Tracking the Fate of Metals in Mining Waste Rock Using Metal Stable Isotopes

Elliott Skierszkan[1], Ulrich Mayer[1], Roger Beckie[1] and Dominique Weis[2]

1. Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Canada
2. Pacific Centre for Isotopic and Geochemical Research (PCIGR), Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia, Canada

ABSTRACT

The characterization of metal release and attenuation in mining waste rock drainage has traditionally relied upon an array of mineralogical and geochemical techniques. Recent advances in analytical instrumentation now allow robust measurements of minute variations in the isotopic composition of metals in environmental samples, which have become a powerful new tracer of their fate. Here we provide an overview of the application of these "non-traditional" stable isotopes to characterize metal release and attenuation in mining waste rock. First, we briefly review the theoretical framework of stable isotope geochemistry and its application to environmental studies. Second, we present results from an isotopic investigation of Mo and Zn at the Antamina mine, Peru. At Antamina, isotopic compositions of Mo and Zn have been determined in waste rock drainage waters and ore-mineral samples as a first step to determine whether isotope analyses can serve as a tool to track the geochemistry of these metals in waste rock dumps. The range in isotopic compositions measured thus far at Antamina spans 1.88‰ for $\delta^{98/95}$Mo and 0.65‰ for $\delta^{66/64}$Zn. This variability confirms that isotopic fractionation is occurring during metal release and/or attenuation reactions and indicates the potential for metal stable isotopes to track the mobility of metals in mining waste rock dumps. Linking this variability to distinct release and attenuation mechanisms (e.g. dissolution, adsorption and secondary mineral precipitation) will require further investigations to characterize the isotopic signatures of these mechanisms.

Keywords: Metal stable isotopes, drainage geochemistry, waste rock

INTRODUCTION

The complex hydrogeological and geochemical nature of waste rock dumps makes a detailed characterization of the fate of metals in this setting particularly challenging to achieve using conventional geochemical methods. An alternative and complimentary tool is stable isotope analysis of metals to track release and attenuation processes which would otherwise be difficult to identify. Subtle but measureable variations in isotopic compositions of metals occur as a result of isotopic fractionation during chemical reactions. By measuring these isotopic variations, metal release and attenuation processes can be unveiled. Over the last sixty years, the stable isotope approach has developed into a mature technique for tracking the fate of elements C, N, H, O and S, often called the "traditional" stable isotopes. Moreover, recent improvements in mass spectrometry permit the analysis of isotopic variations of other elements, including the transition metals, opening the door to their application in environmental studies.

This paper's objective is to introduce the use of metal stable isotope analysis to characterize processes in mining waste rock. Part 1 provides a brief review of isotopic fractionation and its applications and analytical considerations. Part 2 presents early results from a survey of metal stable isotope compositions measured in waste rock drainage, waste rock and ore minerals from the Antamina mine, Peru. These samples were analyzed in order to identify whether variations in isotopic compositions of Mo and Zn are present in Antamina waste rock materials, and consequently whether these can be useful to identify sources and attenuation mechanisms.

THEORY, APPLICATONS AND ANALYTICAL CONSIDERATIONS

Theory

Stable isotopes co-exist for many elements in the periodic table. The isotopes of a given element differ by the number of neutrons they contain, while the number of protons is constant. It is this slight difference in atomic masses and nuclear properties which causes differences in reactivity and result in isotopic fractionation. These isotopic variations are denoted as per mil (‰) deviations in the isotopic ratios of a sample relative to a standard using the delta (δ) notation, where superscripts i and j denote two isotopes of a given element X:

$$\delta^{i/j}X\ (‰) = 1000\ \times \left(\frac{\left(\frac{^iX}{^jX}\right)_{sample}}{\left(\frac{^iX}{^jX}\right)_{standard}} - 1 \right)$$

Mass-*dependent* isotope fractionation occurs as a result of the differences in the strength of chemical bonds involving light and heavy isotopes for a given element: heavy isotopes form bonds which are thermodynamically stronger than those involving light isotopes, and thus are less reactive. Mass-dependent isotopic fractionation is further broken down into two categories, *equilibrium* isotope fractionation and *kinetic* isotope fractionation, an overview of which can be found in (Weiss et al., 2008). Some elements also display mass-*independent* fractionation (MIF) which can be a useful tracer of environmentally-relevant reactions. While not the focus of this work, MIF has been reviewed elsewhere (e.g. Buchachenko, 2013).

