

Available online at www.sciencedirect.com



Geochimica et Cosmochimica Acta

Geochimica et Cosmochimica Acta 75 (2011) 3419-3433

www.elsevier.com/locate/gca

## Calcium isotopes in fossil bones and teeth — Diagenetic versus biogenic origin

Alexander Heuser<sup>a,\*</sup>, Thomas Tütken<sup>a</sup>, Nikolaus Gussone<sup>b</sup>, Stephen J.G. Galer<sup>c</sup>

<sup>a</sup> Steinmann-Institut für Geologie, Mineralogie und Paläontologie, Universität Bonn, Poppelsdorfer Schloss, 53115 Bonn, Germany <sup>b</sup> Institut für Mineralogie, Universität Münster, Corrensstraße 24, 48149 Münster, Germany

° Max-Planck-Institut für Chemie, Abteilung Biogeochemie, Postfach 3060, 55020 Mainz, Germany

Received 5 August 2010; accepted in revised form 15 March 2011; available online 31 March 2011

## Abstract

We present the first systematic study of Ca isotopes ( $\delta^{44/40}$ Ca) in Late Triassic to Late Cretaceous dinosaur bones and teeth (enamel and dentin) from sympatric herbivorous and carnivorous dinosaurs. The samples derive from five different localities, and data from embedding sediments are also presented. Additional  $\delta^{44/40}$ Ca in skeletal tissues from modern reptiles and birds (avian dinosaurs) were measured for comparison in order to examine whether the original Ca isotopic composition in dinosaur skeletal apatite was preserved or might have changed during the diagenesis and fossilization process.

 $\delta^{44/40}$ Ca of fossil skeletal tissues range from  $-1.62_{00}^{\circ}$  (*Tyrannosaurus rex* enamel) to  $+1.08_{00}^{\circ}$  (*Brachiosaurus brancai* bone), while values in modern archosaur bones and teeth range from  $-1.63_{00}^{\circ}$  (caiman enamel) to  $-0.37_{00}^{\circ}$  (ostrich bone). The average  $\delta^{44/40}$ Ca of the three types of fossil skeletal tissue analyzed – bone, dentin and enamel – show some systematic differences: while  $\delta^{44/40}$ Ca in bone exhibits the highest values, while  $\delta^{44/40}$ Ca in enamel has the lowest values, and dentin  $\delta^{44/40}$ Ca falls in between. Values of  $\delta^{44/40}$ Ca in the remains of herbivorous dinosaurs (0.1–1.1<sub>00</sub>) are generally higher than those of bones of modern mammalian herbivores ( $-2.6_{00}^{\circ}$  to  $-0.8_{00}^{\circ}$ ) and from modern herbivorous archosaurs, which exhibit intermediate  $\delta^{44/40}$ Ca ( $-0.8_{00}^{\circ}$  to  $-0.4_{00}^{\circ}$ ). These systematic isotopic shifts may reflect physiological differences between dinosaurs, mammals and reptiles representing different taxonomic groups of vertebrates.

Systematic offsets in skeletal apatite  $\delta^{44/40}$ Ca between herbivorous and carnivorous dinosaurs are not obvious, indicating a lack of a clear-cut Trophic Level Effect (TLE) shift between herbivores and carnivores in dinosaurs. This observation can be explained if the carnivorous dinosaurs in this study fed mainly on soft tissues from their prey and did not ingest hard (calcified) tissue to much extent. The most striking indication that the primary  $\delta^{44/40}$ Ca is actually preserved in most of the fossil teeth is a difference in  $\delta^{44/40}$ Ca of about  $0.35 \pm 0.10\%$  (1SD) between dentin and enamel, based upon 11 of 16 analyzed dentin-enamel pairs. This difference is close to that found in modern reptiles ( $0.28 \pm 0.05\%$ ), and strongly suggests that this tell-tale signature is a primary feature of the fossilized dinosaur material as well. Furthermore, simple mass balance calculations show that changes of the original  $\delta^{44/40}$ Ca in bones and teeth by diagenetically-formed calcium-bearing minerals are either small or would require implausible high original  $\delta^{44/40}$ Ca values in the skeletal apatite. (© 2011 Elsevier Ltd. All rights reserved.

## **1. INTRODUCTION**

Fossil bones and teeth are valuable geochemical archives, and their isotopic and trace elemental compositions

\* Corresponding author.

can be used to reconstruct diet, trophic level, thermophysiology, paleoclimate and the habitat of vertebrates (see overviews by: Kohn and Cerling, 2002; Hedges et al., 2006; Koch, 2007). However, the applicability of the isotopic and trace elemental compositions of skeletal tissues for these reconstructions is limited, as during fossilization (cf. Kohn, 2008) and diagenetic alteration the original chemical and isotopic composition of bones and teeth is changed

E-mail address: aheuser@uni-bonn.de (A. Heuser).

<sup>0016-7037/\$ -</sup> see front matter  $\circledast$  2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.gca.2011.03.032