



Application of heavy stable isotopes to explain (bio)geochemical processes occurring during the formation, transport and remediation of metalliferous mine waters

INTRODUCTION

The exploitation of mineral resources is critical for economic growth and development. At the same time, mineral extraction and processing bear the risk of negatively affecting the environment. When mine wastes such as waste rock and tailings are exposed to ambient conditions, naturally occurring weathering processes such as mineral sulfide oxidation may be accelerated and generate metalliferous potentially acidic mine waters (acid mine drainage, AMD). AMD has been known for centuries (Agricola 1556) and can adversely affect environmental receptors even decades or centuries after mine closure. Therefore, AMD formation, as well as metal mobility, transport and

remediation are widely investigated (Khorasanipour *et al.* 2011; Macias *et al.* 2012; Silva *et al.* 2013). Nonetheless, despite decades of intensive research, many (bio) geochemical processes surrounding AMD are still poorly defined with potentially negative implications for the successful application of AMD prevention and remediation measures. For this reason, the mine water research community has started to apply novel analytical techniques to improve our understanding about these processes that may ultimately also lead us to develop more successful techniques to prevent the formation of acidic mine waters and develop better remediation techniques.

THEORETICAL BACKGROUND

The stable isotopes of an element are characterized by the same number of protons but different numbers of neutrons and consequently different atomic masses. These mass differences may cause a different chemical and physical behaviour of the isotopes and their compounds, leading to mass dependent isotope fractionation. We have been monitoring light stable isotopes (LSI, e.g. H, O, S, C, N) for a number of decades and therefore typically also call them traditional stable isotopes. The lower percentage mass dif-

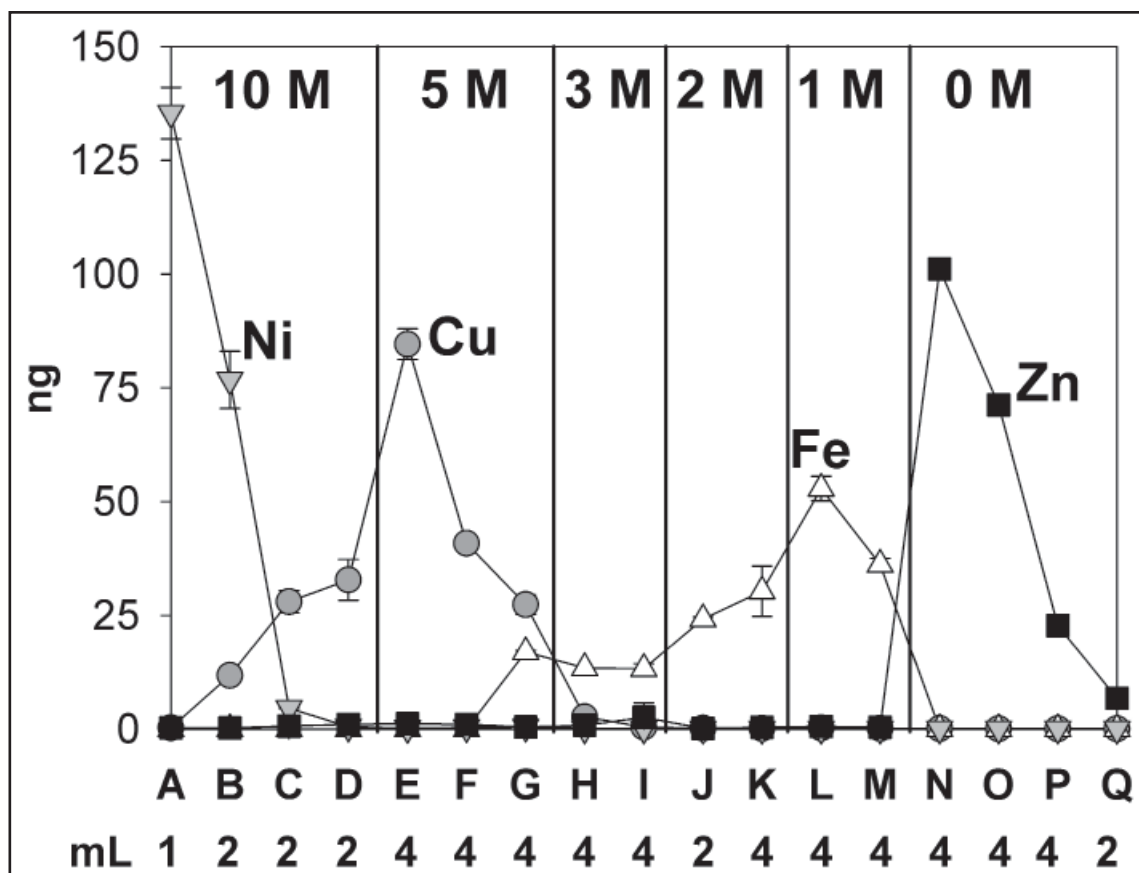


Figure 1. Solid – liquid extraction using anion-exchange resin to separate the target element zinc from the sample matrix consisting of copper, iron and nickel with varying amounts and concentrations of hydrochloric acid.

