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Evidence for rapid climate change in North America during the latest Paleocene thermal maximum: oxygen isotope compositions of biogenic phosphate from the Bighorn Basin (Wyoming)

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Abstract

Oxygen isotope records of Cenozoic sea water temperatures indicate that a rapid warming event known as the Latest Paleocene Thermal Maximum (LPTM) occurred during the otherwise gradual increase in world temperatures during the Late Paleocene and Early Eocene. Oxygen isotope analysis of the carbonate and phosphate components of hydroxyapatite found in mammalian tooth enamel and body scales of river-dwelling fish from the Bighorn Basin in Wyoming were made to investigate corresponding changes in the terrestrial climate. A comparison of carbonate and phosphate isotope data from modern and fossil material indicates that some diagenetic alteration of the fossil material has occurred, although systematically larger intra-tooth ranges in the oxygen isotope composition of carbonate indicate that it is more likely to have been affected than phosphate. Carbonate and phosphate from the ecologically diverse mammals and fishes both record a shift to higher oxygen isotope ratios at the same time and of the same duration as the LPTM. These shifts reflect a change in the isotopic composition of regional precipitation, which in turn provides the first evidence for continental climate change during the LPTM. Assuming the present-day relation between the oxygen isotope composition of precipitation and temperature applies to conditions in the past, and that animal physiology and behavior is relatively invariant over time, the isotopic shift is equivalent to an increase of surface temperature in western North America of several degrees. This result is consistent with the magnitude of high-latitude ocean warming, and provides a basis for relating marine and terrestrial oxygen isotope records to records of terrestrial biotic change. © 1998 Elsevier Science B.V. All rights reserved.

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1. The Latest Paleocene Thermal Maximum

From the Paleocene to the Middle Eocene, ocean water experienced a gradual rise in average surface temperatures which reached levels ~2 to 4°C warmer

than that of the present ocean [1]. Occurring within this interval of gradually increasing temperatures was a rapid, short-term warming event at the end of the Paleocene (~55.5 Ma) known as the Latest Paleocene Thermal Maximum (LPTM). Until now, the only geochemical evidence for this rapid warming was the $\delta^{18}\text{O}$ systematics of high-latitude planktic, and global benthic, foraminiferal tests separated

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from ocean sediment cores around the world [1,2]. In all cases, $\delta^{18}\text{O}$ decreased 2–3‰ over a period of tens of thousands of years [2]. In the absence of global ice sheets, this shift indicates that the temperature of the world's oceans increased by $>4^\circ\text{C}$ during the LPTM. Roughly coeval with the LPTM shift of $\delta^{18}\text{O}$ values is an equally impressive lowering of $\delta^{13}\text{C}$ values of the same benthic forams by $\sim 2\text{‰}$ [2]. Analyses of carbonate from mammalian tooth enamel and soil nodules in North America [3,4], and carbon from organic material in terrestrial sediments in Europe [5] provide evidence that this carbon isotope excursion was global.

An integral, and so far poorly understood, part of understanding the LPTM is the quantitative description of climatic change in continental environments, in particular temperature change. This information is important for two primary reasons. First, it allows estimates to be made of the effects of temperature rise on terrestrial biological systems, such as the well-documented holarctic mammalian dispersal event [6] and increased levels of floral extinction [7] that correspond to the LPTM. In addition, temperature data can provide boundary conditions for the refinement and testing of global and regional climate models.

In this study, we analyzed the oxygen isotope composition of mammalian tooth enamel and freshwater fish scales through the Paleocene–Eocene boundary section in the Bighorn Basin in order to place constraints on continental climate change during the LPTM. The pronounced increase in the $\delta^{18}\text{O}$ values of phosphate and carbonate measured for biogenic apatite provides evidence for continental warming of the same duration and magnitude as that inferred from isotope records of marine sediments.

2. Biogenic phosphate as a proxy for Paleogene continental climate

One of the most useful means of describing climatic conditions on continents is the measurement of the oxygen isotope composition of precipitation ($\delta^{18}\text{O}_{\text{pt}}$), because oxygen isotope variations of precipitation are correlated with local climate variables under present-day climatic conditions. For example, modern observations indicate that precipitation in high-latitude/cooler localities generally

have lower $\delta^{18}\text{O}_{\text{pt}}$ values than precipitation falling in low-latitude/warmer localities [8–10], and there is a strong correlation between mean annual temperature (MAT) and average $\delta^{18}\text{O}_{\text{pt}}$ values at mid- to high-latitude sites located inland from coastal areas [9]. Similarly, $\delta^{18}\text{O}_{\text{pt}}$ values in one location can vary over the course of a year in response to seasonal temperature changes [9], although in both cases the relation can be locally complicated by variations in relative humidity, proportion of winter precipitation, and different transport histories of air-masses formed in different regions.

In order to utilize the $\delta^{18}\text{O}_{\text{pt}}$ –temperature correlation as a thermometer in the geologic past, a proxy must be found for the oxygen isotope composition of past precipitation. One such proxy is the $\delta^{18}\text{O}$ value of oxygen in carbonate hydroxyapatite of teeth and bones [$\text{Ca}_5(\text{PO}_4, \text{CO}_3)_3(\text{OH}, \text{CO}_3)$]. The primary advantage of this biogenic apatite over other proxies for $\delta^{18}\text{O}_{\text{pt}}$ is that phosphate is resistant to oxygen isotope exchange in the diagenetic environment. For example, it has been observed that the oxygen in the phosphate phase of hydroxyapatite is more resistant to isotopic exchange than oxygen in the carbonate phase, and than oxygen in carbonate in general [11,12]. Furthermore, phosphate from skeletal components with little organic material and hence tightly packed crystals, such as tooth enamel, are even less prone to diagenetic exchange than phosphate in bone [13,14].

The biogenic phosphate proxy for $\delta^{18}\text{O}_{\text{pt}}$ works because water ingested from surface reservoirs such as streams, ponds, or plants (stems and leaves) plays the major role in determining the $\delta^{18}\text{O}$ value of animal body water, and hence the $\delta^{18}\text{O}$ value of phosphate ($\delta^{18}\text{O}_{\text{p}}$) and carbonate ($\delta^{18}\text{O}_{\text{c}}$) in biogenic apatite [15–20]. With the exception of leaf water, these water sources have $\delta^{18}\text{O}$ values that reflect those of local precipitation, which in turn provides the connection between $\delta^{18}\text{O}_{\text{p}}$, $\delta^{18}\text{O}_{\text{c}}$, and surface temperature. Leaf water generally has $\delta^{18}\text{O}$ values that are higher than those of water in the stem of plants due to evaporation at the leaf surface [21]. As a result, animals that obtain a large proportion of ingested water from plant leaves can have $\delta^{18}\text{O}_{\text{p}}$ and $\delta^{18}\text{O}_{\text{c}}$ values that are influenced by local relative humidity as well as surface temperature [22,23].

Although the $\delta^{18}\text{O}$ value of ingested water has a strong influence on $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ values, the relation between the two is usually not one-to-one because oxygen from ingested organic matter and the atmosphere also influences the $\delta^{18}\text{O}$ of body water [16,18,20]. In addition, the relation will vary from species to species according to the type of metabolic processes employed by the animal and on the fluxes of H_2O , O_2 and CO_2 into and out of its body [16,18,20]. Relations between the $\delta^{18}\text{O}$ values of precipitation and animal body water, however, can be reasonably approximated using both empirical calibrations and physiological models. Thus it should be possible to use the analyses of animal remains from a single lineage to reconstruct changes in climatic conditions over time using a $\delta^{18}\text{O}_p$ or $\delta^{18}\text{O}_c$ proxy.

