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Historical variations in the isotopic composition of atmospheric zinc deposition from a zinc smelter

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Abstract

In order to test the usefulness of stable zinc isotopes as an atmospheric source tracer, we analyzed the zinc isotopic composition of two sediment cores, taken at 1 km distance of the former zinc smelter in Lommel, Belgium. The peat bog lake sediments accumulate mainly atmospheric particles, have high organic matter contents (12–60 wt.%), are anoxic and highly contaminated with heavy metals (up to 4.7 wt.% Zn, and 1.1 wt.% Pb) with a sulfide mineralogical control on mobility. Down core variations in δ^{66}Zn (relative to the JMC 3-0749L standard) were small, ranging from +0.07‰ to +0.39‰, but are nevertheless eight times the external reproducibility of 0.04‰. Good agreement was found between the two cores, and despite 30% Zn mobilization to deeper layers, no evidence of associated diagenetic Zn isotope fractionation was found. Sediments deposited in the early 20th century have δ^{66}Zn of +0.30‰±0.05‰ (2SD, $n=5$) and a shift takes place between 1945 and 1950 to δ^{66}Zn values of +0.14‰±0.09‰ (2SD, $n=7$) in the 2nd half of the century. In order to understand this shift in δ^{66}Zn we analyzed 32 ore-grade sphalerite (ZnS) samples from African, Australian and European origin. Together with 29 published δ^{66}Zn values for ore-grade ZnS, we find remarkably homogeneous isotopic compositions, which when averaged for mining location gives δ^{66}Zn of +0.16‰±0.20‰ (2SD, $n=10$ mines, $n=61$ analyses). Early 20th century Zn deposition with δ^{66}Zn of +0.30‰ is significantly different ($p<0.001$) from average ZnS δ^{66}Zn of +0.16‰. We suggest that this reflects the presence of an atmospheric smelting residue (slag) component, enriched in the heavy Zn isotopes due to Rayleigh type fractionation during Zn refining.

Keywords: Zinc; Stable isotopes; Fractionation; Smelter; Atmospheric; Sediment

1. Introduction

Exploring the isotopic dimension of elemental cycles is a powerful approach to identify sources and sinks or quantify the physicochemical processes that relate them. Technological advances in inorganic stable isotope measurements, based on multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS), have stimulated the exploration of the isotopic variability of elements such as Fe, Zn, Cu, Si, Mg (Johnson et al., 2004). Numerous physicochemical reactions and transformations, i.e. bio-uptake, surface adsorption, precipitation, are accompanied by isotopic fractionation. In environmental contexts, there is substantial interest in using the isotopic variations of Zn, Cd, Cu, and Hg to better constrain natural and anthropogenic sources and contaminant cycling in the geobiosphere. Zn stable isotope measurements by MC-ICP-MS were developed in F. Albarède's lab (Maréchal et al., 1999), and subsequently used by the same group to explore paleo-

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oceanographic applications (Maréchal et al., 2000; Pichat et al., 2003), ion-exchange mechanisms (Maréchal and Albarède, 2002), and lunar origins (Moynier et al., 2006). Investigations on sample preparation and MC-ICP-MS measurements for Zn have since continued (Archer and Vance, 2004; Mason et al., 2004a,b; Chapman et al., 2006). Zn isotope fractionation has been shown to accompany both inorganic (Pokrovsky et al., 2005) and organic surface complexation (Gelabert et al., 2006), biological uptake and recycling (Zhu et al., 2002; Stenberg et al., 2004; Weiss et al., 2005; Bermin et al., 2006; Viers et al., 2007; Weiss et al., 2007), and ionic diffusion in solution (Rodushkin et al., 2004).

Substantial fractionation of Zn isotopes (δ^{66}Zn of −0.17‰ to +0.64‰) was found among early and late hydrothermal deposits of sphalerite (ZnS) in Ireland (Wilkinson et al., 2005), the Alexandrinka volcanic hosted massive sulfide deposits in the Urals (Mason et al., 2005), and selected samples from mines in the French Cevennes (Albarede, 2004). Tracability of natural and anthropogenic zinc has been evaluated using lichens (Cloquet et al., 2006a; Dolgopolova et al., 2006), aerosols (Cloquet et al., 2006a) and peat deposits (Weiss et al., 2007), the latter showing evidence for both source effects and diagenetic Zn mobilization and Zn isotope fractionation due to plant recycling. Anthropogenic zinc was recently found to have δ^{66}Zn of +0.19‰ ± 0.11‰ (2SD, n = 14) (John et al., 2007), which is similar to sphalerites. The most up to date review of Zn isotopic data is by Cloquet et al. (2008).

