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Natural variation of magnesium isotopes in mammal bones and teeth from two South African trophic chains

Jeremy E. Martin [a,*], Derek Vance [b], Vincent Balter [c]

[a] Bristol Isotope Group, School of Earth Sciences, University of Bristol, BS8 1RJ Bristol, United Kingdom
[b] Institute for Geochemistry and Petrology, Department of Earth Sciences, ETH Zürich, NW D81.4, Clausiusstrasse 25, 8092 Zürich, Switzerland
[c] CNRS UMR 5276, Laboratoire de Géologie de Lyon, Ecole Normale Supérieure de Lyon, 46, Allée d'Italie, 69364 Lyon Cedex 07, France

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Abstract

Isotopic fractionations accompanying element transfer through terrestrial ecosystems have the potential to shed light on ecological interactions between primary producers and consumers, but with the exception of carbon and nitrogen this potential has barely been exploited. Here, the magnesium stable isotope composition of bones and teeth of extant mammals from Kruger National Park (KNP) and Western Cape (WC), South Africa was measured for the first time. The nature of the geological substrate proves to be a major determinant of the ecosystem isotope baseline, as indicated by the lighter magnesium isotope ratios measured in WC mammals (ranging from −1.58‰ to −0.79‰) compared to those from KNP mammals (ranging from −1.01‰ to −0.04‰). Therefore, comparisons between the isotope signatures of taxa must be restricted to a predefined geographic area with a homogeneous substrate. In both parks, Mg shows slight enrichment in heavier isotopes from herbivores to carnivores. Plant remains trapped in the dentition of herbivores provide direct evidence of dietary source and, when available, were measured. In KNP only, δ^{26}Mg of plant remains is systematically lighter than the values for herbivore teeth. These results invite further exploration of the variability of Mg isotopes in vertebrate ecosystems in order to test whether magnesium, a bio-essential element present in relatively large proportions in bone and teeth apatite, may serve as an additional trophic tracer to nitrogen, which is a constituent of collagen that rapidly degrades after burial.

1. INTRODUCTION

Magnesium possesses three stable isotopes, ^{24}Mg, ^{25}Mg and ^{26}Mg with relative abundances of around 78.99%, 10.00% and 11.01% respectively. Earth materials range in δ^{26}Mg from −4.81‰ to 0‰, including rocks (Galy et al., 2002; Young and Galy, 2004; Tipper et al., 2006a,b; Teng et al., 2007 for speleothems; Tipper et al., 2006b for limestones and dolostones), soils (Tipper et al., 2006a; Teng et al., 2010; Bolou-Bi et al., 2012), seawater (Carder et al., 2004; Young and Galy, 2004; de Villiers et al., 2005), precipitation (Bolou-Bi et al., 2012; Tipper et al., 2012), rivers (Tipper et al., 2006a,b; Brenot et al., 2008) and plants (Bolou-Bi et al., 2010 for roots, stem, shoots; Bolou-Bi et al., 2012). It has been shown that fractionation occurs during weathering, with heavier isotopes concentrated in soils while lighter isotopes are carried away in the dissolved phase of river systems (e.g. Tipper et al., 2006a; Teng et al., 2010). In living organisms, magnesium isotopes have been measured in the calcite skeletons of marine invertebrates (e.g. Hippler et al., 2009) and in marine biogenic carbonate sediment (e.g. Wombacher et al., 2011). Variations in magnesium isotope compositions in vertebrate tissue are virtually unquantified.

The role of magnesium in growth has been recognized for a long time (Leroy, 1926). Magnesium, as a bio-essential element for metabolism, is ingested in large quantities (Coudray et al., 2005) and its deficiency leads to severe

* Corresponding author. Tel.: +44 01179545368.
E-mail address: j.e.martin@bristol.ac.uk (J.E. Martin).

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disorders (e.g. Nadler and Rude, 1995). In plants, magnesium also plays an important role as it represents the metal centre of chlorophyll (Black et al., 2006). These observations suggest a link between metabolic processes and magnesium isotope fractionation. Exploration of the isotope variability of this bio-essential element between and within vertebrate communities may provide some insight into biological processes, and may ultimately reveal trophic level effects.

Thus, Mg, like other new isotope systems, could provide evidence for reconstructing food webs among extinct animals, and an opportunity to understand ecological interactions in deep time. In bone apatite ($(Ca,Mg)_{10}(CO_3,PO_4)_6(OH)_2$) magnesium is the second most abundant metal (up to 1.4 wt.%) after calcium, for which it substitutes. Magnesium's occurrence in the calcium site of apatite suggests that it might be resistant to alteration. Thus, potentially, magnesium isotopes might remain unaltered by post-mortem processes in fossil bones, and Mg isotope data could complement other approaches for reconstructing trophic level, for which diagenesis hampers further interpretation (Trueman and Tuross, 2002).

