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Diagenetic effects on the oxygen isotope composition of bones of dinosaurs and other vertebrates recovered from terrestrial and marine sediments

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Abstract: Assessing effects of diagenesis on oxygen isotope composition of bone is essential to its use in reconstructing habitats and lifestyles of ancient vertebrates. These effects are a matter of controversy, particularly in the case of extinct animals such as dinosaurs. To investigate the effects of diagenesis on isotopic composition of fossil bone, bone samples from both marine and terrestrial Campanian sediments from Alberta, Canada, have been analysed. The isotopic compositions of oxygen ($\delta^{18}O_{SMOW}$) were determined in bones sampled from articulated skeletons of exclusively terrestrial animals recovered from the terrestrial Dinosaur Park Formation, and compared with bones from the marine Bearpaw Formation. The articulated skeleton of an exclusively terrestrial dinosaur (hadrosaur) found in marine sediments yielded similar $\delta^{18}O$ values for both structural carbonate and phosphate fractions (mean $\delta^{18}O_{SMOW}$ values 22.6‰ and 16.9‰, respectively) in bone to marine reptiles (mosasaurs) recovered from the same locality (mean $\delta^{18}O_{SMOW}$ values 24.2‰ and 17.3‰, respectively). The isotopic composition of both skeletons recovered from marine sediments was significantly more positive than that of articulated hadrosaur skeletons recovered from contemporaneous terrestrial sediments (mean phosphate $\delta^{18}O_{SMOW}$ value 12.9‰), and outside the range of phosphate $\delta^{18}O_{SMOW}$ values previously reported for terrestrial dinosaur skeletons (*c.* 9–14‰). These data suggest that the isotopic composition of oxygen in the phosphate and structural carbonate ions in the bone apatite was altered during diagenesis and can be used for neither palaeoclimate nor physiological reconstruction.

Keywords: bones, isotope, oxygen, dinosaurs, diagenesis.

The stable isotope composition of biominerals provides a record of the isotopic composition of dietary and environmental sources, potentially modified through physiological fractionation. Stable isotope analyses of biominerals have been used to study a wide range of ecological, biological and physiological processes (e.g. Hobson 1999; Kohn & Cerling 2002). Stable isotope analyses provide data pertaining to the behaviour of individual animals that are otherwise impossible to obtain for extinct taxa. Only the most robust biominerals survive into the fossil record, and the range of isotopic systems available to study is limited. Most analyses of stable isotopes in fossil vertebrate biominerals have therefore focused on the stable isotopes of carbon and oxygen.

The isotopic composition of oxygen in bone is a function of physiology and ingested water (Longinelli 1984; Luz & Kolodny 1985). For extinct taxa, it has been argued that variations in the isotopic composition of oxygen ($\delta^{18}O$) in fossil bones within a single skeleton could provide information about the animal's physiology (Barrick & Showers 1994). Moreover, if the physiology of the animal is known, then the isotopic composition of the local surface water could be deduced. Analysis of fossil bone could therefore provide information on either the environment or the climate at the time of bone formation (Bryant *et al*. 1994; Bryant & Froelich 1995; Kohn 1996).

The physical and chemical nature of bone, however, may be altered significantly during diagenesis (e.g. Kohn *et al*. 1999; Trueman 1999; Trueman & Tuross 2002). Thus the $\delta^{18}O$ value may reflect diagenetic processes rather than a primary biogenic signal (Nelson *et al*. 1986; Iacumin *et al*. 1996; Kolodny *et al*. 1996). This view is challenged by other studies (e.g. Barrick & Showers 1995; Barrick *et al*. 1997; Showers & Barrick 2002) that report isotopic variations between and within bones from single skeletons. It is argued in these studies that such variations are unlikely to be the product of diagenetic alteration, and must relate to physiological factors (e.g. thermoregulation). At present the debate is unresolved, and the information locked up in the $\delta^{18}O$ signal of fossil bone remains difficult to interpret. This study aims to test whether the biogenic $\delta^{18}O$ signal in bone is altered during diagenetic recrystallization of bone mineral.

Testing stability of the oxygen isotope record of bone apatite

Water undergoes oxygen isotopic fractionation during changes in phase such as evaporation or condensation. As fresh water is derived from evaporation of seawater, there is a distinct difference in the isotopic proportions of oxygen present in fresh water compared with sea water (e.g. Dansgaard 1964; Gat 1981).

