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REVIEW

Variation in the isotopic composition of zinc in the natural environment and the use of zinc isotopes in biogeosciences: a review

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Abstract Zinc (Zn) is a trace element that is, as a building block in various enzymes, of vital importance for all living organisms. Zn concentrations are widely determined in dietary, biological and environmental studies. Recent papers report on the first efforts to use stable Zn isotopes in environmental studies, and initial results point to significant Zn isotope fractionation during various biological and chemical processes, and thus highlight their potential as valuable biogeochemical tracers. In this article, we discuss the state-of-the-art analytical methods for isotopic analysis of Zn and the procedures used to obtain accurate Zn isotope ratio results. We then review recent applications of Zn isotope measurements in environmental and life sciences, emphasizing the mechanisms and causes responsible for observed natural variation in the isotopic composition of Zn. We first discuss the Zn isotope variability in extraterrestrial and geological samples. We then focus on biological processes inducing Zn isotope fractionation in plants, animals and humans, and we assess the potential of Zn isotope ratio determination for elucidating sources of atmospheric particles and contamination. Finally, we discuss possible impediments and limitations of the application of Zn isotopes in (geo-) environmental studies and provide an outlook regarding future directions of Zn isotope research.

Keywords Zn isotopes · Isotopic variation · Biogeosciences · Source tracer · Fractionation mechanisms

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Introduction

Zinc (atomic number 30) belongs to the transition metals, even though it has a full *d* shell, with an average concentration in the upper continental crust of 71 μg/g [1]. In the natural environment, it exists in the +2 oxidation state, and its primary sources in the geosphere are the two ore minerals sphalerite (ZnS) and smithsonite ($ZnCO_3$). As a trace nutrient, Zn plays an important role in various biological processes and it is vital for most living organisms. It is an important building block in all six enzyme classes and most of the regulatory proteins [2]. Moreover, Zn is the second most abundant transition metal in seawater, with concentrations up to 15 nmol/l in the deep ocean, but subnanomolar concentrations in surface waters, an observation

that points to the biological utilization of this element during phytoplankton biosynthesis and the fact that it has the potential to modulate primary productivity as a limiting trace nutrient. Zn concentrations span a huge range from a few picograms per gram to some tens of micrograms per gram in the cytoplasm of most cells [3] and it is, after Fe, the most important transition metal in humans.

Zn has five stable isotopes, ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, and ^{70}Zn, with average natural abundances of 48.63, 27.90, 4.10, 18.75, and 0.62%, respectively [4], and an average relative atomic mass of 65.37777(22) [5], yet the exact value of the latter is a matter of debate [6, 7]. The exact determination of the atomic mass of Zn is important for the assessment of the absolute isotopic composition of Zn in various materials, yet it is essentially irrelevant when the Zn isotope composition is expressed relative to a standard reference material, as is the case for most of studies involving the analysis of Zn isotopes. The first attempts to measure variations in the isotopic composition of Zn were done using thermal ionization mass spectrometry (TIMS) [6], but the analytical precision of TIMS was not better than 1–2‰ amu^{-1}, significantly greater than the natural variation itself (see the following sections). With the advent of multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS) in the middle of the 1990s, the precision of Zn isotope ratio measurements improved by more than an order of magnitude, reaching levels lower than 0.05‰ per mass unit [8]. This opened a new and exciting opportunity for studying the biogeochemical cycling of Zn by detecting minor changes in its isotopic composition in nature, which then allowed the chemical or biogeochemical processes responsible for these variations to be elucidated.

The goal of this paper is to provide an up-to-date overview of recent Zn isotope research, and, thus, of a relatively novel isotope system in geochemistry. We review the state-of-the art sample preparation procedures and analytical techniques required to reach the precision and accuracy that are imperative for the detection of the relatively subtle natural variations in Zn isotope ratios. We then discuss the use of natural abundance Zn isotope measurements with regard to their applicability to geological and biological samples, and their potential use as source indicators and biogeochemical tracers.

Materials and methods

Notation, standards, and reference materials

Because variations in the isotopic composition of environmental elements in nature are usually very small, isotope ratios are expressed as the relative deviation with respect to a standard reference, expressed in either parts per 1000 (δ) or parts per 10,000 (ε). For Zn, δ is the preferred notation, with normalization to the most common Zn isotope, ^{64}Zn:

$$\delta^{x}\mathrm{Zn}(\%) = \left(\frac{\left[{}^{x}\mathrm{Zn}/{}^{64}\mathrm{Zn\ sample}\right] - \left[{}^{x}\mathrm{Zn}/{}^{64}\mathrm{Zn\ reference}\right]}{\left[{}^{x}\mathrm{Zn}/{}^{64}\mathrm{Zn\ reference}\right]}\right) \times 1000,$$

where x corresponds to the masses 66, 67, 68, or 70.

Owing to the high relative abundances of ^{64}Zn and ^{66}Zn, their analysis warrants the highest possible precision during isotope ratio determination, typically close to 0.10‰. Because of the very low abundance of the ^{70}Zn isotope, its natural abundance is essentially not measurable with today's sensitivity of instruments; however, applications with ^{70}Zn spikes are common.

To date, an internationally certified Zn isotope standard reference material does not exist. Until now, studies that involve the isotopic analysis of Zn have invoked their own reference material to calibrate measurements, making interlaboratory comparisons difficult. However, many of these studies used a material from the Lyon-CNRS laboratory, a Johnson Matthey (JMC) Zn standard solution, batch 3–0749L, denoted as Zn_{Lyon} below, which is also used as a reference hereafter. The distribution of an internationally accepted monoelemental isotopic standard solution, labeled IRMM-3702, by the Institute for Reference Materials and Measurements (IRMM) is planned for the near future. A standard solution should generally be preferred over solid metal to avoid heterogeneity problems, such as observed for other elements [9]. IRMM-3702 has already been analyzed for both its absolute [5] and its relative Zn isotope composition with respect to Zn_{Lyon} [10], yielding a reported δ^{66}Zn value of 0.32±0.16‰ (Zn_{Lyon}) (Table 1). However, clearly more analyses of the new IRMM material by independent laboratories are imperative for recalibration of the previously published Zn isotope data. A compilation of the standard solutions used thus far in the literature, as well as their normalized δ^{66}Zn value relative to the Zn_{Lyon} material, is provided in Table 1. Commonly used standard solutions span a relatively large range of δ^{66}Zn values between –8.5 and –9‰ for Accutrace solutions [10, 11] and Romil [12–14], and from –7.5 to –2.4‰ for the Specpure [13] and NIST SRM 682 [11, 15] solutions. The δ^{66}Zn values of other standard solutions range between –0.10 and +0.10‰ [13, 15].