Recent Applications of Metal Stable Isotopes

A growing number of studies have successfully used stable isotope analyses to track sources of metal release and attenuation processes in the environment which are summarized in reviews such as (Weiss et al., 2008; Baskaran, 2012). Efforts to apply stable isotopes to track metals in mining environments have begun, including some noteworthy case studies: (Foucher et al., 2009) used mercury stable isotope analyses to identify the release of Hg from a Slovenian mine to riverine sediments and were able to quantify the contribution of the mine to sedimentary Hg downstream from the release site. Copper and Zn isotopes have been useful in identifying processes controlling metal mobility in acid mine drainage such as dilution, weathering and adsorption (Balistrieri et al., 2008; Kimball et al., 2009; Fernandez and Borrok, 2009; Aranda et al., 2012). Strong isotope fractionation during Cr and U removal from groundwater via reduction reactions makes analyses of their isotopic compositions very useful to identify and quantify attenuation of these elements (Heikoop et al., 2014, Baskaran, 2012, A. Shiel, 2013, pers. comm., Oct 16). Taken together, these studies demonstrate the use of stable isotopes to improve our understanding of metal mobility in a variety of environments including mine sites.

Analytical considerations

The stable isotope analysis of metals from environmental samples is not trivial. Analysis is typically done using either thermal ionization mass spectrometry (TIMS), or multi-collector inductively coupled-plasma mass spectrometry (MC-ICP-MS); the latter is becoming the instrument of choice because of the ICP's more efficient ionization ability. Accurate and precise metal isotope ratio measurements require careful sample handling. High-purity grade reagents are used in sample processing, in a metal-free clean laboratory. Samples must undergo chemical purification prior to analysis in order to extract the analyte element from the rest of the sample matrix. Finally, during mass spectrometry, a rigorous correction scheme is required because the MC-ICP-MS system fractionates isotopes during the measurement by as much as three orders of magnitude more than the fractionation present in natural samples. Fortunately, these analytical challenges have been overcome and stable isotope ratio protocols exist for most metals and metalloids of interest to the mining industry (e.g. Cr, Fe, Ni, Cu, Zn, Mo, Cd, Hg, U, Se, W, Ag). At present, analytical capabilities are mainly available within university and government research laboratories where instrumentation is available and knowledge of analytical protocols exists.

STABLE MO AND ZN ISOTOPIC FRACTIONATION AT THE ANTAMINA MINE, PERU

At the Antamina mine a multi-isotope study is currently under way in which the objective is to determine whether stable isotope analyses can be useful to track sources of metal release and processes of metal attenuation in waste rock dumps. The Antamina mine extracts Cu-Zn-(Ag-Mo) ores from one of the world's largest polymetallic skarn deposits, located high in the Peruvian Andes. The deposit formed in association with a quartz monzonite intrusion into carbonate terrain, producing a heterogeneous array of local lithologies which include skarns, hornfels, marbles and intrusives. Good understanding of Mo and Zn release and attenuation processes in waste rock dumps comprised of these materials is critical in order to predict long-term drainage water quality. However, this is a challenging objective to achieve by conventional geochemical and mineralogical approaches, and is further complicated by the geological heterogeneity of waste rock. Stable isotope

analyses could prove useful to gain insights into the fate of metals in waste rock dumps. As a first step, the variability in Mo and Zn isotopic compositions of drainage waters collected from field barrels and experimental waste rock dumps as well as select ore-grade rock samples must be determined to investigate this possibility.

