

SUPPORTING INFORMATION

Biology

Taphonomic and diagenetic pathways to protein preservation, part II: the case of *Brachylophosaurus canadensis* specimen MOR 2598

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This supplement provides: (1) additional details on our LA-ICPMS methods; (2) discussion of potential tetrad effects in the left tibia of MOR 2598; (3) discussion of potential sequestration process that may have limited REE availability to the bones of MOR 2598; (4) discussion of potential causes for the peculiar shapes of Sc and U profiles in the left tibia of MOR 2598; (5) sources for environmental data in Figure 5 of the main text, and; (6) additional data on the trace element composition of the left tibia of MOR 2598 (Figures S1, S2). Raw transect data are provided separately in Data S1 as an Excel XLSX file.

LA-ICPMS Methodology

LA-ICPMS analyses were conducted using a New Wave UP-213 (213 nm wavelength) Nd:YAG laser coupled to a Finnigan Element2 ICPMS at the University of Maryland. The laser was operated at 2–3 J/cm² and a pulse rate of 7 Hz. Transect data were collected using a laser diameter of 30 µm moving at a scan speed of 50 µm/s, and background collection was performed prior to each reading for 20 s. NIST 610 glass was used as an external standard and elemental concentrations were calculated based on normalization to 55.8% CaO in bone apatite.

Potential Tetrad Effects in MOR 2598

Most REE uptake behavior in natural systems can be attributed to charge and radius controls on ion reactions (so-called CHARAC behavior; [1]). Non-CHARAC behavior, in which the behavior of REE ions is also influenced by the configuration of their outer electron shell [2], can produce tetrad effects, including in fossil bones (e.g., [3,4]). Spider diagrams of NASC-

normalized REE concentrations in the tibia of MOR 2598 exhibit subtle yet distinct peaks and/or deflections at europium (Eu) and holmium (Ho) (Figures 3B and 4). These diagrams are not developed into strong M-shaped profiles, but the regular deflections are still apparent. Abundant, positive Y/Ho anomalies in the external and internal cortices (Figure S1) may also be attributable to tetrad effects during uptake [4]. According to Herwartz et al. [4], preferential uptake of LREE in the external cortex may also contribute to these patterns. Abundant evidence of for fractionation in MOR 2598 (e.g., typical intra-bone fractionation trends in the by-laser-run spider diagram [Figure 4B in the main text], low concentrations of MREE and elements with low-moderate diffusivities in the middle cortex [Figure 2A,B in the main text, Data S1]) implies that fractionation was likely a major control on the development of the high Y/Ho ratios, but the clear peaks/deflections at Eu and Ho appear more likely attributable to strong tetrad effects during uptake.

Processes Which Potentially Limited REE Availability

Complexation of dissolved REE with carbonate anions is common in natural waters [5,6], especially in coastal fresh and brackish waters [7,8] due to chemical weathering [9] and the decomposition of abundant organic matter in coastal sediments [10]. Given the geologic and geochemical indications (described herein) that MOR 2598 was buried in an estuarine channel, it is therefore plausible that extensive complexation may have partially suppressed the availability of trace elements during early diagenesis. Humic acids released during the decay of plant debris in the surrounding sediments and of any residual dinosaur tissues (e.g., muscle) may also have formed complexes with dissolved REE [11], further limiting their availability for uptake by the

bone. Dissolved phosphates released from decaying organic matter [12–14] may also have scavenged REE ions from solution via coprecipitation within trace secondary phosphates in the surrounding sediments (cf. [15,16]). We were not able to test quarry sediments for trace phosphatic phases in this study, but they are almost certainly present as lowland/coastal watersheds generally contain more phosphate than upstream regions [13,17]. In the absence of such direct tests, these potential sequestration processes (carbonate complexation and/or coprecipitation with phosphate) remain speculative, but the depositional setting implies that each may have contributed to limiting the supply of trace elements within surrounding early-diagenetic pore fluids.

