Palaeogeography, Palaeoclimatology, Palaeoecology 310 (2011) 84–91

Contents lists available at ScienceDirect

Palaeogeography, Palaeoclimatology, Palaeoecology

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

Triple oxygen isotope analysis of bioapatite as tracer for diagenetic alteration of bones and teeth

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A R T I C L E I N F O

Article history:
Received 24 June 2010
Received in revised form 24 March 2011
Accepted 13 April 2011
Available online 20 April 2011

Keywords:
Diagenesis
Oxygen isotopes
Cenozoic
Mammals
Palaeoclimate

A B S T R A C T

The detection of diagenetic alteration is critical for palaeoclimate reconstruction that is based on the oxygen isotope composition of fossil bones and teeth. So far, no direct chemical proxy has been found to track diagenetic modification of the oxygen isotope ratios. Here, a new approach to identify diagenetic changes of $\delta^{18}O_{PO4}$ values in skeletal apatite of small mammals by means of triple oxygen isotope analysis (^{16}O, ^{17}O and ^{18}O) is presented.
Our method is based on the fact that inhaled air oxygen (O_2) has an isotope anomaly on its rare isotope ^{17}O. Inhaled air O_2 is a major source of oxygen in small land-living mammals. A fraction of the anomaly is transferred via body water to skeletal apatite, where it can be detected by means of $\delta^{17}O$ and $\delta^{18}O$ analyses. The approach, considering the current analytical uncertainty, is restricted to small mammals with body masses ≤ 1 kg. This is due to the low specific metabolic rates of large mammals, resulting in a lower fraction of oxygen inhaled via breathing relative to oxygen from other sources in their body water.
Remnant negative ^{17}O anomalies derived from in vivo inhaled O_2 have been detected in enamel bioapatite of Eocene to Miocene rodent teeth while dentine of the same teeth lacks significant ^{17}O anomalies. This suggests preservation of the original phosphate oxygen isotope composition in enamel of these small mammal teeth. In contrast, ^{17}O anomalies in dentine have been erased due to diagenetic alteration with isotopically normal diagenetic fluids. Triple oxygen isotope analysis of bioapatite thus seems to be a useful new proxy to directly detect diagenetic alterations of the $\delta^{18}O_{PO4}$ values of small mammal teeth.

1. Introduction

1.1. General considerations

Since the pioneering works of Longinelli (1984), Luz et al. (1984) and Luz and Kolodny (1985), palaeotemperature reconstructions based on the $^{18}O/^{16}O$ (expressed as $\delta^{18}O$, see Section 1.2 for definitions) of bioapatite from fossil mammals rapidly became an established method and the number of studies on this topic is increasing continuously (e.g., Fricke, 2003; Grimes et al., 2003, 2004, 2005; Tütken et al., 2006, 2007; Zanazzi and Kohn, 2008; Chritz et al., 2009; Tütken and Vennemann, 2009).

The $\delta^{18}O$ of bioapatite can be used as a proxy for the $\delta^{18}O$ of ingested meteoric water, which is the main source of oxygen in large land-living animals. The oxygen isotope composition of meteoric water provides information about mean annual air temperature, relative humidity and local precipitation (Dansgaard, 1964; Rozanski et al., 1997; Fricke and O'Neil, 1999 and references therein). Skeletal apatite precipitates in equilibrium with body water. For most mammals, skeletal apatite precipitates at a body temperature of 37 °C and has a $\delta^{18}O$, which is ~17.3‰ higher than the $\delta^{18}O$ of the water from which it has precipitated (Longinelli and Nuti, 1973). Therefore, the $\delta^{18}O$ of mammalian bioapatite relates to the $\delta^{18}O$ of ingested meteoric water and can thus be used as a climate proxy for air temperature, aridity and/or drinking behaviour (Longinelli, 1984; Ayliffe and Chivas, 1990; Delgado Huertas et al., 1995; Kohn et al., 1998; Levin et al., 2006; Tütken et al., 2006).

Most studies using $\delta^{18}O_{PO4}$ of mammalian bioapatite for continental palaeoclimate reconstructions have been conducted on teeth of large mammals (Koch et al., 1989; Ayliffe et al., 1992; Bryant et al., 1994; Gaboardi et al., 2005; Tütken et al., 2006, 2007; Chritz et al., 2009; Tütken and Vennemann, 2009). However, the number of studies using small mammals (mainly rodents) has increased over the last few years (Grimes et al., 2003, 2004, 2005; Navarro et al., 2004; Tütken et al., 2006; Ruddy, 2008; Héran et al., 2010). The advantages and disadvantages of using small mammal teeth for continental palaeoclimate reconstructions are reviewed in detail in Grimes et al. (2008).

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doi:10.1016/j.palaeo.2011.04.014