3. Sampling protocol

The northern Bighorn Basin of Wyoming preserves one of the most complete and best studied terrestrial stratigraphic records across the Paleocene–Eocene boundary interval [24,6,25]. Biostratigraphic, magnetostratigraphic and chemostratigraphic constraints on sections from this area allow relatively precise correlations to be made with the marine record. Earlier carbon isotope analyses of carbonate in mammalian tooth enamel and in soil nodules collected from this stratigraphic section provided evidence for the LPTM carbon isotope excursion noted above [3,4]. In addition, a Clarkforkian–Wasatchian transitional fauna (zone Wa-0) has been identified [6] which is now known to coincide precisely with the carbon isotope excursion during the LPTM.

All of the samples analyzed in this study are from either the Clarks Fork Basin or the McCullough Peaks section of the northern Bighorn Basin. Both sections are characterized by thick fluvial and fluvio-lacustrine deposits of the Paleocene Fort Union Formation and Eocene Willwood Formation. The Fort Union–Willwood contact is diachronous across the basin, with the mammalian faunal zone Wa-0 found at the base of the Willwood Formation in the McCullough Peaks section and approximately 350 m above the Fort Union–Willwood contact in the

Clarks Fork Basin. Fossils are generally preserved in overbank mudstone facies which have undergone various amounts of pedogenic alteration.

Each sample was assigned an estimated age on the basis of a model that uses linear interpolation between magnetostratigraphic and chemostratigraphic ($\delta^{13}\text{C}$) correlation points (Table 1). For the Clarks Fork Basin section, the boundaries between Chrons C26N/C25R, C25R/C25N, C25N/C24R [26] and the carbon isotope excursion [3,4] are used as correlation points. For the McCullough Peaks section, the boundaries between Chrons C24R/C24N.3n, C24N.3n/C24N.2r, and C24.2n/C24.1r [25,27] and the carbon isotope excursion (Koch, unpublished data) are used as correlation points. Ages for magnetic correlation points are taken from the most recent geomagnetic polarity time scale [28] and an estimated age of 55.5 million years was used for the carbon isotope excursion [29]. An age model that excludes the carbon isotope event as a calibration point does not differ significantly from the one used here. Initial reports of the excursion [2] used earlier calibrations of the geomagnetic timescale [30] which were significantly different than the most recent calibration [28]. Any future changes in the age estimate of the carbon isotope excursion used here, however, would only affect the calibration of these events in time, not their correlation to one another.

3.1. *Coryphodon*

Mammals are well suited for paleoclimatic studies that utilize $\delta^{18}\text{O}_p$ values because they precipitate biogenic apatite in equilibrium with their body water at a constant temperature of $\sim 37^\circ\text{C}$ [15,16]. Therefore, assuming dietary habits are constant, any change in $\delta^{18}\text{O}_p$ over time should reflect a change only in the $\delta^{18}\text{O}$ of ingested water, and hence a change in local climate variables. For this study, samples were collected from the canine teeth of *Coryphodon* (Mammalia, Pantodonta), a relatively common, large (~ 500 kg estimated body weight), herbivorous mammal which is known from across the entire holarctic region during the Paleogene. Although it is difficult to determine a representative habitat of an extinct species, *Coryphodon* is thought to have lived near, or perhaps in, rivers that flowed through the Bighorn Basin during the Paleogene.

Table 1
Stable isotope data for gar body scales and *Coryphodon* tusks

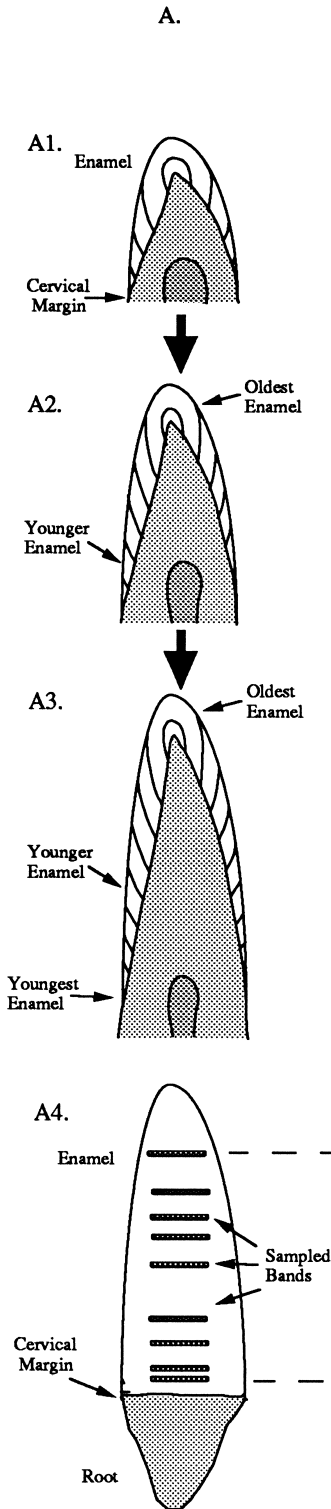
Sample	LMZ/age (Ma)	Height (mm)	Carbonate ($\delta^{13}\text{O}$)	Carbonate ($\delta^{18}\text{O}$)	Phosphate ($\delta^{18}\text{O}$)	Sample	LMZ/age (Ma)	Height (mm)	Carbonate ($\delta^{13}\text{C}$)	Carbonate ($\delta^{18}\text{O}$)	Phosphate ($\delta^{18}\text{O}$)
<i>Coryphodon</i>											
87991-1	CF-2/55.64	46.5	−11.7	17.8	14.19	4016-8	Wa-4/53.67	45.0	−14.2	20.1	
87991-2		41.5	−12.4	19.5	16.9	94016-7		40.5	−14.0	18.8	13.3
87991-3		36.0	−12.7	20.9	15.6	94016-6		35.5	−13.6	19.9	13.6
87991-4		31.5	−13.3	19.9	14.9	94016-5		31.0	−13.6	20.4	13.4
87991-5		26.5	−12.5	19.2	14.0	94016-4		22.5	−14.3	20.0	14.3
87991-6		20.0	−12.1	21.8		94016-3		18.0	−14.4	19.4	13.9
87991-7		14.0	−12.7	21.3	14.5	94016-2		14.0	−14.4	18.8	13.6
87991-8		10.5	−12.0	19.3	15.0	94016-1		10.0	−14.0	18.8	13.5
87991-9		6.5	−11.4	18.4	13.6						
87991-10		3.5	−11.3	19.1	13.8	88268-11	Wa-6/53.01	75.2			16.4
						88268-10		70.1			16.5
80251-10	CF-2/55.64	44.6			14.8	88268-9.5		67.0			15.6
80251-9		39.7			15.0	88268-9		64.0			
80251-8		36.7			14.8	88268-8		58.2	−13.4	19.0	14.7
80251-7		32.7			14.7	88268-7.5		54.9			14.9
80251-6		27.1			16.0	88268-7		51.7	−13.3	19.1	15.3
80251-5.5		25.1			15.0	88268-6		45.7	−12.8	19.0	14.7
80251-5		23.1			14.5	88268-5		40.4	−13.6	17.4	15.5
80251-4		18.5			15.6	88268-4		34.1	−12.8	20.1	15.5
80251-3.6		15.7			14.4	88268-3		28.9	−12.5	20.7	16.3
80251-3.2		13.2			14.8	88268-2		23.5	−13.3	20.4	16.1
80251-3		11.7				88268-1		17.9	−13.5	19.9	15.2
80251-2		7.4									
80251-1		1.8			14.0	96744-8	Wa-6/53.01	42.0			15.3
						96744-7		35.5			14.7
83613-9	Wa-0/55.50	44.3	−15.6	21.6	17.6	96744-6		29.5	−12.6	21.3	15.7
83613-8.5		42.0	16.7			96744-5		24.0	−11.5	20.9	15.3
83613-8		39.7	−15.6	22.0	15.5	96744-4		20.0	−11.3	20.4	14.1
83613-7		35.5	−15.1	22.3	16.5	96744-3		15.0	−11.7	19.7	14.4
83613-6		32.7	16.5			96744-2		9.0	−12.1	19.0	13.3
–	Break	–	–	–	–	96744-1		3.0	−13.9	18.6	13.2
83613-5		23.6	−15.4	21.4	15.9						
83613-4		18.6	−15.6	22.1	15.7	88232-1	Wa-6/53.01	93.0	−13.8	21.5	14.9
83613-3		13.4	−14.4	23.3	16.6	88232-2		78.0	−14.3	18.8	15.1
83613-2		8.3	−14.5	23.3	17.0	88232-3		68.0	−13.0	20.7	16.2
83613-1		2.0			17.5	88232-4		61.0	−13.0	22.0	16.6
						88232-5		52.0	−13.3	21.0	15.2
83517-10	Wa-1/55.31	50.7	−16.0	20.8	15.1	88232-6		43.0	−13.2	19.4	13.9
83517-9		45.6	−15.6	20.8	15.0	88232-7		34.0	−12.2	20.3	14.8
83517-8		40.5	−15.1	20.2	15.5	88232-7.5		29.0			15.3