Here, we present the first database on the variability of magnesium isotope composition in extant mammalian communities and associated plant remains at two locations in South Africa. Although the precise links between metabolic and fractionation processes within a single organism still need to be characterized, we discuss evidence for the suggestion that natural variation of magnesium isotopes in mineralized tissues may be indicative of diet.

2. MATERIALS AND METHODS

2.1. Sample collection

Samples consisted of bones of herbivores and carnivores from the Kruger National Park (KNP) and Western Cape (WC), South Africa. The samples were collected at the Ditsong National Museum of Natural History (Pretoria, South Africa). In addition to bone and teeth, plant residue trapped in the selenodont dentition of herbivorous mammals was extracted with a scalpel and analyzed.

2.2. Analytical techniques

Powdered samples of bone and teeth apatite were completely dissolved in 1 ml double-distilled 15.3 N HNO_3 overnight, then evaporated and re-dissolved in 350 µl 2.0 N HNO_3. Plant samples were dissolved in 1 ml 15.3 N HNO_3 using microwave digestion. An aliquot of all solutions was taken for concentration analysis of magnesium and other elements. This was done on an Element 2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) by peak-height comparison with an in-house standard. Mg, Ca and Sr concentrations on the river standard SLRS-5 reproduce to 7–8% (2SD), and are accurate relative to certified values to 3%.

Magnesium was separated from the remaining solution using cation-exchange resin (AG-50WX-12, 200–400 mesh) with ultrapure 2.0 N HNO_3 as the elution agent (see Pogge von Strandmann, 2008 for details). In order to avoid isotopic fractionation during column separation, over 99% of the magnesium was collected. This was verified by collecting and measuring the Mg content of a separate fraction of the eluant before and after the magnesium elution peak.

The purified Mg fraction was measured for Mg isotopes on a Thermo Neptune Multicollector ICP-MS using an Apex-Q for sample introduction (Foster et al., 2010). Purified samples were diluted in 2% HNO_3 to a concentration of 100 ppb. Measurements were conducted at low resolution and each analysis consisted of 20 four-second integrations of the ^{24}Mg, ^{25}Mg and ^{26}Mg signals in static mode. Each analysis was preceded by a measurement of blank 2% nitric, and the signals for this background were subtracted from analyte signal before calculation of isotope ratios. Delta values were obtained via bracketing analyses of DSM-3 (Galy et al., 2003), with CAM-1 used as a secondary standard. In each analytical session, samples (and occasional CAM-1) bracketed by DSM-3 were measured in turn. This sequence was then repeated three more times so that four separate analyses of the same sample solution were obtained. The uncertainties reported in Table 1 represent 2 standard deviations of these four analyses.

$\delta^{26}Mg$ and $\delta^{25}Mg$ values presented for samples in Table 1 are defined as:

$$\delta^{26}Mg = (((^{26}Mg/^{24}Mg_{sample})/(^{26}Mg/^{24}Mg_{DSM3})) - 1) * 1000 \quad (1)$$

$$\delta^{25}Mg = (((^{25}Mg/^{24}Mg_{sample})/(^{25}Mg/^{24}Mg_{DSM3})) - 1) * 1000 \quad (2)$$

For $\delta^{26}Mg$ the maximum uncertainty is 0.30‰ and for $\delta^{25}Mg$ it is 0.18‰. The CAM-1 standard ($n = 74$ over a period of around 18 months) yielded a mean $\delta^{26}Mg$ of $-2.57‰ \pm 0.16$ (2SD) and a mean $\delta^{25}Mg$ of $-1.33‰ \pm 0.10$. These are close to published values, e.g. $\delta^{26}Mg = -2.58‰ \pm 0.14$ (Galy et al., 2003). The $\delta^{26}Mg$ and $\delta^{25}Mg$ values obtained for all samples and standards measured in this study lie on a line ($R^2 = 0.996$) with a slope of 0.517 ± 0.007 (using a weighted regression, MSWD −0.61), within error of both the value (Young et al., 2002) for pure kinetic processes (0.510) and that for pure equilibrium processes (0.520) (Fig. 1).

3. RESULTS

Magnesium isotope data for samples are reported in Table 1 and in Fig. 1. The total range of measured values for $\delta^{26}Mg$ is 1.54‰, from −1.58‰ to −0.04‰. When available ($n = 6$), tooth enamel and bone were both measured from the same individual. The very slightly more positive values for tooth enamel are not significantly different from the values obtained for bone. A positive offset has been reported for mineral carbon isotopes, with enamel apatite more ^{13}C-enriched than bone apatite by more than 2‰ (Warinner and Tuross, 2009). In contrast, a negative offset of about 1‰ is observed for calcium isotopes between enamel and bone (Heuser et al., 2011).

The KNP offers the biggest sample of mammal species in this study ($n = 12$; Fig. 2a). The lower number of mammal species measured for WC ($n = 4$; Fig. 2b) precludes further discussion on trophic level effect at this site, but the data from WC will be discussed below with regard to the importance of the geological substrate or other sources. In KNP,