



# Zinc stable isotope fractionation upon accelerated oxidative weathering of sulfidic mine waste



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## HIGHLIGHTS

- Controlled oxidative weathering was applied on Kidd Creek mill tailings.
- For the first time  $\delta^{66}\text{Zn}$  was determined in the leachate of the weathering cell.
- $\delta^{66}\text{Zn}$  provided additional information on zinc sources and mobilization.

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## ABSTRACT

Accelerated oxidative weathering in a reaction cell (ASTM D 5744 standard protocol) was performed over a 33 week period on well characterized, sulfidic mine waste from the Kidd Creek Cu–Zn volcanogenic massive sulfide deposit, Canada. The cell leachate was monitored for physicochemical parameters, ion concentrations and stable isotope ratios of zinc. Filtered zinc concentrations ( $<0.45\ \mu\text{m}$ ) in the leachate ranged between  $4.5\ \text{mg L}^{-1}$  and  $1.9\ \text{g L}^{-1}$ —potentially controlled by pH, mineral solubility kinetics and (de)sorption processes. The zinc stable isotope ratios varied mass-dependently within  $+0.1$  and  $+0.52\%$  relative to IRMM 3702, and were strongly dependent on the pH ( $r_{\text{pH-d}^{66}\text{Zn}} = 0.65$ ,  $p < 0.005$ ,  $n = 31$ ). At a pH below 5, zinc mobilization was governed by sphalerite oxidation and hydroxide dissolution—pointing to the isotope signature of sphalerite ( $+0.1$  to  $+0.16\%$ ). Desorption processes resulted in enrichment of  $^{66}\text{Zn}$  in the leachate reaching a maximum offset of  $+0.32\%$  compared to the proposed sphalerite isotope signature. Over a period characterized by  $\text{pH} = 6.1 \pm 0.6$ , isotope ratios were significantly more enriched in  $^{66}\text{Zn}$  with an offset of  $\approx 0.23\%$  compared to sphalerite, suggesting that zinc release may have been derived from a second zinc source, such as carbonate minerals, which compose 8 wt.% of the tailings. This preliminary study confirms the benefit of applying zinc isotopes alongside standard monitoring parameters to track principal zinc sources and weathering processes in complex multi-phase matrices.

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## 1. Introduction

The formation of metalliferous rock drainage (also: acid mine drainage, AMD) is triggered by sulfide mineral oxidation (De La Torre et al., 2011; Taylor et al., 1984). This naturally occurring process may be accelerated by mineral extraction and processing through the increase in reactive surface area and the exposure of mine wastes to ambient conditions ( $\text{O}_2$ ,  $\text{H}_2\text{O}$ ). Due to the elevated potential for contamination

and for impacts on sensitive environmental receptors associated with waters affected by mining activities, it is critical to assess the likelihood of AMD formation from waste rock prior to its final disposal. In the standardized humidity cell method ASTM D 5744 (2001), the mine waste (waste rock or mill tailings) is exposed to accelerated oxidative weathering under dry and wet air cycles to enhance mineral sulfide oxidation. Oxidation products are consequently mobilized through dissolution (Kossoff et al., 2010). This method offers the opportunity to predict potential future leaching behaviour and identify the main contaminants deriving from mine waste. This procedure also offers the opportunity to monitor natural weathering processes under controlled laboratory conditions. The volcanogenic massive sulfide deposit Kidd Creek, Canada, has average concentrations of  $28.6\ \text{mg g}^{-1}$  Cu,  $61.4\ \text{mg g}^{-1}$  Zn,  $2.2\ \text{mg g}^{-1}$  Pb,  $0.085\ \text{mg g}^{-1}$  Ag and minor concentrations of Sn and Cd (Bleeker and Parrish, 1996; Schandl and Wicks,

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1993). A well characterized sample of Kidd Creek mill tailings with zinc as a major component ( $5.98 \text{ mg g}^{-1}$ ) (Al et al., 1997; Jambor and Owens, 1992) was subjected to weathering cycles in a laboratory-scale leaching cell. Zinc is bio-essential and a component in more than 300 enzymes involved in many metabolic pathways. In excess, however, it may have adverse impacts on numerous environmental receptors (Griffith et al., 2012; Mayes et al., 2010). Knowledge about the mobilization of zinc, its transport behaviour and attenuation is therefore critical. Here, we complemented the standard monitoring parameters of the cell leachate of a weathering cell (ASTM D 5744, 2001) with the determination of zinc stable isotope ratios. Zinc is pentanuclear (natural abundance:  $64 > 66 > 68 > 67 > 70$ ) and has an atomic weight of 65.3756 (Gross et al., 2012; Tanimizu et al., 2002). Zinc stable isotope ratios were first analysed by Multi-Collector Inductively-Couple Plasma Mass Spectrometry (MC-ICP-MS) in 1999 (Maréchal et al., 1999). Isotope ratios of zinc are mass-dependently fractionated by numerous natural and anthropogenic, biotic and abiotic processes (Cloquet et al., 2008) in the range of 1 to 2‰. Recently, increasing numbers of mine water and mine waste related studies have applied this isotope system in order to identify zinc sources and discriminate processes connected to the mobilization and attenuation of zinc (Aranda et al., 2012; Borrok et al., 2008; Fernandez and Borrok, 2009). The aim of this study was to gain information on the zinc isotope system during the accelerated oxidation of a well-characterized mill tailings sample. We aimed to investigate zinc isotope fractionation under controlled laboratory conditions and the resulting changes in pH and ionic strength, and identify processes controlling zinc mobility. The results should provide a valuable contribution to understanding the zinc isotope system and its potential application for monitoring weathering processes.