Table 1 (continued)

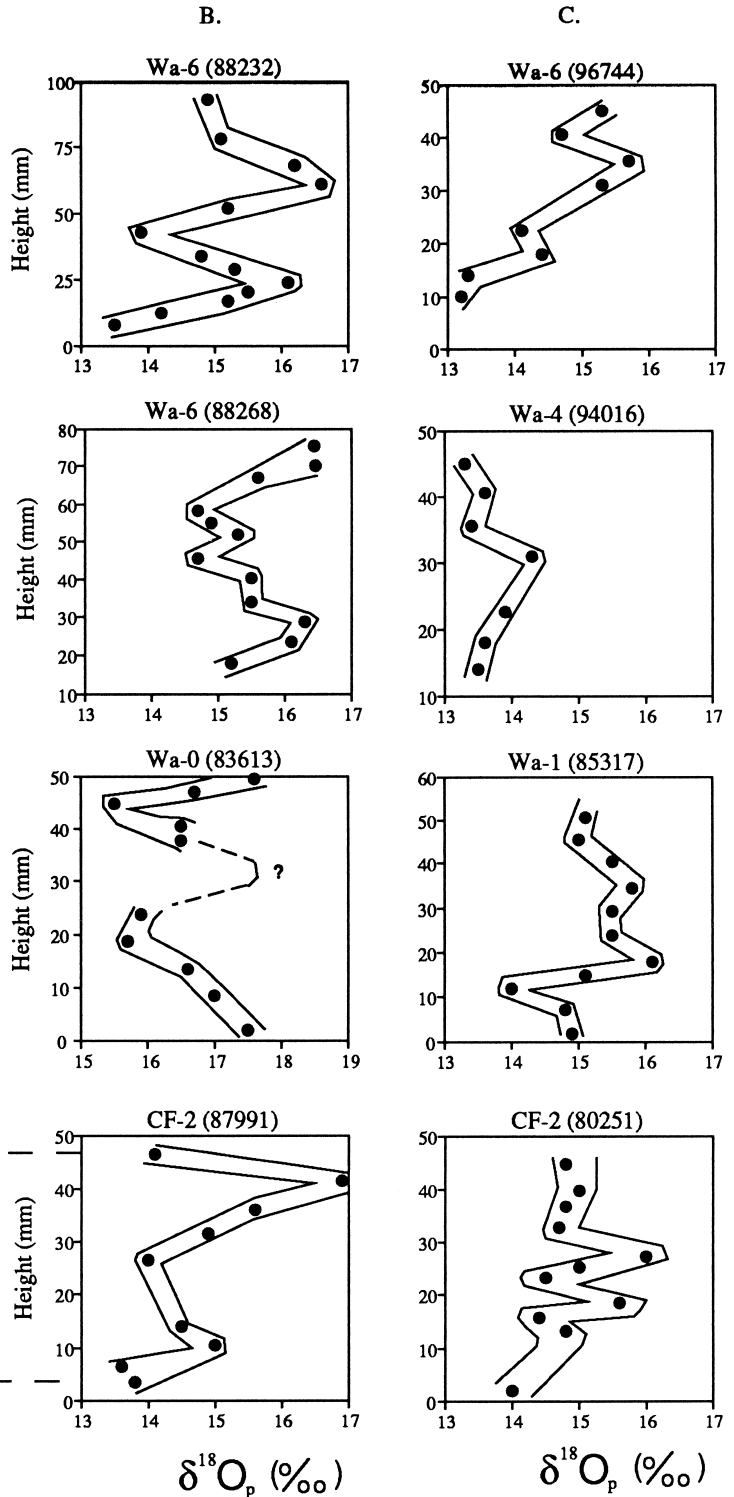
Sample	LMZ/age (Ma)	Height (mm)	Carbonate ($\delta^{13}\text{O}$)	Carbonate ($\delta^{18}\text{O}$)	Phosphate ($\delta^{18}\text{O}$)	Sample	LMZ/age (Ma)	Height (mm)	Carbonate ($\delta^{13}\text{C}$)	Carbonate ($\delta^{18}\text{O}$)	Phosphate ($\delta^{18}\text{O}$)
83517-7		34.3	-15.4	19.7	15.8	88232-8		24.0	-11.8	22.2	16.1
83517-6		29.3	-14.4	22.1	15.5	88232-8.5		20.5			15.5
83517-5		24.0	-15.2	21.7	15.5	88232-9		17.0	-12.6	20.7	15.2
83517-4		17.9	-15.4	20.7	16.1	88232-9.5		12.5			14.2
83517-3.5		15.0			15.1	88232-10		8.0	-12.8	18.9	13.5
83517-3		12.0	-15.9	18.7	14.0						
83517-2		7.0	-15.0	18.9	14.8						
83517-1		1.8			14.9						
<i>Gar</i>											
60816	Tiffanian	56.83	-7.0	19.5	13.7	85988-1	Wa-3	54.85	-11.0	19.1	
87213-1	CF-3	55.57	-3.3	19.8	14.0						
68043-1	CF-3	55.56	-5.0	19.3	13.0	93427-1	Wa-4	53.68	-10.4	17.6	13.4
65078-1	CF-3	55.55	-7.0	18.3	12.2	93386-1	Wa-4	53.68	-10.2	18.0	11.9
67243-1	CF-3	55.52	-8.8	18.7	13.9	94647-1	Wa-4	53.68		12.9	
68786-1	CF-3	55.52	-9.1	18.1	13.0	83371-1	Wa-4	53.68			
98427-1	Wa-0	55.50			15.5	91995-1	Wa-5	53.24	-9.6	18.3	13.6
98427-2	Wa-0	55.50	-9.9	20.9	16.6						
98427-3	Wa-0	55.50	-9.0	21.5	15.8	91513-1	Wa-6	52.83	-8.9	19.3	13.6
86137-1	Wa-0	55.50			14.0	92116	Wa-6	52.83		12.8	
86137/2	Wa-0	55.50	-7.6	20.9	14.5	96510	Wa-6	52.83		13.4	
79893-1	Wa-0	55.50	-8.7	20.8	15.3						
83478-1	Wa-0	55.50	-9.7	20.9	15.0						
83478/2	Wa-0	55.50	-8.4	21.6	15.4						
83569-1	Wa-0	55.50	-9.1	21.1	15.6						
76454-1	Wa-1	55.45	-9.1	19.4	14.1						
68779-1	Wa-1	55.42	-9.2	20.8	14.1						
85435/1	Wa-1	55.36	-12.6	19.8	14.3						
85435/2	Wa-1	55.36	-12.9	21.3	14.4						
85218-1	Wa-1	55.31	-11.8	19.6	13.8						

