



# Evaluation of zinc, cadmium and lead isotope fractionation during smelting and refining

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## ABSTRACT

To evaluate metallurgical processing as a source of Zn and Cd isotopic fractionation and to potentially trace their distribution in the environment, high-precision MC-ICP-MS Zn, Cd and Pb isotope ratio measurements were made for samples from the integrated Zn–Pb smelting and refining complex in Trail, B.C., Canada. Significant fractionation of Zn and Cd isotopes during processing of ZnS and PbS ore concentrates is demonstrated by the total variation in  $\delta^{66/64}\text{Zn}$  and  $\delta^{114/110}\text{Cd}$  values of 0.42‰ and 1.04‰, respectively, among all smelter samples.

No significant difference is observed between the isotopic compositions of the Zn ore concentrates ( $\delta^{66/64}\text{Zn} = 0.09$  to 0.17‰;  $\delta^{114/110}\text{Cd} = -0.13$  to 0.18‰) and the roasting product, calcine ( $\delta^{66/64}\text{Zn} = 0.17$ ‰;  $\delta^{114/110}\text{Cd} = 0.05$ ‰), due to ~100% recovery from roasting. The overall Zn recovery from metallurgical processing is ~98%, thus the refined Zn metal ( $\delta^{66/64}\text{Zn} = 0.22$ ‰) is not significantly fractionated relative to the starting materials despite significantly fractionated fume ( $\delta^{66/64}\text{Zn} = 0.43$ ‰) and effluent ( $\delta^{66/64}\text{Zn} = 0.41$  to 0.51‰). Calculated Cd recovery from metallurgical processing is 72–92%, with the majority of the unrecovered Cd lost during Pb operations ( $\delta^{114/110}\text{Cd} = -0.38$ ‰). The refined Cd metal is heavy ( $\delta^{114/110}\text{Cd} = 0.39$  to 0.52‰) relative to the starting materials. In addition, significant fractionation of Cd isotopes is evidenced by the relatively light and heavy isotopic compositions of the fume ( $\delta^{114/110}\text{Cd} = -0.52$ ‰) and effluent ( $\delta^{114/110}\text{Cd} = 0.31$  to 0.46‰). In contrast to Zn and Cd, Pb isotopes are homogenized by mixing during processing. The total variation observed in the Pb isotopic compositions of smelter samples is attributed to mixing of ore sources with different radiogenic signatures.

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## 1. Introduction

Worldwide production of refined Zn, Cd and Pb metals in 2007 was 11,500,000 t (Tolcin, 2009), 20,400 t (Tolcin, 2008) and 8,280,000 t (Guberman, 2009), respectively. The majority of Zn is used as an anti-corrosion coating (40%), e.g., galvanized steel (Greenwood and Earnshaw, 2001). The majority of Cd is used to produce the metallic Cd electrode plate found in nickel–cadmium (Ni–Cd) batteries (67%); significant Cd is also used in pigments (15%), plastic stabilizers (10%) and coatings (7%) (Greenwood and Earnshaw, 2001). Today, lead-acid battery production accounts for the largest use of Pb; Pb is also used to produce ammunition, building construction materials, communication and power cable coverings and leaded gasoline (still sold for use in automobiles in parts of Eastern Europe, Africa, the Middle East, Asia and Latin America and used to fuel small general aviation aircrafts) (Greenwood and Earnshaw, 2001).

Zinc, Cd and Pb are all chalcophile elements. Zinc and Pb are the major constituents of the ore minerals sphalerite (ZnS) and galena (PbS). Cadmium is the constituent element of the mineral greenockite

(CdS) and also occurs as a significant impurity (usually ~0.2–0.4%) in the ore mineral sphalerite, sphalerite being the important commercial source (Greenwood and Earnshaw, 2001). Sphalerite and galena ores are commonly associated and mined together. The main metallic Zn and Pb components of these ores are separated from other ore and gangue minerals, using methods such as grinding and sulfide flotation, to produce Zn and Pb ore concentrates. These ore concentrates undergo smelting and refining to produce high purity metals. Most of the world's refined Zn is produced from Zn ore concentrates using an electrowinning process, while most Pb is produced from Pb ore concentrates and secondary Pb materials (e.g., spent Pb-acid batteries) using pyrometallurgical processes. Cadmium is recovered primarily as a byproduct of Zn smelting and refining and from the recycling of spent Ni–Cd batteries, alloys and electric arc furnace dust.

