The isotopic composition of some common forms of anthropogenic zinc

Seth G. John [a],*, J. Genevieve Park [b], Zhitong Zhang [b], Edward A. Boyle [b,1]

[a] Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Chemical Oceanography, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

[b] Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

Abstract

Anthropogenic sources account for much of the zinc (Zn) in the environment. Constraining the isotopic composition of anthropogenic Zn is therefore essential to understanding the environmental biogeochemical cycling of Zn isotopes. This study examines the isotopic variability in several different categories of anthropogenic Zn. Pure Zn metal and Zn dust are the raw materials used in many Zn-containing products. We have measured $\delta^{66}Zn$ for Zn dust purified by thermal distillation, electrochemically purified Zn metal, and US pennies which are made from the most common grade of Zn metal (Special High Grade). Zn in galvanized steel and electroplated hardware was studied because this is a common use of Zn, and Zn in these products may be easily released into the environment through corrosion. Vitamins were studied because they are more highly purified than typical Zn metals and are made from processed chemical compounds such as Zn oxide or Zn gluconate. The isotopic composition of samples measured in this study are as follows (reported as $\delta^{66}Zn$ compared to Lyon-JMC Zn): laboratory standards (seven samples): −9.15‰ to +0.17‰; Zn metal dust purified by thermal distillation (three samples): +0.09‰ to +0.19‰; Zn metal shot purified by electrochemically (one sample): +0.22‰; Special High Grade Zn, as represented in US pennies (six samples): +0.14‰ to +0.31‰; galvanized steel (three samples): +0.12‰ to +0.58‰; electroplated hardware (three samples): −0.56‰ to −0.20‰; and health products (five samples): +0.09‰ to +0.24‰. Based on these results, we suggest that the isotopic composition of "common" anthropogenic Zn products ranges from +0.1‰ to +0.3‰. All samples studied here had $\delta^{66}Zn$ values within this range except four laboratory standards, all electroplated hardware samples, and a single galvanized steel sample. The isotopic range for common anthropogenic Zn is much smaller than the total $\delta^{66}Zn$ range found in Zn ore-field hydrothermal samples, demonstrating the effects of Zn isotope homogenization during ore processing and purification. Laboratory standards may have anomalously light $\delta^{66}Zn$ values because they undergo extra purification steps and Zn recovery during these steps is not quantitative. Electroplated hardware was also isotopically light, consistent with previous studies showing that lighter isotopes are electroplated more quickly than heavy isotopes. Our results suggest that isotopically heavy Zn may be incorporated into the waste stream during the electroplating process. By defining the range of $\delta^{66}Zn$ values that is typical for some common Zn products, and discovering some kinds of products that fall outside this range, we will be better able to use Zn isotopes to trace different anthropogenic Zn sources.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Trace metals; Environment; Zinc; Isotopes; Anthropogenic; Man-made

---

* Corresponding author. Tel.: +1 617 253 5739; fax: +1 617 253 8630.
  E-mail addresses: sjohn@mit.edu (S.G. John), eaboyle@mit.edu (E.A. Boyle).
[1] Tel.: +1 617 253 3388; fax: +1 617 253 8630.

1. Introduction

Zinc (Zn) is commonly used in many man-made items and over three million metric tons are estimated to be released into the environment every year (Graedel et al., 2005). It is used in the manufacture of galvanized steel, in alloy with other metals in many objects, in the manufacture of rubber to neutralize acidity, and in agriculture as a crop nutrient (Gordon et al., 2003). Zn is also used in many health products and is a common component in vitamins, sunscreen, cold medicine, and skin creams. The purification of Zn from ores as described by Gordon et al. (2003) is a multi-step process. The first step is a high-temperature roast to convert Zn sulfides into oxides. The resulting calcine is then dissolved in sulfuric acid and impurities may be removed by precipitation. The final purification step is electrowinning, in which high-purity Zn is electroplated from solution onto aluminum cathodes. Zn may then be manually removed from the cathodes and melted for processing into ingots, shot, dust, and other forms. A less common method of Zn refining uses high-temperature distillation in place of electrowinning. Zn oxide is typically made by evaporation and oxidation of Zn and Zn oxide is a precursor to many other Zn compounds (FDA, 2002).

Anthropogenic sources are a major contributor to the Zn found in natural environments. Approximately half of total Zn emissions to the atmosphere are thought to have anthropogenic sources (Pacyna and Pacyna, 2001) and as much as half of the global fluvial flux of Zn to the oceans may be anthropogenic (Shiller and Boyle, 1985). The influence of anthropogenic Zn is seen even in remote locations far from the major sources of Zn pollution. For example, one third of the Zn dry deposition to the ocean near Bermuda is thought to be anthropogenic (Arimoto et al., 2003), and anthropogenic Zn has been measured in ice from both Greenland (Candelone et al., 1995) and Antarctica (Planchon et al., 2002). In order to model the global cycling of Zn isotopes, we need to characterize the isotopic composition of anthropogenic Zn sources. The Zn isotopic composition of environmental samples can then be compared to this anthropogenic baseline (Fig. 1).

