



Molybdenum and zinc stable isotope variation in mining waste rock drainage and waste rock at the Antamina mine, Peru



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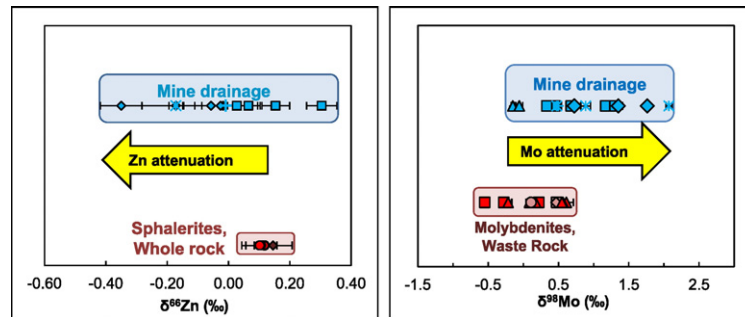
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HIGHLIGHTS

- Metal stable isotopes are promising indicators of attenuation in mine drainage.
- Mine water, waste rock and minerals were analyzed for Mo and Zn isotope ratios.
- Molybdenites had a wide range of $\delta^{98}\text{Mo}$, but sphalerites had invariant $\delta^{66}\text{Zn}$.
- Variations of 2.2‰ in $\delta^{98}\text{Mo}$ and 0.7‰ in $\delta^{66}\text{Zn}$ were measured in mine drainage.
- Attenuation processes drive changes in $\delta^{66}\text{Zn}$ and $\delta^{98}\text{Mo}$ in solution.

GRAPHICAL ABSTRACT



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ABSTRACT

The stable isotope composition of molybdenum (Mo) and zinc (Zn) in mine wastes at the Antamina Copper–Zn–Mo mine, Peru, was characterized to investigate whether isotopic variation of these elements indicated metal attenuation processes in mine drainage. Waste rock and ore minerals were analyzed to identify the isotopic composition of Mo and Zn sources, namely molybdenites (MoS_2) and sphalerites (ZnS). Molybdenum and Zn stable isotope ratios are reported relative to the NIST-SRM-3134 and PCIGR-1 Zn standards, respectively. $\delta^{98}\text{Mo}$ among molybdenites ranged from -0.6 to $+0.6\%$ ($n = 9$) while sphalerites showed no $\delta^{66}\text{Zn}$ variations ($0.11 \pm 0.01\%$, 2 SD, $n = 5$). Mine drainage samples from field waste rock weathering experiments were also analyzed to examine the extent of isotopic variability in the dissolved phase. Variations spanned 2.2‰ in $\delta^{98}\text{Mo}$ (-0.1 to $+2.1\%$) and 0.7‰ in $\delta^{66}\text{Zn}$ (-0.4 to $+0.3\%$) in mine drainage over a wide pH range (pH 2.2–8.6). Lighter $\delta^{66}\text{Zn}$ signatures were observed in alkaline pH conditions, which was consistent with Zn adsorption and/or hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) formation. However, in acidic mine drainage Zn isotopic compositions reflected the value of sphalerites. In addition, molybdenum isotope compositions in mine drainage were shifted towards heavier values ($0.89 \pm 1.25\%$, 2 SD, $n = 16$), with some overlap, in comparison to molybdenites and waste rock ($0.13 \pm 0.82\%$, 2 SD, $n = 9$). The cause of heavy Mo isotopic signatures in mine drainage was more difficult to resolve due to isotopic heterogeneity among ore minerals and a variety of possible overlapping processes including dissolution, adsorption and secondary mineral precipitation. This study shows that variation in metal isotope ratios are promising indicators of metal attenuation. Future characterization of isotopic fractionation associated to key environmental reactions will improve the power of Mo and Zn isotope ratios to track the fate of these elements in mine drainage.