Table 1 also contains a compilation of documented δ^{66}Zn data for other (reference) materials, ranging from rocks (e.g., basalt) to human blood, and including different biological materials (e.g., plankton, bovine muscle, lichen). Unfortunately, most of these materials have been characterized by a single laboratory only, and additional investigations are needed, to assess potentially biasing matrix effects. The reference material with the best established

Table 1 Compilation of the isotopic composition of Zn in standard solutions and in reference materials normalized to the Johnson Matthey (*JMC*) Zn "Lyon solution"

Reference material	References	Type	N	δ^{66}Zn(‰)	2σ	δ^{68}Zn(‰)	2σ
IRMM-3702	[10]	Pure Zn solution	4	0.32	0.16	0.62	0.33
	[11]	Pure Zn solution	4	0.32	0.03	0.57	0.08
NIST SRM 682	[15]	Pure Zn solution	4	–2.40	0.02	–4.75	0.04
	[11]	Pure Zn solution	3	–2.45	0.05	–	–
NIST SRM 683	[15]	Pure Zn solution	4	0.07	0.01	0.10	0.01
JMC 110	[11]	Pure Zn solution	2	–0.05	0.02	–0.17	0.05
Nilaco	[15]	Pure Zn solution	4	0.13	0.02	0.22	0.05
Cica-Merck	[15]	Pure Zn solution for atomic absorption	4	0.07	0.03	0.15	0.05
Romil	[13]	Pure Zn solution	14	–8.96	0.07	–17.2	–
	[12]	Pure Zn solution	21	–9.06	0.08	–	–
	[13]	Pure Zn solution	–	–8.98	0.07	–	–
IMP	[13]	Pure Zn solution	10	0.09	0.07	–	–
Specpure	[13]	Pure Zn solution	–	–7.15	0.01	–	–
Accutrace	[10]	Pure Zn solution	8	–8.66	0.12	–17.03	0.21
	[11]	Pure Zn solution	–	–9.17	0.04	–18.33	0.02
BCR-1	[23]	Basalt	8	0.26	0.05	–	–
	[16]	Basalt	12	0.20	0.09	–	–
	[12]	Basalt	8	0.29	0.12	0.63	0.24
	[10]	Basalt	2	0.32	0.13	0.81	0.22
BEN	[10]	Basalt	1	0.58	0.13	1.01	0.21
BCR-027	[12]	Blende ore	8	0.33	0.07	0.67	0.13
BCR-030	[12]	Calcined calamine ore	8	–0.06	0.09	–0.11	0.3
Nod-P-1	[12]	Manganese nodule	9	0.78	0.09	1.49	0.14
SU-1	[12]	CU-Co ore	6	0.13	0.17	0.30	0.30
BCR 176	This work	Fly ash	1	0.01	0.11	–0.01	0.19
BCR-CRM 482	[23]	Lichen	8	0.14	0.03	–	–
	[10]	Lichen	3	0.07	0.10	0.09	0.18
BCR-CRM 281	[14]	Plant	–	0.81	0.1	–	–
SRM 8414	[65]	Bovine muscle	–	0.56	0.031	–	–
SRM 1577a	[65]	Bovine liver	–	0.04	0.016	–	–
Lot 404108	[22, 65]	Whole blood	–	0.30	0.06	0.63	0.07
Lot MR9067	[22, 65]	Whole blood	–	0.34	0.04	0.66	0.07
Lot OK0336	[22, 65]	Whole blood	–	0.31	0.06	0.62	0.07
GBW 07601	[65]	Human Hair	–	0.07	0.027	–	–
CRM TORT-2	[41]	Lobster liver	–	0.51	–	–	–
CRM 414	[41]	Plankton	–	0.42	–	–	–
CRM 278	[8]	Mussel tissue	–	0.82	–	–	–

N is the number of measurements for the standard solutions and the number of aliquots for the reference materials

δ^{66}Zn so far is the basalt BCR-1, with a reported mean δ^{66}Zn value of 0.25±0.09‰ (2σ) [16] (Table 1). Unfortunately, BCR-1 is no longer available and will be replaced by BCR-2, for which the Zn isotope composition is not yet determined. Given the increasing number of studies involving the measurements of Zn isotope ratios in environmental samples and organic materials, it is fair to say that the scientific community is in dire need of well-constrained reference materials in general, and a plant standard material in particular. As for the isotope analysis of other elements by MC-ICP-MS, it is crucial that isotope ratio measurements are calibrated versus reference materials that have a matrix similar to that of the sample material.

Sample digestion and Zn isolation from the matrix

Two different methods are most commonly used for sample digestion: (1) hot plate acid digestion and (2) microwave-assisted acid digestion. Both methods require the use of concentrated acids. The type of acid mixture used depends on the matrix of the analyte. Choosing the appropriate digestion procedure with quantitative recovery is a prerequisite for reliable results. The most common digestion technique is the hot plate digestion, and a detailed compilation of the sample preparation procedures can be found elsewhere [17, 18]. Briefly, for geological samples, the material is first dissolved in a mixture of concentrated $HF–HNO_3–HClO_4$ in a sealed Teflon beaker, heated on a

hot plate at 120 °C for 24–36 h. The sample solution is then evaporated to dryness, the residue is redissolved in a mixture of concentrated HCl and few drops of concentrated H_2O_2, and then heated again for 24 h or until complete dissolution. Depending on the matrix, an additional digestion step using a mixture of HNO_3 and HCl may occasionally be necessary to ensure complete dissolution. For biological or environmental samples (blood, plants, sediments, soils), microwave-assisted digestion with a mixture of HNO_3 and H_2O_2 or $HClO_4$ and/or HF is most frequently used.

Once digested, Zn has to be isolated from the matrix prior to isotope ratio determination; therefore, it is crucial to remove all components that can potentially result in spectral interferences during mass-spectrometric analysis and/or significant matrix effects. Various chromatographic separation techniques have been developed [19, 20], but the most commonly used protocol involves Zn isolation by ion-exchange chromatography, using strongly basic anion-exchange resins. This separation technique was originally used by Maréchal et al. [8] for the separation of Cu, Fe, and Zn from the sample matrix and has since then been adapted and modified in several other studies [10, 12, 14, 16, 21–23]. Here, after digestion, the sample is dissolved in 7 mol l^{-1} HCl and loaded onto 50 mm polyethylene Bio-Rad PolyPrep columns, containing 2.0 ml of the resin (AGMP-1 Bio-Rad, 100–200-mesh particle size, in chloride form). The matrix components are eluted with 5 ml of 7 mol l^{-1} HCl and dissolved Cu and Fe can be removed from the column with 10 ml of 0.5 mol l^{-1} HCl in the same fraction, prior to the elution of Zn using 10 ml of 0.5 mol l^{-1} HNO_3. Cadmium is eluted simultaneously with Zn; thus, if there are significant amounts of Cd in the sample with respect to Zn, it is advisable to use 0.1 mol l^{-1} HCl for elution of Zn instead, as suggested by Chapman et al. [12], to allow for the quantitative separation of Zn from Cd. As a result of the adapted and more time-efficient "column chemistry" (compared with the "original" version of the isolation procedure [8]) some Fe may also end up in Zn concentrate, inducing matrix effects during subsequent isotope analysis [16], and a second passage through the column may be necessary in order to further reduce the Fe/Zn ratio. Note that the processing of seawater samples or marine sediments requires preconcentration as an additional pretreatment, [21, 24]. The blank for the entire procedure (dissolution and separation) should not excess 50 ng and is in most cases between 20 and 30 ng of Zn. Such a blank can be considered massive compared with, e.g., Pb, but Zn concentrations in the environment are higher than Pb concentrations. Moreover, Zn is less dense, and as a consequence, it is more difficult to remove it from the acids during subboiling.

