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Evaluating zinc isotope fractionation under sulfate reducing conditions using a flow-through cell and *in situ* XAS analysis

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Abstract

A flow-through cell experiment was conducted to evaluate Zn isotope fractionation during ZnS precipitation under microbially-mediated sulfate-reducing conditions. Synthetic groundwater containing 0.90 mM Zn was pumped through a cell containing creek sediment that was biostimulated to promote sulfate reducing conditions. Real-time, *in situ* X-ray absorption spectroscopy (XAS) was applied at the Zn K-edge to collect spectra *via* a Kapton® window in the front of the cell over the course of the experiment. Aqueous effluent samples were collected and analysed to determine concentrations of anions and cations, and Zn isotope ratios. The flow rate was increased step-wise during the experiment to modify the residence time and produce changes in the extent of sulfate reduction, which in turn controlled the extent of ZnS precipitation. Greater enrichment in the heavier isotope in the aqueous phase relative to the input solution was associated with more extensive Zn removal. A Rayleigh curve was fit to the isotope data, where $\varepsilon = -0.27 \pm 0.06‰$ (2σ). Evaluation of Zn isotope fractionation under controlled flow conditions is critical to improve the efficacy of this powerful analytical technique when applied to natural systems or remediation projects in the field.

Keywords: Zinc isotopes; Zinc sulfide; Sulfate reduction; XAS; Passive treatment

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1. INTRODUCTION

Zinc (Zn) is an essential micronutrient that is involved in numerous biogeochemical processes in the environment (Labrenz and Druschel, 2011). However, Zn can be toxic when concentrations become elevated; for example, amphipods have been shown to be impacted by Zn concentrations in the range of 200 µg L^{-1} (Besser and Leib, 2007). Anthropogenic activities such as mining can result in increased Zn concentrations in soil, surface water, and groundwater (Al et al., 1994; Moncur et al., 2005). Release of Zn from mine wastes due to sulfide mineral oxidation is frequently accompanied by elevated concentrations of sulfate (SO_4) and either acidic or neutral pH conditions (Lindsay et al., 2009; Blowes et al., 2014). Passive treatment of Zn *via* ZnS precipitation under microbially-mediated sulfate reducing conditions has been shown to be a viable remediation technique (Waybrant et al., 1998, 2002; Blowes et al., 2000).

Under anaerobic conditions, sulfate-reducing bacteria (SRB) participate in the reduction of sulfate to sulfide,

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coupled with the oxidation of organic carbon (Blowes et al., 2000):

$$2CH_2O_{(s)} + SO^{2-}_{4(aq)} + 2H^+_{(aq)} \rightarrow H_2S_{(aq)} + 2CO_{2(aq)} + 2H_2O_{(l)} \quad (1)$$

The presence of aqueous hydrogen sulfide can lead to the precipitation of ZnS, effectively removing it from solution:

$$Zn^{2+}_{(aq)} + H_2S_{(aq)} \rightarrow ZnS_{(s)} + 2H^+_{(aq)} \quad (2)$$

Provided anaerobic conditions are maintained, this highly insoluble form of Zn (Lawrence and McCarty, 1965) can be a long-term sink.

Zinc has five stable isotopes, ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and ^{70}Zn, with natural abundances of 49.17%, 27.73%, 4.04%, 18.45%, and 0.61% (Meija et al., 2016). First pioneered by Maréchal et al. (1999), Zn isotope ratio analysis has emerged as a powerful technique for tracking geochemical processes in the environment and identifying sources of both natural and anthropogenic Zn contamination (*e.g.*, Pokrovsky et al., 2005; Borrok et al., 2009; Aranda et al., 2012). To apply Zn isotope ratio measurements as a tool to better understand complex natural systems, it is critical to characterize the Zn isotope behavior that is attributed to each reaction mechanism. Controlled laboratory batch experiments provide insight into Zn isotope behavior in pure systems. For example, Pokrovsky et al. (2005) observed very little fractionation during sorption of Zn to Fe and Mn oxides, reporting average shifts of up to 0.2‰ for $^{66}Zn/^{64}Zn$; similar ranges of fractionation were reported for Zn sorption to ferrihydrite (Veeramani et al., 2015). Juillot et al. (2008) reported $\Delta^{66/64}Zn_{sorbed\text{-}aqueous}$ values of +0.29‰ for Zn sorption on goethite and +0.53‰ on 2-Lines ferrihydrite, whereas Balistrieri et al. (2008) reported $\Delta^{66/64}Zn_{soln\text{-}solid}$ values of −0.52‰ for Zn adsorption onto amorphous ferric oxyhydroxide. In contrast, values of $\Delta^{66/64}Zn_{adsorbed\text{-}dissolved}$ up to +2.7‰ were observed for Zn adsorbed to birnessite at high ionic strength (Bryan et al., 2015). Relatively large shifts in Zn isotope composition occur during mineral precipitation reactions. Aqueous Zn is enriched in the heavier isotope during ZnS precipitation, whereas during Zn-carbonate and Zn-phosphate formation, aqueous Zn is depleted in the heavier isotope (Veeramani et al., 2015). Magnitudes of Zn isotope fractionation determined experimentally are in good agreement with those predicted by computational techniques (Black et al., 2011; Fujii et al., 2011, 2014). Building on these pure-system batch experiments, laboratory experiments incorporating greater complexity (*e.g.*, simulated groundwater, natural reactive materials) and saturated flow provides an opportunity to evaluate Zn isotope ratio measurements as a tool under conditions that more closely represent real-world systems.