At Antamina, the hypothesized Mo release mechanism to solution from mining waste rock is oxidative weathering of molybdenite (MoS_2). Upon release to solution as molybdate $(MoO_4^{2})^-$, Mo may be attenuated via adsorption onto (oxy)hydroxide minerals and clays or via precipitation as secondary minerals. Adsorption of molybdate onto various inorganic substrates peaks at a pH range of 3-5 (Goldberg et al., 1998), while it is minimal in alkaline and very acidic conditions. However, Conlan et al., (2012) and Hirsche (2012) showed that Mo solubility in neutral to alkaline conditions can be limited by precipitation of secondary minerals, including wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$).

To date, no studies have examined Mo stable isotope compositions in mining waste. However, a growing body of literature is shedding light on the isotopic behavior of Mo. It has been shown that light isotopes of Mo are preferentially scavenged during adsorption onto Fe and Mn (oxy)hydroxides leaving a residual aqueous Mo pool which is isotopically heavier (Barling & Anbar, 2004; Siebert et al., 2006; Wasylenki et al., 2008; Goldberg et al., 2009; Wasylenki et al., 2011). Molybdenum isotopic fractionation during chemical weathering in various conditions show that Mo leached from rocks may have isotopic compositions which are similar to, or heavier than the parent material by up to 1 ‰ (Siebert et al., 2003; Liermann et al., 2011; Voegelin et al., 2012). The isotopic fractionation occurring during secondary mineral precipitation of Mo has not yet been studied.

Zinc in mining waste rock is released from the weathering of sphalerite (Hirsche, 2012; Matthies et al., 2014a). Possible attenuation mechanisms include adsorption onto (oxy)hydroxide minerals and carbonates and precipitation as secondary minerals (e.g. $ZnCO_3$, $Zn(OH)_2$) (Al et al., 2000; Hirsche, 2012). Zn adsorption shows a strong pH dependency, with minimal adsorption occurring in acidic conditions (<pH 5) and greater adsorption occurring for mildly acidic to alkaline pH values (Pokrovsky et al., 2005).

A small, but growing literature has begun investigating zinc isotopic variations in mining wastes (Balistrieri et al., 2008; Fernandez & Borrok, 2009; Aranda et al., 2012; Matthies et al., 2014a; Matthies et al., 2014b). Zinc adsorption onto Mn, Al and Fe oxides exhibits a small isotopic fractionation of <0.2 ‰ (Pokrovsky et al., 2005). Consistent with Mo, oxidative weathering of sphalerite-rich tailings leads to aqueous Zn which is isotopically heavier by ~0.1-0.2 ‰ (Matthies et al., 2014a). Complexation with carbonates yields residual aqueous solutions which are up to 1‰ lighter than the starting solution (Pichat et al., 2003; Fujii et al., 2011).

Methodology for Antamina Isotope Study

Antamina's geochemical investigation program includes a series of ~10m high experimental waste rock piles (each containing 30,000 tonnes of rock) and ~1m high field barrels (each containing 350kg of rock) which were installed in order to characterize drainage water quality for different waste rock types (Fig. 1). Water samples from these field barrels and experimental waste rock piles were collected in order to determine the range in isotopic compositions associated with different waste rock materials at Antamina. In addition, Mo and Zn ore minerals (molybdenite and sphalerite) from

various locations in the open pit were also sampled for isotope analysis because it is the chemical weathering of these minerals which is expected to be the dominant source of Mo and Zn in waste rock drainage waters.

Figure 1 Experimental field barrels, 1m high and containing ~350 kg of waste rock (left); and experimental waste rock dumps, 10m high and containing ~30,000 kg of waste rock (right) at Antamina.