Except for Wa-0, the height of *Coryphodon* samples is the distance relative to the cervical margin (see Fig. 1A). The Wa-0 remains are fragments that do not include the cervical margin, and the height is given relative to the base of the lowermost fragment. The distance associated with the break between samples is estimated to be 9 mm. Both $\delta^{18}\text{O}_p$ (phosphate) and $\delta^{18}\text{O}_c$ (carbonate) are given relative to SMOW. $\delta^{13}\text{C}$ (carbonate) are given relative to PDB

Enamel Growth



Intra-tooth variations - *Coryphodon*



Living in the riverine environment, *Coryphodon* could have obtained food from terrestrial or aquatic plants, and water from these same plants and the river itself. River water comprises a mixture of local and non-local precipitation, ground water, and soil water, and thus seasonal variations in the $\delta^{18}\text{O}$ value of river water will be dampened relative to seasonal variations in the $\delta^{18}\text{O}$ value of precipitation. The $\delta^{18}\text{O}$ value of water in both the stems and leaves of aquatic plants should track those of the river, as evaporation from submerged leaves will be minimal. In contrast, the $\delta^{18}\text{O}$ value of water in the stems of terrestrial plants should track changes in local precipitation, while the $\delta^{18}\text{O}$ value of leaf water will be shifted to higher values as a result of evaporation. Because *Coryphodon* is extinct, the relative proportion of water it obtained from each of these sources is unknown.

The teeth selected for this study were large canine ‘tusks’ (C_1 and C^1) from eight different individuals, and represent five different land mammal zones of the Bighorn Basin sedimentary sequence. Only two fragments of a *Coryphodon* canine were recovered from zone Wa-0, and they most likely represent the same individual since they were found in close proximity to one another. Multiple samples of tooth enamel were drilled in bands parallel to the cervical margin and along the growth axis of each canine tooth for oxygen isotope analysis of phosphate (Fig. 1). Samples from seven of the eight teeth were split for isotopic analysis of structural carbonate in the apatite.

3.2. Gar

The relation between $\delta^{18}\text{O}$ values of biogenic apatite and environmental water is different for fresh-water fish than for mammals because there appears

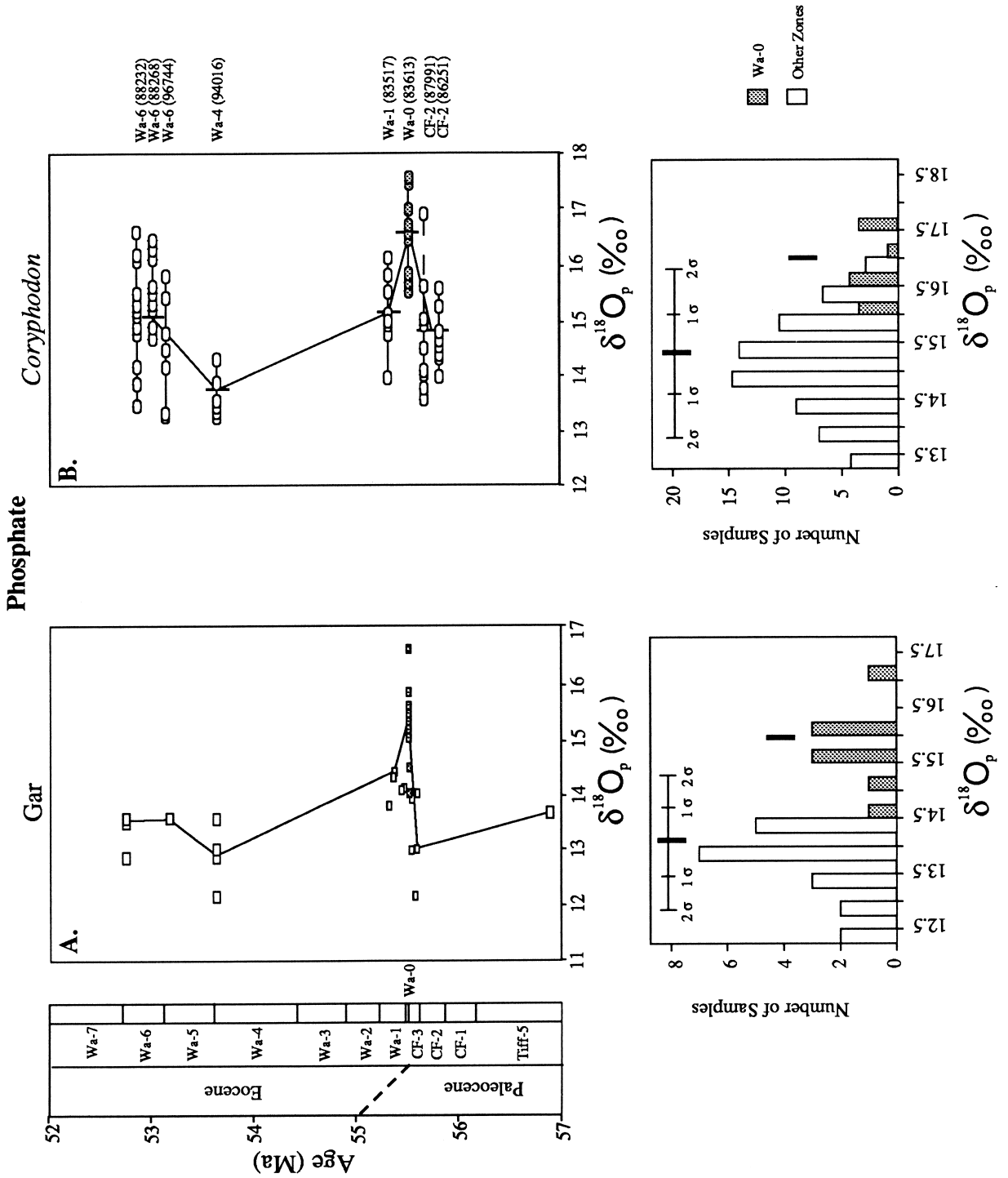
to be little or no metabolic fractionation associated with the formation of biogenic apatite in fish [17] and because fish do not regulate their body temperatures. Therefore $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ values will be determined by both the isotopic composition and the temperature of the water in which it lived. In addition to possible seasonal variations in the $\delta^{18}\text{O}$ value of river water mentioned above, seasonal variations in water temperature on the order of tens of degrees can also occur, depending on the climatic setting. This added uncertainty makes it more difficult to interpret a change in $\delta^{18}\text{O}_p$ or $\delta^{18}\text{O}_c$ in terms of the $\delta^{18}\text{O}$ value of river water/local precipitation exactly.