Previous studies have discovered variations in the δ^{66}Zn of anthropogenic Zn laboratory standards (Tanimizu et al., 2002; Mason et al., 2004). The standards measured by Tanimizu et al. ranged from δ^{66}Zn = $-2.41‰$ to $+0.13‰$ compared to Lyons-JMC Zn. This suggests that isotopic fractionation may be common during the purification of laboratory standards. Tanimizu et al. found that the sample with the greatest deviation from continental material was NIST-SRM

682, also the purest Zn standard tested. They suggest that this large fractionation resulted from the distillation, zone refining, and gasification employed in the final purification of this sample. Zn electroplating may also induce significant isotope effects. Zn elecroplated from a $ZnSO_4$ solution was found to be between $-2.48‰$ and $-3.60‰$ lighter than the solution, depending on the voltage of the electrode (Kavner et al., in preparation). Anthropogenic Zn isotope signals have also been traced into the environment. Samples from a Pb–Zn refinery and a steel mill show variations in δ^{66}Zn from $-0.63‰$ to $+0.58‰$ (Mattielli et al., 2005). In the Pb–Zn refinery, there was a trend towards lighter isotope values near the end of the refining process, with the lightest value found in the chimneystack. Zn isotopes from lichens collected near an ore processing and mining site are heavier than minerals collected from the mining site or the typical mineralogical spread of Zn isotope values (Dolgopolova et al., 2006). The authors suggest that such isotopic signals may be used to trace anthropogenic or natural Zn in aerosols. Zn isotopes in rainwater in France varied between about $-0.2‰$ and $+0.2‰$, and
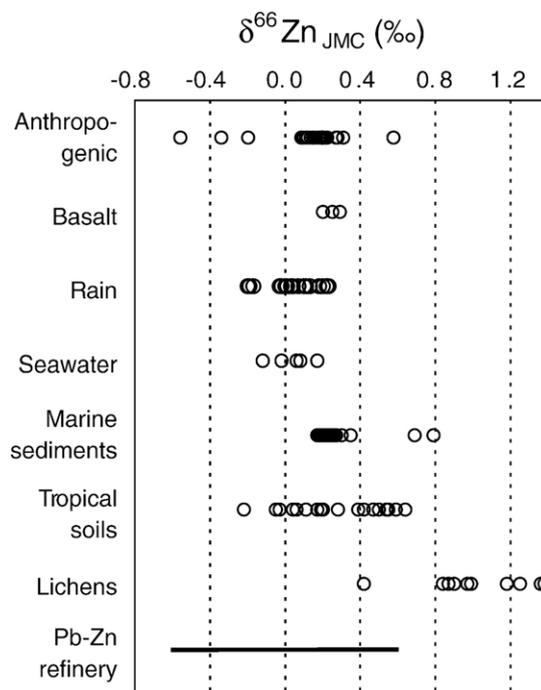

Fig. 1. Anthropogenic Zn isotope samples (this study, excluding laboratory standards) can be compared to the lithogenic baseline of basalt (Archer and Vance, 2004; Ben Othman et al., 2003; Chapman et al., 2006; Maréchal et al., 2000), and to important environmental reservoirs such as rain (Luck et al., 1999), seawater (Bermin et al., 2006), marine sediments (Maréchal et al., 2000), tropical soils (Viers et al., 2007), lichens (Dolgopolova et al., 2006), and samples from a Pb–Zn refinery (Mattielli et al., 2005).

differences were seen between anthropogenically influenced and marine-source rain (Luck et al., 1999). Other trace metals, such as Cd and Pb, are fractionated during purification and this isotopic fractionation of these metals has also been traced in environmental samples (Cloquet et al., 2006; Dolgopolova et al., 2006).

We have undertaken this study in order to determine how widespread Zn isotope variation is among anthropogenic products. Previous studies have shown that anthropogenic $\delta^{66}Zn$ variations can be large, but have not established how common these large variations are. For example, by testing a broader range of anthropogenic samples we can learn whether the large $\delta^{66}Zn$ variations found in laboratory standards are a common feature of refined Zn metal, or if they result from extra purification steps unique to laboratory standards. Measuring Zn isotopes in refined Zn metal may also help us to understand whether the $\delta^{66}Zn$ variations observed in refinery smokestacks are better ascribed to the Zn ores being processed, or fractionation during processing.

By measuring the Zn isotope composition of many different anthropogenic Zn-containing products, we hope to better understand how Zn isotopes may be used as tracers of anthropogenic contamination. Raw Zn metal is the precursor used to make many Zn-containing products such as paints, rubber, hardware, and brassware. Here, we have analyzed Zn manufactured by both electrochemically and thermally purified Zn, as well as a more random sampling of Zn metal represented by Zn-core pennies which are made from Special High Grade (SHG) Zn purchased on the US market (Jasinski, 1994). SHG zinc accounts for 63% of total industrial Zn use in the US, and is the most highly purified of the three common grades of Zn (SHG, High Grade (HG), and Prime Western (PW)) (Jorgenson, 2004). Steel galvanization and Zn electroplating (sometimes called "electrogalvanization") is another major use of anthropogenic Zn. Galvanizing Zn is of particular interest because it is typically exposed to abrasive environmental conditions and is therefore likely to be transported into the environment. Finally, we have studied several health and medical products because they are made from more highly purified Zn than other anthropogenic items. These samples were studied to determine whether, like laboratory standards, the extra purification steps led to large Zn isotope fractionations.

