Earth and Planetary Science Letters 374 (2013) 164–172

Contents lists available at SciVerse ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

Iron, copper and zinc isotopic fractionation up mammal trophic chains

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ARTICLE INFO

Article history:
Received 16 June 2012
Received in revised form
17 May 2013
Accepted 23 May 2013
Editor: J. Lynch-Stieglitz
Available online 19 June 2013

Keywords:
non-traditional isotopes
isotopic fractionation
trophic chain
paleoecology
paleodiet

ABSTRACT

There is a growing body of evidence that some non-traditional elements exhibit stable isotope compositions that are distinct in botanical and animal products, providing potential new tracers for diet reconstructions. Here, we present data for iron (Fe), copper (Cu) and zinc (Zn) stable isotope compositions in plants and bones of herbivores and carnivores. The samples come from trophic chains located in the Western Cape area and in the Kruger National Park in South Africa. The Fe, Cu and Zn isotope systematics are similar in both parks. However, local Cu, and possibly Zn, isotopic values of soils influence that of plants and of higher trophic levels. Between plants and bones of herbivores, the Zn isotope compositions are ^{66}Zn-enriched by about 0.8‰ whereas no significant trophic enrichment is observed for Fe and Cu. Between bones of herbivores and bones of carnivores, the Fe isotope compositions are ^{56}Fe-depleted by about 0.6‰, the Cu isotope compositions are ^{65}Cu-enriched by about 1.0‰, and the Zn isotope compositions are slightly ^{66}Zn-depleted by about 0.2‰. The isotopic distributions of the metals in the body partly explain the observed trophic isotopic systematics. However, it is also necessary to invoke differential intestinal metal absorption between herbivores and carnivores to account for the observed results. Further studies are necessary to fully understand how the Fe, Cu and Zn isotope values are regulated within the ecosystem's trophic levels, but the data already suggests significant potential as new paleodietary and paleoecological proxies.

1. Introduction

Iron (Fe), copper (Cu) and zinc (Zn) are three essential elements for life. These are bound to a variety of ligands to form metalloenzymes and are present under different redox states (Fe and Cu), leading an organism to have heterogeneous isotopic composition in the body. The range of variations of δ^{56}Fe, δ^{65}Cu and δ^{66}Zn[1] values within an organism, being vegetal or animal, is of similar amplitude than those reported so far for most geological terrestrial materials (δ^{56}Fe: −2.7‰ to +1‰ Johnson et al., 2003; Zhu et al., 2000; δ^{65}Cu −3‰ to +2.5‰, Larson et al., 2003; Markl et al., 2006; δ^{66}Zn: −0.5‰ to +1.4‰, Pons et al., 2011). In plants, the metal isotope compositions vary between seeds, stem and leaves, all these organs being isotopically different than the growth media (Weiss et al., 2005; Guelke and von Blanckenburg, 2007; Moynier et al., 2009; Weinstein et al., 2011; Jouvin et al., 2012). The overall variability reported so far for plants ranges from 0‰ to −1.6‰ for δ^{56}Fe (Guelke and von Blanckenburg, 2007; von Blanckenburg et al., 2009), from −1‰ to +0.4‰ for δ^{65}Cu (Weinstein et al., 2011; Jouvin et al., 2012), and from −0.6‰ to +1.3‰ for δ^{66}Zn (Weiss et al., 2005; Moynier et al., 2009). In animals, metal isotope compositions vary among organs (Walczyk and von Blanckenburg, 2002; Balter et al., 2010; Albarède et al., 2011; Hotz et al., 2011; Jaouen et al., 2012). For iron, the whole body is ^{56}Fe-depleted relative to the diet due to a strong isotopic fractionation during Fe intestinal absorption (Walczyk and von Blanckenburg, 2002). In experimental pigs, the δ^{56}Fe values range from −0.4‰ in liver to −1.8‰ in blood for a dietary δ^{56}Fe value of 0‰ (Hotz et al., 2011). In humans, the δ^{56}Fe values can range from −3.5‰ in hair and muscle (Walczyk and von Blanckenburg, 2002) to +0.4‰ in bone (Jaouen et al., 2012). Concerning Cu, the δ^{65}Cu values range from −1.5‰ in liver to +1.5‰ in kidney of experimental sheep and mice for a diet δ^{65}Cu value of 0‰ (Balter and Zazzo, 2011). Human blood is characterized through its constituents, serum and erythrocytes, by a range of the Cu isotope compositions of about 1.6‰, the lowest δ^{65}Cu value of serum being −0.7‰ and the highest δ^{65}Cu value of erythrocytes being +0.9‰ (Albarède et al., 2011). Bodily variations of the δ^{66}Zn values range from −0.5‰ in liver to +0.5‰ in bone, muscle and serum, for a diet δ^{66}Zn value of +0.2‰ (Balter et al., 2010). The spread of the δ^{66}Zn value is about 2‰ in humans, liver being characterized by negative value down to −1‰