We sampled material from the body scales of *Lepisosteus* (Pisces, *Lepisosteiformes*), a fresh-water fish commonly known as gar. Gar scales are commonly found as well preserved and isolated elements in ancient fluvial sequences, and their outer surfaces are covered by an enamel-like aggregate of apatite crystals known as ganoine. Twenty-nine scales from eight different levels in the Bighorn Basin stratigraphic section were sampled but, because gar scales are often found as isolated elements, it is not possible to estimate the number of individuals represented in any one locality. Both $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ values were measured for each scale (3 to 10 mm in length), which required the removal of all of the ganoine from the outer surface. Because ganoine forms sequentially over the course of several years [31], these $\delta^{18}\text{O}$ values represent a homogenized seasonal signal.

4. Methods

The oxygen isotope composition of phosphate from tooth enamel and ganoine was analyzed using the technique of O’Neil et al. [32]. After a series

Fig. 1. Enamel growth and intra-tooth variations in $\delta^{18}\text{O}_p$ values for *Coryphodon* teeth. Column A represents the relative timing of enamel formation during tusk growth. During tooth eruption, enamel is progressively added at the cervical margin creating a pattern where the oldest enamel (formed earliest in life history) is preserved at the top of the tooth, and the youngest enamel (formed later in life history) is preserved at the base of the tooth, as seen in cross-section (A1 to A3). Sampling along the length of the tooth surface (A4) thus results in a time-series of $\delta^{18}\text{O}_p$ values such as those in columns B and C, in which the vertical axis represents the distance of the sample from the cervical margin, and the horizontal axis represents its $\delta^{18}\text{O}_p$ value. Intra-tooth variations in $\delta^{18}\text{O}_p$ values for the *Coryphodon* teeth are relatively regular in some cases (column B) and more irregular in others (column C), which is probably due to changes in the isotopic composition of ingested water. Note that the vertical scales are not the same for each tooth, and that the horizontal scale for the Wa-0 sample is shifted relative to the other teeth.



of simple chemical steps the phosphate radical is isolated as Ag_3PO_4 , which is reacted with graphite in silica-glass tubes at 1400°C to form CO_2 , which in turn is introduced to the inlet system of a mass spectrometer. Using this technique we obtain a value of $21.8 \pm 0.25\text{‰}$ (2σ) for NBS-120c, which is comparable to values obtained using the conventional fluorination method. For carbonate analyses, about 1 mg of enamel/ganoine was separated and soaked in a buffered acetic acid solution (pH ~ 5) for 24 h to remove surficial carbonate material [33]. The samples were then reacted with anhydrous phosphoric acid at 73°C in an automated Kiel carbonate preparation system directly coupled to a mass spectrometer. All analyses were normalized to recommended values of the international reference standards SMOW, SLAP, and NBS-19. Precision of the isotopic data is better than 0.2‰ (2σ). The isotopic analyses of phosphate and carbonate determined for this study are presented in Table 1.

5. Results

One of the most striking aspects of the data is the significant variation in $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ within all *Coryphodon* tusks. When plotted versus height on the tooth, regular variations in $\delta^{18}\text{O}_p$ values are observed in about half of the sampled tusks, while the other tusks are characterized by more irregular and sometimes less variable changes in $\delta^{18}\text{O}_p$ (Fig. 1). $\delta^{18}\text{O}_p$ values of the Wa-0 fragments are plotted together as the fragments are likely from the same individual. Intra-tooth variations in the $\delta^{18}\text{O}_c$ values are also observed, and for both carbonate and phosphate there is no apparent relation between the age of the sample and the pattern of intra-tooth variations. The intra-population range in $\delta^{18}\text{O}_p$ of gar scales from a single land mammal zone is $\sim 2\text{‰}$, a range that is similar to that observed within a single

Coryphodon tooth. For both *Coryphodon* and gar, $\delta^{18}\text{O}_c$ values are only $\sim 6\text{‰}$ higher than the corresponding $\delta^{18}\text{O}_p$ values (Table 1), indicating that diagenetic alteration of carbonate or phosphate oxygen may have occurred.

A stratigraphic/temporal comparison of the phosphate analyses of gar scales is presented in Fig. 2A and of *Coryphodon* teeth in Fig. 2B. Both oxygen isotope records reveal a shift to higher average $\delta^{18}\text{O}_p$ values during the Wa-0 land mammal zone, with a 2.0‰ increase in the mean $\delta^{18}\text{O}_p$ value of gar scales, and an increase in the mean $\delta^{18}\text{O}_p$ value of *Coryphodon* teeth of 1.8‰ relative to values measured for samples from the Cf-3/Cf-2 land mammal zones (Table 2). The significance of the shift can be determined by comparing mean $\delta^{18}\text{O}_p$ values for Wa-0 gar with the mean $\delta^{18}\text{O}_p$ values of samples from the other land mammal zones (Fig. 2). Another important aspect of the data is the difference between $\delta^{18}\text{O}_p$ values of *Coryphodon* teeth and gar scales within a single land mammal zone. For each zone, mean $\delta^{18}\text{O}_p$ values of *Coryphodon* teeth are higher than mean $\delta^{18}\text{O}_p$ values of gar scales, reflecting physiological or behavioral differences between the two species. These same isotopic trends are mirrored by the $\delta^{18}\text{O}$ values of gar and *Coryphodon* carbonate, although the isotopic shift at Wa-0 and the difference between $\delta^{18}\text{O}_c$ values of *Coryphodon* teeth and gar scales is more difficult to resolve due to more scatter in the carbonate data (Fig. 3).

The Wa-0 land mammal zone has been correlated with the marine record of the LPTM by means of carbon isotope chemostratigraphy [3]. Measurements of $\delta^{13}\text{C}$ values of the *Coryphodon* samples are limited (Table 1), but provide further evidence that the carbon isotope shifts in the terrestrial environment are correlated with those observed in marine samples of the same period. Average $\delta^{13}\text{C}$ values of the Cf-2 and Wa-6 samples are -12.2 and -12.8‰ , respectively, while the average $\delta^{13}\text{C}$ value of the Wa-0

Fig. 2. Stratigraphic and statistical comparison of the isotopic composition of phosphate in gar and *Coryphodon* hydroxyapatite. $\delta^{18}\text{O}$ values of phosphate from ganoine in the body scales of gar (A) and *Coryphodon* tooth enamel (B) versus age in epoch, land mammal zone and year with lines connecting mean $\delta^{18}\text{O}$ values (vertical bar through the data) for each land mammal zone. The higher average $\delta^{18}\text{O}_p$ values for both *Coryphodon* and gar material from Wa-0 provides evidence for climate change across the LPTM. The significance of the higher values is illustrated using histograms of the $\delta^{18}\text{O}_p$ data along with mean $\delta^{18}\text{O}_p$ values (vertical bars) and standard deviations (1σ and 2σ). Data for Wa-0 are compared with data from all the other land mammal zones except Wa-4. The lower $\delta^{18}\text{O}_p$ values for the Wa-4 *Coryphodon* and gar scales may represent a post-LPTM cooling episode previously identified by foliar physiology [41].