The quantitative recovery (more than 98 %) of Zn after chromatographic separation in the ion-exchange columns is of key importance because adsorption to and elution from the ion-exchange resin can induce significant mass-dependent isotopic fractionation for Zn [8], but also for other elements [25–27], with δ^{68}Zn biases of up to 1‰.

Zn isotope analysis by MC-ICP-MS

In order to obtain reliable results and high accuracy during Zn isotope analysis, raw measurements need to be corrected for mass discrimination during MC-ICP-MS measurements (Fig. 1), as well as for the potential occurrence of spectral and non-spectral interferences. Different methods may be applied to correct for mass bias: (1) the standard sample bracketing technique, (2) external normalization, and (3) the double-spike technique. A large number of papers presented and discussed the numerous correction techniques applied to Zn isotope analyses in more detail [8, 13, 16, 24, 28–32], and an in-depth discussion on spectral interferences potentially affecting Zn isotope ratio measurements has been presented by Mason et al. [30]. Here, only the most common techniques regarding corrections for mass bias and spectral interferences are reviewed. ^{64}Zn, ^{66}Zn, ^{67}Zn, and ^{68}Zn isotopes are simultaneously measured, along with ^{63}Cu, ^{65}Cu, and ^{62}Ni. ^{62}Ni is monitored in order to correct for the isobaric interferences of ^{64}Ni with ^{64}Zn measurements (mass-dependent discrimination for Ni isotopes is assumed). Similarly $^{130}Ba^{2+}$, $^{132}Ba^{2+}$, $^{134}Ba^{2+}$, and $^{136}Ba^{2+}$ (with mass-to-charge ratios ranging from 65 to 68) can cause isobaric interferences with ^{65}Cu, ^{66}Zn, ^{67}Zn, and ^{68}Zn, respectively, and $^{135}Ba^{2+}$ and $^{138}Ba^{2+}$ need to be determined in order to calculate the contribution of these interfering isotopes (Fig. 2). After duplicate element separation in the ion-exchange column, isobaric interference from other metals is most often negligible, or is reduced to such an extent that the necessary corrections are unproblematic.

To correct for mass discrimination during isotopic analysis of Zn via MC-ICP-MS, external normalization

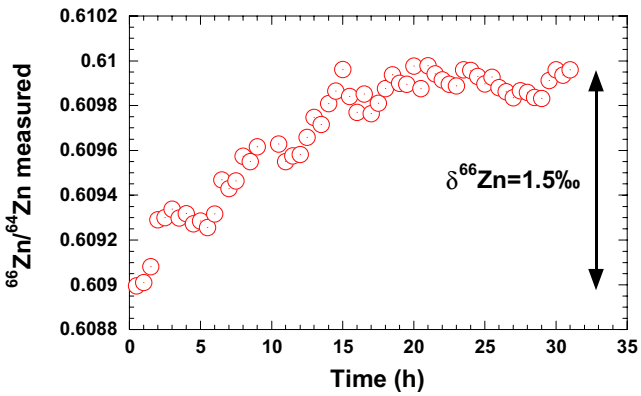

Fig. 1 Mass bias evolution of measured ^{66}Zn/^{64}Zn ratios with time. The observed variation in δ^{66}Zn is up to 1.5‰, and analysis run times of several hours are needed to reach a stable mass bias. This figure demonstrates the necessity and importance of adequate mass bias correction

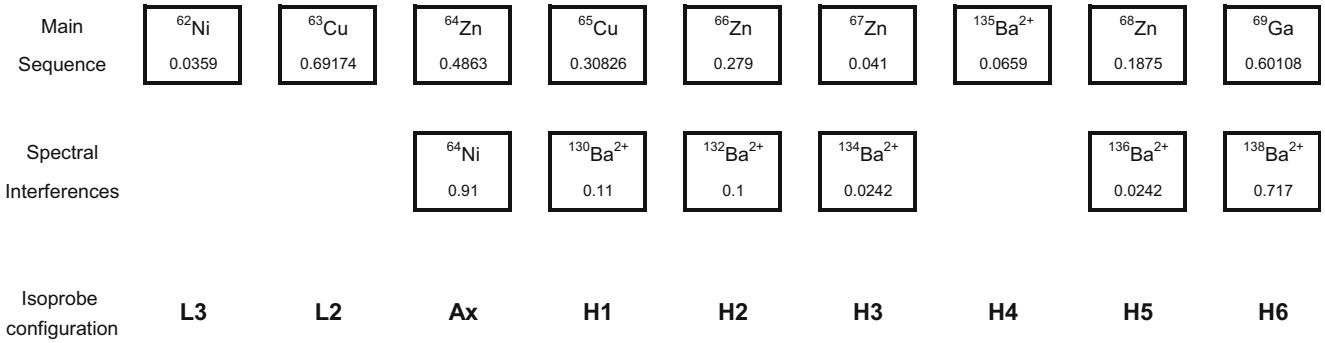

Fig. 2 Zn data acquisition scheme for the Isoprobe multicollector inductively coupled plasma mass spectrometry instrument. The configuration with nine faraday collectors enables the measurement of the four Zn isotopes (masses 64, 66, 67, and 68) the two Cu isotopes (masses 63, 65) which are needed for mass bias correction, as well as Ni and doubly charged Ba ions at mass-to-charge ratios of 62, 68.5, and 69 (together with Ga), respectively. The monitoring of the latter is necessary to correct for potential spectral overlap of the Zn analyte signal with Ni and Ba^{2+} signals for mass-to-charge ratios of 64, 65, 66, 67, and 68, respectively. The relative abundance of each isotope is also indicated

using Cu NIST SRM 976 as an external element, combined with the standard bracketing technique (previously called modified SSB [13]) is commonly applied. This combined approach seems to provide the best results with regard to long-term precision and accuracy (less than 0.05‰ amu^{-1}); yet, even measurement results corrected using either the modified SSB or the external normalization alone produce satisfying results, with generally good agreement between the two techniques [14] in particular when the mass bias is stable. The degree of mass discrimination can be quantified using the mass discrimination factor β, the detailed calculation of which can be found elsewhere [29]. The slope of a linear regression line in a plot of the mass discrimination correction factor β_{Cu} for Cu versus β_{Zn}, the mass discrimination correction factor for Zn (based on analysis of standard solutions where Zn was mixed with Cu SRM 976), may display significant day-to-day variability and is not always 1:1. Thus, for each analytical session, it is crucial to assess the respective β_{Cu}/β_{Zn} relationship in order to ensure the accurate mass bias correction of raw data (Fig. 3) (based on the certified value for the $^{65}Cu/^{63}Cu$ ratio of 0.4456±0.0021 [33] and a value of 0.5737 for $^{66}Zn/^{64}Zn$ [4, 6]), as well as the measured $^{65}Cu/^{63}Cu$ ratios in the standard and in the samples (both Cu-spiked)), and in order to yield reliable $\delta^{66}Zn$ values. In most cases, this correction strategy is to be preferred over the simple sample standard bracketing technique, because Cu and Zn are affected by matrix effects in a very similar way, thus decreasing the potential influence of the latter. Zn isotope ratios have been successfully measured using various brands of MC-ICP-MS instrumentation, the Axiom (VG Instruments), the Plasma 54 (VG Instruments), the Nu Plasma (Nu Instruments), the Neptune (ThermoFinnigan) and the Isoprobe (Micromass), mainly in soft extraction mode, with comparable precision and similarly reliable results [10, 13, 23]. The typical sensitivity for Zn and Cu isotope analyses are within the range of 5–10 V μg^{-1} g^{-1} and a target Zn/Cu ratio of approximately 1 (reference and samples) is used in most cases. The Zn isotope composition may be determined using either wet or dry plasma conditions.