2. Materials and methods

2.1. Zinc samples

Dissolved Zn standards were NIST-SRM 682 and a 1000 ppm Zn standard (AccuTrace, AccuStandard Inc.,

Lot#B2075078). Laboratory-grade Zn metal samples were 10 mesh (Metal #1: B&A, Lot D355Z077R) and 30 mesh (Metal #2: J.T. Baker, Lot G42701). Laboratory Zn acetate standards were from Mallinckrodt (Acetate #1: Lot WALP, and Acetate #2: Lot KDSJ) and Baker Scientific (Acetate #3: Lot H20157). Zn metal purified by thermal distillation was obtained as Zn metal dust (98.5% purity) from US Zinc Corp. (Houston, TX) as regular (USZ #1), regular superfine (USZ #5), and low Pb Zn (USZ #1 XL). Electrochemically purified Zn was obtained as high-purity Zn shot (99.995%) from the Canadian Electrolytic Zinc (CEZ shot) refinery (Salaberry-de-Valleyfield, Québec) through Falconbridge Limited. For a more random sampling of Special High Grade (SHG) Zn metal available on US markets, US pennies were selected from circulation, noted by the year in which they were minted. "Hot-dip" galvanized metal samples were a construction tie plate (Simpson plate: Simpson Strong-Tie # TP15), a hanger strap (Prairie Home strap: Prairie Home Products # 20313), and a siding nail (Sterling nail: Georgia Pacific Products). Electroplated hardware was Zn-plated screws (Allied screw: Allied Bolt and Screw Corp., and Fran-dan screw: Fran-dan Bolt and Screw Corp.) and chain (Blu-Krome chain: Cooper Hand Tools # 0721727). Health and medical products were obtained from local commercial sources and include Benadryl Itch Stopping Cream (Pfizer Consumer Healthcare, Lot #23454L), Centrum Silver multivitamins (Wyeth Consumer Healthcare, Control #A98404), Dr. Zinc lozenges (McKesson, Lot #3KVO305), Nature's Bounty zinc tablets (Nature's Bounty, Inc., Lot #20515101), and ColdEeze zinc lozenges (The Quigley Corporation).

2.2. Sample preparation

Samples were handled under Class-100 clean air flow conditions. Water was deionized and distilled in a borosilicate glass still (Corning MegaPure), and all acids were triply-distilled in Vycor glass to remove contaminants. All labware was acid cleaned PFA (Savillex), polypropylene or polyethylene. Metal samples were prepared by dissolving directly in 2% HNO_3 for analysis, or by dissolving in 2 N HCl prior to purification by anion exchange chromatography. Zn acetate samples were twice dissolved in 2% HNO_3 and evaporated to drive off acetic acid before redissolution in 2% HNO_3. Pennies were washed with 2% Citranox® detergent, rinsed with distilled water, and dissolved in 2 N HCl prior to anion exchange purification. Health and medical products were dissolved in 2% nitric acid and small aliquots were removed and evaporated to

dryness. These subsamples were then combusted for 8 h at 450 °C to remove all organic material and the remaining material was dissolved in 2 N HCl for purification by anion exchange chromatography.

Between 10 to 200 µg of each sample was purified by anion exchange chromatography according to a procedure based on methods previously used for the purification of Fe, Cu, and Zn for isotopic analysis (Maréchal et al., 1999). Instead of loading samples in 7 N HCL, samples were loaded onto the column directly in 2 N HCl to save time and reduce the total amount of HCl used. Zn affinity for the anion exchange resin is highest at a Cl^- concentration of 2 N (Kraus and Moore, 1953). The samples were rinsed with 15 mL of 2 N HCl to elute other elements, and then the Zn fraction was eluted in 12 mL 0.5 N HNO_3. The eluent was evaporated and reacted with 200 µL of 14 N HNO_3 and 100 µL of H_2O_2 (Ultrex II, J.T. Baker), to oxidize organics that may have leached from the resin. With every group of samples processed by column chromatography, two process blanks and one or two isotope standards were run to assess the magnitude of contamination and matrix effects during measurement. Zn recovery was determined by graphite furnace atomic absorption spectrometry using a Hitachi Z-8100 spectrophotometer. Samples were analyzed by ICP-MS to ensure that Cu and Fe had been removed.
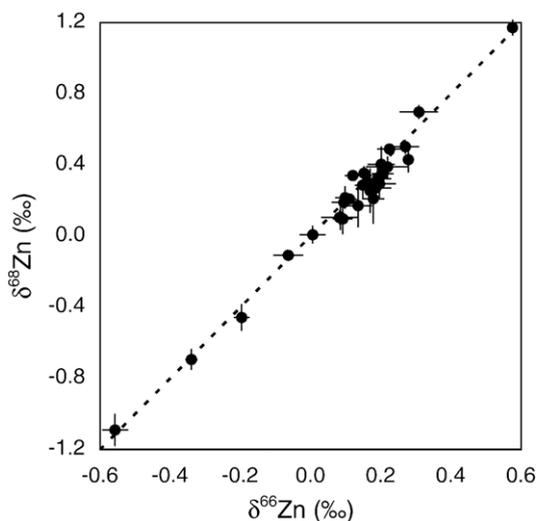