Water samples were filtered in 0.22 μm filters and acidified prior to shipment to the laboratory for analysis. Molybdenites and sphalerites were hand-picked from ore-grade rock samples and dissolved in inverse *aqua regia*. Mo and Zn concentrations were determined using an ICP-MS (Agilent 7700x, Agilent, USA). Sample aliquots were then reconstituted in 7N HCl and processed through an anion-exchange purification scheme modified from Shiel et al. (2013) which isolates Mo and Zn from the sample matrix. In order to correct for instrumental and laboratory mass fractionation, a ^{97}Mo-^{100}Mo double-spike was equilibrated with samples prior to ion-exchange purification (Siebert et al., 2001). Zn instrumental mass fractionation was corrected using a combined standard-sample bracketing and external normalization procedure as in Shiel et al. (2013). Isotopic analyses were conducted using a Nu Plasma MC-ICP-MS (Nu Instruments Ltd., UK) hosted at the Pacific Centre for Isotopic and Geochemical Research (PCIGR), University of British Columbia, Vancouver, Canada. Isotopic compositions in this study were normalized using the NIST-SRM-3134 for Mo and using PCIGR-1 for Zn as delta-zero per mil standards. PCIGR-1 is ~0.11 ± 0.05 ‰ heavier than the commonly used JMC-Lyon Zn isotope standard. All reagents used in the laboratory were prepared using ultra-pure <18.2 MΩ H_2O and commercial environmental-grade acids were sub-boiled in PFA sills to reduce contaminants to trace levels. Laboratory work was carried out in metal-free Class 1000 clean laboratories at PCIGR.

Results and Discussion

Isotopic compositions of Mo and Zn measured in Antamina samples show variations of up to 1.88‰ for $\delta^{98/95}$Mo and 0.65‰ $\delta^{66/64}$Zn. These isotopic ranges are well in excess of the analytical precision of <0.10‰ and <0.12 ‰ for $\delta^{98/95}$Mo and $\delta^{66/64}$Zn, respectively, indicating that significant and resolvable isotopic fractionation is occurring during release and/or attenuation of Mo and Zn at Antamina.

Molybdenum isotopes

Isotopic compositions of molybdenites exhibit a range of 1.09‰ among various ore samples collected in the deposit (Fig. 2) The range in isotopic composition of molybdenites analyzed here bear some relationship with the lithological origin of its host rock: intrusive-hosted molybdenite spans –0.79 to -0.04 ‰ while skarn-hosted molybdenite is isotopically heavier (-0.46 to 0.37 ‰), though there is some overlap. The observed variability in $\delta^{98/95}$Mo in molybdenites at Antamina is consistent with studies of other molybdenite deposits worldwide, and is thought to be caused by a kinetic isotope fractionation associated with Mo reduction from Mo(VI) to Mo(IV) in hydrothermal fluids during molybdenite hydrothermal precipitation (Hannah et al., 2007; Greber et al., 2014).
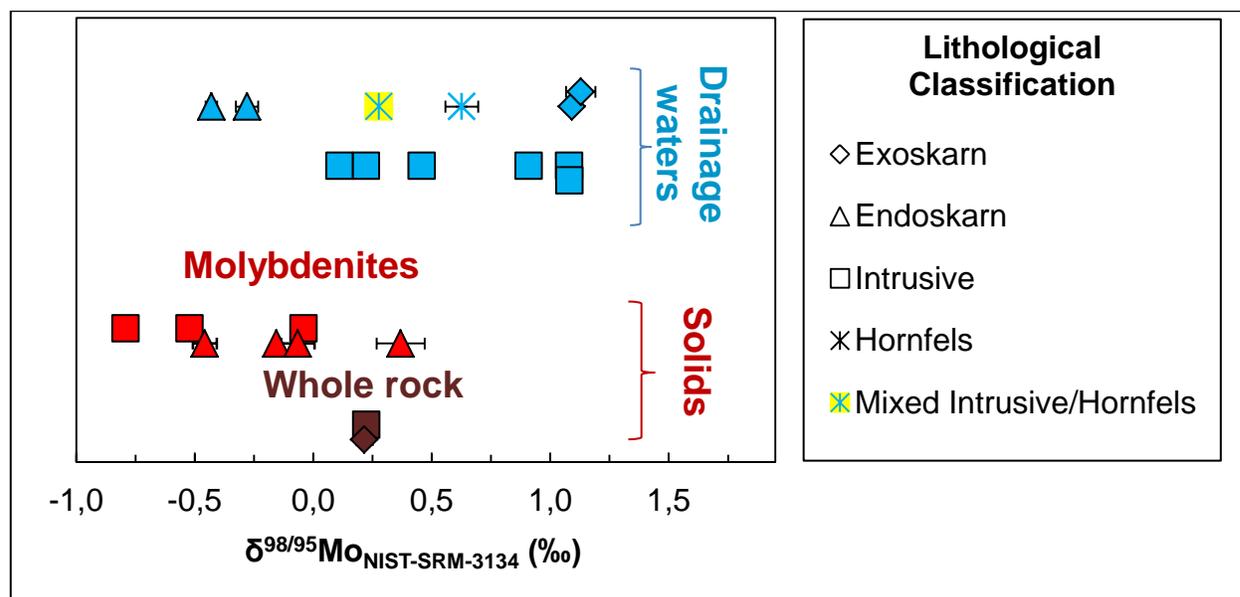