Origin of natural Zn isotope variations

Variations in the isotopic composition of Zn can find their origin in both physical processes and (bio)chemical reactions involving Zn. Zn isotope fractionation may be of either kinetic origin or due to isotope equilibrium effects. An in-depth review of fractionation mechanisms for various elements, which can also be applied to Zn has been recently presented by Johnson et al. [34] and the potential fractionating processes for Zn and the degree of Zn isotope fractionation are schematized in Fig. 4. The main processes affecting the Zn isotope composition are evaporation–

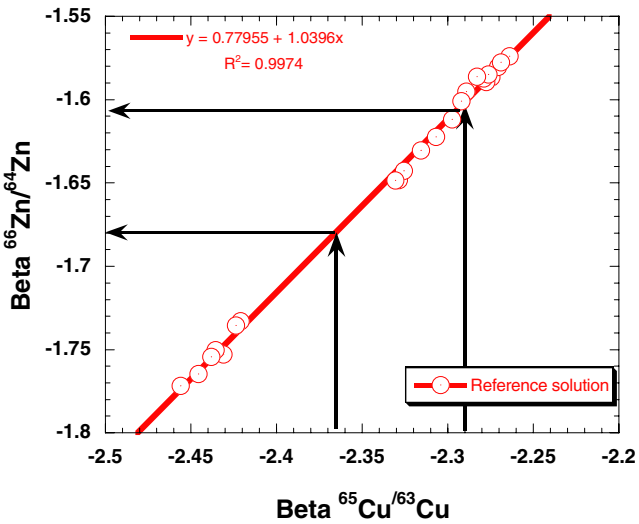

Fig. 3 The external normalization technique for Zn isotopes. Cu is added to standards and samples. A regression line is calculated based on the results on reference materials. β_{Cu} for analyzed samples is then used to derive β_{Zn} needed for the final $\delta^{66}Zn$ correction

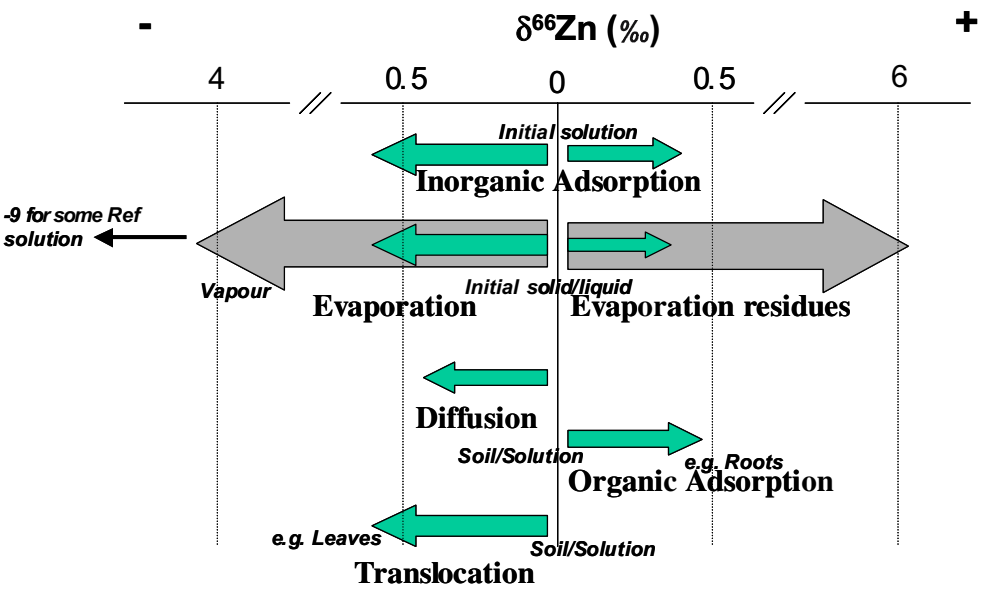

Fig. 4 The principal processes inducing Zn isotope fractionation. The length of the arrows indicates the range of observed δ^{66}Zn values as an approximation of the degree of Zn isotope fractionation. In the case of evaporation, the *big arrows* refer to extraterrestrial materials, while the *small arrows* refer to ore-related anthropogenic processes. Note that the standard reference solution with extreme isotopic composition possibly reflecting evaporation is excluded from this figure

condensation processes governed by Rayleigh dynamics, organic and inorganic adsorption, diffusion, and translocation. A general review concerning these isotope fractionation mechanisms (for Fe) can be found in Dauphas and Rouxel [35]. In all cases, the partitioning of the isotopes during biogeochemical cycling is mass-dependent, that is, directly proportional to mass differences between the respective isotopes, with the following relationships: $\delta^{66}Zn/^{64}Zn \approx 2/3\times\delta^{67}Zn/^{64}Zn \approx 1/2\times\delta^{68}Zn/^{64}Zn \approx 1/4\times\delta^{70}Zn/^{64}Zn \approx \delta^{68}Zn/^{66}Zn$. A review compiling Zn isotope values for cosmochemical and geological materials has recently been provided by Albarède [28] and another compilation (in a different context) has been provided by Cloquet et al. [10]. In the sections that follow, we provide an updated compilation of reported Zn isotope values in nature, with particular emphasis on environmental samples and biomaterials.

Variability of Zn isotope ratios in geological and cosmochemical materials

The largest variations in δ^{66}Zn thus far observed have been in extraterrestrial materials, i.e., in meteorites [6, 36] and in lunar materials [37]. δ^{66}Zn values range from 6 to –4‰, and the prime explanation for the large spectrum of Zn isotope ratios observed is Zn isotope fractionation during evaporation–condensation processes, with the vapor phase becoming depleted in the heavier isotopes with ongoing reaction. This effect has been known for Zn since 1972 [6] and is also known for other elements (e.g., Cd [38]). As will be discussed further later, such physically mediated fractionation may also apply to Zn cycling reactions involving anthropogenic activities (e.g., smelting), providing the basis for the use of Zn isotopes as a tracer of Zn contaminant sources (see "The use of the isotopic composition of Zn in environmental studies"). It has also been shown that the δ^{66}Zn values for lunar basalts [37] are in the same range as those for terrestrial basalts [8, 10, 16, 23, 39–41], suggesting that lunar Zn is not significantly fractionated relative to Zn on Earth. However, all reports on lunar basalt δ^{66}Zn were derived from only one set of sample material, and, thus, it is not yet possible to conclusively discard the possibility of lunar basalts being fractionated relative to those on Earth.