continued on page 3

Application of heavy stable isotopes to explain (bio)geochemical processes...

continued from page 1

ference of two isotopes of heavier, non-traditional, elements (HSI = heavy stable isotopes) commonly leads to much lower isotopic fractionation. We therefore require analytical techniques with improved precision than those applied for LSI. A number of methods are now available for the analysis of these non-traditional stable isotopes. However, the development of Multi-Collector Inductively-Coupled Plasma Mass Spectrometry (MC-ICP-MS) in the early 1990s (Walder & Freedman 1992) has been a breakthrough for HSI research because of the higher precision compared to other ICP-MS instruments and improved ionization compared to Thermal Ionization Mass Spectrometry (Albarede & Beard 2004; Walczyk 2004). The multi-collectors consist of four main components (Albarede & Beard 2004): i) the sample introduction system ; ii) the inductively-coupled argon plasma to ionize the sample; iii) the mass spectrometer interface to establish high vacuum; and iv) the mass analyser that

separates the ions by their kinetic energy. MC-ICP-MS requires the sample to be in a dissolved state unless coupled to a laser ablation system (e.g. Standish *et al.* 2012). For this purpose, most samples have first to be digested. The target element can then be separated by solid - liquid extraction (Fig. 1). Trace contaminants remaining in the sample may cause interferences that can bias the isotope results. As with LSI, heavy stable isotopes are commonly reported in delta notation (e.g. Cu in eq. 1) where the ratio of the heavy over the light isotope of an element in a sample is compared to the same isotope couple in an international standard.

$$1) \delta^{65}\text{Cu} = \left(\frac{{}^{65}\text{Cu}}{{}^{63}\text{Cu}} \right)_{\text{sample}} \left(\frac{{}^{65}\text{Cu}}{{}^{63}\text{Cu}} \right)_{\text{standard}}^{-1} - 1$$

APPLICATION OF HSI IN MINE WATER RESEARCH

Traditional stable isotopes have found wide application in mine water research. They have been used to trace pollution sources (Frandsen *et al.* 2009;

continued on page 4

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Application of heavy stable isotopes to explain (bio)geochemical processes...

continued from page 3

Herbert & Björnström 2009), identify the origin and infiltration behaviour of water (Gammons *et al.* 2010; Wisskirchen *et al.* 2010), assess transportation processes and residence times in underground mines and passive treatment systems (Wolkersdorfer 2006) and clarify a variety of (bio)geochemical processes such as mineral sulfide oxidation and bacterial sulfate reduction taking place in waste rock dumps and passive treatment systems (Tröger *et al.* 2005; Fonyuy & Atekwana 2008; Guo & Blowes 2009; Knöller *et al.* 2011). Since the development of MC-ICP-MS, we have seen an exponential increase in studies using HSI in diverse fields of the natural sciences (Douthitt 2008). Studies on heavy stable isotopes in AMD research are still scarce, but have already led to an enhanced understanding of mine water related processes as the following examples show.

REDOX PROCESSES

Chromium, uranium, iron and copper are redox sensitive elements. It has been observed that during oxidation, reduction, or both, a significant isotopic fractionation occurs that could be used to track redox processes during metal (im)mobilization. Jamieson-Hanes *et al.* (2012) studied the reduction and immobilization of Cr (VI) to Cr (III) in batch and column experiments using organic carbon as a reducing agent. Whereas the batch experiments showed that the isotope fractionation followed the general Rayleigh-type of closed systems, the column experiments were much less conclusive, suggesting that the flow patterns within the columns as well as other chromium removal mechanisms, such as sorption, had a significant influence on the isotope fractionation. Similarly, the reduction of uranium from U (VI) to U (IV) leads to a decrease in mobility. Shiel *et al.* (2013) investigated uranium immobilization and its isotope fractionation during *in situ* experiments at an uranium mine in Colorado. Bacterial iron and sulfate reduction led to significant isotope fractionation ($\Delta^{238}\text{U}_{\text{max}} = -1.3 \text{ ‰}$) and an enrichment of light isotopes in the non-reduced phase. The study by Egal *et al.* (2008) on iron isotope fractionation in the Iberian Pyrite Belt was somewhat less conclusive because of a multitude of overlying processes such as mineral sulfide oxidation, the speciation of mobilized iron and the type of secondary hydroxide precipitate. The primary sulfide minerals showed a rather homogeneous isotopic fingerprint (Tharsis: $\delta^{56}\text{Fe} = -0.56 \pm 0.08 \text{ ‰}$; Rio Tinto: $\delta^{56}\text{Fe} = 0.25 \pm 0.1 \text{ ‰}$). However, the isotope ratios of the iron hydroxides precipitated in surface water