Figure 2 1-D representation of Mo isotopic composition of drainage waters (blue symbols), molybdenites (red symbols) and whole-rock (maroon symbols) by lithology (indicated by symbol shape) in Antamina waste rock material. Data are spread vertically for clarity. Error bars are ±2SD for a triplicate analysis on the MC-ICP-MS.

The range in $\delta^{98/95}$Mo in leachate water samples collected from field barrels and experimental waste rock piles is considerable, spanning 1.56 ‰. Leachate tends to be isotopically heavier than molybdenites, assumed to be the source of Mo. While at this point it is not possible to say specifically what causes this shift, it is possible to formulate hypotheses based on current knowledge of Mo isotope behavior. Heavier $\delta^{98/95}$Mo in drainage waters are consistent with previous studies, which have attributed this phenomenon to isotopic fractionation during oxidative weathering and adsorption onto (oxy)hydroxide minerals (Siebert et al., 2003; Barling and Anbar, 2004; Goldberg et al., 2009; Liermann et al., 2011; Voegelin et al., 2012). Sequential extractions and SEM analyses performed on Antamina waste rock dump material performed by Laurenzi (in prep.) show an association of Mo with oxidized mineralogical phases including Fe/Mn (oxy)hydroxides.

However, adsorption alone cannot fully explain Mo isotope compositions found in Antamina waters because the isotopically heaviest waters in this study included samples with pH ranges from 7.2-8.0, where Mo adsorption is expected to be minimal. Therefore another fractionating process can be invoked to explain this isotopic shift. Previous work shows that Mo attenuation via powellite

(CaMoO₄) mineral precipitation is possible in these geochemical conditions (Conlan et al., 2012), although it is kinetically limited. While we cannot confirm which process is causing this isotopic shift at this point in time, a powellite precipitation hypothesis can be invoked as a possible explanation to explain this data: Ca- and Mo- bearing exoskarn is releasing Mo and Ca to solution, which then precipitate as CaMoO₄ albeit with a kinetic limitation. Kinetic isotope fractionation theory predicts that lighter Mo isotopes will be scavenged in this precipitation process, resulting in an isotopically heavy solution. Experimental testing of this hypothesis is an obvious next step. Finally, the endoskarn field barrel sampled in this campaign exhibited an opposite behavior to all other samples: water was isotopically lighter (-0.43 to -0.28 ‰) relative to molybdenite found in that field barrel (-0.16 ‰), suggesting another as of yet unknown process is causing isotopically light waters.