In terrestrial geological materials, δ^{66}Zn values are closely clustered around 0.5‰, ranging from –0.4‰ in ore samples from the Alexandrinka deposit [42] to 1.4‰ in marine carbonate rocks [21]. Such a small variability in the isotopic composition of Zn is, most likely, partially due to the fact that there is only one oxidation state. But more importantly, it probably reflects the low capacity of igneous processes to fractionate Zn isotopes. Indeed, except for ore minerals and ore-bearing granites from Orlovka-Spokoinoe [43], igneous rocks analyzed so far display surprisingly invariant δ^{66}Zn values, with δ^{66}Zn=0.2–0.5‰ for basalts [8, 10, 12, 16, 23, 39, 41] and δ^{66}Zn=0.4–0.6‰ for more acidic rocks, like granodiorites, granites [23], and andesites, [19] which is quite close to the range reported so far for Fe isotopes (see [35] for a compilation). Reported δ^{66}Zn values for carbonate rocks and loess [44], clay minerals, sediments from the Pacific and Atlantic oceans, shales, eolian dust, etc. [41] also fall in the same range, as does the δ^{66}Zn of water from the English Channel [24]. There is some evidence that mineral phases having different Zn isotope compositions may be separated during physical weathering, leading to different Zn isotope signatures in the alteration products [45], in direct analogy to the Fe isotope system [46]. However, more or less invariant δ^{66}Zn values

found for terrestrial sediment particles in marine cores [19] argue against such physical weathering fractionation mechanisms for Zn. It is fair to say, that, given the limited amount of data available, it is to date not yet possible to draw clear conclusions regarding Zn isotope effects due to physical weathering. Similarly, chemical alteration of the rocks seems to result, if at all, in only a negligibly small isotope fractionation towards heavier δ^{66}Zn values [23]. As a consequence, a well-constrained mean δ^{66}Zn value of 0.3‰ (integrating terrestrial igneous and sedimentary rocks, dust, loess, etc.) should reflect the Zn isotope composition of terrestrial Zn supplied to the ocean. While published values of δ^{66}Zn for Zn dissolved in northeast Pacific ocean water, which are not significantly different from 0.3‰, support this assumption [47], more variable (higher *and* lower) values have been reported from other regions of the Pacific [24, 47, 48]. Moreover, more elevated and relatively variable δ^{66}Zn values have been observed in marine sediments [21] and in ferromanganese nodules, suggesting Zn isotope fractionation during the chemical precipitation of marine sedimentary particles and nodules, during adsorptive processes, and/or biological transformations. Indeed, it has been suggested that, analogous to Fe isotope fractionation in hydrothermal systems [49], kinetic Zn isotope fractionation (depending on the ambient temperature [42], or not [50]) can occur, following Rayleigh distillation kinetics, during mineral precipitation along fluid pathways. It has also been demonstrated that Zn adsorption onto oxides and hydroxides is associated with both positive and negative isotope effects, depending on mineral species and pH [51]. Laboratory experiments involving marine diatom species [52] suggest that complexation and sorption of Zn onto diatom frustules is generally accompanied by an enrichment in the heavier Zn isotopes in the solid phase with respect to the growth medium. While isotope fractionation during adsorption and desorption of Zn could result in the alteration of the bulk sedimentary δ^{66}Zn during sedimentary diagenesis, the observed shifts in the Zn isotope composition of marine sediments are much greater than can be solely explained by these sorption processes [21]. It is more plausible that changes in the Zn isotope fractionation during biological processes, i.e., the uptake of Zn during biosynthesis of marine algal material, contributes most to the observed δ^{66}Zn variations in marine sediment cores (see later).

Variations in the Zn isotope composition of biological materials

The total range of reported values of δ^{66}Zn for biological materials (excluding lichens and peat bogs, which will be discussed separately in the next section) is quite significant, with the lowest δ^{66}Zn values found for palm leaves (–0.9‰) [23], and the highest δ^{66}Zn values of approximately 0.8‰ being found for mussel tissue (CRM 278) [8] and rye grass (BCR CRM 281) [14] (Table 1).

Zn in marine and continental aquatic systems

As mentioned already, biological processes have been invoked in order to explain the variation in the isotopic composition of Zn observed in marine carbonaceous sediments. It has been suggested that during uptake by marine algae, the lighter Zn isotopes are preferentially consumed, resulting in a relative enrichment of δ^{66}Zn in the residual seawater Zn pool and ultimately in that of shell carbonate, which is formed in isotopic equilibrium with ambient seawater [21]. In the same line, the remineralization of marine particulates and the associated release of adsorbed or incorporated Zn may cause a decrease in the seawater δ^{66}Zn. For example, Zn isotope depth profiles from the northeast Pacific Ocean revealed a depletion of water column δ^{66}Zn that has been attributed to the liberation of isotopically light cellular Zn [24].

The preferential uptake of the lighter isotopes of Zn has recently been demonstrated experimentally for diatoms [47, 48, 53, 54], with Zn isotope effects up to –0.8‰ (δ^{66}Zn), and for plankton in the natural environment [48, 53]. In the latter case, it was demonstrated that the δ^{66}Zn value for marine phytoplankton material can display significant spatial variability in the Pacific and Atlantic oceans, most likely as a function of the degree of Zn utilization and the associated Zn isotope fractionation [48]. A similar explanation may apply to the seasonal variations observed for δ^{66}Zn of sinking particulate material (mostly algal material) from sediment traps deployed in a Swiss lake. The δ^{66}Zn values of particulate matter from sediment traps show distinct variations from 0.15 to 0.75‰ between May and July, with the highest values observed at the end of the spring productive period. We did not have access to the water samples and it cannot be completely ruled out that the observed δ^{66}Zn variations are partially due to changes in the amount and quality of external inputs of Zn into the lake (see later). Yet, initial changes in δ^{66}Zn towards lower values during early spring may most likely be attributed onto preferential adsorption of ^{64}Zn to sinking particles at moderate particle flux. The subsequent positive trend starting by the end of May is consistent with the preferential uptake of the lighter Zn isotopes during photosynthesis and incorporation of Zn into the algal material. High primary productivity during late spring algal blooms, resulting in high fluxes of phytoplankton particles out of the photic zone (as indicated by the organic C and N fluxes (Fig. 5) [55, 56]), most likely results in the depletion of Zn in the surface waters and the concomitant enrichment of the heavier Zn isotopes in the residual dissolved Zn pool