Fig. 2. Comparison of $\delta^{66}Zn$ values and $\delta^{68}Zn$ values for each sample (●). Samples generally lie upon the expected mass-fractionation line (•••), indicating the absence of isobaric interferences during analysis. Some highly fractionated laboratory standards are not pictured, though they also conform to the expected mass-dependant relationship. Error bars are the internal error for triplicate analysis of each sample (2σ S.D.).
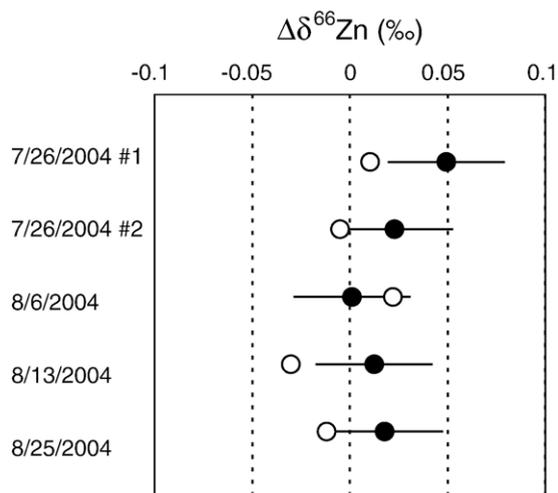

Fig. 3. On several separate dates, NIST-SRM 682 standards were processes alongside samples. $\Delta\delta^{66}Zn$ (the difference between $\delta^{66}Zn$ of the NIST-SRM 682 bracketing standard and the same standard after purification as a sample) was calculated both by sample-standard bracketing alone (○) and using both sample-standard bracketing and Cu normalization (●). Error bars represent the pooled standard deviation for the Cu-normalized samples compared to the expected isotope ratio (2σ).

2.3. Isotope analysis

All samples were diluted to 200 ppb Zn in 2% HNO_3 for isotope analysis and spiked with 100 ppb Cu (Ultra Scientific, Lot #D00204) to monitor instrumental mass bias. Because Cu is more efficiently ionized than Zn, a 2:1 Zn:Cu ratio was chosen to provide roughly equivalent voltages on each mass. Data was collected on an IsoProbe multi-collector ICP-MS (Thermo Electron, formerly Micromass), using Faraday collectors to monitor signals on masses 60, 63, 64, 65, 66, 67, and 68. Typical signals on the Faraday collectors were around 0.2 mV, 2.5 V, 2.2 V, 1.2 V, 1.3 V, 0.2 V, and 0.9 V, respectively. Samples were introduced into the plasma by an Apex Q inlet system with a desolvating membrane (ESI) using a 75 µL/min MicroMist® (Glass Expansion) nebulizer. On-peak acid blank subtraction was applied to all samples by monitoring the signal from 2% HNO_3 during one sixty second block, 3 min before sample analysis. Sample and standard data was collected in fifteen cycles of ten seconds, and up to two cycles that were more than two standard deviations from the mean were discarded.

The only spectral interference for which we apply a correction is ^{64}Ni (overlapping with ^{64}Zn). This correction is made by monitoring the abundance of ^{60}Ni, assuming natural isotopic abundances, and correcting for instrumental mass bias with an internal

Table 1
Zn isotopic composition of anthropogenic samples compared to Lyon-JMC Zn

Sample name	Sample-standard bracketing (SSB) corrected data		Cu empirical external normalization (EEN) corrected data		Cu empirical external normalization (EEN) corrected data	
	$\delta^{66}Zn_{JMC}$	S.D. (2σ)	$\delta^{66}Zn_{JMC}$	S.D. (2σ)	$\delta^{68}Zn_{JMC}$	S.D. (2σ)
Laboratory standards						
NIST-SRM 682	−2.45		−2.45			
AccuTrace Std	−9.14	0.02	−9.17	0.04	−18.33	0.02
Metal #1	0.16	0.03	0.17	0.00	0.26	0.12
Metal #2	0.08	0.03	0.09	0.03	0.19	0.03
Acetate #1	0.16	0.24	0.01	0.04	0.01	0.05
Acetate #2	0.16	0.10	0.08	0.05	0.10	0.04
Acetate #3	0.06	0.06	−0.06	0.04	−0.11	0.02
Industrial raw metal (distillation refined)						
USZ #1	−0.04	0.09	0.15	0.02	0.29	0.07
USZ #5	0.01	0.02	0.19	0.04	0.32	0.07
USZ #1 XL	0.03	0.08	0.09	0.03	0.10	0.09
Industrial raw metal (electrochemically refined)						
CEZ shot	0.21	0.02	0.22	0.03	0.49	0.02
Industrial raw metal (SHG)						
1983 penny	0.06	0.07	0.15	0.02	0.35	0.04
1983 penny #2	0.11	0.03	0.14	0.04	0.17	0.12
1985 penny	0.09	0.07	0.20	0.04	0.40	0.10
1985 penny #2	0.11	0.03	0.18	0.03	0.21	0.14
1991 penny	0.04	0.11	0.22	0.06	0.39	0.06
1991 penny #2	0.14	0.03	0.19	0.05	0.27	0.05
1999 penny	0.10	0.06	0.17	0.01	0.30	0.05
2000 penny	0.24	0.07	0.31	0.05	0.70	0.04
2000 penny #2	0.24	0.02	0.28	0.02	0.43	0.07
2002 penny	0.16	0.06	0.20	0.05	0.29	0.09
Galvanized hardware						
Simpson plate	0.17	0.04	0.12	0.02	0.34	0.02
Prairie Home strap	0.75	0.03	0.58	0.01	1.17	0.04
Sterling nail	0.31	0.02	0.21	0.03	0.35	0.05
Electroplated hardware						
Allied screw	−0.19	0.01	−0.34	0.02	−0.69	0.06
Fran-dan screw	−0.21	0.08	−0.20	0.02	−0.46	0.08
Blu-Krome chain	−0.55	0.01	−0.56	0.04	−1.09	0.09
Health products						
Benadryl	0.09	0.01	0.11	0.02	0.21	0.02
Centrum	0.08	0.05	0.09	0.02	0.11	0.07
Dr Zn	0.18	0.03	0.20	0.02	0.34	0.08
Nature's Bounty	0.14	0.24	0.10	0.03	0.22	0.06
ColdEeze	0.16	0.07	0.27	0.04	0.50	0.04

