

Chapter 2

The isotopic composition of some common forms of anthropogenic zinc

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 kinds of anthropogenic Zn. Laboratory standards are highly purified and can be significantly fractionated from natural Zn. Industrial Zn dust and U.S. pennies, which are made from the most common grade of Zn metal (Special High Grade), were studied to represent common Zn metal. Vitamins were studied because they are more highly purified than typical Zn metals and are made from chemical compounds such as Zn oxide or Zn gluconate. The isotopic composition of laboratory standards ranged in $\delta^{66}\text{Zn}$ from -9.15‰ to +0.17‰ compared to Lyon-JMC Zn. Zn dust and pennies ranged from +0.09‰ to +0.31‰, and vitamins ranged from +0.09‰ to +0.27‰. External

reproducibility was 0.052‰ (2σ s.d.) based on several standards, and was similar to internal error. The isotopic range for non-laboratory standards is much smaller than the total range seen in Zn ore deposits, but has a similar average Zn isotope ratio. This data presents a first look at the range of $\delta^{66}\text{Zn}$ values that is typical of common anthropogenic Zn products.

2.1 Introduction

Zinc (Zn) is commonly used in many man-made items and over 3 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 alloys 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 of metallic Zn 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.

Previous studies have found large variations in the Zn isotope composition of anthropogenic Zn standards (Mason et al., 2004; Tanimizu et al., 2002). The standards measured by Tanimizu et al. ranged from $\delta^{66}\text{Zn}_{\text{JMC}} = -2.41\text{‰}$ to $+0.13\text{‰}$. 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, which was 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. Metal reduction during electroplating may also have a significant kinetic isotope effect (Kavner et al., 2005), suggesting that electrolytically-purified Zn could also have a unique anthropogenic signature.

Non-electrolytic processes may also fractionate Zn isotopes. Analysis of Zn isotopes samples from a Pb-Zn refinery and a steel mill show variations in $\delta^{66}\text{Zn}$ from -0.63‰ to $+0.58\text{‰}$. 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 (Mattielli et al., 2005). 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 (Dolgoplova 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 by about 0.3‰, and differences were seen between anthropogenically influenced and marine-source rain (Luck et al., 1999).

Mineral ores may also be a source of variability in anthropogenic Zn. Samples collected at ancient hydrothermal sites, the source of modern Zn ores, range from $\delta^{66}\text{Zn} = -0.43\text{‰}$ to $+1.33\text{‰}$ (Mason et al., 2005; Wilkinson et al., 2005). Wilkinson et al. compiled Zn isotope data for all terrestrial samples measured to date to show that they span the entire range between the heaviest and lightest hydrothermal sample. Three homogenized ore samples have a smaller isotopic range, between $\delta^{66}\text{Zn} = -0.06\text{‰}$ and $+0.33\text{‰}$ (Chapman et al., 2006). Zn isotopes are variable on spatial scales of centimeters and millimeters (Mason et al., 2005), so the lesser variability found in ores may represent the effects of homogenization.

While the total variability in anthropogenic Zn isotopes including laboratory standards and aerosols may be several permil, the variability of Zn isotopes in the most common forms of anthropogenic Zn has not previously been investigated. Several grades of Zn are manufactured and used in the US including Special High Grade (SHG), High Grade (HG), Prime Western (PW) with minimum purities of 99.99%, 99.95% and 98.50%, respectively. Together, these three grades account for 94% of the reported Zn use in the US during 2004 and SHG Zn alone accounted for 63% of Zn use during this time (Jorgenson, 2004). U.S. pennies, which have been made from Zn with a thin coating of Cu since 1982, are made with SHG Zn and are therefore representative of the majority of Zn used in the US (Jasinski, 1994). If there is isotopic fractionation associated with industrial Zn refining and production processes, we expect this to be most apparent in SHG Zn compared to less purified HG and PW grade Zn. We have also measured some health and medical products; although they represent only a small portion of Zn use, they require the most highly purified Zn used in common anthropogenic

products and are made from Zn compounds such as Zn oxide and Zn gluconate rather than Zn metal (FDA, 2002).

