The zinc stable isotope signature of waste rock drainage in the Canadian permafrost region

Romy Matthies [a,b,*], Sean A Sinclair [b,1], David W Blowes [b,1]

[a] School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK
[b] Department of Earth and Environmental Sciences, University of Waterloo, 200 University Avenue West, Waterloo ON N2L 3G1, Canada

ARTICLE INFO

ABSTRACT

Leachate from a well-instrumented experimental-scale waste-rock pile (test pile) at the Diavik Diamond mine, Northwest Territories, was monitored. The well-characterized waste rock consists of granite, pegmatitic granite and biotite schist with an average total sulfur and carbonate carbon concentration of 0.053 and 0.027 wt.%, respectively. The leachate emerging from the southern basal drain of the waste rock pile has been monitored since 2007. The zinc stable isotope footprint was characterized alongside standard monitoring parameters during two field seasons, May to November 2011 and 2012. The pH ranged between 4.3 and 6.8 and carbonate alkalinity was low or undetectable (<35 mg L^{-1} CaCO$_3$). The pH was governed by the oxidation of sulfide minerals and the dissolution of primary carbonate minerals and secondary Al and Fe oxyhydroxysulfates and hydroxides. Dissolved Al and Fe concentrations averaged 6.78 mg L^{-1} and 175 µg L^{-1}, respectively. The main processes controlling Zn concentrations in the range of 0.4 and 4.7 mg L^{-1} (average = 2.2 mg L^{-1}) were the oxidative dissolution of sphalerite (ZnS) and the attenuation by secondary Fe and Al hydroxides. Zinc isotopes were fractionated mass dependently. Zinc isotope ratios, ranging between −0.16 and +0.18‰ (average = +0.05‰, $n = 43$) were consistent with values reported for sphalerite from other deposits. The deviations in isotope ratios ($\Delta = 0.36‰$) were significant in comparison to analytical uncertainties (0.06‰). Zinc isotope ratios and concentrations were largely uncorrelated, suggesting that the processes affecting Zn mobility had little or no impact on the Zn isotope signature. These data suggest that the Zn isotope ratios of the waste-rock leachate may be used as a fingerprint to track anthropogenic, mine-derived Zn sources in an environment under fluctuating pH, temperature and ionic strength.

1. Introduction

Zinc is pentanuclidic, bio-essential and occurs predominantly in one oxidation state (Zn^{2+}). In many mine waters, however, particularly in those emerging from coal and massive sulfide deposits, Zn reaches concentrations potentially harmful for sensitive environmental receptors (Clyde et al., 2010; Solis-Domínguez et al., 2011). Since the development of Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) (Walder and Freedman, 1992), the Zn stable isotope system has been used to assess anthropogenic Zn sources, modes of metal transport and attenuation pathways of Zn (Shiel et al., 2013; Sivry et al., 2008; Sonke et al., 2008). Zinc has been shown to fractionate mass

dependently in numerous processes including biogenic and inorganic reactions in the order of 1.0–2.0‰ (Cloquet et al., 2008). The Zn isotope system may be used to identify contaminant sources and to elucidate processes that effect metal mobility. Therefore, Zn isotope ratio measurements are used increasingly in studies focused on the release of dissolved metals associated with the metal extraction industry (Aranda et al., 2012; Borrok et al., 2008; Dolgopolova et al., 2006). The aim of our study was to extend on the recent research by monitoring Zn isotopes in drainage derived from a well instrumented and characterized experimental waste-rock pile (Smith et al., 2013a,c) under Arctic climatic conditions over the course of two field seasons. Zinc had previously been identified as a potential contaminant associated with waste rock at the site (Smith et al., 2013a). Our objectives were to assess the variability of the Zn isotope ratios associated with varying (a) pH and ionic strengths, (b) temperature effects in Arctic climate and (c) the variability over different field seasons. Ultimately, we aim to assess whether Zn isotope ratios can be used to fingerprint the bulk Zn source of the waste rock and enable