Standard deviations are the internal error reported for triplicate analysis of individual samples (2σ).

Cu spike (see below). Ni corrections were insignificant at our analytical precision. We first determine Zn isotope ratios by sample-standard bracketing alone and then correct these data for sample matrix effects on instrumental mass bias using an internal Cu spike. The relationship between Zn and Cu mass bias can differ from that expected based on the exponential mass bias law alone (Maréchal et al., 1999; Albarède and Beard, 2004). Following their suggestion, we determine the linear relationship between the natural log of measured $^{66}Zn/^{64}Zn$ versus measured $^{65}Cu/^{63}Cu$ for all standards run during an analysis session, a procedure termed
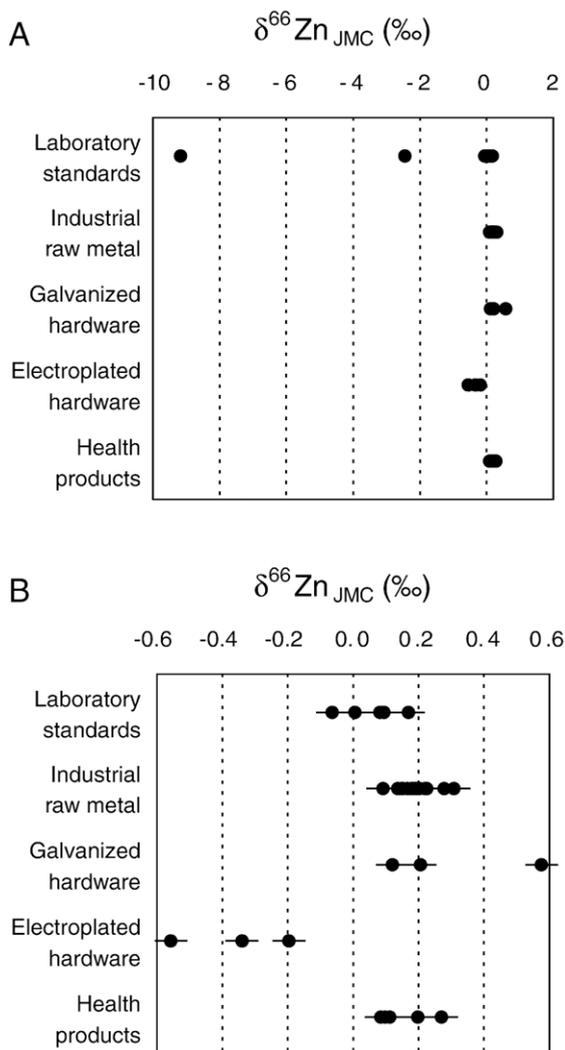
Fig. 4. Zn isotopic composition of anthropogenic samples showing A) the entire measured range and B) the smaller range in which all non-laboratory standards fall. Error bars (2σ S.D.; ± 0.05‰) give the external reproducibility calculated based on the analytical error for processed laboratory standards and the error in δ^{66}Zn for running standard compared to JMC Zn.

empirical external normalization (EEN) (Clayton et al., 2002; Mason et al., 2004). We apply this correction to both samples and standards, for a 'modified' EEN sample-standard bracketing technique. All samples were measured in triplicate and ^{68}Zn/^{64}Zn ratios were measured to verify mass-dependent fractionation and the absence of Zn spectral interferences (Fig. 2).

The Zn isotope ratio of NIST-SRM 682 compared to Lyon-JMC Zn (Maréchal et al., 1999) has been measured in triplicate six times, during three separate analytical sessions, and our NIST-SRM 682 standard was determined to be lighter by δ^{66}Zn$_{JMC}$=-2.45 ± 0.02‰ (2σ S.E.). All

measurements are corrected with this offset so that isotope ratios may be reported compared to Lyon-JMC Zn.