The $\delta^{18}O$ of ocean water is relatively constant as the ocean acts as a large isotopic reservoir (e.g. Faure 1986), and is given the mean value of zero when referenced on the V-SMOW scale (Vienna-Standard Mean Ocean Water) As the isotopic composition of water varies with salinity, animals in exclusive contact with fresh water such as terrestrial herbivores produce bone apatite with a lighter oxygen isotopic ratio (more negative $\delta^{18}O$

value) than contemporaneous animals in exclusive contact with marine waters (Nelson *et al*. 1986).

After death, any diagenetic growth of apatite within the animal's bone will inherit an isotopic signal controlled by the local pore water. Diagenetic minerals that form in exclusive contact with meteoric pore waters typically have more negative $\delta^{18}O$ values than the same minerals forming in marine settings. As noted by Kolodny *et al*. (1996), if bones from two animals that had similar biogenic $\delta^{18}O$ values experience diagenesis in environments with distinct isotopic compositions of pore water, it should be possible to determine the extent of diagenetic alteration. Any divergence in the isotopic signal of the fossil apatite between the two animals would be expected to reflect the influence of the environment of burial.

Vertebrate assemblages from the Upper Cretaceous non-marine Dinosaur Park Formation and the coeval marine Bearpaw Formation of Alberta, Canada provide the ideal geological setting to investigate the effects of diagenesis on the primary isotopic signatures of bone (Fig. 1). The Dinosaur Park Formation contains abundant remains of exclusively terrestrial herbivorous dinosaurs. In addition, partial to complete dinosaur skeletons are occasionally found in marine sediments of the Bearpaw Formation (e.g. Horner 1979). These apparently represent the carcasses of terrestrial animals that were washed out to sea (see Schwimmer 1997). The Dinosaur Park Formation therefore yields dinosaur specimens that were buried in sediments with pore waters with broadly similar isotopic composition to the animal's ingested water, whereas dinosaurs recovered from the Bearpaw Formation were buried in sediments with pore waters that were very different from those typically encountered in the animal's original habitat. The palaeogeographical position of the Dinosaur Provincial Park during the Campanian was *c*. 60°N. As the $\delta^{18}O$ value of ocean water has not altered significantly since the Campanian (Shackleton & Kennett 1975), a significant difference between $\delta^{18}O$ values of Campanian fresh water and sea water is to be expected at these palaeolatitudes. This difference will be reflected in any biogenic or diagenetic minerals that formed in contact with both fresh and marine waters.

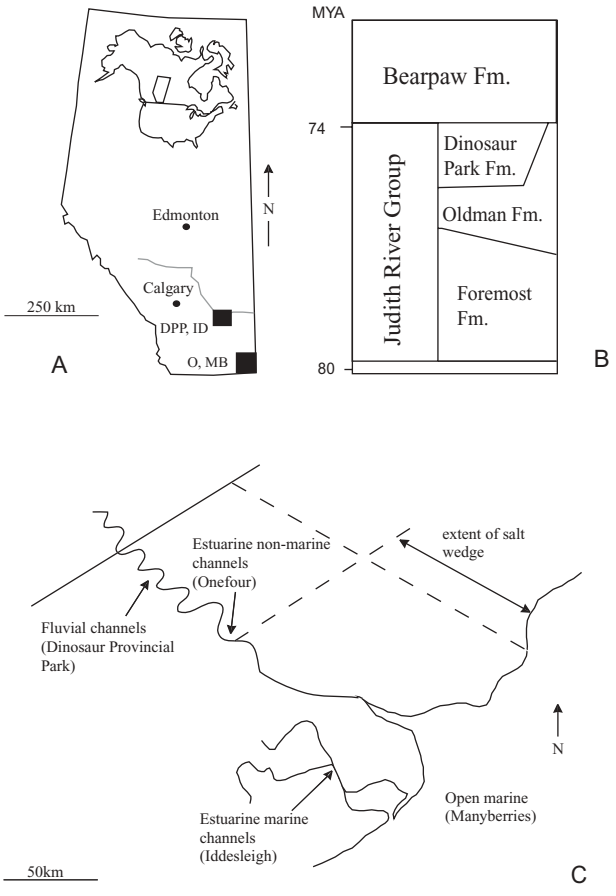

Fig. 1. Location (**a**), stratigraphy (**b**), and simplified palaeogeographical model (**c**) of study area. Samples were taken from Dinosaur Provincial Park (DPP), Iddesleigh (ID), Onefour (O) and Manyberries (MB) in Alberta, and were derived from the Campanian Bearpaw and Dinosaur Park Formations. Study area represents a transect from freshwater fluvial conditions in the Dinosaur Park Formation, to open marine conditions in the Bearpaw Formation. All figures after Eberth (1996).