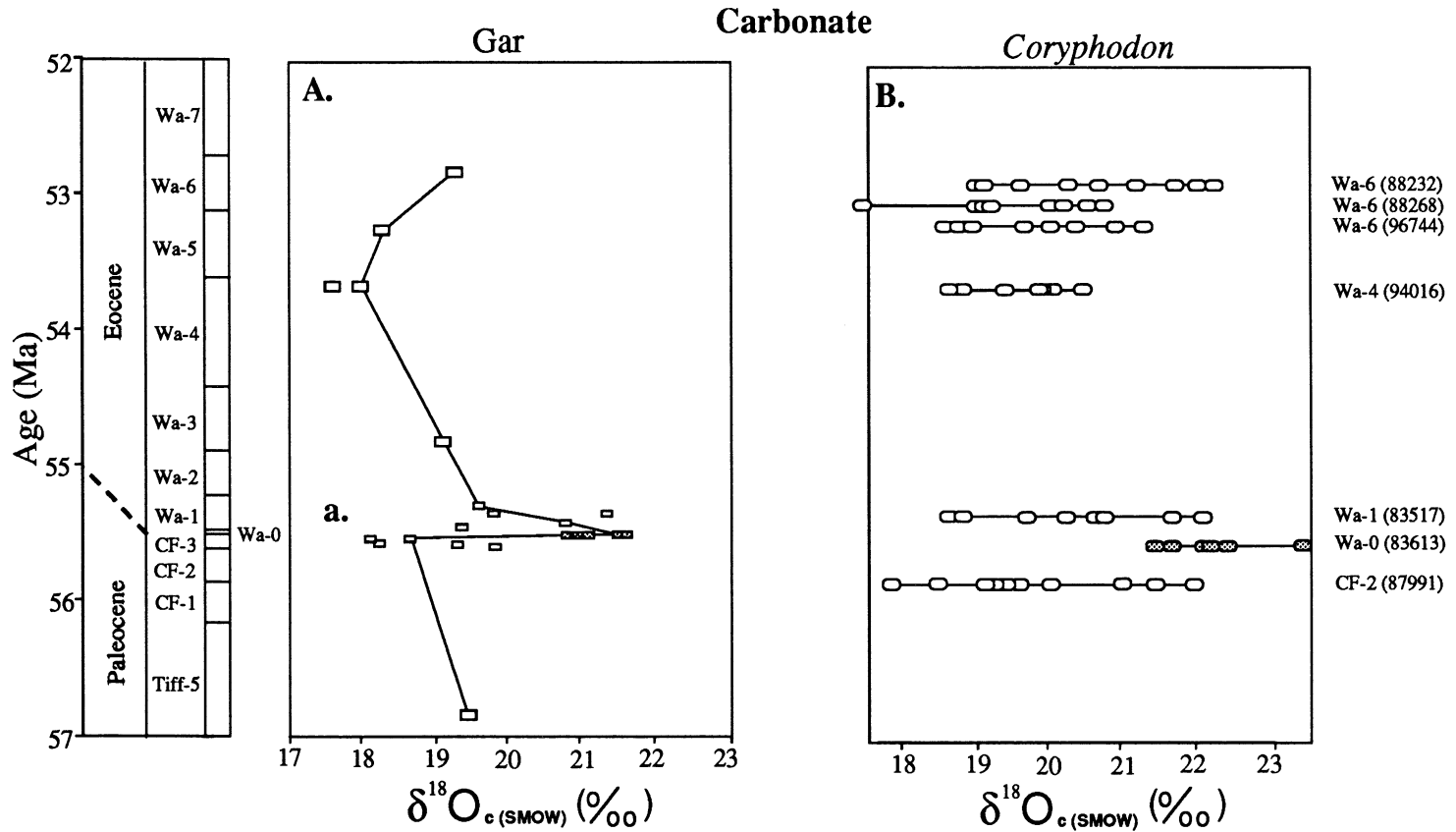


Fig. 3. Stratigraphic and statistical comparison of the isotopic composition of carbonate in gar and *Coryphodon* hydroxyapatite. $\delta^{18}O$ values of carbonate from ganoine in the body scales of gar (A) and tooth enamel of *Coryphodon* (B) versus age in epoch, land mammal zone and year. These isotope records for carbonate mirror those for phosphate, although there is more scatter in the data, particularly within single *Coryphodon* teeth. This scatter may represent partial diagenetic resetting of carbonate $\delta^{18}O$ values.

Table 2
Estimated change in temperature during the LPTM

Interval	Time span (Ma)	$\Delta(\delta^{18}\text{O}_{\text{p,cory}}, \text{‰})$	$\Delta(\delta^{18}\text{O}_{\text{ingt}}, \text{‰})$		$\Delta(\delta^{18}\text{O}_{\text{pt}}, \text{‰})$	ΔT_{s}
<i>Coryphodon</i>						
Cf2–Wa0	55.86–55.50	+1.8	+2.4	→	+2.4	+4.0
Wa0–Wa1	55.50–55.48	–1.4	–1.9	→	–1.9	–3.3
Wa1–Wa4	55.48–53.59	–1.4	–1.9	→	–1.9	–3.3
Wa4–Wa6	53.59–52.71	+1.3	+1.7	→	+1.7	+2.9
		0.75%			0.58‰/°C	
Interval	Time span (Ma)	$\Delta(\delta^{18}\text{O}_{\text{p,gar}}, \text{‰})$	$\Delta(\delta^{18}\text{O}_{\text{river}}, \text{‰})$		ΔT_{r}	
<i>Gar</i>						
Cf3–Wa0	55.62–55.50	+2.0	+2.4		+1.7	
Wa0–Wa1	55.50–55.48	–1.2	–1.9		–3.0	
Wa1–Wa4	55.48–53.59	–1.2	–1.9		–3.0	
Wa4–Wa6	53.59–52.71	+0.4	+1.7		+5.7	
				L&N, 1973		

For *Coryphodon*, the change (Δ) in $\delta^{18}\text{O}$ values of phosphate (p,cory) over time is assumed to be 75% of the change in the $\delta^{18}\text{O}$ value of ingested (ingt) water. In turn, ingested water is assumed to have the same $\delta^{18}\text{O}$ value as local precipitation. The change in surface temperature (ΔT_{s}) between land mammal zones is then estimated using the present-day $\delta^{18}\text{O}_{\text{pt}}$ –MAT relation of 0.58‰/°C [9]. In the case of gar, the $\delta^{18}\text{O}$ value of river water is assumed to be the same as the $\delta^{18}\text{O}$ value of precipitation inferred from the *Coryphodon* data. The change in river water temperature (ΔT_{r}) between zones is then estimated using the equation $T_{\text{r}} = 111.4 - 4.3(\delta^{18}\text{O}_{\text{p,gar}} - \delta^{18}\text{O}_{\text{river}})$ [43]. The duration of time intervals was determined using the age model discussed in the text.

samples is -15.2‰ . This $\sim 2.8\text{‰}$ shift to lower $\delta^{13}\text{C}$ values is identical to the shift reported previously for different mammalian species [3,4]. The average $\delta^{13}\text{C}$ value of the Wa-1 samples is the same as of the Wa-0 samples, but this observation is not unexpected in light of more recent data for the Bighorn Basin where relatively low $\delta^{13}\text{C}$ values were also measured for paleosol carbonates from the Wa-1 land mammal zone (Koch, pers. commun.). Significant intra-tooth variations in $\delta^{13}\text{C}$ of *Coryphodon* tusks are observed, but their discussion is beyond the scope of this paper, and will be addressed elsewhere. Carbon isotope analyses of gar samples are not as useful for chemostratigraphy given the more complicated nature of the carbon cycle in riverine environments.