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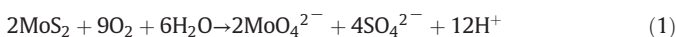
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1. Introduction

Leaching of metals during sulfide oxidation reactions in mining waste rock dumps presents a global environmental challenge, the mitigation of which requires a detailed understanding of the geochemical behavior of metals in these systems. Molybdenum (Mo) and zinc (Zn) are two metals which can be released at elevated concentrations during weathering of sulfidic waste rock (e.g. Kaback, 1976; Sahu et al., 1994). Both of these elements are important micronutrients, but can cause toxic effects at elevated environmental concentrations: excess Mo is particularly harmful to ruminants which are susceptible to molybdenosis (Barceloux, 1999) and Zn toxicity has been reported in plants, humans, cattle, and invertebrates (Canadian Council of Ministers of the Environment, 1999; Valko et al., 2005).

Molybdenum and zinc are released from mine wastes during the oxidative weathering of the sulfide ore minerals molybdenite (MoS_2) and sphalerite (ZnS), respectively:



Because aqueous Mo forms an anionic molybdate species (MoO_4^{2-}) while Zn forms a weakly-hydrolyzing cation (Zn^{2+}), the response of these metals to changes in pH in mine drainage is distinct (Dockrey and Stockwell, 2012) and their mobility may be reduced by different attenuation processes (e.g. adsorption, secondary mineral formation). Molybdate (MoO_4^{2-}) is strongly adsorbed onto oxyhydroxide minerals in moderately acidic conditions (Goldberg et al., 1996; Gustafsson, 2003; Xu et al., 2006), but is mobile in neutral to alkaline pH conditions where its adsorption is minimal. In alkaline mine drainage, molybdate minerals powellite (CaMoO_4) and wulfenite (PbMoO_4) can act as Mo solubility controls (Conlan et al., 2012). In contrast, Zn exhibits an opposite response to pH relative to Mo: it is mobilized in acidic conditions while attenuation processes reduce its mobility in alkaline conditions. Attenuation mechanisms for Zn in mine drainage include adsorption onto oxyhydroxide and carbonate minerals (Gupta et al., 1987; Iavazzo et al., 2012; Laurenzi et al., 2015), and the formation of a variety of secondary minerals such as $\text{Zn}(\text{OH})_2$, carbonates (e.g. smithsonite (ZnCO_3), hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$), silicates (e.g. willemite Zn_2SiO_4 , hemimorphite $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) and sulfates (e.g. zincosite, ZnSO_4) (Hirsche, 2012; Iavazzo et al., 2012; Jacquat et al., 2008; Wanty et al., 2013a, 2013b).

Conventional geochemical and mineralogical investigations have yielded some insights into which processes are responsible for metal attenuation in mining waste rock dumps. However, uncertainty remains with regard to the long-term fate of metals in mine wastes, in large part due to the difficulty in accessing the interior of dumps for sampling, and also due to the inherent mineralogical and hydrological heterogeneity of waste rock (Amos et al., 2015). Recent analytical improvements in mass spectrometry now permit the accurate and precise measurement of small variations in metal isotope ratios, which have been increasingly utilized as tracers of metal attenuation processes in the environment (Wiederhold, 2015). Metal isotope ratios may therefore become useful monitoring parameters for the characterization of mine drainage effluent (Matthies, 2015) by recording the geochemical history of attenuation processes which occur within waste rock dumps, provided these processes impart distinct isotopic signatures on the residual dissolved metal pool.

A small number of studies have investigated the applicability of Zn isotopes as tracers of Zn geochemistry in mine drainage. Matthies et al. (2014b) monitored Zn isotopic compositions of moderately acidic (pH ~4–6.5) mine drainage in an experimental waste rock pile and found small variations in $\delta^{66}\text{Zn}$ which averaged $+0.06 \pm 0.08\%$ (2 SD, $n = 43$) relative to the IRMM 3702 Zn isotope standard over a 2-year monitoring period, suggesting little effect of secondary processes

