Application of Zn isotopes in environmental impact assessment of Zn–Pb metallurgical industries: A mini review

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ABSTRACT

Zn and Pb smelters are the major contributors to Zn and Pb emissions among all anthropogenic sources, thus, it is essential to understand Zn isotopic variations within the context of metallurgical industries, as well as its fractionation in different environments impacted by smelting activities. This mini review outlines the current state of knowledge on Zn isotopic fractionation during the high-temperature roasting process in Zn and Pb refineries; δ^{66}Zn values variations in air emissions, slags and effluents from the smelters in comparison to the geogenic Zn isotopic signature of ores formation and weathering. In order to assess the environmental impact of these smelters, the available and measured δ^{66}Zn values are compiled for smelter impacted natural water bodies (groundwater, stream and river water), sediments (lake and reservoir) and soils (peat bog soil, inland soil). Finally, the discussion is extended to the fractionation induced during numerous physicochemical reactions and transformations, i.e. adsorption, precipitation as well as both inorganic and organic surface complexation.

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1. Introduction

The global mining industries produced 4,140,000 metric tons of lead (Guberman, 2012) and 12,000,000 metric tons of zinc (Tolcin, 2012) in 2010 where the principal use of lead is heavily reliant on the lead-acid battery industry, and the automotive sector (Guberman, 2012) and the primary demand for zinc is galvanizing, in which a zinc coating is applied to steel to prevent corrosion (Tolcin, 2012). Other uses of zinc include the production of brass and bronze, zinc-based alloys for die-casting, chemicals, and zinc semi-manufactures.

Zn becomes widespread in the natural environment due to the major anthropogenic inputs from vehicle emission, sewage sludge and pig slurry spreading, road runoff, industrial emission, and the geogenic input from the weathering of Zn-bearing rocks (John et al., 2007; Juillot et al., 2011). Among all the anthropogenic sources, Zn and Pb smelters are large contributors to Zn and Pb emissions (Shiel et al., 2010). Many studies have highlighted the pollution associated with lead and zinc metallurgical activities in many environmental compartments: atmospheric heavy metal emissions and deposition (van Alphen, 1999), surface and ground water contamination (Parsons et al., 2001), agricultural topsoil (Pelfrene et al., 2011) and river sediment (Vdovic et al., 2006).

Due to active participation of Zn in multiple biological and low temperature inorganic–chemical reactions (Marechal et al., 2000; Pokrovsky et al., 2005), isotopic variations of Zn can be used as a tracer of biogeochemical and chemical processes and sources of pollution (Cloquet et al., 2008; Sivry et al., 2008). The variations of Zn isotope composition from different anthropogenic activities (thermal distillation or electrochemical purification) were reviewed by John et al. (2007), variations in different aquatic systems (rain, fresh water, seawater, fresh and marine sediments) and terrestrial organic materials (algae, phytoplankton, rice and tomato plants to palm trees) were reviewed by Cloquet et al. (2008). In this contribution, we endeavor to better understand the Zn isotope fractionation within the context of metallurgical industries and activities. Thus, this mini review is especially dedicated to the Zn isotopes fractionation occurring during Zn–Pb ore formation, smelting processes of these ores, smelter related air emissions, slags (solid wastes), and smelter-impacted environmental

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compartments (water, air, soil and biological samples).

2. Contribution of analytical development to the understanding of Zn isotopes system

Zinc has five stable isotopes: ^{64}Zn (48.6%), ^{66}Zn (27.9%), ^{67}Zn (4.1%), ^{68}Zn (18.8%), and ^{70}Zn (0.6%) with their relative abundances in nature given in %. Zinc isotopes and their natural abundances were first determined by Rosman (1972), however due to the limitation in analytical precision no further work had been done on terrestrial samples. During the late 1990s, the technical development of multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) made it possible to measure Zn isotopes simultaneously and accurately (Marechal et al., 1999) in a wide range of samples such as biological materials, sediments, ores and silicate minerals (Maréchal et al., 2000). Similarly to O and Mg isotopes (Young et al., 2002), the kinetic and equilibrium mass-dependent fractionation laws that govern Zn isotope fractionation were then discussed by Sonke et al. (2008).

Later, the analytical challenges of measuring mass-dependent isotopic variations in nature was further addressed in many studies such as the spectral interferences (Mason et al., 2004a) and mass discrimination effect (Mason et al., 2004b) during analysis of Cu and Zn isotopes by plasma source mass spectrometry. The studies have been extended to different non-traditional isotopic systems: Li, Mg, Ca, Cr, Fe, Se, Cl and Mo (Albarède and Beard, 2004). Following the first development in ion-exchange separation techniques for isolation of Cu and Zn isotopes (Marechal and Albarede, 2002), the techniques later evolved for more complex and concentrated aqueous samples like acid mine drainage (Borrok et al., 2007), and for very dilute aqueous samples like river waters (Chen et al., 2009). In addition, the matrix effect due to resin-derived contaminants during column separation was evaluated as well (Shiel et al., 2009). Although the extent of Zn isotopes fractionation of environmental samples in nature is quite small ($\delta^{66}Zn$~1.7‰) compared to the other transitional metal isotopes ($\delta^{65}Cu$~9‰), thanks to MC-ICP-MS, the measured range of $\delta^{66}Zn$ is approximately from 20 to 50 times larger than the analytical precision (Wilkinson et al., 2005; Cloquet et al., 2008). The magnitude of Zn stable-isotope fractionation is usually expressed as $^{66}Zn/^{64}Zn$, $^{67}Zn/^{64}Zn$, $^{68}Zn/^{64}Zn$ with normalization to the most abundant Zn isotope, ^{64}Zn (48.6% in abundance). It is expressed as the relative deviation with respect to a standard reference: the Johnson Matthey Company (JMC) Zn standard solution (batch 3–0749L), in parts per 1000 (δ) as mentioned in Equation (1) (Black et al., 2011):

$$\delta^{66}Zn_{JMC} = \left[\left({}^{66}Zn/{}^{64}Zn \right)_{sample} \Big/ \left({}^{66}Zn/{}^{64}Zn \right)_{JMC} \right] - 1 * 1000 (‰) \tag{1}$$