2.4. Error analysis

The measured isotope ratio of samples compared to unprocessed bracketing standards can be affected by Zn contamination of the samples, isotopic fractionation during the purification procedure, or analytical changes resulting from matrix residues or incomplete purification of the samples. We discount the effect of Zn contamination because process blank concentrations were low (<10 ng and never more than 0.1% of the sample concentrations). Assuming that contamination sources have an isotopic ratio similar to other continental and anthropogenic samples, this amount of contaminant Zn is too small to have a measurable effect on the isotope ratio of samples. With Zn recoveries greater than 98%, there should be no isotopic fractionation associated with column purification and other processing steps. NIST-SRM 682 process standards were treated by the same purification protocol as samples in order to gauge the accuracy and precision of our analytical methods (Fig. 3). After purification, isotope analysis samples were checked for Fe and Cu by ICP-MS. Concentrations of these elements were always below detectable limits (<1 ppb in the solution with 200 ppb Zn). Most of the Cu-corrected Zn isotope ratios are higher than the Zn isotope ratios corrected by sample-standard bracketing alone. Although the magnitude of this correction is small, it indicates that column matrix may have a small effect on instrumental mass bias.

In our experience, the main source of analytical error is occasional appearance of a systematic offset between pre-column and post-column standards, as has also been observed in other studies (Archer and Vance, 2004). In some analytical sessions, use of the desolvating membrane attached to the APEX resulted in systematic offsets in all post-column samples of as much as +0.2‰. In this study, careful post-column treatment of the samples to remove organics seems to have prevented this problem.

Internal reproducibility for triplicate analysis of individual samples was usually in the range 0.00‰ to 0.06‰ (2σ S.D.) (Table 1). $\Delta\delta^{66}$Zn, the difference in measured isotope ratio between standards used for sample-standard bracketing and the same standards run through the full sample purification protocol, was used to estimate external reproducibility. The standard deviation of $\Delta\delta^{66}$Zn for the five process standards was 0.052‰ (2σ), greater than the internal reproducibility within triplicate analyses for nearly all of our samples.

We are wary of applying the error calculated for post-column standards to samples with a potentially more complicated matrix, but we believe that this error is, at worst, more appropriate than the smaller errors calculated from internal reproducibility. The error in the isotopic offset between our NIST-SRM 682 running standard and JMC Zn must also be taken into account, for a total external error of 0.05‰ (2σ S.D.) Several samples were run in different analytical session months apart, these replicate analyses give the same δ^{66}Zn values within the analytical error (Table 1).

3. Results and discussion

3.1. Zn isotope measurements

Zn isotope ratios were measured for thirty-two anthropogenic samples (Table 1, Fig. 4). The isotopic compositions of the laboratory standards ranged from $\delta^{66}\text{Zn}_{\text{JMC}} = -9.15$‰ to $+0.17$‰. The AccuTrace standard has the lightest Zn isotope ratio reported to date. NIST-SRM 682 and two of the Zn acetate samples (#1 and #3) were also lighter than most other anthropogenic products. The δ^{66}Zn of Zn metal ranged from $+0.09$‰ to $+0.30$‰. No systematic differences were discovered between Zn metal refined by thermal distillation or electrochemical purification, or in the Special High Grade Zn found in pennies. Hot-dip galvanized steel δ^{66}Zn ranged from $+0.12$‰ to $+0.58$‰. Electroplated hardware samples had δ^{66}Zn from -0.56‰ to -0.20‰, and all three samples were isotopically lighter than other Zn metal samples. Health and medical products δ^{66}Zn ranged from 0.09‰ to 0.27‰, a similar range discovered for Zn metals. Based on this data, we find that the δ^{66}Zn of "common" anthropogenic Zn products varies between about $+0.1$‰ and $+0.3$‰.

3.2. Isotopic variability within "common" Zn

The ultimate source of isotopic variability for common Zn products may be either variability in the Zn ores, or isotopic fractionation imparted during the purification process. The variability discovered so far within hydrothermal Zn ores from two separate ore fields is large, from $\delta^{66}\text{Zn} = -0.43$‰ to $+1.33$‰, much greater than the variability seen in common anthropogenic samples (Mason et al., 2005; Wilkinson et al., 2005). Interestingly, the average isotopic composition of our common Zn is $\delta^{66}\text{Zn} = +0.18$‰, quite similar to the $+0.15$‰ average isotope composition of samples measured in these two Zn ore fields. Homogenization during processing may account for the smaller range in

isotopic composition of common Zn compared to ore-field samples. δ^{66}Zn variability within Zn ores may be the primary cause of the $+0.1$‰ to $+0.3$‰ δ^{66}Zn variability seen in common anthropogenic products. In fact, the δ^{66}Zn of three homogenized ore samples ranged between -0.06‰ and $+0.33$‰, similar to the isotopic range discovered here for common anthropogenic Zn (Chapman et al., 2006). If Zn recovery from ores during purification is not complete, however, isotope fractionation during refining may also impact the δ^{66}Zn of common anthropogenic Zn.

3.3. Isotopically "uncommon" Zn products

Samples with δ^{66}Zn values outside the range for "common" anthropogenic products include laboratory standards, electroplated hardware, and one of our galvanized steel samples. The methods used to purify laboratory standards, electrochemical purification and thermal distillation, are similar to methods used to purify common Zn metal from ores. The reason for the larger isotopic fractionations seen in laboratory standards may be that Zn recovery during purification is not quantitative. Industrial processes are optimized to attain nearly complete recovery of the Zn from the starting material, so that even if there is isotopic fractionation during purification, the δ^{66}Zn of purified metal will match the δ^{66}Zn of the original Zn ores. Differences in the purification method used, or use of multiple additional purification steps, may also contribute to the great variability in δ^{66}Zn found in laboratory standards compared to common Zn.