In 2007, Canada was the second largest producer of refined Zn and the fourth largest producer of refined Cd in the world, producing ~7% (Tolcin, 2009) and ~10% (Tolcin, 2008), respectively. Canada also produced ~3% of the world's Pb (Guberman, 2009). Teck is Canada's largest mining, mineral processing and metallurgical company. Their operations in Trail, B.C. include one of the world's largest fully integrated Zn and Pb smelting and refining complexes, which contributed an estimated 36%, 33% and 67% of Canada's Zn, Pb and Cd metals production in 2007, respectively (calculated from

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Fthenakis, 2004; Teck Cominco Ltd., 2008; Tolcin, 2008, 2009; Guberman, 2009).

Zinc and Pb smelters, together with refineries, are large contributors to anthropogenic Zn, Cd and Pb emissions. Releases to air and water vary with the Zn and Pb ores used, type of metallurgical processing and the abatement measures in place. In this contribution, we endeavor to better understand the behavior of Zn, Cd and Pb isotopes during metallurgical processing and we explore the potential use of new geochemical tools, such as Zn and Cd isotopes, to source and trace these metals in the environment.

For elements with two or more stable isotopes, physical and chemical reactions may result in mass-dependent isotopic fractionation. This leads to natural variations in the isotopic compositions of many elements. The stable isotopic composition of a sample reflects that of the source and/or isotopic fractionation introduced by physiochemical reactions (Peterson and Fry, 1987). The extent of natural isotopic variability for an element is primarily determined by the relative mass difference for isotopes of that element (i.e., the mass difference for an isotope pair,  $\Delta m$ , relative to the average mass of the isotopes of the element) (Johnson et al., 2004). The extent of isotopic variability for an element will decrease with increasing atomic weight; for  $\Delta m = 1$ , the relative mass difference is, e.g., 8.0% for C, 3.1% for Zn, 0.9% for Cd and 0.5% for Pb. However, heavier elements tend to have more isotopes, and so the  $\Delta m$ , and subsequently the relative mass difference, for two isotopes of an element, may be much larger than that for  $\Delta m = 1$ . Due to the extended mass range of Cd isotopes relative to that of Zn isotopes, both Zn and Cd have total relative mass differences of 9.0% for  $\Delta m = 6$  and  $\Delta m = 10$  (i.e.,  $\Delta m =$  mass range for all isotopes of the given element), respectively, despite the heavier mass of Cd. For Pb, this total relative mass difference is significantly smaller, 1.9% for  $\Delta m = 4$ . Only with modern instruments, primarily the multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) with its enhanced ionization efficiency, has the precision needed to measure the small isotopic variations of most heavy stable elements (e.g., Zn and Cd) in terrestrial materials been available. In the case of Pb, any isotopic mass-dependent fractionation is very small in contrast to the variation in isotopic abundance among the world's ore deposits (0.61% for  $^{204}\text{Pb}$ , 6.64% for  $^{206}\text{Pb}$ , 6.03% for  $^{207}\text{Pb}$  and 4.93% for  $^{208}\text{Pb}$ ; Böhlke et al., 2005). Lead has four stable isotopes, three ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) the stable end products of radioactive decay chains ( $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$ , respectively) and one non-radiogenic isotope ( $^{204}\text{Pb}$ ). The Pb isotopic composition of an ore deposit is that of the initial Pb-isotopic composition of the host-rock/source material at the time of formation, plus new radiogenic Pb if any, which would have accumulated from the radioactive decay of U and Th since the time of formation (i.e., the age of the deposit; Faure and Mensing, 2005). The Pb isotopic composition of anthropogenic emissions resulting from high temperature processes (e.g., fossil fuel combustion, smelting and refining) reflects the isotopic composition of the source. As a result, Pb isotopic composition can be used to trace the source of Pb emissions in a technique called Pb isotope fingerprinting.