Potential Explanations for Sc and U Profile Shapes

Sc and U are the only trace elements examined in MOR 2598 to exhibit broad peaks in concentrations across the middle cortex (Figure 2B in the main text). The causes(s) of this are unclear. Although the internal “boundary” of their peaks (near 25 mm) spatially corresponds with a transition in histologic structure from more random Haversian bone with numerous secondary osteons (internal cortex) to denser, more organized, fibrolamellar, laminar bone (middle cortex) (see thick section inlays in Figure 2 of the main text), there is no similar apparent transition in histologic microstructure between the middle and external cortices. Lack of permineralization implies that there were no spatial contrasts in fluid flow potential either. Therefore, the only potential explanation we can advance is that simultaneous pore fluid diffusion toward the middle cortex from both outside the bone and the medullary cavity during early diagenesis may have caused heavily-fractionated groundwaters to ‘pool’ in the middle

cortex, which over time led to the development of elevated concentrations of U and other elements still abundant in solution (i.e., Sc) in this region of the cortex.

Sources for Environmental Data in Figure 5

Literature data for environmental samples in Figure 5A of the main text are as follows: river waters (green field; [18–37]); suspended river loads (dull pink field; [19,38]); groundwaters (bright pink field; [24,39–47]); lakes (purple field; [24,27,28,31,40,43,48,49]); estuaries (yellow field; [20,46,50–52]); coastal waters (light blue field; [18,20,21,32,53,54]); seawater (dark blue field; [55–73]); sea floor particles (gray field; [59,67]); marine pore fluids (orange field; [53,71,74,75]).

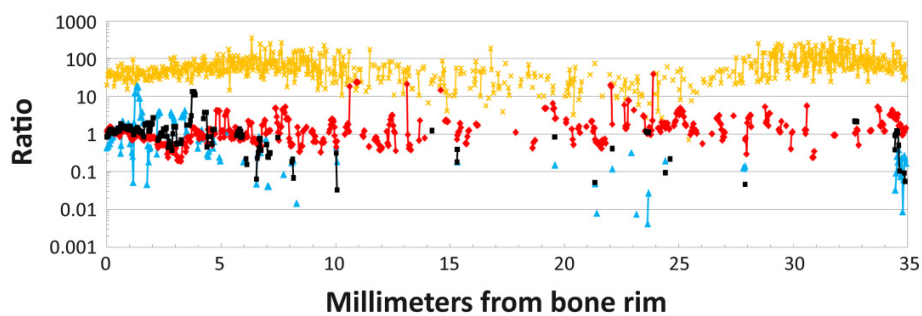


Figure S1. Intra-bone patterns of $(\text{Ce}/\text{Ce}^*)_{\text{N}}$, $(\text{Ce}/\text{Ce}^{**})_{\text{N}}$, and $(\text{La}/\text{La}^*)_{\text{N}}$ anomalies and Y/Ho ratios within the tibia of MOR 2598. $(\text{Ce}/\text{Ce}^*)_{\text{N}}$ values (red curves), $(\text{Ce}/\text{Ce}^{**})_{\text{N}}$ values (black curves), and $(\text{La}/\text{La}^*)_{\text{N}}$ anomalies (blue curves) were calculated as outlined in the Materials and Methods. Y/Ho ratio data are presented as the orange curve. Absence of $(\text{Ce}/\text{Ce}^*)_{\text{N}}$, $(\text{Ce}/\text{Ce}^{**})_{\text{N}}$, and $(\text{La}/\text{La}^*)_{\text{N}}$ anomalies occurs at 1.0.

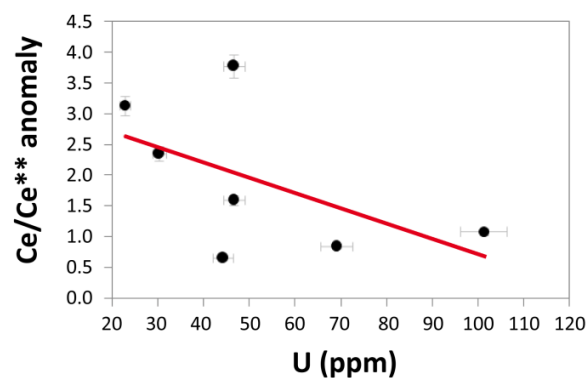


Figure S2. Cerium anomaly $(\text{Ce}/\text{Ce}^{**})_{\text{N}}$ values plotted against uranium (U) concentrations in the tibia of MOR 2598. Absence of the cerium anomaly is at a value of 1.0. Error bars, in gray, are based on analytical reproducibility of $\pm 5\%$. The trendline in red has a very poor fit ($r^2 = 0.29$), suggesting different timescales for uptake of U and Ce (according to [76]).

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