulfate is isotopically *heavy* by about 4.48 ‰ relative to reactant sulfite. Variations in the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ values approach the limits of detection, although small positive shifts in $\Delta^{33}\text{S}$ may accompany these reactions. The change in the direction of the fractionation based on speciation appears to be a new observation. It is clear that the isotope effects associated with these reactions are more complex than previously recognized.

| pH | $10^3 \ln(\alpha)$ (‰) | $\Delta^{33}\text{S}$ (‰) | $\Delta^{36}\text{S}$ (‰) |
|---------------|------------------------|---------------------------|---------------------------|
| 4.6 (2 exp.) | -5.32±0.10 | 0.018 ± 0.010 | -0.1 ± 0.2 |
| 12.5 (4 exp.) | 4.48±0.29 | 0.011 ± 0.040 | -0.1 ± 0.1 |

Table 1: Fractionations ($\alpha = {}^{34}\text{R}_{\text{product}}/{}^{34}\text{R}_{\text{reactant}}$) determined for bisulfite (pH=4.6) and sulfite (pH=12.5) oxidation experiments at 5.00 ± 0.01 °C. Uncertainties are 2σ standard deviations of repeat experiments (duplicate or quadruplicate).

[1] J-Z. Zhang & F.J. Millero (1993) *GCA* **V. 57**, 1705-1718.

[2] D.E. Canfield (2001) *Rev. in Min. & Geochem.* **V.43** 607-636.

Microbial-mineral-metal interactions in suspended aquatic floc

ELLIOTT, A.V.^{1*}; PLACH, J.M.¹; DROPPA, I.G.^{2,1};

AND WARREN, L.A.¹

¹McMaster University, Hamilton, Canada, elliottav@mcmaster.ca (* presenting author)

²National Water Research Institute, Environment Canada, Burlington, Canada

Characterization of suspended floc trace element (TE) abundance and partitioning for Ag, As, Cu, Ni and Co across 6 variably impacted aquatic ecosystems identify floc to be a key trace element sequestration phase, concentrating TEs ~55x above that of surficial bed sediments. Further, floc TE geochemical partitioning patterns were highly conserved across systems, with amorphous Fe oxyhydroxides (FeOOH) consistently the most important sorbent phase for TE retention, regardless of physico-chemical conditions or elements involved. In contrast, surficial (0-0.5cm) bed sediment TE partitioning was more classically reflective of both system geochemical parameters and element-specific reactivity, indicating differing controls on TE sequestration by suspended versus bed sediment system compartments. Results indicate that floc TE uptake is biologically linked to floc microbial components. Imaging analysis of floc architecture reveals bacterial extracellular polymeric substances (EPS) as the major constituent of floc organics and physical bridging mechanism between floc-associated organic and inorganic constituents. Moreover, floc organic concentrations (live cells, EPS) directly predict floc-FeOOH concentrations. Thus while floc-FeOOH are the dominant TE sequestration phase, floc-associated organic and microbial constituents provide the critical foundation underpinning enhanced floc TE uptake through their structure role in the nucleation, precipitation and/or trapping of TE-reactive FeOOH; ultimately creating a distinctly different solid than surficial sediments in close proximity with differing controls on trace element uptake.

[1] Author Last Name (Year) *Publication Name* **Volume#**, pp-pp.

[2] Author Last Name (Year) *Publication Name* **Volume#**, pp-pp.