on Zn isotope ratios in waste rock drainage under those conditions. However, a subsequent study found a range in $\delta^{66}\text{Zn}$ of 0.4‰ during experimental leaching of sulfidic mine tailings, which was hypothesized to be caused by release of Zn from distinct mineral phases bearing different isotopic compositions (Matthies et al., 2014a). Other studies have examined Zn isotope compositions in surface waters downstream of historical acid-rock drainage (ARD) sites where limited variations in $\delta^{66}\text{Zn}$ were found, which led to the proposition that Zn stable isotope ratios were more likely to be tracers of Zn sources rather than attenuation processes, due to its conservative isotopic and geochemical behavior in such conditions (Aranda et al., 2012; Borrok et al., 2008; Fernandez and Borrok, 2009). All of these studies pointed to a relatively narrow range in $\delta^{66}\text{Zn}$ in ARD. No studies so far have expanded analyses to directly include alkaline pH mine drainage where Zn attenuation processes including adsorption and secondary Zn carbonate and hydroxide mineral formation are of greater importance. However, studies by Wanty et al. (2013a, 2013b) in an alkaline-pH river (pH ~8) with an elevated dissolved Zn load from mining activities showed that Zn was removed during precipitation of hydrozincite and amorphous Zn-silicate minerals which had $\delta^{66}\text{Zn}$ values that were 0.35 to 0.5‰ heavier compared to the dissolved Zn load. Laboratory experiments have also confirmed that hydrozincite precipitation removes heavy Zn isotopes from solution (Veeramani et al., 2015).

There have been no studies of Mo isotope compositions in waste rock drainage to date. However, a compilation of natural and experimental samples measured thus far showed a substantial degree of fractionation in $\delta^{98}\text{Mo}$ exceeding 6‰ (Goldberg et al., 2013). Mo adsorption is known to drive changes in Mo isotope ratios in solution: Fractionation factors for Mo adsorption ($\alpha_{\text{solution-adsorbed}}$) range from 1.00083 to 1.00276 depending on the adsorbent mineral (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2008). Molybdate (MoO_4^{2-}) conversion to thiomolybdate ($\text{MoO}_x\text{S}_4^{2-x}$) in sulfidic waters can also drive a preferential removal of light Mo isotopes from solution (Nägler et al., 2011), although this Mo removal pathway is not expected in oxidized waste rock drainage where sulfur speciation is dominated by SO_4^{2-} .

These previous studies of Mo and Zn indicate that their isotopic variation may be useful parameter to track the geochemical fate of these metals in waste rock drainage. However, more measurements of $\delta^{66}\text{Zn}$ are necessary to constrain our understanding of its isotopic behavior in waste rock drainage, in particular in alkaline-pH mine drainage where Zn attenuation is stronger. In addition, $\delta^{98}\text{Mo}$ has yet to be explored as a tracer of Mo in mine wastes. Therefore, the objectives of the present study were twofold: (1) to evaluate the extent of isotopic variability of Mo and Zn source minerals at a mine site with lithological heterogeneity in its waste rock, and (2) to evaluate whether isotopic fractionation in mine drainage was occurring after release of Mo and Zn to solution via sulfide mineral oxidation. The Mo and Zn isotopic compositions of source minerals were characterized by analyzing solid phase samples that included waste rock, ore minerals collected from drill core, and ore concentrate. The role of secondary processes on Mo and Zn isotopic compositions in mine drainage was investigated by analyzing water samples from small- to intermediate-scale waste rock weathering experiments under field conditions covering a range in pH from acidic to alkaline. Samples were collected at the Antamina Cu–Zn–Mo–(Pb–Ag–Bi) mine, Peru, where multi-scale weathering experiments are under way to assess metal release and transport processes in mining waste rock dumps.

2. Study site

The Antamina deposit is a polymetallic skarn emplaced during a mid-Cenozoic quartz monzonite porphyry intrusion into Late Cretaceous limestone (Lipten and Smith, 2004). It is located at high elevation (4100–4700 m) in the Peruvian Andes (9° 32 S, 77° 03 W) (Fig. 1). The average annual temperature is between 5.5 and 6.0 °C, and annual

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