## 2. Materials and methods

### 2.1. Kidd Creek mill tailings

Unoxidized, oven dried ( $100 \text{ }^\circ\text{C}$ , Table 1) mill tailings were received from the metallurgical plant of the Kidd Creek mine for mineralogical and geochemical characterization (Jambor and Owens, 1992; Jambor et al., 1993; Jurjovec et al., 2002).

One kilogram of homogenized, riffle-split tailings material was subjected to 33 weeks of 7-day cycles of oxidative weathering in a standard humidity cell (200 mm diameter) under controlled laboratory conditions ( $T = 20.8 \pm 0.6 \text{ }^\circ\text{C}$ ). The purpose of the test is to accelerate the oxidation of sulfide minerals, the generation of acidity and metal leaching under varying sample humidity and flushing. For this purpose, in 7-day cycles the sample was exposed to dry air during days 1 to 3 and moisturized air during days 4 to 6 dry followed by flooding with 1 L of deionized water on day 7. After 2 hours reaction time, the water was drained at the bottom of the cell and recovered for analysis.

### 2.2. Physico-chemical parameters and ion concentrations

The leachate was analysed for physicochemical parameters (pH, Eh, T, electrical conductivity (EC), alkalinity). Cation and anion

concentrations and zinc stable isotope ratios were determined on the leachate water as described in the electronic supplement (Sppl).

### 2.3. Calculations

The leachate chemistry was interpreted with the assistance of the USGS equilibrium geochemical/mass transfer model PhreeqC (version 2.18.00). The WATEQ4F thermodynamic database (Ball and Nordstrom, 1991) was updated with thermodynamic data for ankerite, ferrihydrite, schwertmannite and lepidocrocite (Al, 1996; Bigham et al., 1996; Bonneville et al., 2009; Majzlan et al., 2004). Calculation results are expressed as the saturation index values ( $\text{SI} = \log \text{IAP} - \log \text{K}$ ; IAP = ion activity product; K = solubility constant). An SI greater than zero suggests supersaturation, whilst an SI below zero suggests that water is potentially undersaturated with respect to the mineral. An SI value of 0 indicates that equilibrium has been attained.

### 2.4. Zinc stable isotope ratios

Dissolved Zn was concentrated and separated from the matrix by liquid–solid extraction. Isotope ratios were continuously analysed on a Thermo Fisher Neptune MC-ICP-MS. A double spike method (Isoflex, San Francisco, USA,  $^{67}\text{Zn}:^{70}\text{Zn} = 0.43:0.57$ , spike:sample ratio of 0.37) was used to adjust for analytical isotope fractionation and instrumental mass bias. A detailed description of the sample preparation as well as measuring conditions on the MC-ICP-MS can be found in the electronic supplement. Isotope ratios are reported as delta notation ( $\delta^{66}\text{Zn} = R_{\text{sample}} \times R_{\text{standard}}^{-1} - 1$ ,  $R = {}^{66/64}\text{Zn}$ ) relative to the international Zn isotope standard IRMM 3702. Zinc isotope ratios in the literature referring to non-IRMM reference standards and cited in this publication were recalculated to IRMM 3702 ( $\delta^{66}\text{Zn}_{\text{IRMM/JMC}} \approx +0.32\text{‰}$ ) (Cloquet et al., 2008) to facilitate comparison. The Zn isotope ratios 67/64 and 70/64 were checked to verify mass-dependent fractionation and the possibility of spectral interferences (Sppl). The total procedural blanks (incl. chemical purification and mass spectrometry) of Zn contributed in average 2.8% to the total Zn signal.

## 3. Results

### 3.1. Physicochemical parameters and ion concentrations

Over the course of the experiment, pH values ranged between 3.7 and 6.6 (Fig. 1). After an initial pH of 3.7 (week 0), pH values increased to circum-neutral values within three weeks. During weeks 7 to 18, the pH varied around  $6.3 \pm 0.2$ , and subsequently (weeks 21 to 33) decreased to pH values of  $4.5 \pm 0.2$ . Most dissolved metal concentrations, including zinc, showed a negative correlation to pH (Figs. 2 to 4, Sppl). The highest dissolved metal concentrations were observed during week 0. During weeks 7 to 18, most element concentrations were low or close to detection limit. The dissolved element concentrations increased during the later part of the experiment. Aluminium concentrations ranged from detection limit to  $71 \text{ mg L}^{-1}$  and iron concentrations varied between 0.4 and  $767 \text{ mg L}^{-1}$ , respectively. Depending

**Table 1**  
Mineralogical composition of the Kidd Creek mill tailings (Al, 1996; Jambor et al., 1993).

Mineral group	Minerals <sup>a</sup>	Mineral group	Minerals <sup>a</sup>
Sulfides (151 mg/g)	Pyrite Pyrrhotite Chalcopyrite Sphalerite	Gangue minerals (769 mg/g)	Quartz Chlorite Muscovite Biotite Albite Silpnomelane Gypsum
Carbonates (80 mg/g)	Siderite Ferroan dolomite-ankerite Calcite		

$S_{\text{measured}}$ : 56 to  $138 \text{ mg g}^{-1}$ ,  $C_{\text{calculated}}$  based on  $\text{FeCO}_3$ :  $\approx 8.3 \text{ mg g}^{-1}$ , porosity: 0.44 (Al et al., 1997; Jambor and Owens, 1992).

<sup>a</sup> Minerals in decreasing order of abundance.

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