Sulfate reduction and zinc isotope fractionation observed using a flow-through cell and in situ XAS analysis

JULIA H. JAMIESON-HANES[1], HEATHER K. SHRIMPTON[1], HARISH VEERAMANI[1,2], CAROL J. PTACEK[1], ANTONIO LANZIROTTI[3], MATTHEW NEWVILLE[3], DAVID W. BLOWES[1]*

[1] Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON, N2L 3G1, Canada (jhjamies@uwaterloo.ca, hshrimpt@uwaterloo.ca, ptacek@uwaterloo.ca, *correspondence: blowes@uwaterloo.ca)

[2] Present address: School of Engineering, University of Glasgow, Glasgow, G12 8QQ, United Kingdom (harish.veeramani@glasgow.ac.uk)

[3] Center for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637, USA (lanzirotti@cars.uchicago.edu, newville@cars.uchicago.edu)

Zinc isotope fractionation and secondary Zn-sulfide precipitation under microbially-mediated sulfate reducing conditions was evaluated using a synchrotron-based flow-through cell experiment. The flow-through cell was constructed with a Kapton window to allow real-time, *in situ*, collection of X-ray absorption spectroscopy (XAS) at the Zn K-edge over the course of the experiment. Creek sediment, biostimulated with synthetic groundwater containing sulfate, was packed into the cell. This synthetic groundwater solution, augmented with 0.90 mM Zn, was pumped through the cell to promote Zn removal under sulfate reducing conditions. The residence time was modified by increasing the flow rate step-wise during the experiment to produce changes in the extent of Zn removal. Aqueous effluent samples showed that the greatest degree of Zn removal occurred at the slowest flow rate. As the flow rate increased, the degree of Zn removal decreased. Effluent monitoring showed an increase in $\delta^{66}Zn$, with the greatest enrichment associated with more extensive Zn removal. A Rayleigh curve was fit to the isotope data, where $\varepsilon = -0.26 \pm 0.06$ ‰ (2σ). The results from this study are consistent with fractionation of Zn observed during Zn-sulfide precipitation in batch experiments, where $\varepsilon = -0.30 \pm 0.04$ ‰ [1]. Assessment of Zn isotope fractionation under controlled conditions provides an important foundation for application of Zn isotope measurements to field systems.

[1] Veeramani et al. (2015) *Environ. Sci. Technol. Letters* **2(11)**, 314-319.