6. Discussion

6.1. Intra-tooth variations in $\delta^{18}\text{O}_{\text{p}}$

Cyclic variation in $\delta^{18}\text{O}_{\text{p}}$ in a single tooth is not unique to *Coryphodon* teeth, and regular variations have been observed in the tusks and teeth of a number of modern herbivore species from around

the world [34–38]. Such variations are preserved in mammalian tooth enamel because it forms incrementally from crown to base prior to or during tooth eruption, and thus preserves a time series of $\delta^{18}\text{O}_{\text{p}}$ values along the direction of growth. They are interpreted to result primarily from the ingestion of surface and plant water whose isotopic composition varies seasonally in response to changing climate variables such as temperature and relative humidity [34–37], and not from a seasonal change in metabolic processes [38].

Regular variations in $\delta^{18}\text{O}_{\text{p}}$ of *Coryphodon* teeth (Fig. 1, column B) are similar to those observed for extant herbivore species [35,36,38], including the stream-dwelling beaver [37]. More uniform $\delta^{18}\text{O}_{\text{p}}$ values that characterize some of the other *Coryphodon* teeth (Fig. 1, column C), however, have yet to be described for a modern species, and probably reflect the use of larger and isotopically more homogeneous rivers by some *Coryphodon*. In general, the different patterns of intra-tooth $\delta^{18}\text{O}_{\text{p}}$ variability highlight the importance of both mammalian behavior/ecology and surface hydrology in determining $\delta^{18}\text{O}_{\text{p}}$ values of tooth enamel, and act as a reminder that both factors need to be considered

whenever using $\delta^{18}\text{O}_p$ values to infer the isotopic composition of local precipitation.

6.2. Retention of primary $\delta^{18}\text{O}$ values over time

We tested our Cenozoic-age samples for degree of isotopic preservation by comparing $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ values of biogenic apatite from modern and fossil samples. There is a linear correlation between $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ for modern, presumably unaltered, samples whereby $\delta^{18}\text{O}_c$ is consistently $\sim 8.5\%$ higher than $\delta^{18}\text{O}_p$ [19,39,40]. For *Coryphodon* tooth enamel, however, all paired $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ values lie below this trend (Fig. 4), indicating that either or both carbonate and phosphate components of fossil samples were diagenetically altered. Unfortunately, neither stable isotope data nor any geochemical data can be used to make an unambiguous determination of the extent of alteration for either phase.

It can be argued, on the basis of previously published measurements [13,14], that carbonate in enamel is more likely than phosphate to undergo isotopic exchange with fluids during diagenesis, and patterns of intra-tooth variations in $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ lend credence to this idea. Both phosphate and carbonate are characterized by intra-tooth variation in $\delta^{18}\text{O}$ (Fig. 1, Table 1), but the range in $\delta^{18}\text{O}_c$ for each tooth is

systematically larger than the corresponding range in $\delta^{18}\text{O}_p$ by $\sim 1\%$ (compare Fig. 2 and Fig. 3). In his study of radial variations in the $\delta^{18}\text{O}$ of carbonate from belemnites, Longinelli [41] observed a similar increase in the range of $\delta^{18}\text{O}$ for altered relative to unaltered specimens and showed that alteration of carbonate in belemnites corresponded with a lowering in average $\delta^{18}\text{O}$ values relative to unaltered samples. If the isotopic alteration of carbonate in fossil belemnites is analogous to that of carbonate in *Coryphodon* tooth enamel, then patterns of intra-tooth variations in $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ are consistent with carbonate being more susceptible than phosphate to oxygen isotope exchange reactions with diagenetic fluids. Furthermore, it becomes clear that the simple existence of intra-tooth variations in $\delta^{18}\text{O}$ cannot be used as definitive evidence for a lack of isotopic alteration of either phase.

Regardless of the extent to which carbonate oxygen may have been more altered than phosphate oxygen, in neither case does diagenesis appear to have had a major effect on records of $\delta^{18}\text{O}$ change over time. For both phases, offsets in $\delta^{18}\text{O}$ are observed between *Coryphodon* and gar samples from each land mammal zone (Figs. 2 and 3). These offsets represent the behavioral and physiological differences between the two animals when they were living. In addition, temporal changes in carbonate $\delta^{18}\text{O}$ of both *Coryphodon* and gar mirror those of phosphate almost exactly. The implication is that the $\delta^{18}\text{O}$ of any carbonate and/or phosphate formed during early diagenesis still tracks that of local precipitation, and that once these secondary minerals formed they were not overprinted by later events that involved isotopic exchange.

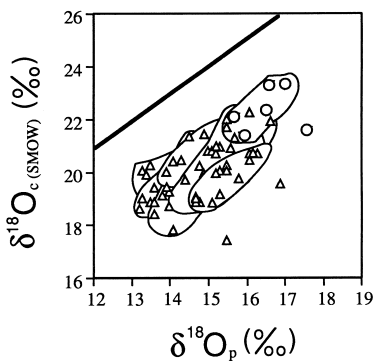


Fig. 4. $\delta^{18}\text{O}_p$ versus $\delta^{18}\text{O}_c$ values for tooth enamel of *Coryphodon* teeth. The data are grouped together (except for five outliers with exceptionally low $\delta^{18}\text{O}_c$ values). Samples from Wa-0 are shown as circles, while those from other land mammal zones are in triangles. The diagonal line represents the region where $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_c$ values of modern/unaltered tooth enamel would lie [19,40], indicating that the oxygen isotope composition of carbonate, and perhaps phosphate, in the biogenic apatite of *Coryphodon* teeth has been altered to some degree.

6.3. $\delta^{18}\text{O}_p$ and climate change during the LPTM

Coincident shifts in $\delta^{18}\text{O}_p$ for two physiologically and behaviorally different animals such as *Coryphodon* and gar (Fig. 2) are not likely to be due to independent modifications of their respective behaviors, diets, or habitats. Instead, the shifts must have their basis in a fundamental change in the $\delta^{18}\text{O}$ value of precipitation on a regional scale during the LPTM time interval, which in turn is influenced by change in climate variables such as temperature. In order to make quantitative interpretations of the

phosphate data it is necessary to (1) relate shifts in $\delta^{18}\text{O}_p$ of *Coryphodon* enamel to corresponding shifts in $\delta^{18}\text{O}_{pt}$, and (2) determine how much temperature change is represented by the $\delta^{18}\text{O}_{pt}$ shifts.