Geological setting

The sedimentology, taphonomy and palaeoecology of the Dinosaur Park Formation have been studied in detail (Eberth & Brinkman 1997; Wood *et al*. 1988; Brinkman 1990; Eberth 1990, 1996; Eberth & Hamblin 1993; Eberth *et al*. 2001). The Dinosaur Park Formation forms an eastward-thinning clastic wedge that reflects deposition on a low-slope coastal plain bordering the Campanian-age Interior Seaway (Fig. 1c). The Dinosaur Park Formation was deposited during a transgressive interval of the Interior Seaway. At this time, shorelines advanced westward from the interior of Saskatchewan to SW Alberta. The 80 m thick section of the Dinosaur Park Formation preserved at Dinosaur Provincial Park consists of a lower sandy zone of strictly alluvial origin and an upper, muddy succession of alluvial and estuarine origin. The Dinosaur Park Formation is sharply overlain by marine mudstones of the Bearpaw Formation.

Characteristic facies of the Dinosaur Park Formation include 1–10 m thick, straight-to-meandering palaeochannel deposits consisting of trough cross-bedded sandstone, inclined heterolithic strata, carbonaceous drapes, *in situ* and reworked siderite, and fossils of articulated, associated and disarticulated vertebrates, including dinosaurs (Eberth & Hamblin 1993). Near the top of this unit, a tidally influenced and mixed fresh–brackish–marine succession includes mud-filled incised valleys, marine flooding surfaces, and a variety of trace fossils, palynomorphs, microfossils, and plant and vertebrate fossils (Eberth 1996; Eberth *et al*. 2001).

Fossils of dinosaurs occur throughout the Dinosaur Park Formation section and exhibit preservational states that range from disarticulated bones and teeth (single occurrences and bonebeds) to fully articulated skeletons with skin impressions (Eberth *et al*. 2001). The sheer abundance of dinosaur fossils in sediments of the Dinosaur Park Formation exposed within Dinosaur Provincial Park, and the broad variety of their taphonomic states and facies associations suggest that most of the animals lived close to where they were finally buried (Eberth 1990).

In SE Alberta, the Bearpaw Formation consists largely of brown sandy mudstones and minor sandstone lenses and sheets, and yields an estuarine to fully marine fossil assemblage of microfossils, ammonites, marine molluscs and crustaceans, fish and marine reptiles (e.g. Russell & Landes 1940; Russell 1993). As mentioned above, partial to complete dinosaur skeletons are occasionally found in this unit (Horner 1979).

To test for diagenetic alteration of the biogenic $\delta^{18}O$ signal in fossil bone, the isotopic composition of apatite in bones from articulated skeletons of terrestrial animals recovered from terrestrial fluvial sediments (Dinosaur Park Formation) and con-

temporaneous marine sediments (Bearpaw Formation) was determined. Only articulated skeletons were used, to minimize the possibility that bones were reworked from older horizons. Samples were taken from hadrosaurs, dinosaurs with exclusively terrestrial life habitats, so that all animals lived in contact with fresh waters. Different species of hadrosaurs probably occupied similar ecological niches, so interspecific variation in biogenic isotopic signals is expected to be relatively low. Articulated skeletons of exclusively terrestrial animals are rare in marine sediments, and a single hadrosaur skeleton was sampled from marine sediments. Bones were also sampled from articulated skeletons of exclusively marine animals (mosasaurs) found in the same marine sediments as the allochthonous hadrosaur skeleton. Isolated bones from terrestrial herbivores recovered from estuarine channels were also sampled. For each bone, samples of cortical and spongy (cancellous) bone were taken. Previous studies (e.g. Barrick *et al*. 1997) found that $\delta^{18}O$ values may be altered more extensively in porous cancellous bone than in dense compact cortical bone as a result of the greater pore volume available for addition of diagenetic apatite.

Little is known about the possible variation in isotopic composition of body water of contemporaneous dinosaur taxa. To provide comparative data, a compilation of $\delta^{18}O$ values measured in the phosphate fraction of bone mineral from various Cretaceous dinosaur and reptile taxa recovered from Alberta and Montana (Barrick & Showers 1995; Barrick *et al*. 1996) was made. This dataset consists of 180 analyses of $\delta^{18}O$ values from six genera, including both herbivorous and carnivorous taxa. These animals were recovered from a wide geographical and temporal range, and thus if fossil bones preserve a biogenic isotopic signal, the variation in isotopic composition within this dataset will provide a first approximation for levels of isotopic variation both between and within diverse reptilian and dinosaurian taxa living in Cretaceous times in Alberta and Montana.