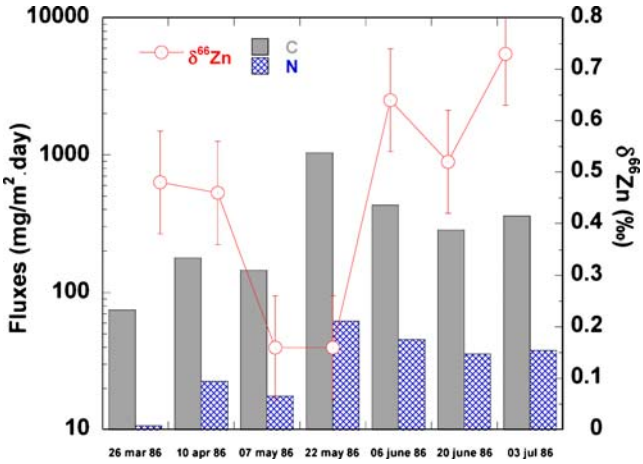

Fig. 5 Zn isotope composition of sediment trap material and organic C and N fluxes in a Swiss lake. The significant increase in δ^{66}Zn during the high productivity (i.e., high-flux) period at the end of May is consistent with Rayleigh distillation dynamics in association with the preferential uptake of the lighter Zn isotopes during photosynthesis and incorporation of Zn into the algal material (see text)

(according to Rayleigh distillation dynamics), and, in turn, in the algae contributing to the sedimenting particles (from 0.15 to 0.75‰) (Fig. 4).

Zn isotope fractionation and bioaccumulation in plants

The strongest variation in the Zn isotope composition of terrestrial organic materials recorded so far has been found in land plants and trees [23, 57], with differences of up to 1.6‰ between the shoot and the leaf δ^{66}Zn of a palm tree [23], the leaves being depleted in heavy Zn. The pioneering work by Weiss et al. [57] provided the first conclusive evidence that plant uptake represents an important source of isotopic variation in the biogeochemical cycling of Zn. It also permitted insight into the fundamental mechanisms of Zn fractionation during the incorporation and translocation of Zn in vascular plants. Three different species of higher plants (tomato, lettuce, rice) were chosen for experiments in hydroponic cultures with different nutrients solutions, containing various mixtures of metal-binding ligands. In general, independent of the experimental setup and species investigated, roots and shoots showed the same δ^{66}Zn dynamics during the incubation period, with a similar extent of heavy Zn isotope enrichment in roots relative to the nutrient solution (0.08–0.2‰), and a plant-specific internal fractionation of Zn isotopes during membrane transport and cell uptake in the shoots, leading to depletion of the heavier isotopes from root to shoot of –0.13 to –0.26‰. The Zn isotope shift between solutions and roots has been attributed to the preferential adsorption of heavier isotopes at the root surface, analogous to observations made during experiments with diatom frustules [52]. The degree of Zn isotope discrimination during the root-to-shoot transfer was not only a function of the Zn speciation in solution, but was also dependent on the plant species, with the strongest depletion in the heavier isotopes observed for tomatoes and the weakest enrichment for rice. Similarly, Zn isotope fractionation in higher plants and its species-specific variability have been reported for herbaceous species and trees in the field [23]. For both plant families, a much more negative δ^{66}Zn value was found in leaves with respect to the roots; yet, the overall Zn isotope fractionation was significantly more pronounced for trees. These two studies suggest a correlation between the height of the plants and the degree of Zn fractionation during Zn uptake: The higher the plants (rice<lettuce<tomato and herbs<trees), the lower the ultimate δ^{66}Zn value with respect to substrate δ^{66}Zn. This correlation can possibly be explained by the variation in the plant-specific diffusive distances, controlling the Zn isotope partitioning during passive (apoplastic) transport within the plant. Viers et al. [23] reported that during the uptake of Zn by plants, Zn crosses the root cell plasma membrane and diffuses from the root to the shoots through the xylem, from where it is incorporated into the plant cells. The diffusive transport of Zn in the xylem solution and ultimately through the cell membranes (i.e., the transport from roots to the aerial parts of the plant) probably fractionates the Zn isotopes [58], and the degree of Zn fractionation is a function of the diffusive distance, which can be directly related to the height of the plant. While probably both the adsorption of Zn ions or ion complexes onto cell layers (the cell wall of roots or the plasma membranes) and the passive transport of Zn within the plant by diffusion act to modulate Zn isotope discrimination during plant uptake, it is very likely that the ultimate binding of Zn by enzymes within the plant cells (Zn serves as an important cofactor in a number of enzymes) is also associated with an isotope effect, as the heavier isotopes are generally complexed preferentially [46, 52, 59]. Analogous to other uptake systems (e.g., CO_2 fixation [60, 61], denitrification—[62]), it is reasonable to assume, however, that the expression of the enzyme-level Zn isotope fractionation (in higher and lower plants) depends on whether Zn uptake in the cell is complete (no Zn efflux) or not, which, in turn, may be a function of both the Zn availability and the transport distance to the active sites.

Zn isotope fractionation and bioaccumulation in animals

Since Zn isotope fractionation occurs in diatoms and various higher plants, we can assume that such isotope discrimination takes also place in other living organisms. Unfortunately, the literature regarding Zn isotope fractionation by animals or plants is currently still scarce and

information on the isotopic composition of Zn in animal tissues is most often limited to reference materials (Table 1). Nevertheless, a few studies exist that indicate that Zn isotope fractionation indeed occurs during animal metabolism and organ building. For example, Büchl et al. [63], reported δ^{66}Zn values around –0.4‰ in mouse brains and Maréchal et al. [8] reported δ^{66}Zn values of 0.8‰ in mussel tissue, a range that essentially spans the total reported terrestrial variability of Zn isotope compositions. Similarly, a huge discrepancy in δ^{66}Zn has been reported for various bovine standards (0.56‰ for the SRM 8414 bovine muscle and 0.04‰ for the SRM1577a bovine liver standards, respectively) (Table 1), suggesting Zn isotope partitioning and fractionation in higher animals, but, source effects cannot be ruled out. Along the same line, Maréchal et al. [8] noted that the δ^{66}Zn of lobster liver and mussel tissue is significantly different from the Zn isotope composition of ambient seawater and plankton. Existing Zn isotope data for human samples are essentially limited to blood and hair [8, 22, 64, 65]. These studies revealed that the Zn isotope composition of bulk blood shows little variation, with a range of reported values from 0.3 to 0.4‰. Moreover, significant Zn isotope differences have neither been observed between red blood cells (RBC) and bulk blood, nor between RBCs from male and female test persons, contrary to differences for Fe isotopes in human blood [66]. δ^{66}Zn values reported thus far for RBC range from 0.4 to 0.5‰, and they do not display systematic temporal variations, e.g., over one annual cycle [64]. The apparent invariance and homogeneity in δ^{66}Zn found for blood and blood components, as well as the possible link (or its absence) to changes in dietary conditions, should be motivation for further work. While the isotopic invariance of δ^{66}Zn values in blood (and other human organs) still has to be verified through more comprehensive studies with higher numbers of samples, it already suggests a certain uniformity (1) in the way humans use and metabolize Zn and (2) of the source of Zn in the daily diet. A "baseline δ^{66}Zn" for human blood can be of great value because it may allow the detection of Zn isotope anomalies that can potentially be related to specific diseases or gene mutations. In a pioneering study, Stenberg et al. [22] provided putative evidence that the mutation in the human HFE gene (hemachromatosis) induced a small, but systematic, shift of 0.1‰ in the δ^{66}Zn value of blood. Even though this effect is very subtle, it seems to be real, and thus should encourage further studies that test the usefulness of the isotopic composition of Zn as a diagnostic tool in health sciences in general, and to trace gene malfunctions in humans in particular. As has been shown for various animals (see earlier), some evidence exists that suggests that partitioning of Zn isotopes in the human body occurs. Reported values for Zn isotope ratios in human hair indicate a consistent depletion in the heavier isotopes, with δ^{66}Zn values between 0.07 and –0.46‰ with respect to values for blood [65]. It is not certain, however, whether this observation is indeed the result of Zn isotope fractionation in the human body or whether it is due to external factors. δ^{66}Zn for human hair is clearly more variable than that for blood and RBCs, an observation that might be attributed to the variable use of shampoo, dyeing (even if relatively subtle δ^{66}Zn variation, 0.09–0.24‰, in some health products seems to argue against this hypothesis [11]), and/or to air pollution rather than to changes in the degree of Zn isotope discrimination during hair growth.

