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WEB ALERT

Application of heavy stable isotopes in mine water research

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Abstract Metal and coal mining are essential for economic development. However, the metalliferous, acidic waters often emerging from these industrial sites, may also cause significant environmental damage. Multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) was developed in the early 1990s. MC-ICP-MS allows for the first time the simultaneous detection of many heavy stable isotopes of elevated ionization potential. Here, I outline the potential of this technique to improve our understanding on the mobilization and transport of metals and the remediation of metalliferous mine waters.

Keywords Heavy stable isotopes · Isotope fractionation

1 Introduction

The mineral extracting and processing industry creates bigger waste streams than any other industry (Rauch and Pacyna 2009; Rauch 2010). When those wastes (e.g. waste rock and tailings) are exposed to ambient, oxidizing conditions, weathering processes enhance the leaching of metals. The oxidation of mineral sulfides like pyrite (Eq. 1) and pyrrhotite (Eq. 2) may also lead to a release of ferrous iron that, once oxidized, may act as an additional oxidizing agent for other sulfide minerals. Further, hydrogen ions are released that can lead to a decrease in pH when buffering minerals (e.g. carbonates, aluminosilicates, Al-/Fe-hydroxides) are absent or exhausted. Ultimately, these processes can lead to the generation of metalliferous waters of low pH; commonly termed acid mine drainage (AMD).

$$FeS_2 + 2O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \tag{1}$$

$$FeS + O_2 + 2H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 4H^+ \tag{2}$$

AMD has been known for centuries (Agricola 1556). It is considered to be the main environmental concern of the mining industry and may lead to potentially devastating impacts on environmental receptors (US EPA 2005; Peplow and Edmonds 2006; Casiot et al. 2009). Therefore today, AMD generation, prevention, transport and mitigation are topics widely investigated (see for instance the International Conference on Acid Rock Drainage, the Congress of the International Mine Water

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Association and the International Applied Geochemistry Symposium).

2 MC-ICP-MS

Despite the extensive research, many biogeochemical processes connected to metal (im) mobilization are ill defined. We therefore started to support our research by applying novel analytical techniques. In the early 1990s, multi-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS) was developed (Walder and Freedman 1992). The MC-ICP-MS consists of four main parts (Albarede and Beard 2004): a sample introduction system; the inductively coupled argon plasma to ionize the sample; an ion transfer system to establish a high vacuum and the mass analyser to produce a mass spectrum with flat topped peaks (Fig. 1). This technique enables the simultaneous monitoring of stable isotopes of heavy elements (HSI).

Before, the method of choice for HSI determination was thermal ionization mass spectrometry (TIMS) (Walczyk 2004). TIMS, however, was unable to quantitatively ionize HSI of high ionization potential such as mercury, selenium and zinc. In consequence, the development of MC-ICP-MS has triggered a new wave of research in a multitude of areas of the natural sciences and beyond.

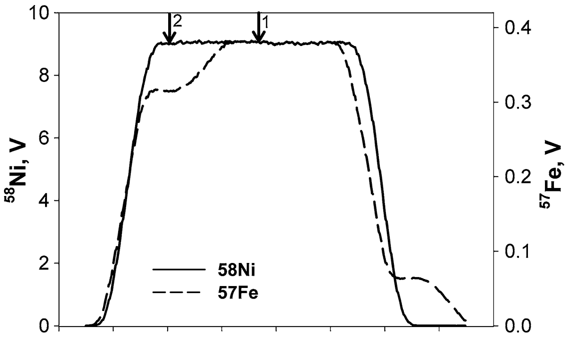

Fig. 1 The most abundant nickel isotope (^{58}Ni) has an isobaric interference with ^{58}Fe which we are unable to resolve with current analytical techniques. We therefore monitor a second iron isotope (here ^{57}Fe) to assess the amount of ^{58}Fe via their natural abundance ratio and discount ^{58}Fe from the ^{58}Ni scan. However, the heavier side of the ^{57}Fe scan shows a polyatomic interference deriving from the argon plasma. We therefore need to shift the monitoring beam from the centre position (*1*) to the left shoulder (*2*) to avoid the argon interference

In order to monitor heavy stable isotopes by MC-ICP-MS, the target element needs to be present in dissolved state and be isolated from the matrix. For this purpose, samples need to be digested to destroy biological and mineral components. In a second step, the element is concentrated and separated from the matrix by solid/liquid extraction (Korkisch and Ahluwalia 1967). If trace contaminants are not completely removed, a number of intraspectral interferences may bias the isotope results as shown in the mass scan of Fig. 1. This example shows how critical it is to quantitatively separate the target element from the sample matrix.