Sampling sites and analytical methods

Terrestrial fluvial sites

Three articulated hadrosaur (Ornithischia, Ornithopoda) skeletons were sampled from terrestrial fluvial sediments in the central regions of Dinosaur Provincial Park (Fig. 1c). Bone samples were recovered in the field from articulated skeletons contained within inclined bedded strata of point-bar deposits.

Estuarine sites

Disarticulated vertebrate materials were sampled from an estuarine site located near Onefour in SE Alberta (Complex MFIV-1 of Eberth 1996; Fig. 1). Sediments at this site contain a dominantly freshwater fauna, and are believed to have formed $<$100 km from the palaeoshoreline (Eberth 1996). No articulated vertebrate material was available from this site, so sampling was restricted to channel lag deposits, and consequently taxonomic identification was poor. A similar restricted sampling was undertaken at Iddesleigh (Sample MFIV-3 of Eberth 1996), with basal lag samples yielding disarticulated ceratopsian and hadrosaur remains. This site contains a restricted brackish–marine fauna, and is reconstructed at $<$50 km from the palaeoshoreline (Eberth 1996).

Marine sites

Several samples were taken from a single articulated hadrosaur skeleton recovered from the Bearpaw Formation near the town of Manyberries. Three articulated mosasaur (Mosasauridae) skeletons were also sampled at this locality. All marine samples were taken from the collections of the Royal Tyrell Museum of Palaeontology.

Analytical methods

The authigenic mineral suite developed in all bone samples was determined before preparation for isotopic analysis by light microscopy and XRD analysis. XRD analyses were performed on a Philips PW1800 diffractometer operating at 45 kV and 40 mA. The relative abundance of calcite and apatite in each sample was estimated with reference to the ratio of intensity of the (211) apatite reflection and the (104) calcite reflection after calibration with mixtures of calcite and apatite at known ratios.

Mineral separations for isotopic analysis

Apatite contains oxygen in three main lattice sites: within the phosphate ion, within the carbonate ion that substitutes for phosphate in the minerals dahllite and francolite (structural carbonate), and within the hydroxyl site (e.g. Mann 2001). In addition, fossil bones also frequently contain diagenetic calcite. The phosphate–oxygen bond is relatively strong compared with the carbon–oxygen bond, so phosphate-bound oxygen is considered to be more resistant to diagenetic alteration than carbonate-bound oxygen (e.g. Iacumin *et al*. 1996). Diagenetic calcite forms *post mortem*, and cannot reflect the original isotopic composition of the bone. The nature of diagenetic alteration can be investigated, therefore, by comparing the isotopic composition of oxygen in the carbonate and phosphate ions in fossil bone apatite, and in the carbonate ions from associated diagenetic calcite.

To determine the isotopic composition of oxygen in the structural carbonate and phosphate fractions of apatite, and in diagenetic calcite associated with fossil bones, separate samples were taken from cortical and cancellous regions of each bone, and split into two portions. One portion was reacted with phosphoric acid at 25 °C, and the CO_2 released was analysed. This fraction is dominated by diagenetic calcite (e.g. Barrick & Showers 1995) and is termed the free carbonate extraction ($\delta^{18}O_{cc}$). The other portion was treated with tri-ammonium citrate to remove diagenetic carbonate (Silverman *et al*. 1952), and further divided into two subsamples. One subsample was reacted with phosphoric acid at 90 °C, and the CO_2 released was analysed. CO_2 released during this reaction is derived from the structural carbonate component of carbonate apatite (McArthur *et al*. 1980), and is termed the structural carbonate extraction ($\delta^{18}O_{sc}$). The other subsample was reacted with ClF_3 using a laser, and the oxygen gas released was converted to CO_2 and analysed. This fraction contains oxygen from structural carbonate, hydroxyl and phosphate fractions of apatite. Apatite with a typical 5 wt% CO_3^{2-} substituted in the lattice contains oxygen in the phosphate, carbonate and hydroxyl anions in a ratio of *c*. 17:2:1. Consequently, the $\delta^{18}O$ value obtained by this method will be dominated by oxygen held in the phosphate anion, and $\delta^{18}O$ values are reported as the phosphate oxygen extraction ($\delta^{18}O_p$).

All sample gases were analysed on a V.G. Isotech Optima dual inlet isotope ratio mass spectrometer, and analytical precision and accuracy were monitored with laboratory and international standards. The analytical precision determined from repeated standard analysis was $<\pm$0.1‰ (1σ) for phosphoric acid digestions and $<\pm$0.2‰ (1σ) for laser fluorination methods.