A few previous studies have examined the Zn and Cd isotopic variability among sulfide ores (Wombacher et al., 2003; Mason et al., 2005; Sonke et al., 2008; Mattielli et al., 2009; Schmitt et al., 2009), constraining the range in isotopic compositions of smelter source materials. Potential use of Zn and Cd isotopes as tracers has been increasingly explored since Wombacher et al. (2004) and Cloquet et al. (2005) identified that high temperature processes (e.g., evaporation of Cd) cause isotopic fractionation. More recently, Mattielli et al. (2009) identified successive steps of pyrometallurgical processing, particularly evaporation, as a source of Zn isotopic fractionation in resulting airborne particles. Zinc isotopes can therefore be used as a tracer of atmospheric Zn emissions released from these processing plants. Most recent studies have focused on the isotopic fractionation imparted to environmental samples taken from

the vicinity of ore processing plants (Dolgoplova et al., 2006) and refineries (Cloquet et al., 2006a; Gao et al., 2008; Sivry et al., 2008; Sonke et al., 2008; Mattielli et al., 2009). By contrast, process samples have been the focus of fewer studies (Cloquet et al., 2005; Sivry et al., 2008; Mattielli et al., 2009).

Several studies have evaluated the use of Zn or Cd isotopes to source anthropogenic emissions of these elements in the environment. The coupled use of Zn and Pb isotopes traced the source of enriched Zn in lichens and leaves (Russia) to local activities related to mining and ore processing as well as long-range transport of dust from other anthropogenic activities or natural processes (Dolgoplova et al., 2006). Enriched Zn in sediments and soils was traced using Zn isotopes to emissions from local metallurgical processing plants in the polluted Lot watershed in SW France (Sivry et al., 2008) and in a peat bog lake near Lommel, Belgium (Sonke et al., 2008). A trend between proximity to a Pb and Zn refinery plant (N France) and Cd isotopic composition was identified in topsoils (from proximal and a light Cd isotopic composition consistent with emissions from the refinery, to distal and a heavier isotopic composition consistent with natural sources) demonstrating Cd isotopes can be used as an environmental tracer (Cloquet et al., 2006a).

The primary focus of this study is to determine the presence and degree of Zn, Cd and Pb isotopic fractionation introduced during the metallurgical processing of Zn and Pb ore concentrates in one of the world's largest integrated Zn and Pb processing plants (Teck's operations in Trail, B.C.). We obtained samples of source materials, end products and intermediate products (e.g., roaster calcine) chosen to represent significant steps in processing (especially high temperature processes), which may result in isotopic fractionation. The thermal recovery of Cd in the recycling of Ni–Cd batteries was evaluated as a source of Cd isotopic fractionation by comparing the Cd isotopic compositions of recycled Cd metal, recovered from Ni–Cd batteries at INMETCO's Cd recovery plant (Ellwood City, PA), and refined Cd metal (Teck), chosen to exemplify the refined Cd metal used to make the metallic Cd electrode plate found in Ni–Cd batteries. The process of calcination, used to produce CdS pigments, was evaluated as a source of isotopic fractionation by comparing the Cd isotopic compositions of CdS pigment and Cd bearing minerals.

## 2. Materials and methods

### 2.1. Sample materials and collection

Samples were collected from the Zn and Pb operations at Teck's integrated Zn and Pb smelting and refining complex in Trail, B.C. in December 2008. Teck's Trail facility also produces Cd, Ge and In as byproducts of Zn production and Ag, Au, Bi, Cu and As as byproducts of Pb production and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) produced from  $\text{SO}_2$  off-gases. Zinc and Pb ore concentrates comprise the primary feeds for Zn and Pb operations. These ore concentrates are produced at mining sites from ores using crushing, grinding and selective flotation to isolate ZnS and PbS and reject gangue minerals (including FeS) to mine tailings (Fthenakis, 2004). Although the focus of this paper is to study the Zn, Cd and Pb isotopic fractionation imparted by smelting and refining of Zn and Cd, due to the integrated nature of the processing at Teck's Trail facility, both Zn and Pb processing must be considered as sources of Zn, Cd and Pb isotopic fractionation in smelting and refining products and emissions.

Zinc and Cd refining, as relevant to this study, is summarized in Fig. 1. For Zn, Teck's Trail facility employs an electrolytic Zn process, which consists of parallel high temperature roasting (Z1) and pressure leaching (not shown in Fig. 1), leaching with  $\text{H}_2\text{SO}_4$  (Z2), purification (Z4), electrodeposition (Z5) and melting/casting (Z6) (Fthenakis, 2004). Although, Zn ore concentrates are normally treated in parallel with two processes, roasting (80–85%) and pressure leaching (20–25%), the pressure leaching plant was not in operation

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