The use of the isotopic composition of Zn in environmental studies

Relatively new is the application of Zn isotope ratio measurements in environmental and contamination studies, in which the isotopic composition of Zn is used for the assessment of the contribution from various potential Zn sources (analogous to the use of Pb isotopes). Luck et al. [44] conducted the first systematic investigations into the variability of the isotopic composition of Zn in rainwater in urban and rural areas. In their study conducted in the south of France, the authors identified significant differences in the δ^{66}Zn of rainwater from rural areas (0 and 0.15‰) with respect to that for urban precipitation (–0.2 to –0.1‰), and explained the observed discrepancy by inferring spatial variations in Zn contamination due to anthropogenic activities rather than variations in natural Zn inputs (i.e., rocks, loess, eolian dust). The potential of Zn isotopes to trace Zn contamination and atmospheric metal deposition was further verified by a more recent study, in which the Zn isotope composition of ambient aerosol particles (or PM-10) and bus-air filter particles was determined in a city in northeastern France [10]. In general, the main Zn sources are assumed to be various industries (e.g., metal refinery, steel industry, coal power plants) automotive traffic, and urban waste incineration. The authors reported δ^{66}Zn values ranging from 0 to 0.3‰ for δ^{66}Zn in urban aerosols, with a mean value of 0.12‰. Such a signal seems contradictory to the lower δ^{66}Zn found for urban compared to rural precipitation [44], but may simply be explained by the spatial variability in the quality of atmospheric Zn deposition, for example, more or less contamination from fossil fuel combustion. Indistinguishable from the δ^{66}Zn of aerosol particles, Cloquet et al. [10] found that the Zn isotope composition of lichens collected in the same study area has a mean δ^{66}Zn of 0.1‰. However, for individual lichen samples that carried a clear gasoline fingerprint (as identified by Pb isotopes [67]) the δ^{66}Zn found was significantly lower [10], suggesting that Zn isotopes can

potentially be used to trace and reconstruct past automotive circulation activity. Similarly, the potential to use lichen δ^{66}Zn values as contaminant tracers in mining-industry-dominated areas has been demonstrated by Dolgopolova et al. [43]. Close to a mining and mineral processing plant in Russia, the authors found δ^{66}Zn values for lichens between 0.4 and 1.4‰. The δ^{66}Zn analysis of various local rocks and ores permitted the identification of mining and processing activities in the plant as the main contributor to the Zn deposition in the nearby environment, yet a straightforward interpretation of the δ^{66}Zn data was complicated by the fact that additional sources of Zn, such as soil dusts and long-range transport from other anthropogenic activities or atmospheric particles, may have masked the local mining-associated Zn isotope signatures. The impact of other anthropogenic activities besides fossil fuel combustion and ore mining are not that well documented. Analysis of the BCR 176 city waste incineration fly ash reference material (Table 1) resulted in δ^{66}Zn values close to 0‰, and measurements of urban waste incineration flue gases revealed an average δ^{66}Zn value of 0.13‰ [10]. These flue gases have been shown to have an integrated mean Pb isotope composition that is representative for the average composition of industrial Pb, and the same may hold true for Zn. Matielli et al. [68] recently reported a strong depletion in the heavier Zn isotopes in dust of a refinery in northern France (δ^{66}Zn as low as –0.63‰), and attributed the strong variability in δ^{66}Zn to evaporation–condensation processes within the refinery during ore refining. From the same refinery, a variation in the δ^{66}Zn is observed between dust (–0.13‰) and slag (0.02‰) sampled the same day (Fig. 6). Mattielli et al. [68] also showed that the δ^{66}Zn of atmospheric dry aerosols varied significantly as a function of the distance to the refinery. The closest samples, representing large Zn-rich particles derived from the remobilization of ore and slag, displayed a positive δ^{66}Zn between 0.02 and 0.19‰, while more distant and thus smaller particles had a δ^{66}Zn between –0.52 and –0.02‰, most likely representing chimney emission dust.

In our ongoing efforts to better constrain anthropogenic Zn isotope signatures, and in turn, to reconstruct Zn contamination in the past, investigations into the Zn isotope composition in environmental "archives" may be of great help. In this context, the source of Zn and pollution fluxes may be determined through the study of soils and sediments. Agriculture soil samples collected within 5 km around a Pb and Zn refinery in northern France contained several hundreds micrograms of Zn per gram of dry soil, decreasing with the distance to the refinery, and δ^{66}Zn values ranged from 0.05 to 0.56‰ (Fig. 6b). Zn and Cd concentrations in these soils are positively correlated (Fig. 6a), suggesting the mixing from common sources for the two metals. However, the Cd/Zn isotope ratio relation-