Results

All samples contained authigenic calcite, with minor aragonite, hematite and siderite present in some cases. The principal apatite mineral present was carbonate fluorapatite (francolite), with peak intensities in descending order of (211,112), 300, 202. Authigenic calcite made up no more than *c*. 5% of the total sample before cleaning.

$\delta^{18}O_{V\text{-}SMOW}$ signals determined from diagenetic calcite, structural carbonate and phosphate components of the fossil bones studied are shown in Table 1 and Figure 2. $\delta^{18}O$ values in phosphate range from 9.5 to 13.2‰ (mean 12.3‰) in bones recovered from terrestrial environments, from 7.9 to 13.6‰ (mean 11‰) in estuarine environments, and from 16.1 to 18.1‰ (mean 17.2‰) in marine environments. $\delta^{18}O$ values in apatite structural carbonate range from 18.6 to 20.2‰ (mean 19.3‰) in bones recovered from terrestrial environments, from 18.9 to 22‰ (mean 19.8‰) in estuarine environments, and from 20.4 to 26.8‰ (mean 23.3‰) in marine environments. Diagenetic calcite recovered from fossil bones yielded $\delta^{18}O$ values from 18.5 to 21.2‰ (mean 20.3‰) in bones recovered from terrestrial environments, from 18.9 to 21.7‰ (mean 20.3‰) in estuarine environments, and from 23.4 to 25.7‰ (mean 24.4‰) in marine environments. Each sampled component shows more positive $\delta^{18}O$ signals in bones and diagenetic calcite recovered from marine sediments compared with those recovered from terrestrial sediments. Diagenetic calcite recovered from estuarine localities closer to the palaeoshore shows more positive $\delta^{18}O$ values than diagenetic calcite recovered from estuarine channels showing greater freshwater influence. This distinction is not clear in $\delta^{18}O$ values recovered from phosphate or structural carbonate fractions. The samples from the articulated (exclusively terrestrial) hadrosaur skeleton recovered from marine sediments yield $\delta^{18}O$ values similar to those found in exclusively marine vertebrates.

Table 1. *Isotopic composition of oxygen (‰ SMOW) in structural carbonate and phosphate fractions of fossil bone apatite, and in diagenetic calcite (free carbonate) associated with fossil bones*

		Free carbonate		Structural carbonate		Phosphate	
Sample code	Environment	Cortical	Cancellous	Cortical	Cancellous	Cortical	Cancellous
TF-DPF-'DB'	TF	20.8	21.2	20.2	18.9	13.2	12.8
TF-DPF-H	TF	20.3	18.5	19.3	18.6	9.5	n.d.
TF-DPF-T	TF	20.8	20.3	20.0	18.9	13.1	12.7
ECT-98-08-A-1	ENM	19.6	n.d.	n.d.	n.d.	12.1	11.0
ECT-98-08-B	ENM	19.9	19.8	18.9	19.7	9.3	11.2
ECT-98-08-C	ENM	19.8	18.9	19.6	19.3	11.1	11.3
ECT-98-01	EM	20.7	21.6	20.1	22.0	12.0	13.6
ECT-98-03-1	EM	21.7	21.1	19.1	19.8	11.0	7.9
TMP-83-64-3-1&2	M	n.d.	n.d.	20.4	n.d.	n.d.	n.d.
TMP-83-64-3-114	M	24.3	24.1	23.3	22.8	16.1	17.7
TMP-83-64-3-35	M	n.d.	n.d.	23.4	23.1	n.d.	n.d.
TMP-92-74-1-1	M	25.7	23.4	23.8	22.7	17.3	16.2
TMP-93-3-39-1-1	M	24.6	n.d.	23.6	26.8	17.7	18.1

Environmental code specifies the palaeoenvironmental interpretation of the sediments from which the bones were recovered: TF, terrestrial fluvial; ENM, estuarine, non-marine influenced; EM, estuarine, marine influenced; M, open marine. Specimen TMP-83-64-3 is a terrestrial animal (hadrosaur dinosaur) recovered from marine sediments. n.d., not determined.