3. Zinc and lead smelters

3.1. Ore signatures

The primary sources of Zn and Pb production are from the minerals sphalerite (ZnS) and galena (PbS) where Zn and Pb are the major constituents of the ores. Variations of Zn isotopes in sulfide-rich ores have been reported by many researchers (Fig. 1) where $\delta^{66}Zn$ values are ranging from −0.17–1.33‰ in sphalerite rich samples from Ireland (Wilkinson et al., 2005), from −0.4–1.2‰ in ores from Orlovka and Spokoinoe mining site (Dolgopolova et al., 2006), from 0.1 to 0.5‰ in ores from Finland (Weiss et al., 2007), from 0.00 to 1.14‰ in sphalerite rich base metal deposits from Northern Alaska (Kelley et al., 2009), from −0.43 to 0.23‰ in Alexandrinka ore deposit from Russia (Mason et al., 2005), from 0.1

to 0.37‰ in ZnS ores from Europe (Pašava et al., 2014; Sonke et al., 2008; Mattielli et al., 2009), compared to the initial hydrothermal fluid composition of 0.0 ± 0.1‰ (Wilkinson et al., 2005). Despite of such variations, the $\delta^{66}Zn$ signatures of ores used in Pb and Zn smelters have remarkably homogeneous isotopic compositions where the average $\delta^{66}Zn$ is 0.16 ± 0.20‰ (2SD, n = 10 mines, n = 61 analyses) considering different mine locations and initial ore compositions (Sonke et al., 2008).

3.2. Smelting processes

The typical primary lead refining is by means of lead blast furnace technology (LBF) where the roasting of ores, mainly sinter, coke and fluxes moves through a vertical shaft in counter-current to the ascending gas flow. The descending ore concentrates successively pass through the preheating zone (at 200 °C), the reaction or reduction zone (at 900 °C), the melting zone (at 1150 °C), and finally the combustion zone (Verguts, 2005). Production of zinc uses the imperial smelting technology (ISF) which includes the multiple-hearth, suspension, or fluidized bed. Zinc ore concentrate is introduced into a multiple-hearth roaster (at about 690 °C) to produce calcine which is later blown into a suspension roaster or fluidized-bed roaster (at about 980 °C) (Gordon et al., 2003).

The high-temperature roasting process is closely followed by the electrolytic processes where the calcine is leached with sulfuric acid. The zinc sulfate electrolyte is circulated continuously in the leach tanks with lead/silver alloy anodes and aluminum cathodes, where zinc is recovered and stripped from the cathodes, melted, and casted into slabs (Gordon et al., 2003). Imperial smelting technology (ISF) was first developed in England and deployed since 1952. It is known to be accounted for 80% of the world's primary zinc production (Gordon et al., 2003).

Some smelters are integrated to produce both Zn and Pb metals while individual smelters stand alone to produce either Zn or Pb metals. However, the availability of Zn isotopic data regarding each step of the smelting process either from integrated Zn + Pb smelters or individual Zn or Pb smelters are very limited. Therefore, Fig. 2 refers to the Zn isotopic fractionation induced at different steps of smelting at integrated Pb and Zn smelters.

The Zn isotopic compositions were evaluated during the smelting activities of zinc and lead ores (Shiel et al., 2010). Zn ore concentrates were normally treated in two parallel processes: roasting (80–85%) and pressure leaching (15–20%), the residue from the Zn leaching plant went to Pb smelters and was fed together with Pb ore concentrate. $\delta^{66}Zn$ values from Zn smelters ranged from 0.09 to 0.17‰ in Zn ore concentrate, 0.17 ± 0.06‰ in calcine (~100% recovery from ore to calcine), 0.22 ± 0.06‰ in refined Zn (~98% recovery from overall process), and 0.41 to 0.51 ± 0.08‰ in smelter effluent. On the other hand, the mixed feed of Zn residues to Pb ore concentrate had $\delta^{66}Zn$ values of 0.33 ± 0.15‰ and ZnO fuming plants (0.43 ± 0.06‰). No significant fractionation was observed between ore and refined Zn product despite the significant fractionation in the effluent which is easily explained by the very high recovery of the overall process.

3.3. Slags

The Zn isotopes signature related to slag materials at Pb and Zn smelting sites can exhibit a large range of $\delta^{66}Zn$: 0.81 ± 0.20‰ (Juillot et al., 2011), 0.37–0.43‰ from Pb–Zn refinery (Couder et al., 2008), 0.85 ± 0.74‰ from Belgian Zn refinery (Sonke et al., 2008), 0.18–1.49 ± 0.04‰ for tailings at a former French Zn refinery site (Sivry et al., 2008), 0.78 ± 0.13‰ in Pb slags and 0.13 ± 0.05‰ in Zn slags (Yin et al., in preparation). Thus, Zn slags from Zn–Pb refineries display heavier Zn isotopic signatures ranging from