Electroplated hardware is lighter than common Zn metal, consistent with previous experimental results showing that there is a negative isotope effect for Zn electroplating (Kavner et al., in preparation). The fact that these samples are lighter than common metal implies that not all Zn added to the plating bath is converted to electroplated Zn. The isotope ratio of electroplated Zn can be used to estimate the amount of Zn that is lost into the waste stream during processing. At steady state, the isotopic ratio of plated Zn will be given by:

$$\delta^{66}\text{Zn}_{\text{plated}} = \delta^{66}\text{Zn}_{\text{starting}} - \varepsilon(f)$$

where $\delta^{66}\text{Zn}_{\text{starting}}$ is the isotope ratio of the Zn added to the plating bath, ε is the isotope effect for plating, and f is the fraction of Zn lost to the waste stream. Assuming that $\delta^{66}\text{Zn}_{\text{starting}}$ is $+0.2$‰, and taking the isotope effect (ε) measured for electroplating at the highest voltage studied by Kavner et al. (in preparation), -2.48‰ at

800 mV, we calculate values of f between 0.16 and 0.31 for our three samples. Such high losses of Zn seem unlikely in an industrial process, the fractionation of Zn during electroplating warrants further study.

One of the three "hot-dip" galvanized samples measured was isotopically heavy ($\delta^{66}Zn=+0.58‰$) compared to common Zn metal. This may be due to isotopic fractionation during the plating process, or the starting Zn used in this process may have been isotopically heavy.

4. Conclusions

When studying Zn isotopes in the environment, for example in seawater (Bermin et al., 2006), marine materials (Maréchal et al., 2000), plants (Weiss et al., 2005), or soils and trees (Viers et al., 2007), there may be both natural and anthropogenic sources of Zn (Fig. 1). Our study of $\delta^{66}Zn$ in many different anthropogenic materials provides a framework for predicting the isotopic composition of some different Zn sources. We predict that most anthropogenic Zn will have an isotopic composition in the range of +0.1‰ to +0.3‰. Although many common Zn-containing materials were not studied, for example rubbers, paints, and brass, our data provides a basis for predicting what the isotopic composition of these materials might be. If there is no fractionation during the production process, or if the raw Zn starting materials are completely consumed during production, the Zn isotope ratio of these products should match the Zn isotope ratio the Zn raw material, with an expected $\delta^{66}Zn$ from +0.1‰ to +0.3‰. When the $\delta^{66}Zn$ of anthropogenic products falls out of this range, it may be because the raw Zn starting material had an unusual isotope ratio, or it may be an indication that isotopic fractionation has occurred during manufacture.

By constraining the isotopic composition of common anthropogenic Zn, and discovering some of the processes that lead to large deviations from this composition, Zn isotopes may be better used as an environmental tracer. For example, very negative $\delta^{66}Zn$ values (<0‰) may indicate Zn that has been electroplated from solution. Conversely, Zn in the waste stream from electroplating operations may be isotopically heavy. The heavy $\delta^{66}Zn$ values found in lichens (Dolgopolova et al., 2006), may also indicate a Zn source that has been somehow isotopically fractionated compared to common Zn. Measuring Zn isotopes in other anthropogenic materials, and in Zn products from other countries, will increase our understanding of the likely isotopic composition of different forms of anthropogenic Zn.

References

Albarède, F., Beard, B., 2004. Analytical methods for non-traditional isotopes. Geochemistry of Non-traditional Stable Isotopes, pp. 113–152.

Archer, C., Vance, D., 2004. Mass discrimination correction in multiple-collector plasma source mass spectrometry: an example using Cu and Zn isotopes. Journal of Analytical Atomic Spectrometry 19, 656–665.

Arimoto, R., Duce, R.A., Ray, B.J., Tomza, U., 2003. Dry deposition of trace elements to the western North Atlantic. Global Biogeochemical Cycles 17 (1) Art. No. 1010.

Ben Othman, D., Luck, J.M., Tchalikian, A., Albarède, F., 2003. Cu–Zn isotope systematics in terrestrial basalts. Geophysical Research Abstracts 5, 09669.

Bermin, J., Vance, D., Archer, C., Statham, P.J., 2006. The determination of the isotopic composition of Cu and Zn in seawater. Chemical Geology 226 (3–4), 280–297.

Candelone, J.P., Hong, S.M., Pellone, C., Boutron, C.F., 1995. Postindustrial revolution changes in large-scale atmospheric-pollution of the Northern-Hemisphere by heavy-metals as documented in Central Greenland snow and ice. Journal of Geophysical Research -Atmospheres 100 (D8), 16605–16616.

Chapman, J.B., Mason, T.F.D., Weiss, D.J., Coles, B.J., Wilkinson, J.J., 2006. Chemical separation and isotopic variations of Cu and Zn from five geological reference materials. Geostandards and Geoanalytical Research 30 (1), 5–16.

