



Zinc isotope systematics in snow and ice accretions in Central European mountains



Petra Voldrichova^{a,b}, Vladislav Chrastny^a, Adela Sipkova^a, Juraj Farkas^a, Martin Novak^{a,*}, Marketa Stepanova^a, Michael Krachler^c, Frantisek Veselovsky^a, Vladimir Blaha^a, Eva Prechova^a, Arnost Komarek^d, Leona Bohdalkova^a, Jan Curik^a, Jitka Mikova^a, Lucie Erbanova^a, Petra Pacherova^a

^a Division of Geochemistry and Laboratories, Czech Geological Survey, Geologicka 6, 152 00 Prague 5, Czech Republic

^b Department of Analytical Chemistry, Faculty of Science, Charles University, Albertov 6, 128 43 Prague 2, Czech Republic

^c European Commission Joint Research Centre, Institute for Transuranium Elements, 76125 Karlsruhe, Germany

^d Faculty of Mathematics and Physics, Charles University, Sokolovska 83, 186 75 Prague 8, Czech Republic

ARTICLE INFO

Article history:

Received 18 March 2014

Received in revised form 2 September 2014

Accepted 5 September 2014

Available online 16 September 2014

Editor: Carla M. Koretsky

Keywords:

Zinc
Isotopes
Deposition
Atmosphere
Snow
Ice accretion

ABSTRACT

Zinc (Zn) pollution negatively affects human and ecosystem health. We quantified atmospheric Zn inputs at six remote mountain-top locations in the Czech Republic (Central Europe), and used $\delta^{66}\text{Zn}$ isotope ratios to identify Zn from different pollution sources. The study sites were located at an elevation of approximately 1000 m near the state borders with Germany and Poland. During two winter seasons (2009–2010), over 400 samples of vertical deposition (snow) and horizontal deposition (ice accretions) were collected. Zinc pollution levels were generally low. Zinc concentrations in snow and ice accretions were less than twice as high in the east, compared to the west. Across the sites, over 90% of Zn was present in a weak-acid soluble form. Zinc concentrations were 5 times higher in ice accretions, which formed from small droplets originating in the basal cloud layer, rich in pollutants, than in snow. In contrast, droplets resulting in snow formation were larger and scavenged less pollution due to their smaller surface area. $\delta^{66}\text{Zn}$ of Pribram sphalerite (west) and smelter-derived fly ash (west) were low, -0.23 and -0.47% , respectively. Olkusz sphalerite (east) had a higher $\delta^{66}\text{Zn}$ of 0.02% . $\delta^{66}\text{Zn}$ of snow ranged from -0.60 to 0.68% . Ice accretions had $\delta^{66}\text{Zn}$ between -0.67 and 0.14% . At the three eastern sites, $\delta^{66}\text{Zn}$ of ice accretions was lower than $\delta^{66}\text{Zn}$ of snow, suggesting the presence of volatilized smelter-derived or coal-burning derived Zn. $\delta^{66}\text{Zn}$ of ice accretions at two of the three western sites was higher than $\delta^{66}\text{Zn}$ of snow. Different $\delta^{66}\text{Zn}$ values of snow and ice accretions from the same site reflected different pollution sources, which may have been situated at different distances from the receptor site. $\delta^{66}\text{Zn}$ of the soluble Zn fraction was higher than $\delta^{66}\text{Zn}$ of the insoluble Zn fraction, possibly also indicating a different origin of these two Zn fractions. Zinc isotope heterogeneity in the atmosphere of remote areas indicates that $\delta^{66}\text{Zn}$ can be a useful tool in pollution provenance studies.

© 2014 Published by Elsevier B.V.

1. Introduction

Zinc is the second most important transition metal in the human body, due to its unique role in enzymes and proteins (Viers et al., 2007). Excessive supply of Zn, however, has a detrimental effect on living organisms (Cloquet et al., 2008). Despite its only moderate overall toxicity, Zn pollution is of concern in many industrial and developing countries (Shiel et al., 2010). Metallurgy, coal burning, tire wear, zinc-coated roofs, fertilizers and pesticides can be major sources of Zn to the environment (Borrok et al., 2008). Air pollution by a suite of trace metals, including Zn, has been quantified in many countries over the past 40 years (Freydier et al., 1998; Simonetti et al., 2000; Luck and Ben Othman, 2002). Zinc contamination of urban atmospheres is still

increasing, in contrast to many other trace metals (Thapalia et al., 2010). Anthropogenic Zn emissions in developing countries are also increasing (Dolgopolova et al., 2006).