To our knowledge, no experimental high temperature studies exist on Zn evaporation or condensation, so we summarize work on other elements in the following. A study on the evaporation of molten Cd into a vacuum at 180 °C showed evaporative fraction of Cd isotopes to be enriched in lighter isotopes by a combined equilibrium/kinetic mechanism (Wombacher et al., 2004). Subsequently, Cloquet et al. (2005) reported a heavy Cd isotope depletion, δ^{114}Cd of −0.6‰, in dust phases from a lead smelter, and a concomitant δ^{114}Cd of +0.4‰ enrichment of the residual slag phases. A subsequent study on Cd in surficial soils surrounding the zinc smelter in question suggested 3-component mixing between atmospheric dust, slag and a natural source (Cloquet et al., 2006b). Similar evaporative enrichment of the vapor phase in the lighter isotopes exists for mercury (Brönsted and von Hevesy, 1920; Estrade et al., 2007). Mattielli et al. (2006) found that fine particles from a Pb–Zn smelter chimney were enriched in the lighter Zn isotopes with δ^{66}Zn up to −0.63‰, and our group recently found Zn refinery slag materials to be enriched in the heavier isotopes with δ^{66}Zn up to +1.49‰ (Sivry et al., in revision). These studies suggest that industrial high T evaporation and condensation of Zn, Cd and Hg can induce significant isotopic fractionation and offers a potential for anthropogenic source tracing of the dust and slag phases.

In this paper we evaluate the source tracer and industrial fractionation hypothesis by investigating historical variations in Zn isotopes emitted from the Lommel zinc smelter (Belgium). The atmospheric smelter emissions have been deposited during the 20th century in the accumulating sediments of a nearby peat bog lake, and detailed mineralogical, heavy metal, lead isotope and ^{210}Pb age dating information is available elsewhere (Sonke et al., 2002; Sonke et al., 2003). To constrain the interpretation we have also determined the δ^{66}Zn of 32 ore-grade sphalerite and 3 galena mineral samples, and their variation will be discussed.

2. Sampling and methods

2.1. Sampling location and context

Two, sediment cores, labeled B1 and M3 throughout the text, were obtained in 1996 in a small (30 m diameter) peat bog lake within the Maatheide Nature Reserve. The lake is situated 100 m East from the former Lommel zinc smelter area, and 1000 m East from the original smelter chimneys. The prevailing wind direction is from the West and has directly carried historical chimney dust as well ore dust from temporary open-air stock deposits over the targeted lake. Sediment accumulation is considered to be exclusively of atmospheric origin, due to absence of small streams feeding the lake. Post-industrial (after 1974) lack of re-vegetation on the heavy metal contaminated soils (up to 2 wt.% Zn, (Vangronsveld et al., 1995; Nachtegaal et al., 2005)) has caused continued exposure of the site to metal inputs by wind-erosion. The two sediment cores were extremely contaminated, with maximum Zn, Pb and Cd concentrations of 4.7, 1.1, and 0.1 wt.% respectively. Age-dating was done with combined ^{210}Pb and ^{137}Cs analysis (Sonke et al., 2003). Down core trends in metal concentrations revealed close correlations with historical events, such as World War's I and II, and overall Belgian Zn production. Radiogenic lead isotope profiles confirmed the industrial activities as a source of the contaminated sediments, and suggested distinct presence of Australian and possible African–Canadian lead; for further details, see Sonke et al. (2002). Only core M3 probed deeper pre-industrial layers, while core B1 had a higher sedimentation rate and thus better temporal resolution; the cores are regarded as complementary.

Sphalerite (ZnS) specimens were obtained from the Belgian Geological Survey (Brussels, Belgium), the Royal Museum for Central Africa (Tervuren, Belgium) and the Museum of Natural History (Toulouse, France) as well as two academic collections at UC Santa Cruz and the University of Adelaide. Specimens were crushed, handpicked and checked by X-ray diffraction for purity (>90%).

2.2. Sample preparation

Sediment sampling, and measurements of major and trace metal concentrations by quadrupole ICP-MS are detailed elsewhere (Sonke et al., 2003); here we used non-sieved, finely powdered sub samples. Sphalerite (ZnS) and galena (PbS) minerals were finely crushed in an agate mortar. All sediment and mineral samples were dissolved using ultra pure acids. 30–300 mg of sediment and 20 mg of minerals were weighed into 15 ml Savillex beakers such that abundant Zn was available for analysis (1–40 µg). Sediments were digested using the following protocol: 1 ml HNO_3 (25 °C), evaporate to dryness,