2.2 Materials and methods

2.2.1 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 (#1: B&A, Lot D355Z077R) and 30 mesh (#2: J.T. Baker, Lot G42701). Laboratory Zn acetate standards were from Mallinckrodt (#1: Lot WALP, and #2: Lot KDSJ) and Baker Scientific (#3: Lot H20157). Industrial Zn metal dust samples of 98.5% purity were obtained from the US Zinc (Austin, TX) as regular (USZ # 1), regular superfine (USZ # 5), and low Pb Zn (USZ #1 XL). Industrial high purity Zn shot (99.995%) was obtained from the Canadian Electrolytic Zinc (CEZ) refinery (Salaberry-de-Valleyfield, Québec) through Falconbridge Limited. U.S. pennies were obtained from circulation and are noted by the year in which they were minted. 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).

2.2.2 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% HNO₃ for analysis, or by dissolving in 2N HCl prior to purification by anion exchange chromatography. Zn acetate samples were twice dissolved in 2% HNO₃ and evaporated to drive off acetic acid before redissolution in 2% HNO₃. Pennies were washed with 2% Citranox detergent, rinsed with distilled water, and dissolved in 2N 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 hours at 450°C to remove all organic material and the remaining material was dissolved in 2N HCl prior to anion exchange purification.

Between 10 to 200 µg of each sample was purified by anion exchange chromatography on AG-MP1 resin (BioRad) according to a method previously used for the purification of Fe, Cu, and Zn for isotopic analysis (Maréchal et al., 1999). Because samples were not being processed for Fe and Cu isotope analysis, samples were loaded in 2N HCl. The sample was rinsed with 15 mL of 2N HCl to elute other elements, and then the Zn fraction was eluted in 12 mL 0.5N HNO₃. The eluent was evaporated and reacted with 200 µL of 14N HNO₃ and 100 µL of H₂O₂ (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 processed and analyzed to assess the magnitude of contamination and matrix effects during measurement.

2.2.3 Isotope analysis

All samples were diluted to 200 ppb Zn in 2% HNO₃ for isotope analysis and spiked with 100 ppb Cu (Ultra Scientific, Lot #D00204) to monitor instrumental mass bias. 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. Samples were introduced into the plasma by an Apex Q inlet system with a desolvating membrane (ESI) using a 75 $\mu\text{L}/\text{min}$ MicroMist® (Glass Expansion) nebulizer. On-peak acid blank subtraction was applied to all samples by monitoring the signal from 2% HNO_3 during one 60 second block, three minutes before sample analysis. Sample and standard data was collected in fifteen cycles of ten seconds, and up to two cycles 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 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 (Albarède and Beard, 2004; Maréchal et al., 1999). Following their suggestion, we determine the linear relationship between the natural log of measured $^{66}\text{Zn}/^{64}\text{Zn}$ versus measured $^{65}\text{Cu}/^{63}\text{Cu}$ for all standards analyzed during a single session, a procedure termed 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 $^{68}\text{Zn}/^{64}\text{Zn}$ ratios were measured to verify mass-dependent fractionation and the absence of Zn spectral interferences.

NIST-SRM 682 has been measured repeatedly against the Lyon-JMC Zn (Maréchal et al., 1999) and is lighter by $\delta^{66}\text{Zn}_{\text{JMC}} = -2.45 \text{ ‰}$. All measurements are corrected with this offset so that isotope ratios may be reported compared to Lyon-JMC Zn.

2.3 Results and Discussion

2.3.1 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. We discount the effect of Zn contamination because process blank concentrations were low (consistently between 0 and 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. Zn recoveries were always greater than 98%, so 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 (Figure 1). Most of the Cu-corrected ratios are higher than the raw data corrected by sample-standard bracketing alone. Although the magnitude of this correction is small (the average $\Delta\delta^{66}\text{Zn} = +0.02 \text{ ‰}$ for the five standards), it may reflect a genuine systematic matrix effect on the Cu isotope ratio in samples.