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[1] $\delta^{65}Cu=[(^{65}Cu/^{63}Cu)_{sample}/(^{65}Cu/^{63}Cu)_{standard}-1]\times 10^3$. All δ^{65}Cu values in the text are with respect to the NIST-SRM 976 standard. $\delta^{x}Fe=[(^{x}Fe/^{54}Fe)_{sample}/(^{x}Fe/^{54}Fe)_{standard}-1]\times 10^3$and $x=56$ or 57. All δ^{x}Fe values in the text are with respect to the IRMM 14 standard. $\delta^{x}Zn=[(^{x}Zn/^{64}Zn)_{sample}/(^{x}Zn^{64}Zn)_{standard}-1]\times 10^3$and $x=66$, 67 or 68. All δ^{x}Zn values in the text are with respect to the JMC 3-0749L standard.

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http://dx.doi.org/10.1016/j.epsl.2013.05.037

and bone by positive values up to +1‰ (Albarède et al., 2011; Jaouen et al., 2012).

The above preliminary data suggest that biological activity heterogeneously redistributes metal isotopes in the organism, leading the different organs to be isotopically fractionated. The two major potential factors of the isotopic fractionation of metals are thought to be the oxidation state and the nature of ligands. Briefly, for metals bearing various oxidation states (as for Fe and Cu), oxidized compounds should be isotopically heavier than their reduced equivalent (Bigeleisen and Goeppert-Mayer, 1947). Zinc exists as Zn^{2+} solely, and Zn isotopic fractionation is expected to occur only during Zn exchange between ligands of distinct bond energies.

The existence of widespread isotopic fractionations of Fe, Cu and Zn between diet and animal organs, suggests that the metal isotope compositions can be used as potential dietary tracers in natural contexts. This has been previously suggested by Walczyk and von Blanckenburg (2005) concerning the Fe isotope compositions. In the present study, we report the results of Fe, Cu and Zn stable isotope compositions for plants and bones of herbivores and carnivores coming from two trophic chains in South Africa, the Kruger National Park (KNP) and Western Cape (WC).

2. Material and method

The sampling consists of fresh bones of herbivores and carnivores coming from the Kruger National Park (KNP) and Western Cape (WC), South Africa (Fig. 1). Also included are samples of plants debris that were found stuck in the dentine grooves of the occlusal surface in teeth of herbivores. The samples were collected at the Ditsong National Museum of Natural History (Pretoria, South Africa). Bone aliquots were sampled in jaws. All the samples belonging to protected species by the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES) were exported to France and re-exported to South Africa according to the international agreements between the French and the South African governments.

Samples were dissolved in a 1:1 mixture of sub-boiled distilled concentrated HNO_3 and 30% H_2O_2 (analytical grade), evaporated to dryness and further redissolved in 1 mL of 7 N HCl+0.001% H_2O_2. The solution was processed for isotope analysis according to the technique of Maréchal et al. (1999), fully described in Maréchal and Albarède (2002). Using quartz column filled with the AG MP-1 anion-exchange resin (100–200 mesh, Bio-Rad), Cu was eluted with 20 mL of 7 N HCl+0.001% H_2O_2, Fe with 10 mL of 2 N HCl +0.001% H_2O_2, and Zn with 10 mL of 0.5 N HNO_3. This procedure constitutes the first method (thereafter labeled method *M*1) for extracting Zn from the matrix. A second method (thereafter labeled method *M*2) was also tested for comparative purposes. The starting solution is evaporated to dryness and re-dissolved in 1 mL of 1.5 N HBr, and Zn is further purified on 0.5 mL of AG-1x8 resin (200–400 mesh) using 3 mL of 0.5 N HNO_3. Whatever the procedure and the element, the chemical extraction was repeated once to get rid of residual trace elements.