streams downstream of the deposits ($-1.98 - 1.57 \text{ ‰}$) and the mine waters ($-1.76 - 0.43 \text{ ‰}$) showed a wider scatter with significant variations in separation factors ($\Delta = -0.98 - 2.25 \text{ ‰}$) between the iron isotopes in the water and those of the secondary hydroxide precipitates. Kimball *et al.* (2009) investigated the fractionation of copper during (a)biotic oxidation of enargite and chalcopyrite and compared the isotope fractionation factors with those of a watershed affected by mine drainage. The authors found, that because of the preferential oxidation of ^{65}Cu , abiotic oxidation caused a fractionation of up to 1.37 ‰ ($\Delta^{65}\text{Cu}$) whereby the mobilized copper in the leachate was more isotopically heavy than the copper in the source minerals. If the leaching was promoted by microorganisms (e.g. *Acidithiobacillus ferrooxidans*), minimal fractionation was observed for enargite ($\Delta^{65}\text{Cu}_{\text{aq-min}} = 0.14 \text{ ‰}$) whereas for chalcopyrite the leachate was enriched in light copper isotopes ($\Delta^{65}\text{Cu}_{\text{aq-min}} = -0.57 \text{ ‰}$). Observations of copper isotopes from the field suggested that the dominant process connected to copper mobilization was likely of abiotic nature, which may be interesting from an AMD prevention perspective.

ANTHROPOGENIC PROCESSES

The identification of (bio)geochemical processes of non-redox sensitive HSI can be more difficult because the isotopic fractionation is smaller and a primary process causing enhanced fractionation is lacking as observed by Cloquet *et al.* (2008) for zinc. This makes the interpretation of the isotope data obtained in natural settings — with multiple processes occurring in parallel — challenging. It has, however, been shown that a number of anthropogenic processes may cause a significant isotope fractionation, which may be used to trace these pollution sources and differentiate them from other sources. Sivry *et al.* (2008) and Juillot *et al.* (2011), suggested that mineral processing and the efficiency of zinc extraction may lead to a distinct fractionation of zinc isotopes in the tailings material as compared to the unprocessed ore, permitting discrimination of Zn derived from tailings from other natural and anthropogenic sources. It is currently under investigation whether similar fractionation may occur for the nickel isotope system (Quantin *et al.* 2012). Despite several recent studies on iron (Herbert & Schippers 2008; Pérez Rodríguez *et al.* 2013), zinc (Sonke *et al.* 2007; Aranda *et al.* 2012), copper (Balistrieri *et al.* 2008; Borrok *et al.* 2008) and lead isotopes (Choi *et al.* 2013), more research is needed to better understand

continued on page 6

Application of heavy stable isotopes to explain (bio)geochemical processes...

continued from page 4

the underlying isotope fractionation mechanisms. In addition, effective element-matrix separation methods as well as analytical methods on the multi-collector are still needed for a number of HSI. Further, for many of these elements no certified international isotope standards exist, which makes it difficult to compare isotopic data obtained by different laboratories. The presented studies, however, have shown that HSI provide a tool for improved understanding of many biogeochemical and anthropogenic processes during AMD formation and metal transport and may also be valuable to improve our understanding of many passive mine water treatment systems that otherwise may not have been achieved.

At the University of Waterloo's *Hydrogeology, Geochemistry and Remediation* research group, we have started to apply a number of HSI (e.g., Cu, Cr, Hg, Ni, Se, Zn) to investigate in lab and field-scale experiments the fractionation behaviour of these elements during their mobilization from sulfidic mine wastes from various North American massive sulfide and kimberlite deposits and their attenuation through interaction with organic and inorganic substances. In a study investigating the potential to prevent AMD generation from mine waste by the amendment of organic substrates, we assess the potential of HSI to trace microbial induced reduction processes. We also apply HSI to discriminate anthropogenic, mine derived one-point pollution sources and investigate diffuse pollution and related isotope fractionation on a catchment scale.

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continued on page 7

Application of heavy stable isotopes to explain (bio)geochemical processes...

continued from page 6

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continued on page 8

Application of heavy stable isotopes to explain (bio)geochemical processes...

continued from page 7

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