* Corresponding author at: School of Civil Engineering and Geosciences, Newcastle University, Newcastle upon Tyne NE1 7RU, UK. Tel.: +44 191 222 4869; fax: +44 191 222 692.
E-mail addresses: romy_matthies@gmx.net (R. Matthies), sean.a.sinclair@uwaterloo.ca (S.A Sinclair), blowes@uwaterloo.ca (D.W Blowes).
[1] Tel.: +1 519 888 4567; fax: +1 519 746 7484.

discrimination of dissolved Zn derived from waste rock from other natural and anthropogenic Zn sources and to determine whether processes effecting Zn mobility affect the Zn isotopic signature.

1.1. The study site

The Diavik Diamond Mine is located in the Northwest Territories, Canada (64°29″N, 110°18″W, 440 m asl). The open pit and underground mine is located in a semi-arid, permafrost area with an annual precipitation of 280 mm, 60% occurring as snow, and mean annual air temperatures of $-8.5\,°C$ (18 °C in July, $-31\,°C$ January/February) (Environment Canada, 2010). Mining commenced in 2003. At the end of the lifetime of the mine, about 105 Mt of waste rock will be produced. The waste rock consists of country rock that surrounds the diamondiferous kimberlite dykes and is mostly composed of granite and pegmatitic granite that are composed of K-feldspar, albite, and quartz, with <5 % biotite and muscovite (Jambor, 1997). The granite contains xenoliths of meta-sedimentary biotite schist, which is composed of quartz (20–50%), albite (35–55%) and biotite (10–25%) and contains disseminated pyrrhotite ($Fe_{0.852}Ni_{0.004}Co_{0.001}S$) and traces of pyrite, sphalerite, chalcopyrite and calcite.

The waste rock at the Diavik site is segregated into three types on the basis of the sulfide content. Type I waste rock is composed of granite and contains <0.04 wt.% S, Type II waste rock, which is composed of granite with a small proportion of biotite schist contains 0.04–0.08 wt.% S and Type III waste rock, which contains a greater proportion of biotite schist contains >0.08 wt.% S. It is anticipated that the Type III rock may constitute up to 24 Mt of waste rock at closure (Smith et al., 2013c). This project was part of an integrated field and laboratory research programme that focused on monitoring the evolution of hydrology, geochemistry, biogeochemistry, internal temperatures and gas transport in waste rock under Arctic climatic conditions (Smith et al., 2013c). Three experimental waste-rock piles (test piles) were constructed at the Diavik site, including the Type I test pile, which contains run-of-mine Type I rock, the Type III test pile, which contains run-of-mine Type III rock, and the Covered test pile, which was constructed to evaluate an approved closure strategy. This study focuses on the Type III waste-rock test pile. The Type III test pile was constructed at the mine site between 2004 and 2006. The waste rock in this test pile has a total sulfur content in the <50 mm fraction of 0.053 wt.% ($n = 327$, $\sigma = 0.037$, range: 0.0085–0.27 wt.% S) and a carbonate content of 0.027 wt.% C (range: 0.008–0.32 wt.% C) (Smith et al., 2013b). Given the low carbonate content, this rock is considered to be potentially acid generating (Smith et al., 2013a,b). Automated measurements of pore-gas pressures made at 49 locations within the Type III test pile indicate that there are no pressure fluctuations that can be attributed to exothermic sulfide oxidation. In addition, automated measurements of pore-gas O_2 and CO_2 concentrations, made and the same locations, and manual measurements made a numerous other locations, indicate that concentrations of these gases have remained at atmospheric levels since the initiation of monitoring (Amos et al., 2009). Temperature measurements made at more than 150 locations within the Type III test pile show seasonal oscillations with no indication of temperature increases due to exothermal sulfide oxidation (Pham et al., 2013).