Zinc isotopes

In contrast with molybdenites, sphalerites at Antamina have a remarkably homogeneous Zn isotopic composition of 0.11 ± 0.01 ‰ (Fig. 3), which is consistent with a worldwide survey of Zn isotopic compositions in sphalerites by (Sonke et al., 2008). The range in Zn isotopic compositions measured in drainage water samples spans from -0.35 to 0.30 ‰, indicating that Zn isotopes are fractionated after release into solution from sphalerite oxidation. The isotopic composition of drainage waters is dependent upon the waste rock type: exoskarn and hornfels drainage is isotopically light, ranging from -0.35 to -0.02 ‰, while intrusive drainage is isotopically heavier, spanning from 0.03 to 0.30 ‰. One sample collected from an experimental waste rock pile (Pile 5-D) containing a mixture of hornfels and intrusive material had an intermediate isotopic composition of -0.01 ‰.
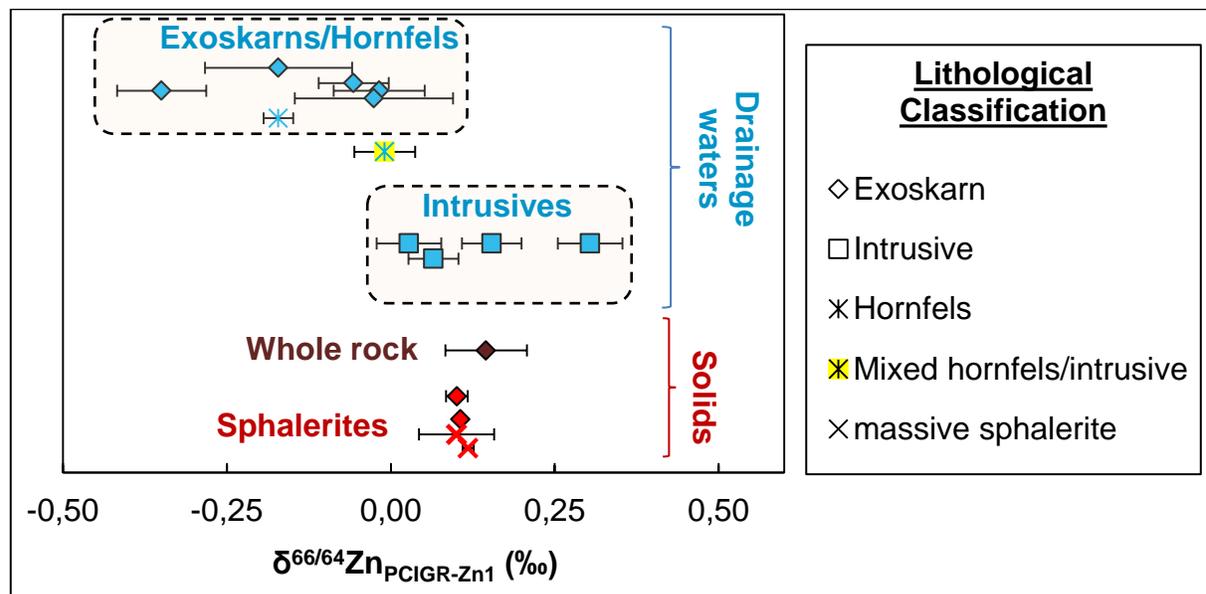

Figure 3 1-D representation of Zn isotopic composition of drainage waters (blue symbols), sphalerites (red symbols) and whole-rock (maroon symbols) in Antamina waste rock material by lithology (indicated by symbol shape). Data are spread along vertically axis for clarity. Error bars are ±2SD.

As is the case with Mo isotopes, at this point it is only possible to suggest hypotheses for the isotopic Zn variability measured at Antamina. Oxidative weathering, adsorption and precipitation of Zn-bearing carbonate minerals are all expected to cause some shifts in $\delta^{66/64}$Zn (Pichat et al., 2003; Fujii et al., 2011; Matthies et al., 2014a) and the variability measured here is likely an expression of one or several of these processes. The association of $\delta^{66/64}$Zn to waste rock lithology shows that Zn isotopes are a promising indicator for the provenance of Zn in waste rocks dumps which contain a mixture of different rock types. The intermediate isotopic composition of the hornfels/intrusive sample (Pile 5-D) could be an example of this application.

Laurenzi (in prep) has found evidence of Zn attenuation via adsorption onto Fe oxides and association with carbonate minerals in waste rock material collected from Antamina's waste rock dumps. Both of these attenuation mechanisms are possible in exoskarn waste rock material, because of its high carbonate content (2.8-31.3% by weight, (Peterson, 2014) and pH range (pH ~7-8) which is favorable for Zn adsorption (Pokrovsky et al., 2005). However, the shift towards isotopically light $\delta^{66/64}$Zn values in leachates from carbonate-rich waste exoskarn and hornfels materials are consistent with the precipitation of a Zn-carbonate mineral as an attenuating process (Pichat et al., 2003; Fujii et al., 2011).