6.3.1. Relating $\delta^{18}\text{O}_p$ and $\delta^{18}\text{O}_{pt}$ values — *Coryphodon*

As described above, the relation between $\delta^{18}\text{O}$ values of biogenic apatite and ingested water is not one-to-one for mammals, and it can differ from species to species depending on diet and physiology. These differences pose a problem, especially when considering an extinct animal such as *Coryphodon*. Empirical studies of modern herbivores [20], however, indicate that with the exception of mammals living in extremely arid environments, the *slope* of the relation between the $\delta^{18}\text{O}$ value of biogenic apatite and the $\delta^{18}\text{O}$ values of ingested water for large herbivores is ~ 0.75 , regardless of diet and habitat. A slope of ~ 0.75 is also in agreement with estimates made for large herbivores using physiological models developed on the basis of known metabolic processes and the fluxes of H_2O , O_2 and CO_2 in and out of the mammal [18,20]. Therefore it is not unreasonable to assume that shifts in the $\delta^{18}\text{O}_p$ values of *Coryphodon* between land mammal zones were also about 75% of the shifts in the $\delta^{18}\text{O}$ value of ingested water (Table 2).

It is more problematical to demonstrate that shifts in the $\delta^{18}\text{O}$ value of ingested water can be equated to shifts in the $\delta^{18}\text{O}$ value of local precipitation. This difficulty arises because the proportion of water ingested by *Coryphodon* from sources that do not track precipitation directly, such the leaves of land plants, is not known. In the absence of detailed information regarding where *Coryphodon* obtained its water, we must assume that shifts in the $\delta^{18}\text{O}$ value of ingested water calculated above are equivalent to the shifts in local $\delta^{18}\text{O}_{pt}$ values (Table 2).

6.3.2. Relating changes in $\delta^{18}\text{O}_{pt}$ values to changes in temperature

The relation between $\delta^{18}\text{O}_{pt}$ and MAT [9,10] can be used to infer the temperature change associated with the shifts in $\delta^{18}\text{O}_{pt}$ values estimated above. As an inland and middle-latitude ($\sim 45^\circ\text{N}$) location during the Paleogene, the Bighorn Basin is an ideal location for estimates of this sort to be made. There

are, however, two important caveats that must be mentioned. First, it is not known with any certainty if the present-day slope of the global $\delta^{18}\text{O}_{pt}$ –MAT relation of $\sim 0.58\text{‰}/^\circ\text{C}$ that exists today for middle latitudes is the same as that appropriate for the Paleogene given the different distribution of land, sea, and ice, and the warmer oceans that existed during that period. If the relation is significantly different, estimates of temperature change will be inaccurate. Secondly, the present-day $\delta^{18}\text{O}_{pt}$ –MAT relation is characterized by scatter in $\delta^{18}\text{O}_{pt}$ of several per mil at any given temperature due to the regional influence of climate variables other than temperature on $\delta^{18}\text{O}_{pt}$ values. It is therefore possible that climate change may cause $\delta^{18}\text{O}_{pt}$ values to change for reasons other than surface temperature. In order to determine the effect of these factors during the Paleogene more precisely, it will be necessary to analyze animal remains from sites located over a range of paleolatitudes. By doing so, a more quantitative description of latitudinal gradients in temperature and $\delta^{18}\text{O}_{pt}$ values during this time can be constructed.

Until this work is done, however, we will rely on the present-day average $\delta^{18}\text{O}_{pt}$ –MAT relation of $0.58\text{‰}/^\circ\text{C}$ to infer temperature change between land mammal zones. The results of these calculations are presented in Table 2. The largest positive shift is $\sim 4^\circ\text{C}$ between Cf-2 and Wa-0, which is similar to the estimated magnitude of warming of high-latitude oceans [2]. This increase is immediately followed by a gradual fall of $\sim 6^\circ\text{C}$ to a cool episode represented by analyses of the Wa-4 sample. Although only one *Coryphodon* tusk from this zone was analyzed, the data obtained for this tusk support the findings of Wing et al. [42], who suggested on the basis of floral assemblages that a cooling episode followed the LPTM in the Bighorn Basin. Because the inferred warming therefore appears to be restricted to the $\sim 20,000$ years represented by the Wa-0 land mammal zone time interval, it is also of the same duration as the warming of high-latitude oceans [2]. Following this cooling, there was a return to pre-LPTM temperatures at the time corresponding to the Wa-6 land mammal zone.

6.3.3. Changes in temperature — *gar*

There is an alternative method of determining temperature change between land mammal zones

that can be compared with the above estimates. It does not rely on the present-day $\delta^{18}\text{O}_{\text{pt}}$ -MAT relation, and thus provides a check on the temperature records presented above. In this approach, $\delta^{18}\text{O}_{\text{pt}}$ shifts inferred from *Coryphodon* data are assumed to be the same as concurrent shifts in the $\delta^{18}\text{O}$ of river water. Given these values, it is then possible to use the average $\delta^{18}\text{O}_{\text{p}}$ values of gar from each land mammal zone with the phosphate paleothermometer of Longinelli and Nuti [43] to estimate associated changes in the temperature of the river over time [11]. As illustrated in Table 2, temperature changes estimated in this manner mirror the Wa-0 warming and Wa-4 cooling trends estimated using the *Coryphodon* data and the present-day $\delta^{18}\text{O}_{\text{pt}}$ -MAT relation, although the magnitudes of the shifts are slightly different.

The reasons that estimated temperature changes are different using the two different methods are complex, and may be related to the number of assumptions that had to be made, or to the lack of resolution resulting from the limited number of sampled *Coryphodon* tusks. Thus $\delta^{18}\text{O}_{\text{p}}$ values cannot be used to provide exact determinations of temperature change given the information currently available to us. Nevertheless, the similarity in magnitude and duration of our temperature estimates compared to those deduced from the marine record provide credence for the conclusion that $\delta^{18}\text{O}_{\text{p}}$ data do provide strong evidence for temperature change on the order of several degrees in the Bighorn Basin region during the LPTM.

6.4. Summary and conclusions

This study provides the first evidence that isotopic analysis of phosphate in tooth enamel and ganoine can provide a reliable oxygen isotope record at least as far back as the early Cenozoic. An intra-tooth and multi-species approach to determine $\delta^{18}\text{O}$ values of precipitation during different time periods is promising because it reduces the possibility that observed change in $\delta^{18}\text{O}_{\text{p}}$ values is due to the alteration of the behavior, diet or habitat of a single animal over time or to diagenesis. Analyses of material from animals that are physiologically and ecologically very different, such as *Coryphodon* and gar, are most useful in this regard.

Carbon isotope stratigraphy and magnetostratigraphy were used to correlate the Wa-0 land mammal zone in the Bighorn Basin with the LPTM observed in isotopic analyses of ocean sediment cores. The observed shift to higher $\delta^{18}\text{O}_{\text{p}}$ values of both *Coryphodon* teeth and gar scales during the LPTM is strongly indicative of changes in regional $\delta^{18}\text{O}_{\text{pt}}$ values and hence climate change. Assuming that the global relation between $\delta^{18}\text{O}_{\text{pt}}$ values and temperature during the Paleogene was similar to that of today, and that animal diets did not change dramatically, the oxygen isotope data indicate that the North American interior experienced a brief warming event at this time. This implied warming is similar in magnitude and duration to that found in high-latitude marine environments, and also provides compelling evidence that the coincident terrestrial biotic turnover observed during the LPTM was indeed a result of climatic change.

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