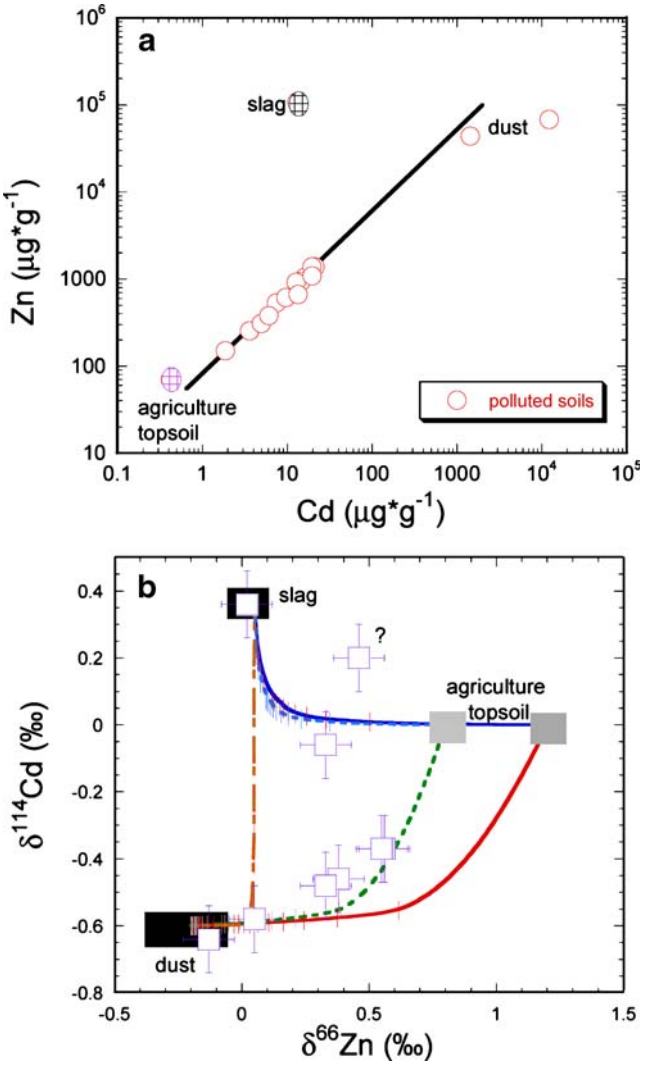

Fig. 6 **a** Zn and Cd concentrations in soils surrounding a Pb and Zn refinery in northern France. Slag and dust samples were obtained the same day within the refinery. The agriculture topsoil is an uncontaminated soil from the same area reported by Sterckeman [71]. **b** Zn and Cd isotope composition of soils, slag and dust (Cd data from [66]). Theoretical mixing curves were calculated according to the measured or estimated isotopic compositions and concentrations of Cd and Zn for the three end members: dust (measured: Cd concentration 6,000 mg g^{-1}, δ^{114}Cd=–0.6‰; Zn concentration 50,000 mg g^{-1} from [71], δ^{66}Zn=–0.2‰), slag (measured: Cd concentration 13 mg g^{-1}, δ^{114}Cd=0.36‰; Zn concentration 107,638 mg g^{-1} from [71], δ^{66}Zn=0.05‰), agriculture topsoil (measured: Cd concentration 0.5 mg g^{-1}; estimated: δ^{114}Cd=0‰; measured: Zn concentration 70 mg g^{-1} from [64], estimated: δ^{66}Zn=0.8 and 1.2‰). Estimation for the uncontaminated topsoil δ^{114}Cd was based on the fact that many natural geological samples have δ values very close to zero as reported by Cloquet et al. [25]. The δ^{66}Zn values for the uncontaminated topsoil were estimated from the composition of lichens and surface peat bog samples as reported in the literature [43, 69]. A δ^{66}Zn lower than 0.6‰ for the uncontaminated topsoil would exclude many soil samples from the proposed mixing

ship (Cd isotope data from [69]) (Fig. 6b) argue against a simple conservative mixing of Zn isotopes. Obviously, atmospheric Zn stored in soils may undergo significant isotope alteration as a result of fluid migration and diffusion in soil solutions or owing to bioaccumulation (see earlier). For example, the work of Weiss et al. [14] strongly suggests that the diffusion of dissolved Zn in ombrotrophic peat bogs alters its isotopic composition, with Zn species containing the heavier Zn isotopes diffusing slower than the lighter Zn isotopologues. They observed the highest δ^{66}Zn values (up to 1.7‰, higher than any local or background atmospheric Zn sources) at the bottom of the peat cores, where diffusion-related Zn isotope partitioning is expected to be most pronounced. Nonetheless, since the top core samples were most likely less affected by postdeposition alteration, Weiss et al. [14] concluded that here, the low δ^{66}Zn was representative of anthropogenic Zn sources from nearby smelting and mining activities.

Zn samples retrieved from a river sediment core sampled in southern France appear to be less affected by postdepositional isotopic alteration [70], and thus are more suitable to trace Zn contamination in the near past. Changes in anthropogenic activities in the surrounding environment during the last 60 years could plausibly be invoked to explain the large variations observed in δ^{66}Zn (between 0.33 and 1.4‰). A constant δ^{66}Zn value of approximately 1‰ measured in sediments deposited between 1952 and 1975 and the subsequent trend towards more ^{66}Zn-enriched sediments thereafter can most likely be attributed to the industrial exploitation of a local Zn ore.

These examples demonstrate the potential of Zn isotopes for source assessment in environmental samples. On several occasions, the δ^{66}Zn of industrial emissions seems to be variable enough to allow for the disentanglement of various end-member Zn sources. However, the existing studies also highlight the fact that atmospheric Zn can undergo significant isotope alteration during its transport and after deposition. That is, fractionation during both physical (e.g., diffusion) and biogeochemical (plant uptake in soils) postdepositional processes can significantly complicate the assessment of Zn emission sources.

Conclusions and future directions

In this review we compiled results of the first "wave" of investigations into the natural variation of Zn isotope composition in various geological and biological samples. Although we are still at the beginning of exploring all the possibilities of the Zn isotope system in geological, biological, environmental, and life sciences, it seems evident that, analogous to other isotope systems, Zn isotope measurements are indeed a powerful analytical tool to assess a variety of questions in various scientific fields, for example, enzyme-level biochemistry, (paleo-) oceanography, and contaminant source assessment. For the future, it will be imperative that the scientific community establishes internationally accepted, common standards to allow for interlaboratory comparison and reliable quality control of analyses (e.g., the establishment of the δ^{66}Zn value for the JMC Zn "Lyon standard" with respect to IRMM-3702 is needed for the renormalization of previous results). Reference materials for the analyses of biological materials are particularly desirable.

The most pronounced variations in δ^{66}Zn thus far reported seem to be controlled by evaporation–condensation processes, during which extraterrestrial materials are formed, as well as by specific ore-industry-related anthropogenic activities that produce slag, dust, fly-ash highly concentrated in Zn. While the impact of redox reactions on the distribution of Zn isotopes is probably negligible, adsorption and diffusion processes are likely to be associated with relatively strong Zn isotope fractionation. The single most important process responsible for Zn isotope variations on Earth is the preferential uptake of the lighter Zn isotopes during biosynthesis of plants. While we think we know that various physicochemical and biological processes induce Zn isotope fractionation and thus lead to relatively large variations in δ^{66}Zn in nature, we often neither understand the exact mechanism that leads to this observed fractionation nor do we know, with some exceptions, the degree of Zn isotope fractionation (i.e., the Zn isotope fractionation factors for specific reactions). Future work should not only aim at better constraining the Zn isotope composition of various compartments and materials on Earth and at assessing the sources of Zn in the atmosphere, but also should aim at gaining a mechanistic understanding of Zn isotope fractionation during Zn cycle reactions. For example, laboratory experiments are desirable, which aim at elucidating the controls on, and degree of, Zn isotope fractionation during phytoplankton consumption and particle–water interaction in the ocean. Knowledge of these isotope effects is a prerequisite for the use of Zn isotopes in marine sedimentary archives in order to reconstruct paleoenvironmental conditions. Highly promising are initial attempts to use Zn isotopes to study the Zn partitioning in different compartments of the human body. Yet, clearly, more work is needed in order to gain a more complete understanding of the Zn isotope fractionation in humans, and to further test and ultimately establish Zn isotopes as a diagnostic tool to identify protein or enzyme dysfunctions.

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