SU MMARY AND CONCLUSION

Recent analytical improvements in MC-ICP-MS instrumentation allow the application of stable isotope analysis of heavy metals to track geochemical processes in mining waste rock and tailings. Mo and Zn isotope variations measured in Antamina waste rock materials are considerable and show that fractionation processes are occurring. Further experimental work will constrain the isotopic signature of environmentally relevant processes (e.g. adsorption, oxidative dissolution, secondary mineral precipitation) and improve our ability to use isotopes to diagnose the fate of these metals in full-scale waste rock dumps.

REFERENCES

Al T. A., Martin C. J. and Blowes D. W. (2000) Carbonate-mineral / water interactions in sulfide-rich mine tailings. Geochim. Cosmochim. Acta 64, 3933–3948.

Aranda S., Borrok D. M., Wanty R. B. and Balistrieri L. S. (2012) Zinc isotope investigation of surface and pore waters in a mountain watershed impacted by acid rock drainage. Sci. Total Environ. 420, 202–13.

Balistrieri L. S., Borrok D. M., Wanty R. B. and Ridley W. I. (2008) Fractionation of Cu and Zn isotopes during adsorption onto amorphous Fe(III) oxyhydroxide: Experimental mixing of acid rock drainage and ambient river water. Geochim. Cosmochim. Acta 72, 311–328.

Barling J. and Anbar A. D. (2004) Molybdenum isotope fractionation during adsorption by manganese oxides. Earth Planet. Sci. Lett. 217, 315–329.

Buchachenko A. L. (2013) Mass-Independent Isotope Effects. J. Phys. Chem. 117, 2231–2238.

Baskaran, M. (Ed.) (2012) Handbook of Environmental Isotope Geochemistry. Springer Heidelberg Dordrecht London New York. 951 p.

Conlan M. J. W., Mayer K. U., Blaskovich R. and Beckie R. D. (2012) Solubility controls for molybdenum in neutral rock drainage. Geochemistry Explor. Environ. Anal. 12, 21–32.

Fernandez A. and Borrok D. M. (2009) Fractionation of Cu, Fe, and Zn isotopes during the oxidative weathering of sulfide-rich rocks. Chem. Geol. 264, 1–12.

Foucher D., Ogrinc N. and Hintelmann H. (2009) Tracing mercury contamination from the Idrija mining region (Slovenia) to the Gulf of Trieste using Hg isotope ratio measurements. Environ. Sci. Technol. 43, 33–9.

Fujii T., Moynier F., Pons M.-L. and Albarède F. (2011) The origin of Zn isotope fractionation in sulfides. Geochim. Cosmochim. Acta 75, 7632–7643.

Goldberg S., Lesch S. M. and Suarez D. L. (1998) Predicting Molybdenum Adsorption by Soils Using Soil Chemical Parameters in the Constant Capacitance Model. Soil Sci. Soc. Am. J. 66,1836–1842.

Goldberg T., Archer C., Vance D. and Poulton S. W. (2009) Mo isotope fractionation during adsorption to Fe (oxyhydr)oxides. Geochim. Cosmochim. Acta 73, 6502–6516.

Greber N. D., Pettke T. and Nägler T. F. (2014) Magmatic–hydrothermal molybdenum isotope fractionation and its relevance to the igneous crustal signature. Lithos 190-191, 104–110.

Hannah J. L., Stein H. J., Wieser M. E., de Laeter J. R. and Varner M. D. (2007) Molybdenum isotope variations in molybdenite: Vapor transport and Rayleigh fractionation of Mo. Geology 35, 703.

Heikoop J. M., Johnson T. M., Birdsell K. H., Longmire P., Hickmott D. D., Jacobs E. P., Broxton D. E., Katzman D., Vesselinov V. V., Ding M., Vaniman D. T., Reneau S. L., Goering T. J., Glessner J. and Basu A. (2014) Isotopic evidence for reduction of anthropogenic hexavalent chromium in Los Alamos National Laboratory groundwater. Chem. Geol. 373, 1–9.