In our experience, though, 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

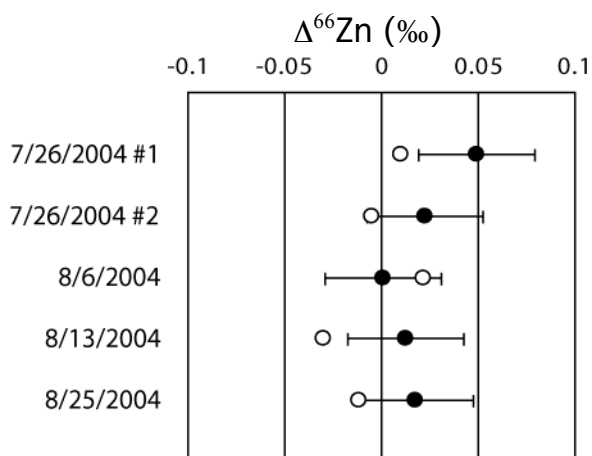


Figure 2.1. Sample-standard bracketing corrected (O) and sample corrected (●) Zn isotope ratios of standards processed alongside samples on several different dates.

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 with HNO₃/H₂O₂ to remove organics seems to have largely prevented this problem. In other experiments, we found that removing the desolvating membrane appears to eliminate this problem.

Reproducibility for triplicate analysis of individual samples was between 0.00‰ and 0.06‰ (2σ s.d.) (Table 1). The difference in measured isotope ratio (Δ) between standards used for sample-standard bracketing and standards run through the full sample purification protocol was used to estimate external reproducibility. The standard deviation of Δ⁶⁶Zn for the five process standards was 0.052‰ (2σ), greater than the internal reproducibility within triplicate analyses for nearly all of our

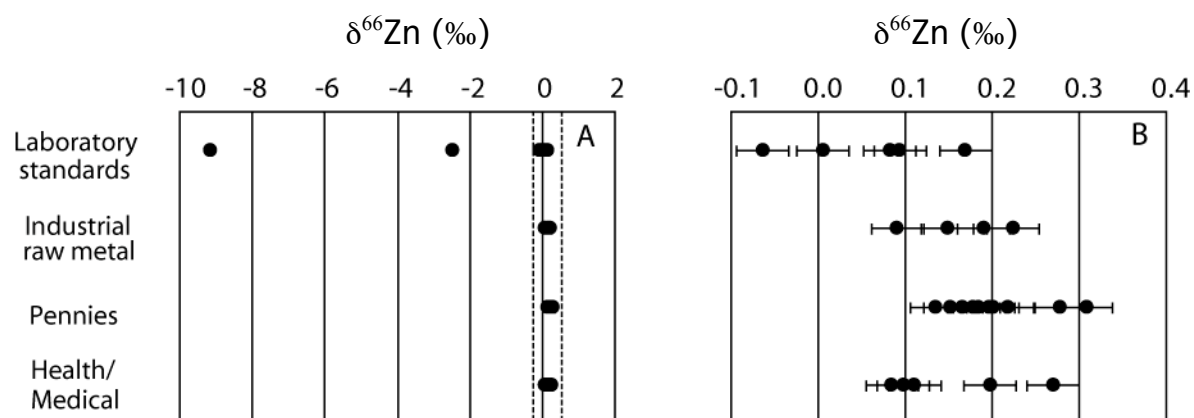


Figure 2.2. Zn isotopic composition of anthropogenic samples showing A) the entire measured range and B) the smaller range in which all non-laboratory standards fall.

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 more appropriate than the smaller errors calculated from internal reproducibility. A standard deviation of 0.052‰ is equivalent to a standard error of 0.030‰ (2σ) for triplicate analysis. Several samples were run in different analytical sessions months apart, these replicate analyses give the same $\delta^{66}\text{Zn}$ values within the analytical error.