Clayton, R., Andersson, P., Gale, N.H., Gillis, C., Whitehouse, M.J., 2002. Precise determination of the isotopic composition of Sn using MC-ICP-MS. Journal of Analytical Atomic Spectrometry 17 (10), 1248–1256.

Cloquet, C., Carignan, J., Libourel, G., Sterckeman, T., Perdrix, E., 2006. Tracing source pollution in soils using cadmium and lead isotopes. Environmental Science & Technology 40 (8), 2525–2530.

Dolgopolova, A., Weiss, D.J., Seltmann, R., Kober, B., Mason, T.F.D., Coles, B., Stanley, C.J., 2006. Use of isotope ratios to assess sources of Pb and Zn dispersed in the environment during mining and ore processing within the Orlovka–Spokoinoe mining site (Russia). Applied Geochemistry 21, 563–579.

FDA, 2002. Code of Federal Regulations, Title 21, 73.1991 Zinc oxide.

Gordon, R.B., Graedel, T.E., Bertram, M., Fuse, K., Lifset, R., Rechberger, H., Spatari, S., 2003. The characterization of technological zinc cycles. Resources Conservation and Recycling 39 (2), 107–135.

Graedel, T.E., van Beers, D., Bertram, M., Fuse, K., Gordon, R.B., Gritsinin, A., Harper, E.M., Kapur, A., Klee, R.J., Lifset, R., Memon, L., Spatari, S., 2005. The multilevel cycle of anthropogenic zinc. Journal of Industrial Ecology 9 (3), 67–90.

Jasinski, S.M., 1994. Zinc, Minerals Yearbook. The Bureau of Mines, Washington, D.C.

Jorgenson, J.D., 2004. Zinc, Minerals Yearbook. The Bureau of Mines, Washington, D.C.

Kavner, A., John, S., Sass, S., Boyle, E., in preparation. Voltage dependent stable isotope separation during Zn electroplating.

Kraus, K.A., Moore, G.E., 1953. Anion exchange studies. VI. The divalent transition elements manganese to zinc in hydrochloric acid. Journal of the American Chemical Society 75, 1457–1460.

Luck, J.M., Ben Othman, D., Albarède, F., Telouk, P., 1999. Pb, Zn, and Cu isotopic variations and trace elements in rain. Geochemistry of the Earth's Surface. Balkema, Rotterdam.

Maréchal, C.N., Telouk, P., Albarède, F., 1999. Precise analysis of copper and zinc isotopic compositions by plasma-source mass spectrometry. Chemical Geology 156 (1–4), 251–273.

Maréchal, C.N., Nicolas, E., Douchet, C., Albarède, F., 2000. Abundance of zinc isotopes as a marine biogeochemical tracer. Geochemistry Geophysics and Geosystems 1 1999GC000029.

Mason, T.F.D., Weiss, D.J., Horstwood, M., Parrish, R.R., Russell, S.S., Mullane, E., Coles, B.J., 2004. High-precision Cu and Zn isotope analysis by plasma source mas spectrometry — Part 2. Correcting for mass discrimination effects. Journal of Analytical Atomic Spectrometry 19 (2), 218–226.

Mason, T.F.D., Weiss, D.J., Chapman, J.B., Wilkinson, J.J., Tessalina, S.G., Spiro, B., Horstwood, M.S.A., Spratt, J., Coles, B.J., 2005. Zn and Cu isotopic variability in the Alexandrinka volcanic-hosted massive sulphide (VHMS) ore deposit, Urals, Russia. Chemical Geology 221 (3–4), 170–187.

Mattielli, N., Yao N'Guessan, M., Rimetz, J., Petit, J., Weis, D., Debout, K., Flement, P., 2005. Isotopic study of two biolimiting metals (Zn and Cu) in industrial aerosols. Geophysical Research Abstracts 7, 10030.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. Environmental Reviews 9, 269–298.

Planchon, F.A.M., Boutron, C.F., Barbante, C., Cozzi, G., Gaspari, V., Wolff, E.W., Ferrari, C.P., Cescon, P., 2002. Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to the late-20th century. Earth and Planetary Science Letters 200 (1–2), 207–222.

Shiller, A.M., Boyle, E., 1985. Dissolved zinc in rivers. Nature 317 (6032), 49–52.

Tanimizu, M., Asada, Y., Hirata, T., 2002. Absolute isotopic composition and atomic weight of commercial zinc using inductively coupled plasma mass spectrometry. Analytical Chemistry 74 (22), 5814–5819.

Viers, J.R.M., Oliva, P., Nonell, A., Gélabert, A., Sonke, J., Freydier, R.M., Gainville, R., Dupré, B., 2007. Evidence of Zn isotopic fractionation in a soil–plant system of a pristine tropical watershed (Nsimi, Cameroon). Chemical Geology 239, 124–137.

Weiss, D.J., Mason, T.F.D., Zhao, F.J., Kirk, G.J.D., Coles, B.J., Horstwood, M.S.A., 2005. Isotopic discrimination of zinc in higher plants. New Phytologist 165 (3), 703–710.

Wilkinson, J.J., Weiss, D.J., Mason, T.F.D., Coles, B.J., 2005. Zinc isotope variation in hydrothermal systems: Preliminary evidence from the Irish Midlands ore field. Economic Geology 100 (3), 583–590.