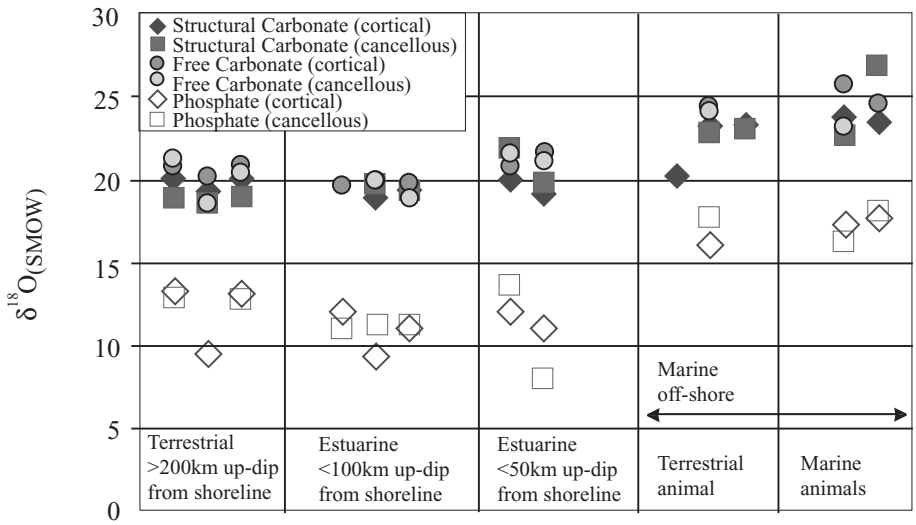

Fig. 2. Plot of isotopic composition of oxygen in structural carbonate ($\delta^{18}O_{sc}$) and phosphate ($\delta^{18}O_p$) fractions of bone apatite, and diagenetic calcite ($\delta^{18}O_{cc}$) recovered from fossil bones. Samples recovered from various sedimentary environments representing a salinity gradient in the Dinosaur Park Formation and coeval Bearpaw Formation, south–central Alberta. Reconstructed salinity of burial pore waters increases from freshwater fluvial on the left-hand side of the plot, to marine on the right. Isotopic values obtained from bones from an exclusively terrestrial organism (hadrosaur dinosaur) recovered from marine sediments are separated from those recovered from *in situ* marine mosasaur bones. Distance fields relative to the palaeoshoreline given by Eberth (1996, p. 473), Eberth & Brinkman (1997, p. 48) and Eberth (1996).

Mean $\delta^{18}O$ values in bones from the hadrosaur are 16.9‰, 22.6‰ and 24.2‰ in phosphate, structural carbonate and diagenetic calcite, respectively; mean $\delta^{18}O$ values in exclusively marine vertebrates are 17.3‰, 24.2‰ and 24.6‰ in phosphate, structural carbonate and diagenetic calcite, respectively. One sample of cortical bone (TMP-83-64-3-1&2) from the hadrosaur retains a relatively negative isotopic value (20.4‰) in the structural carbonate fraction of bone apatite.

Discussion

The isotopic composition of bone from an exclusively terrestrial animal (hadrosaur dinosaur) recovered from marine sediments is indistinguishable from that of associated exclusively marine animals (mosasaurs), and significantly different from that of contemporaneous terrestrial animals (hadrosaur dinosaurs) preserved in terrestrial sediments. These data strongly suggest that the isotopic composition of oxygen in both phosphate and structural carbonate fractions of bone apatite is altered during diagenesis. It is possible that the relatively high $\delta^{18}O$ values found in the phosphate fraction of bones from the single hadrosaur skeleton recovered from marine sediments reflect an unusually positive *in vivo* isotopic composition in this individual, and therefore that biogenic isotope signals are preserved. If fossil bone does preserve an unaltered biogenic signal, then one would expect all hadrosaurs to fall within the range of isotopic signals recorded for a variety of contemporaneous dinosaur taxa. With one exception, all values of $\delta^{18}O$ from dinosaurs recovered from terrestrial and estuarine sediments determined in our study lie within the range previously reported for a range of herbivorous and carnivorous terrestrial dinosaurs recovered from contemporaneous sediments in Montana and Alberta (Fig. 3). All samples recovered from open marine conditions fall outside this range, however, including samples from the hadrosaur recovered from open marine sediments. It is likely, therefore, that the unusually positive $\delta^{18}O$ values found in bones from the hadrosaur recovered from marine sediments indicate diagenetic alteration of a previous (relatively negative) terrestrial biogenic signal. A similar conclusion was reached by Nelson *et al*. (1986). It follows that all fossil bones are similarly affected by diagenesis, and therefore that the relatively low levels of isotopic variation seen in fossil dinosaur and reptile bones from Alberta and Montana reflect diagenetic recrystallization in contact with relatively homogeneous meteoric pore waters.