The Type III waste rock has a rock-like character and consists of particles between meters and sub-milimeters. About 14% of the waste rock has a grain size <5 mm. This material is dominated by gravel and sand and constitutes the majority of the reactive surface area of the waste rock. The saturated hydraulic conductivity of the matrix material of the waste rock ranged in the order of 2×10^{-6} to $2 \times 10^{-5}\,m\,s^{-1}$ (Neuner et al., 2009).

The waste-rock pile is frozen during early autumn to late spring. It thaws at rates of $0.2–0.4\,m\,d^{-1}$ (Neuner et al., 2013). Leachate monitoring is generally performed between May to October. The Type III test pile has basal dimensions of 50×60 m and a height of 15 m. The entire test pile is constructed on an impermeable liner, which captures water exiting at the base of the waste rock. This discharge is captured in a basal drainage system which directs water along the north, south and eastern margins of the test pile and is collected at the SE (South Basal Drain) and NE (North Basal Drain) corners of the test pile. Because of similarities between the effluent from the two basal drains, this study focused only on the South Basal Drain.

2. Material and methods

2.1. Physicochemical parameters and ion concentrations

Sampling methods were previously described (Smith et al., 2013a). Samples were collected from the heat-traced conduits of the basal drainage collection system underneath the South end of the waste rock pile (3BSxdrn15). Field parameters (pH, electrical conductivity (EC), Eh, T, flow (Q), alkalinity, PO_4^{3-}, S^{2-}, Fe^{2+}) and ion concentrations were determined.

2.2. Calculations

The leachate chemistry was interpreted by the modified USGS PHREEQC equilibrium geochemical/mass transfer model (version 2.18.00, WATEQ4F database) (Al, 1996; Ball and Nordstrom, 1991; Bigham et al., 1996; Bonneville et al., 2009; Majzlan et al., 2004). Mineral saturation is expressed as the saturation index (SI = log IAP − log K; IAP = ion activity product; K = solubility constant).

2.3. Zinc stable isotope ratios

Eighty-five samples were collected from the basal drain during 2011 and 2012. Zinc stable isotope ratios were determined on 43 of these samples. The procedure for Zn-matrix separation and isotope ratio determination was described in detail before (Matthies et al., 2014). The 0.45 µm filtered and HNO_3-acidified samples were used for isotope analysis. Sample preparation and zinc – matrix separation was performed in a clean laboratory environment and under a HEPA-filtered laminar floor hood. Each sample, blank and standard check (IRMM 3702) was spiked with a ^{67,70}Zn double spike (DS, Isoflex, San Francisco, USA, ^{67}Zn:^{70}Zn = 0.43:0.57) with a sample-DS ratio of ≈ 1.7. Continuously, the samples were evaporated and redissolved multiple times in concentrated HCl. Solid–liquid separation was performed with AG-1-X8 anion exchange resin and sequentially mobilized from the resin with 2 mL 10 M HCl, 16 mL 7 M HCl and 18 mL 1 M HCl. Zinc was eluted with 30 mL of 0.1 M HCl. The Zn phase was evaporated and redissolved in nitric acid. One quarter of each sample was used to monitor trace contaminants. The remainder was used for isotope analysis. Each sample was purified in duplicate. Each duplicate was analysed on a Thermo Fisher Neptune MC-ICP-MS during three analytical events. During each analytical event, two purified DS-IRMM standards, one purification blank and a maximum of nine samples were analysed. Each sample, standard and purification blank was bracketed with a blank solution (0.5 M HNO_3) to correct for background noise. The double spike was used to adjust for analytical isotope fractionation and instrumental mass bias. The contribution of ^{64}Ni and ^{70}Ge was subtracted assuming $^{66/64}$Ni = 3.903225806 and $^{70/72}$Ge = 0.756717501 via double-nested iteration (Siebert et al., 2001). Isotope ratios are reported as delta notation (δ^{66}Zn $= R_{sample} \times R_{standard}^{-1} - 1$,