Over the past 15 years, Zn isotope ratios have been used to trace sources and transport pathways of pollution (Albarede, 2004). Zinc has five stable isotopes (^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn , and ^{70}Zn). Zinc isotope abundances are measured by thermal ionization mass spectrometry (TIMS), or multi-collector plasma-source mass spectrometry (MC ICP MS). The ratio of the two most abundant Zn isotopes ($^{66}\text{Zn}/^{64}\text{Zn}$; abundances of 28 and 48%, respectively) is used to report Zn isotope systematics. The commonly used $\delta^{66/64}\text{Zn}$ ($\delta^{66}\text{Zn}$) ratio expresses the relative ‰ deviation of the Zn isotope composition of a sample from that of a standard.

Zinc exists in nature in only one oxidation state (+2). The range of $\delta^{66}\text{Zn}$ values of geological materials on Earth is relatively narrow, not exceeding 2‰. Several authors (Pokrovsky et al., 2005; Borrok et al.,

* Corresponding author.

E-mail address: martin.novak@geology.cz (M. Novak).

2009; Cloquet et al., 2006, 2008) have compared the ranges of $\delta^{66}\text{Zn}$ values among various rock types and environmental sources. Weiss et al. (2007) have summarized our current knowledge of Zn isotope fractionations in nature. Igneous processes in the mantle and crust do not fractionate Zn isotopes. Zinc is a relatively volatile element, and its condensation occurs under lower temperatures compared to other base metals, such as copper (Sivry et al., 2008). Due to a kinetic fractionation, Zn vapor emitted from a smelter is isotopically light (i.e., has low $\delta^{66}\text{Zn}$ values; Juilliot et al., 2011). Whereas globally distributed sphalerites exhibit an average $\delta^{66}\text{Zn}$ value of 0.20‰ (Marechal and Albarède, 2002), smelter emissions are characterized by values close to -0.30% (Sonke et al., 2008). $\delta^{66}\text{Zn}$ values of rocks and unpolluted environmental samples cluster between 0.20 and 0.50‰ (Thapalia et al., 2010). Most anthropogenic Zn samples are isotopically lighter (0.10 to 0.30‰; John et al., 2007).

Zinc isotopes have been successfully applied as tracers in many polluted and unpolluted ecosystems (Luck et al., 1999; Mattioli et al., 2006; Weiss et al., 2007; Viers et al., 2007; Bigalke et al., 2010). Some features of Zn isotope systematics, however, complicate the use of $\delta^{66}\text{Zn}$ as a tracer. It has been shown, for example, that $\delta^{66}\text{Zn}$ values in a single ore deposit may vary by as much as 0.70‰ (Mason et al., 2005). Similarly, the zinc isotope composition of an individual plant may vary by as much as 1.60‰ (Cloquet et al., 2008). With no clear-cut isotope composition of mixing end-members, source apportionment at a receptor site may be difficult (Chen et al., 2008).

The Czech Republic has been known for a sharp (5- to 10-fold) pollution gradient, with an industrialized, polluted northwest, and nearly unpolluted rural south (Novak et al., 2008). After the years of peak industrial pollution (the late 1980s), industrial emission rates of various pollutants have decreased substantially. Recently, a 300-km shift in the highest industrial pollution has been reported from the northwest to the northeast, from the North Bohemian soft-coal basin to the Lower Silesia stone-coal basin (Bohdalkova et al., 2012). The most visible legacy of the North Bohemian industrialization is spruce die-back, caused by acid rain (Novak et al., 2007; Oulehle et al., 2013a). The Lower Silesian conurbation is notorious for the highest air-borne dust levels in today's Europe, and low life expectancy (Erbanova et al., 2008).

Atmospheric input of pollutants into ecosystems is comprised of wet and dry deposition. The main forms of wet deposition are vertical deposition (rain and snow) and horizontal deposition (fog and ice accretions; Moldan and Cerny, 1994). Dry deposition increases with surface roughness, and may bring considerable amounts of pollutants. Larger particles tend to be deposited closer to the pollution source than finer particles. In industrial regions, ice accretions are often characterized by higher concentrations of pollutants, compared to snow (Dousova et al., 2007). Snow and ice accretions have never been analyzed for Zn isotope composition, despite their potential for isotope fingerprinting in environmental health studies. Here we present $\delta^{66}\text{Zn}$ values of snow and ice accretions collected at 6 mountain-top locations in the Czech Republic, Central Europe. Winter seasons were chosen because higher demand for electricity results in higher emissions from coal-burning power plants, compared to other seasons. Furthermore, frequent temperature inversions slow the dispersion of pollutants from the industries, and the concentrations of pollutants in the air increase. Our objective was to compare the Zn isotope composition between vertical and horizontal deposition in a region characterized by a sharp spatial gradient in industrial pollution. We hypothesized that Zn isotope systematics may differ between vertical and horizontal deposition, possibly reflecting different provenance of these two pools of Zn. Our second objective was to quantify and compare input fluxes of soluble and insoluble Zn at remote upland locations of Central Europe. Previous literature often used the *insoluble* form of Zn for isotope analysis, using total HF digests (Dong et al., 2013). The soluble form was rarely analyzed for $\delta^{66}\text{Zn}$, yet it was unclear which form supplies higher fluxes of atmospheric Zn into ecosystems.