The isotopic composition of phosphate oxygen in bones recovered from estuarine sediments does not differ significantly from that in bones recovered from terrestrial settings (mean $\delta^{18}O_p$ values are 11‰ in bones from estuarine sediments and 12.3‰ in bone from terrestrial sediments). This suggests that bones recovered from estuarine settings do not reflect the influence of saline waters. All bones recovered from estuarine environments, however, were disarticulated remains recovered from lag deposits. These bones may have been reworked from previous depositional settings in contact with meteoric ground waters. The isotopic composition of diagenetic calcite recovered from fossil bone is higher in bones recovered from the Iddesleigh locality. Sediments from this locality yield a mixed freshwater and saline fauna (Eberth 1996). Diagenetic calcite in these bones formed in contact with mixed fresh and saline waters, and therefore shows $\delta^{18}O$ values intermediate between 'end-member' values from terrestrial and marine localities. Structural carbonate (but not phosphate) $\delta^{18}O$ values are also intermediate between freshwater and marine-water end-members, indicating isotopic exchange between apatite structural carbonate and pore waters after the initial recrystallization of bone apatite.

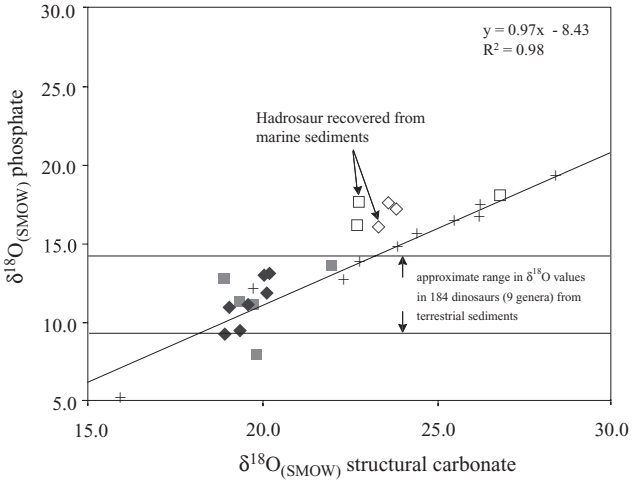

Fig. 3. Cross plot of structural carbonate $\delta^{18}O$ ($\delta^{18}O_{sc}$)and phosphate $\delta^{18}O$ ($\delta^{18}O_p$) values of fossil bones from Cretaceous sediments from Alberta, together with the biogenic equilibrium relationship between $\delta^{18}O_{sc}$ and $\delta^{18}O_p$ determined from analyses of modern mammals (Iacumin *et al*. 1996). Filled symbols indicate samples recovered from terrestrial fluvial or estuarine environments; open symbols indicate samples recovered from open marine environments. Values obtained from hadrosaur remains recovered from marine sediments are arrowed. Linear regression on $\delta^{18}O_{sc}$ and $\delta^{18}O_p$ values determined from analyses of fossil bones yields the relationship $\delta^{18}O_p = 1.19 \times \delta^{18}O_{sc} - 11.8$ ($R^2 = 0.7$). Boxed area indicates the range of $\delta^{18}O_p$ values of fossil dinosaur bones from Cretaceous sediments from Montana and Alberta (Barrick & Showers 1995; Barrick *et al*. 1996). It should be noted that all dinosaur bones recovered from marine sediments fall outside the previously reported range of $\delta^{18}O_p$ values of dinosaur bones from terrestrial sediments.

The free carbonate fraction is dominated by calcite that probably precipitated during early diagenesis (Trueman *et al*. 2002), in contact with diagenetic pore water. The isotopic composition of calcite in our samples varies from 18 to 26‰ (SMOW). Pore water in equilibrium with this calcite (calculated using the fractionation equation of O'Neil *et al*. (1969), and an assumed temperature of 20 °C) ranges from −7‰ SMOW in freshwater settings to −2‰ SMOW in marine settings, reflecting the range between marine and terrestrial water conditions. The isotopic composition of Cretaceous sea water has been estimated as −1‰ SMOW (Shackleton & Kennett 1975).

The isotopic composition of phosphate in our samples ranges from 9 to 18‰ SMOW. Pore water in equilibrium with these measured $\delta^{18}O_p$ values (using the phosphate fractionation equation of Longinelli & Nuti (1973) modified by Friedman & O'Neil (1977), and a temperature of 20 °C) ranges from −13‰ to −5‰ SMOW. Evidently the phosphate and diagenetic calcite values do not reflect isotopic equilibrium with the same pore water source. The phosphate fraction of these fossil bones reflects a major influence of low $\delta^{18}O$ fresh waters in comparison with the fluid associated with the bone during diagenesis. It is possible that these low $\delta^{18}O$ values reflect a remnant biogenic signal, and hence that bone phosphate contains both biogenic apatite and apatite forming in isotopic equilibrium with early diagenetic pore waters. A similar result was noted during burial of fish remains (Kolodny & Luz 1991), and in fossil bone (Nelson *et al*. 1986).