Hirsche D. T. (2012) A field and humidity cell study of metal attenuation in neutral rock drainage from the Antamina mine, Peru. M.Sc. Thesis, University of British Columbia, 152 p.

Kimball B. E., Mathur R., Dohnalkova A. C., Wall A. J., Runkel R. L. and Brantley S. L. (2009) Copper isotope fractionation in acid mine drainage. Geochim. Cosmochim. Acta 73, 1247–1263.

Laurenzi, L., in prep. Metal attenuation studies in operational waste rock piles: A combined mineralogical and geochemical approach. ICARD conference, Santiago, Chile, April 20-25 2015.

Liermann L. J., Mathur R., Wasylenki L. E., Nuester J., Anbar a. D. and Brantley S. L. (2011) Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. Chem. Geol. 281, 167–180.

Matthies R., Krahé L. and Blowes D. W. (2014a) Zinc stable isotope fractionation upon accelerated oxidative weathering of sulfidic mine waste. Sci. Total Environ. 487, 97–101.

Matthies R., Sinclair S.A and Blowes D. W. (2014b) The zinc stable isotope signature of waste rock drainage in the Canadian permafrost region. Appl. Geochemistry 48, 53–57.

Peterson H. E. (2014) Unsaturated hydrology, evaporation and geochemistry of neutral and acid rock drainage in the highly heterogeneous mine waste rock at the Antamina mine, Peru. PhD Thesis, University of British Columbia, 307 p.

Pichat S., Douchet C. and Albarède F. (2003) Zinc isotope variations in deep-sea carbonates from the eastern equatorial Pacific over the last 175 ka. Earth Planet. Sci. Lett. 210, 167–178.

Pokrovsky O. S., Viers J. and Freydier R. (2005) Zinc stable isotope fractionation during its adsorption on oxides and hydroxides. J. Colloid Interface Sci. 291, 192–200.

Shiel A. E., Weis D., Cossa D. and Orians K. J. (2013) Determining provenance of marine metal pollution in French bivalves using Cd, Zn and Pb isotopes. Geochim. Cosmochim. Acta 121, 155–167.

Siebert C., McManus J., Bice A., Poulson R. and Berelson W. M. (2006) Molybdenum isotope signatures in continental margin marine sediments. Earth Planet. Sci. Lett. 241, 723–733.

Siebert C., Nägler T. F., von Blanckenburg F. and Kramers J. D. (2003) Molybdenum isotope records as a potential new proxy for paleoceanography. Earth Planet. Sci. Lett. 211, 159–171.

Siebert C., Nägler T. F. and Kramers J. D. (2001) Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. Geochemistry Geophys. Geosystems 2, 2000GS000124.

Sonke J., Sivry Y., Viers J., Freydier R., Dejonghe L., Andre L., Aggarwal J., Fontan F. and Dupre B. (2008) Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter. Chem. Geol. 252, 145–157.

Voegelin A. R., Nägler T. F., Pettke T., Neubert N., Steinmann M., Pourret O. and Villa I. M. (2012) The impact of igneous bedrock weathering on the Mo isotopic composition of stream waters: Natural samples and laboratory experiments. Geochim. Cosmochim. Acta 86, 150–165.

Wasylenki L. E., Rolfe B. A., Weeks C. L., Spiro T. G. and Anbar A. D. (2008) Experimental investigation of the effects of temperature and ionic strength on Mo isotope fractionation during adsorption to manganese oxides. Geochim. Cosmochim. Acta 72, 5997–6005.

Wasylenki L. E., Weeks C. L., Bargar J. R., Spiro T. G., Hein J. R. and Anbar a. D. (2011) The molecular mechanism of Mo isotope fractionation during adsorption to birnessite. Geochim. Cosmochim. Acta 75, 5019–5031.

Weiss D. J., Rehkämper M., Schoenberg R., Mclaughlin M., Kirby J., Campbell P. G. C., Arnold T., Chapman J., Peel K. and Gioia S. (2008) Application of nontraditional stable-isotope systems to the study of the sources and fate of metals in the environment. Environ. Sci. Technol. 42, 665–664.