As for the traditional light stable isotopes (LSI: S, C, H, O, N), HSI results are presented in the delta notation (Eq. 3 for zinc), where the ratio of the heavy over the light isotope in the sample is compared to the same isotope couple of an international standard (Bureau International des Poids et Mesures 2011).

$$\delta^{66}\mathrm{Zn} = \left(\left({}^{66/64}\mathrm{R}\right)_{\mathrm{sample}}\left({}^{66/64}\mathrm{R}\right)_{\mathrm{standard}}\right)^{-1} - 1 \qquad (3)$$

R = ratio of isotope abundance.

3 Application of MC-ICP-MS

Traditional, light stable isotopes have already been used widely in mine water research. Water isotopes (δD_{H_2O}, $\delta^{18}O_{H_2O}$) were used to identify water sources, infiltration behaviour and flow paths into waste rock dams, tailings impoundments and underground mines (Gammons et al. 2010; Wisskirchen et al. 2010). LSI have also been used as tracers to identify transportation processes and residence times in underground mines and passive treatment sites (Wolkersdorfer 2006). Sulfur and oxygen isotopes of sulfate and sulfide ($\delta^{18}O_{SO_4}$, $\delta^{34}S_{SO_4}$, $\delta^{34}S_{H_2S}$) helped to clarify mineral sulfide oxidation and bacterial sulfate reduction. The latter is a critical process in many passive mine water treatment systems as it generates alkalinity to buffer pH and enhances the retention of metals as secondary mineral sulfides (Tröger et al. 2005; Knöller et al. 2012). Nitrogen isotopes (δ^{15}N) have been used to discriminate nitrogen contamination deriving from blasting processes from other natural and anthropogenic nitrogen sources (Frandsen et al. 2009; Herbert and Björnström 2009). Carbon isotopes (δ^{13}C) enabled the identification of alkalinity sources in passive mine water treatment systems (Fonyuy and Atekwana 2008; Guo and Blowes 2009).

Despite the exponential increase of studies using HSI over the last two decades (Douthitt 2008), so far few studies have been directly linked to mine water related research. The following list of publications is not aimed to be exhaustive but rather to provide a snapshot of the application of HSI in mine water research.

A number of studies used HSI as a tracer to track contamination. Ettler et al. (2006) monitored lead isotopes to discriminate lead sources from mining and smelting to those from other anthropogenic and natural lead sources. Sonke et al. (2007) used zinc isotopes to track smelter emissions. A number of studies have shown that ore processing, in particular pyrometallurgical processes, create a distinct isotope footprint of some elements in the mine waste which is different from the isotope ratio of the original ore material (Sonke et al. 2007; Sivry et al. 2008; Quantin et al. 2012). This characteristic helped to track element mobilization from tailings impoundments were these wastes were stored. By the application of copper isotopes, Kimball et al. (2009) identified the preferential mobilization processes of copper from mine wastes that had been washed into a surface water stream. Similarly, Balistrieri et al. (2008) applied copper and zinc isotopes to discriminate whether the decrease of copper and zinc pollution downstream of a mine site was connected to dilution and mixing processes or whether active element sequestration had taken place.

The reduction of chromium and uranium leads to a decrease in mobility of these elements. Shiel et al. (2013) investigated the isotope fractionation behaviour of uranium in *on site* experiments at an uranium mine in Colorado, USA. Similarly, Jamieson-Hanes et al. (2012) analysed chromium stable isotopes during the reduction of Cr(VI)–(III). The authors of both studies found that the element reduction was accompanied by significant isotope fractionation. This characteristic may be used to trace element reduction in natural reduction zones as well as in passive treatment systems.

Much remains to be done to improve our understanding of processes connected to the mobilization and immobilization of metals and their interaction with other inorganic and organic components. Nonetheless, if we enhance the understanding of isotope fractionation processes, HSI promise to have wide application potentials. The cited publications show that MC-ICP-MS has given us a tool to help clarifying critical biogeochemical processes. Ultimately, it is hoped that this information will be effectively used to minimize the environmental footprint of the mining industry.

4 Training of young researchers

I undertook my Ph.D. in applied geosciences at Newcastle University, UK. During the project, I investigated the passive remediation of metalliferous coal mine drainage under the application of traditional stable isotopes (S, O, C, H). Upon completion and with the help of a JSPS postdoctoral fellowship, I joined Tohoku University in Japan to investigate the application of passive remediation of mine water in Japan. During my Marie Curie International Outgoing Fellowship at the Universities of Waterloo, Canada, and Newcastle, UK, I am monitoring zinc, copper and nickel stable isotopes to investigate processes related to metal mobilization from mine wastes, metal transport and remediation.

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