There is a significant co-variation between $\delta^{18}O$ in apatite structural carbonate and diagenetic calcite ($r^2 = 0.84$, Fig. 4). This co-variation strongly suggests that there is no difference in fractionation of oxygen between water and diagenetic calcite, nor between water and apatite structural carbonate. The isotopic composition of both diagenetic calcite and apatite structural carbonate therefore appears to reflect diagenetic pore-water values. The relationship between $\delta^{18}O$ values in diagenetic calcite and the phosphate fraction of apatite is weaker, however, again suggesting that the $\delta^{18}O$ value of phosphate-bound oxygen reflects both diagenetic and original biogenic components.

These data suggest that the isotopic evolution of bone mineral in the Cretaceous Dinosaur Park and Bearpaw Formations of southern Alberta occurred in two stages. Initially, growth of authigenic apatite occurred within bones in isotopic equilibrium with local pore waters. The isotopic composition of these recrystallized bones is therefore a mixture between two end-member compositions, one biogenic and one diagenetic. Subsequently, the structural carbonate fraction of recrystallized bone apatite underwent further later diagenetic exchange. In marine environments, isotopic exchange with fluids of meteoric origin (or at elevated temperatures) yielded late diagenetic carbonate with relatively negative $\delta^{18}O$ values, and therefore decreased the isotopic separation between structural carbonate and phosphate fractions in fossil bone apatite.

These observations are consistent with current models of bone diagenesis, which suggest that bones preserve their morphological features after early diagenetic growth of apatite within bone pore spaces that in life are occupied by collagen fibrils (Hubert *et al*. 1996; Kolodny *et al*. 1996; Trueman & Martill 2002). These models suggest that *c*. 30% of the volume of a fossil bone may be diagenetic apatite. Fossil bones therefore contain both biogenic apatite deposited *in vivo* in contact with the body fluid, and additional diagenetic apatite that occludes pore space. As diagenetic growth of authigenic apatite continues within a bone, the isotopic composition of the whole bone will trend towards a purely diagenetic signal.

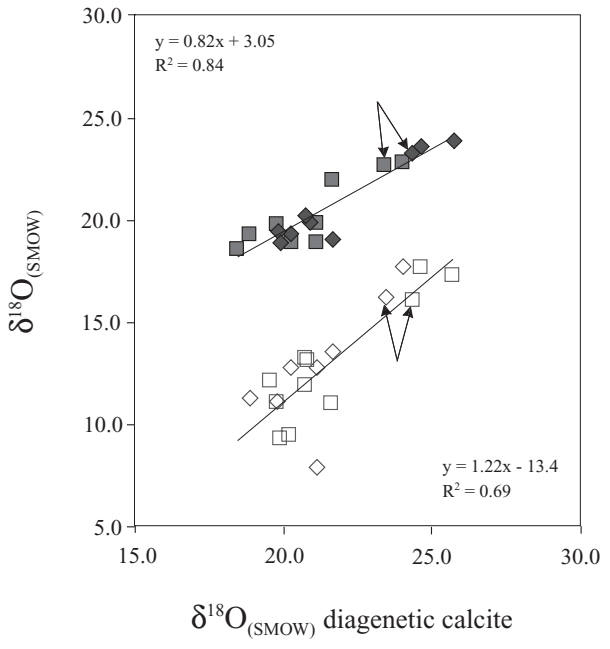

Fig. 4. Relationship between $\delta^{18}O$ values in diagenetic calcite and (1) structural carbonate (filled symbols), and (2) phosphate (open symbols) in fossil bones from Cretaceous sediments from Alberta. Values obtained from hadrosaur remains recovered from marine sediments are arrowed.

Conclusions

All bones investigated in this study record $\delta^{18}O$ compositions that reflect both biogenic and diagenetic components. The isotopic composition of fossil bone partially reflects the environment of burial, and does not record a pristine biogenic signal.

Diagenetic recrystallization tends to homogenize the isotopic composition of bone, therefore measurements of the variation in isotopic composition within and between bones must be taken as minimum estimates of the original biogenic variation. Inferences on palaeoclimate or environment based on the isotopic composition of bone apatite are unreliable.

These results support the conclusion that diagenesis consists of replacement, oxygen isotope exchange, and mixing of oxygen isotopes from different reservoirs rather than the simple addition of components having different oxygen isotope compositions.

Tooth enamel has long been recognized as a potentially more robust source for retrieval of biogenic isotopic signals than bone, and we suggest that a similar test to that described in this study should be attempted using enamel samples.

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