2.3.2 Zn isotopes in anthropogenic samples

Zn isotope ratios were measured for twenty-two anthropogenic Zn samples (Figure 2). The isotopic compositions of the laboratory standards ranged from $\delta^{66}\text{Zn}_{\text{JMC}} = -9.15\text{‰}$ to $+0.17\text{‰}$. The AccuTrace standard has the lightest Zn isotope ratio reported to date. NIST-SRM 682 and two of the

Sample name	Sample-Standard Bracketing (SSB) corrected data			Sample-Standard Bracketing/ Cu Empirical External Normalization (EEN) corrected data		
	$\delta^{66}\text{Zn}_{\text{NIST-SRM 682}}$	$\delta^{66}\text{Zn}_{\text{JMC}}$	s.d. (2 σ)	$\delta^{66}\text{Zn}_{\text{NIST-SRM 682}}$	$\delta^{66}\text{Zn}_{\text{JMC}}$	s.d. (2 σ)
NIST SRM-682				0.00	-2.45	
AccuTrace Std				-6.70	-9.15	
Metal (10 mesh)	2.61	0.16	0.03	2.62	0.17	0.00
Metal (30 mesh)	2.53	0.08	0.03	2.54	0.09	0.03
Acetate #1	2.61	0.16	0.24	2.46	0.01	0.04
Acetate #2	2.61	0.16	0.10	2.53	0.08	0.05
Acetate #3	2.51	0.06	0.06	2.39	-0.06	0.04
Std Dust	2.41	-0.04	0.09	2.60	0.15	0.02
Fine Dust	2.46	0.01	0.02	2.64	0.19	0.04
Low Pb dust	2.48	0.03	0.08	2.54	0.09	0.03
CEZ shot	2.66	0.21	0.02	2.67	0.22	0.03
1983 Penny	2.51	0.06	0.07	2.60	0.15	0.02
1983 Penny #2	2.56	0.11	0.03	2.59	0.14	0.04
1985 Penny	2.54	0.09	0.07	2.65	0.20	0.04
1985 Penny #2	2.56	0.11	0.03	2.63	0.18	0.03
1991 penny	2.49	0.04	0.11	2.67	0.22	0.06
1991 Penny #2	2.59	0.14	0.03	2.64	0.19	0.05
1999 Penny	2.55	0.10	0.06	2.62	0.17	0.01
2000 Penny	2.69	0.24	0.07	2.76	0.31	0.05
2000 Penny #2	2.69	0.24	0.02	2.73	0.28	0.02
2002 Penny	2.61	0.16	0.06	2.65	0.20	0.05
Benadryl	2.54	0.09	0.01	2.56	0.11	0.02
Centrum	2.53	0.08	0.05	2.54	0.09	0.02
Dr Zn	2.63	0.18	0.03	2.65	0.20	0.02
Nature's Bounty	2.59	0.14	0.24	2.55	0.10	0.03
ColdEeze	2.61	0.16	0.07	2.72	0.27	0.04

Table 2.1. Zn isotopic composition of anthropogenic samples compared to NIST SRM-682 and Lyon-JMC Zn. Standard deviations are reported for triplicate analysis of individual samples.

Zn acetate samples (#1 and #3) were lighter than any of the non-laboratory Zn samples measured. The $\delta^{66}\text{Zn}$ of Zn dust ranged from +0.09‰ to +0.22‰, $\delta^{66}\text{Zn}$ for pennies ranged from 0.14‰ to 0.31‰, and the health and medical products $\delta^{66}\text{Zn}$ ranged from 0.09‰ to 0.27‰.

All common types of anthropogenic Zn (excluding laboratory standards) fell within a small range of isotope compositions. The total range in $\delta^{66}\text{Zn}$ that we measured for common Zn is +0.09‰ to +0.28‰, more than an order of magnitude smaller than the range seen in hydrothermal samples discussed in Section 1. Interestingly, the average isotopic composition of our “common” Zn is $\delta^{66}\text{Zn} = +0.18\text{‰}$, quite similar to the +0.15‰ average isotope composition of samples measured in two Zn ore fields (Mason et al., 2005; Wilkinson et al., 2005). Based on this, we suggest that the $\delta^{66}\text{Zn}$ variability we see in different anthropogenic samples represents isotopic differences between ores, modified by homogenization during processing. We do not find evidence of a large isotope effect associated with the purification of Zn ore into metal.

2.4 Conclusions

When studying Zn isotopes in the environment (for example, in seawater (Bermin et al., 2006), marine materials (Maréchal et al., 2000), or plants (Weiss et al., 2005), there may be both natural and anthropogenic sources of Zn. We believe that the samples analyzed here are broadly representative of both the average isotopic composition and the variability that will be found in common forms of anthropogenic Zn.

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