Body temperatures of modern and extinct vertebrates from ^{13}C-^{18}O bond abundances in bioapatite

Robert A. Eagle[a,1], Edwin A. Schauble[b], Aradhna K. Tripati[a,b,c], Thomas Tütken[d], Richard C. Hulbert[e], and John M. Eiler[a]

[a]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125; [b]Department of Earth and Space Sciences, University of California, Los Angeles, CA 90095; [c]Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom; [d]Steinmann-Institut für Geologie Mineralogie und Paläontologie, Universität Bonn, Poppelsdorfer Schloss, 53115 Bonn, Germany; and [e]Florida Museum of Natural History, University of Florida, Gainesville, FL 32611

Edited by Mark H. Thiemens, University of California, San Diego, La Jolla, CA, and approved April 16, 2010 (received for review October 1, 2009)

The stable isotope compositions of biologically precipitated apatite in bone, teeth, and scales are widely used to obtain information on the diet, behavior, and physiology of extinct organisms and to reconstruct past climate. Here we report the application of a new type of geochemical measurement to bioapatite, a "clumped-isotope" paleothermometer, based on the thermodynamically driven preference for ^{13}C and ^{18}O to bond with each other within carbonate ions in the bioapatite crystal lattice. This effect is dependent on temperature but, unlike conventional stable isotope paleothermometers, is independent from the isotopic composition of water from which the mineral formed. We show that the abundance of ^{13}C-^{18}O bonds in the carbonate component of tooth bioapatite from modern specimens decreases with increasing body temperature of the animal, following a relationship between isotope "clumping" and temperature that is statistically indistinguishable from inorganic calcite. This result is in agreement with a theoretical model of isotopic ordering in carbonate ion groups in apatite and calcite. This thermometer constrains body temperatures of bioapatite-producing organisms with an accuracy of 1–2 °C. Analyses of fossilized tooth enamel of both Pleistocene and Miocene age yielded temperatures within error of those derived from similar modern taxa. Clumped-isotope analysis of bioapatite represents a new approach in the study of the thermophysiology of extinct species, allowing the first direct measurement of their body temperatures. It will also open new avenues in the study of paleoclimate, as the measurement of clumped isotopes in phosphorites and fossils has the potential to reconstruct environmental temperatures.

apatite | isotope | paleoclimate | thermophysiology | paleothermometry

The mechanisms by which animals regulate their body temperatures are among the most fundamental aspects of their biology. The acquisition of endothermy, the ability to maintain high and stable body temperatures through internal heat production, is a major physiological change that occurred at an unknown stage during the evolutionary transition to mammals and birds from their ancestors among the nonmammalian therapsids and nonavian dinosaurs, respectively (1). Approaches to understanding the physiology of extinct animals and the evolution of endothermy have largely focused on biophysical modeling, anatomical observations, growth rate analysis from bone histology, and behavioral studies such as estimating predator/prey ratios (1–7). The validity of each of these approaches is uncertain (for contrasting viewpoints on approaches to dinosaur thermoregulation see refs. 4 and 5).

Modern endothermic mammals and ectotherms, such as alligators and crocodiles, generally have significant differences in average body temperatures. With rare exceptions, mammals have high and stable body temperatures around 36–38 °C regardless of their environment, whereas the body temperatures of ectotherms are generally lower on average and often fluctuate depending on environmental temperatures (1). While not a completely unambiguous indicator of physiology, the ability to measure the body temperature of extinct vertebrates would provide crucial information in tracing the evolution of thermoregulation. However it has been widely assumed that it would not be possible to make a direct measurement of the body temperatures of extinct organisms (2, 8).

An indirect geochemical approach to reconstructing temperature is based on the oxygen isotope composition ($\delta^{18}O$) of minerals such as calcite, aragonite, and apatite (9–12). However, the $\delta^{18}O$ values of these minerals depend on both growth temperature and the $\delta^{18}O$ of the water from which the mineral formed. Because waters are rarely preserved in the geologic record, it is generally necessary to assume a value for the $\delta^{18}O$ of water in order to draw conclusions regarding biomineral growth temperatures.

The oxygen isotope composition ($\delta^{18}O$) of the phosphate and carbonate component of bioapatite in bone, teeth, and scales reflects both the body temperature of the animal and the oxygen isotope composition of its body fluids (13–19). The $\delta^{18}O$ of body waters, and hence bioapatite, can be influenced by local meteoric water compositions (14, 15, 19, 20), humidity (20–23), diet (24, 25), and physiology of the animal (19, 20, 24, 25). The complex factors influencing body water $\delta^{18}O$ mean that it is difficult to make robust assumptions regarding the body water $\delta^{18}O$ of an extinct species. Attempts have been made to address thermoregulation in extinct species with the oxygen isotope thermometer. However, these studies are to some extent ambiguous due to the requirement for assumptions regarding body water $\delta^{18}O$ (26–28) and the preservation of primary oxygen isotope compositions when fossil bone was analyzed (29, 30).

Here we describe the application of a previously undescribed approach to bioapatite—the carbonate "clumped-isotope" thermometer—that holds promise for overcoming some of the drawbacks of oxygen isotope paleothermometry and providing a relatively assumption-free measurement of body temperatures of extinct species. Clumped-isotope thermometry relies on the propensity of ^{13}C and ^{18}O to form bonds, or "clump," with each other in a carbonate molecule. This effect is independent of bulk isotopic compositions but is dependent on temperature (31–33). The abundance of ^{13}C-^{18}O bonds in carbonate can be determined from the abundance of mass 47 CO_2 produced on phosphoric acid digestion of carbonate-containing minerals. The relationship between temperature and ^{13}C-^{18}O bond abundance is defined by the deviation of the measured abundance of mass 47 CO_2 compared to the abundance of mass 47 CO_2 expected for a random distribution of isotopes and is given the notation Δ_{47} (34). As $\delta^{13}C$

Author contributions: R.A.E., E.A.S., and J.M.E. designed research; R.A.E. and E.A.S. performed research; R.A.E., E.A.S., A.K.T., and J.M.E. analyzed data; T.T. and R.C.H. contributed new reagents/analytic tools; and R.A.E. and E.A.S. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission.

[1]To whom correspondence should be addressed. Email: robeagle@caltech.edu.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.0911115107/-/DCSupplemental.

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