Metal isotopic ratios were measured by multiple-collector inductively coupled plasma mass spectrometry (MC-ICPMS) at ENS-Lyon, using either a VG Plasma 54 (P54) or a Nu Plasma HR (Nu500) for Zn, a Nu500 for Cu, and a large radius Nu Plasma 1700 (Nu1700) for Fe. Analytical conditions for Zn isotopic ratios are provided in Maréchal et al. (1999) and in Balter et al. (2010) for measurements by means of the P54 and the Nu500 MC-ICPMS, respectively. In both cases, instrumental mass fractionation was corrected using Cu-doping (Cu NIST-SRM 976) and standard-sample bracketing (Zn JMC 3-0749L). Copper isotopic ratios were determined on the Nu500 by Zn-doping (Zn JMC 3-0749L) and standard-sample bracketing (Cu NIST-SRM 976). The Cu/Zn doping technique requires Cu and Zn isotope measurements using wet plasma due to large isotopic effects on the desolvator devices (Aridus and DSN). For Fe, isotopic ratios were run using dry plasma and instrumental mass fractionation was controlled by standard-sample bracketing (Fe IRMM14). Metal concentrations were measured at ENS-Lyon using an Agilent 7500CX quadrupole ICPMS.

Several in-house standards were routinely analyzed for the assessment of the precision. The results are shown in Table 1, and give a typical external reproducibility (2σ, where σ is the standard deviation of the results) of 65 ppm for Zn, 60 ppm for Cu and 110 ppm for Fe. Isotopic fractionation was mass dependent for Zn whatever the MC-ICPMS used for analysis (Fig. 2A and B), because the δ^{66}Zn vs. δ^{67}Zn values and the δ^{66}Zn vs. δ^{68}Zn values fall on mass fractionation lines close to the theoretical value of 1.5 and 2, respectively. The δ^{56}Fe vs. δ^{57}Fe values fall on a mass fractionation line of slope 1.54 (± 0.03) close to the theoretical value of 1.5 (Fig. 2C). In all cases, offsets are negligible (Fig. 2A–C).

3. Results

The isotopic and concentration results are presented in Table 2 and the isotopic results for Zn, Cu and Fe graphically represented as a function of sample type in Figs. 3, 4, and 5, respectively.

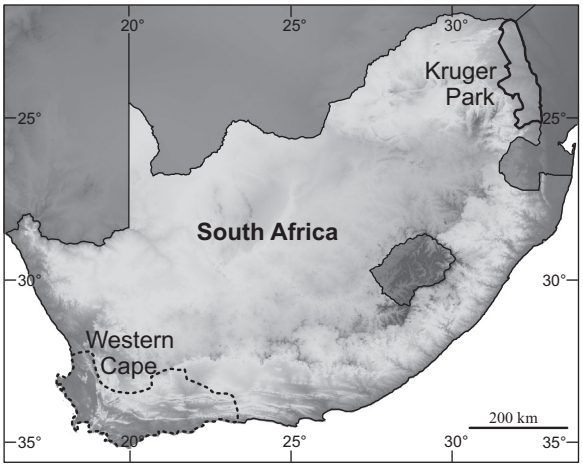

Fig. 1. Localization of the Kruger National Park (KNP) and Western Cape (WC) areas in South Africa.

Table 1
Zn, Cu and Fe isotopic values for the several in-house standards used during the course of the study. The external reproducibility is expressed as 2σ, where σ is the standard deviation of the results.

Sample	Mean (‰)	Min (‰)	Max (‰)	$\pm 2\sigma$	*n*
δ^{66}Zn					
ZnO (sheep muscle)	0.64	0.57	0.67	0.08	8
Zn49 (fossil bone)	0.65	0.64	0.67	0.02	7
3L (sheep liver)	−0.66	−0.72	−0.63	0.08	4
ZnST4 (soil)	0.36	0.28	0.41	0.08	6
δ^{65}Cu					
gb (copper coin)	0.14	0.10	0.20	0.04	16
CuO (sheep muscle)	−0.31	−0.36	−0.25	0.06	13
Cu49o (fossil bone)	−0.30	−0.25	−0.36	0.06	21
Cu49 (fossil bone)	−0.40	−0.49	−0.32	0.08	23
δ^{56}Fe					
3H (sheep blood)	−1.87	−2.10	−1.67	0.12	60
L1 (human blood)	−2.90	−3.01	−2.80	0.10	49