The objective of this study was to identify the mechanism of aqueous Zn removal under microbially-mediated sulfate reducing conditions, and to evaluate the concomitant Zn isotope behavior during Zn removal by natural sediment under saturated flow conditions. Following the experimental design pioneered by Jamieson-Hanes et al. (2014), a flow-through cell experiment was conducted to acquire real-time, *in situ* speciation of the Zn removed from solution, and to simultaneously collect aqueous Zn for isotopic analysis. Solid-phase Zn and sulfur (S) X-ray absorption spectroscopy (XAS) was combined with aqueous pH and redox measurements, cation and anion concentrations, Zn isotopic analyses, and microbiological characterization to provide a more complete understanding of the biogeochemical processes during Zn removal by natural sediment under sulfate-reducing conditions. Assessment of Zn isotope fractionation in this system is critical for the application of isotope analyses to understand Zn cycling in natural systems, which will also aid remediation endeavors.

2. MATERIALS AND METHODS

2.1. Cell design

A flow-through cell (FTC) was fabricated using high-density polyethylene (HDPE) following a similar design to that used in Jamieson-Hanes et al. (2014). The dimensions of this cell were greater than that used in a previous study, with the open-faced indentation measuring 3.8 × 7.6 × 1.3 cm (37.5 mL internal volume, 28.9 cm^2 face area; Fig. 1). A HDPE frame was affixed to the face of the cell to hold in place an 80 μm-thick sheet of Kapton® film allowing X-ray penetration; a rubber O-ring provided a fluid-tight seal. The outer dimensions of the cell were 17.8 × 14.0 × 6.4 cm. Synthetic groundwater was passed through the cell via 2 mm ports installed at the bottom and top of the cell.

2.2. Experimental setup

Natural sediment was collected from the anaerobic zone of Columbia Lake in Waterloo, Ontario, Canada (43° 28′30.6″N 80°33′15.0″W) to provide a natural source of microbial communities. The sediment was biostimulated in synthetic groundwater containing 3.5 mM sodium sulfate and 250 mM sodium lactate. The sediment was incubated at 25 °C; the solution was replaced once a week with fresh synthetic groundwater. Within one week, the sediment was found to be reducing as indicated by formation of black iron sulfide precipitates and a hydrogen-sulfide-like smell; however, the sediment was allowed to continue to reduce for several more weeks. The biostimulated sediment was mixed with acid-washed silica sand (20–30 mesh) at a ratio of 40%: 60% by volume, to increase permeability and allow water to flow through the material. The sediment-sand mixture was packed into the FTC under a 3.5% H_2/balance N_2 atmosphere in an anaerobic glovebox (Coy Laboratory Products Inc., Grass Lake, MI). Glass wool and Nitex mesh screen with 210 μm openings were used to prevent clogging of the influent and effluent ports.

An input solution of synthetic groundwater containing 0.90 mM Zn as $ZnSO_4{\cdot}7H_2O$ was prepared following the composition listed in Table 1. Lactate was added as the organic carbon source (250 mM as Na-lactate), while Na_2SO_4 was added to increase the initial SO_4 concentration to 4.44 mM. This solution was purged with high-purity Ar