2. Materials and methods

2.1. Study sites

In 2009, we established a new hydrogeochemical monitoring network in high-elevation regions of the Czech Republic, less than 1 km from state borders with Germany, Poland and Slovakia. All study sites were situated on mountain peaks at elevations of about 1000 m, and were unforested. For this study, we collected data at six sites (Fig. 1, Table 1). Three sites (KAP, LOU and PRA) were situated in the western part of the Czech Republic. The other three sites (POM, VRH and ELK) were located in the eastern part of the country. The study sites were remote from local pollution sources, approximately 5–10 km away from the nearest settlement, road, or trail.

2.2. Sampling

Snow and ice accretions were collected during two winter seasons between February 2009 and April 2010. The mean interval between snow samplings was 7 days, and the mean interval between ice accretion samplings was 8 days. Both sample types on each sampling date were collected in triplicate. The snow samples were taken from snowpack surfaces (30 by 10 by 3 cm) on the mountain summit. The distance between replicate snow samples was 20 to 50 m. Three wooden poles carrying ice accretion samplers (Figs. S1–S3; Electronic Annex) were erected at fixed positions at mutual distances of 20 to 50 m. Each sampling device consisted of a horizontal wooden bar attached to a wooden pole 1.5 m above the snow pack surface. The samplers were polyethylene (PE) rectangles (14 by 8 by 2 cm) with a high surface area. Each PE rectangle was covered by 784 “thorns” (14 by 2 by 0.6 mm) on both sides. Each stand carried two pairs of these rectangles, installed perpendicularly (N–S, E–W), and one additional pair of rectangles made of PE mesh (14 by 8 by 0.1 cm), also installed perpendicularly. As we found by *in-situ* trials, under some meteorological conditions, large-surface mesh was a more efficient rime scavenger than the thorns. Under other meteorological conditions, the opposite was true. The distance between adjacent pairs of rectangles on the bar was 25 cm. All six rectangles (four with thorns, two made of mesh) were used to collect one combined sample of ice accretions. Three ice accretion samples were collected simultaneously at each study site.

In all, we collected 237 snow samples and 179 ice accretion samples. These samples were analyzed for Zn and Sc concentrations. Thirty five selected snow samples and 9 selected ice accretion samples were analyzed for Zn isotope ratios. Relatively Zn-rich samples were selected for the isotope analysis. At each site, snow samples selected for $\delta^{66}\text{Zn}$ measurements included both winters, and were complemented by at least one ice accretion sample.

Pre-cleaning of ice accretion samplers took 48 h. The PE rectangles were submerged in semiconductors-purity HNO_3 , diluted with deionized water (DW; Milipore, MilliQ 18.2 M Ω cm) in a 1:6 ratio, for 24 h. After rinsing, the rectangles were submerged in DW for another 24 h. Each snow and ice accretion sample was placed in a 1.5 L pre-cleaned polypropylene (PP) container and kept at -20°C .

Three samples of sphalerite (ZnS), one sample of hemimorphite [$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$], and one sample of tetrahedrite [(Cu,Fe,Ag,Zn) $_{12}\text{Sb}_4\text{S}_{13}$] finely intergrown with chalcopyrite (CuFeS_2) were selected from private collections, and analyzed for $\delta^{66}\text{Zn}$. Fly ash from the Příbram base-ores smelter and soft coal from Sokolov–Antonín were also analyzed for $\delta^{66}\text{Zn}$. Additionally, 4 samples of the <0.05 mm fraction of the O horizon of forest soils from two Zn mining regions, Olkusz (Poland) and Příbram (Czech Republic), were analyzed for $\delta^{66}\text{Zn}$. The soil sampling procedure was described in detail by Chrastny et al. (2012).

Download English Version:

<https://daneshyari.com/en/article/4698702>

Download Persian Version:

<https://daneshyari.com/article/4698702>

[Daneshyari.com](https://daneshyari.com)