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Can fossil turtle bone apatite be used to reconstruct paleoclimates?

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INTRODUCTION

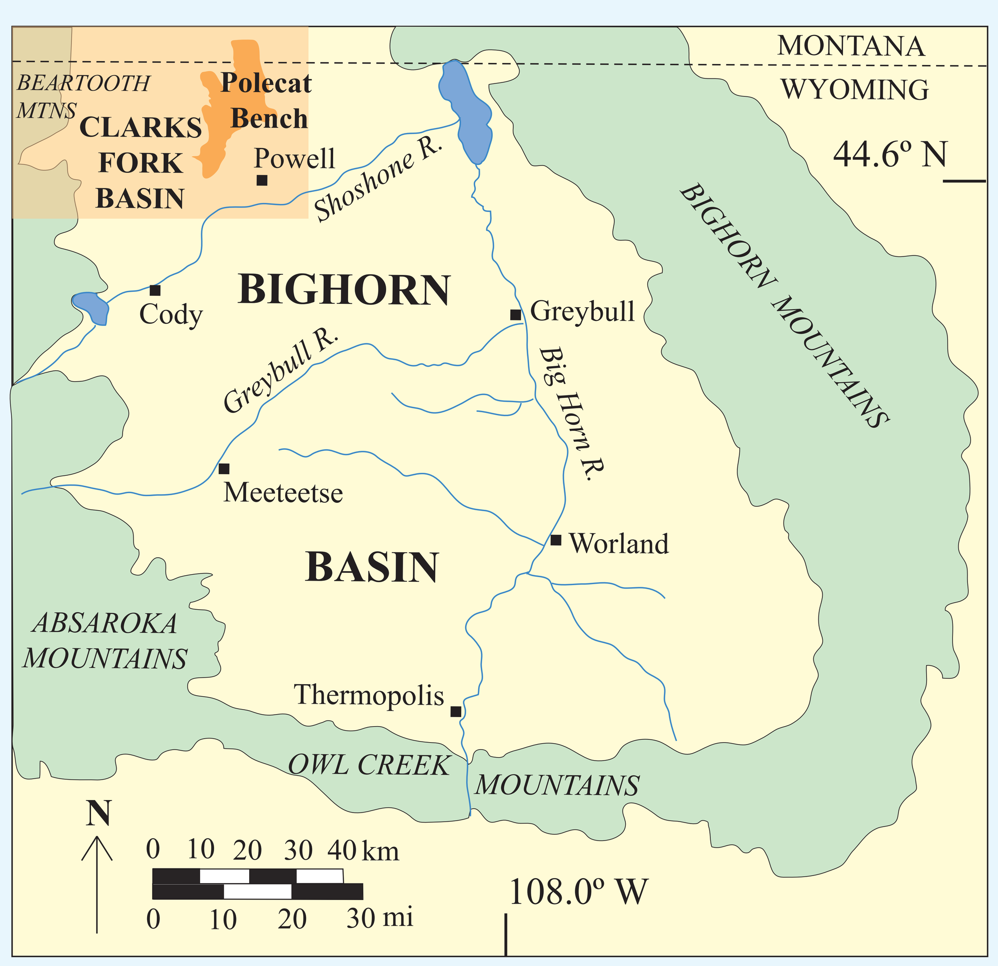
A complication to using the oxygen isotope composition ($\delta^{18}O$) of vertebrate hydroxylapatite (HA) in paleoclimate studies is the need to distinguish variation due to temporal changes in the $\delta^{18}O$ of surface waters from that due to temperature-dependent fractionation during biomineraliztion. One solution is multiple-taxon comparisons using data from coexisting homeothermic (i.e., mammals) and heterothermic animals. Fossil emydid turtles have been suggested to be potentially useful as functional homeotherms (Barrick et al., 1999) because 1) modern emydids employ behaviors, such as basking, to restrict skeletal growth a narrow temperature range, 2) their aquatic habitat constrains the isotopic variability of dietary inputs, and 3) emydids have a dense fossil record. However, because turtles lack teeth and therefore tooth enamel, sampling must focus on bone, which is potentially more susceptible to diagenetic alteration.

This study examines the oxygen isotopes from the carbonate ($\delta^{18}O_c$) and phosphate ($\delta^{18}O_p$) fractions of hydroxylapatite from co-occurring emydids and two groups of known heterotherms (crocodilians and gar) from the Paleocene and Eocene (P-E) of the Clarks Fork Basin, Wyoming. Previous isotopic studies of this area provide an extensive dataset for comparison with the results of this study. Carbonate coulometry and X-ray diffraction measurements of bone carbonate content and apatite crystallinity were performed to examine the possibility of diagenetic alteration of turtle bone.

MATERIALS AND METHODS

Turtle, crocodilian, and gar fossils used in this study come from the collections of the U. Michigan Museum of Paleontology. Approximately 10-50 mg of powdered (HA) was obtained from each specimen using a hand-held rotary drill. For analysis of $\delta^{18}O_c$, aliquots of HA powder were treated with 2-3% NaOCl to oxidize organic matter and then treated with 1 M acetic acid buffered with 1 M Ca-acetate The samples were then analyzed using a Kiel II automatic carbonate preparation device coupled to a Finnigan MAT-252 IRMS. For analysis of $\delta^{18}O_p$, 5-10 mg aliquots were each dissolved in 1 ml of 2 M HF and then neutralized with 430 ml of 10% NH_4OH and 300 ml of distilled, deionized H_2O. CaF_2 precipitate was removed through centrifugation and decantation, and 1 ml of 2 M $AgNO_3$ was added to each sample to rapidly precipitate finely crystalline Ag_3PO_4. The Ag_3PO_4 samples were then analyzed using a TC/EA coupled to a Finnigan Delta-Plus IRMS. Carbonate content of the turtle bone samples was measured through Total Inorganic Carbon coulometry. The crystallinity index (CI) of the turtle bone samples was measured through X-ray diffraction and defined according to the method of Person et al. (1995).

STUDY AREA



RESULTS

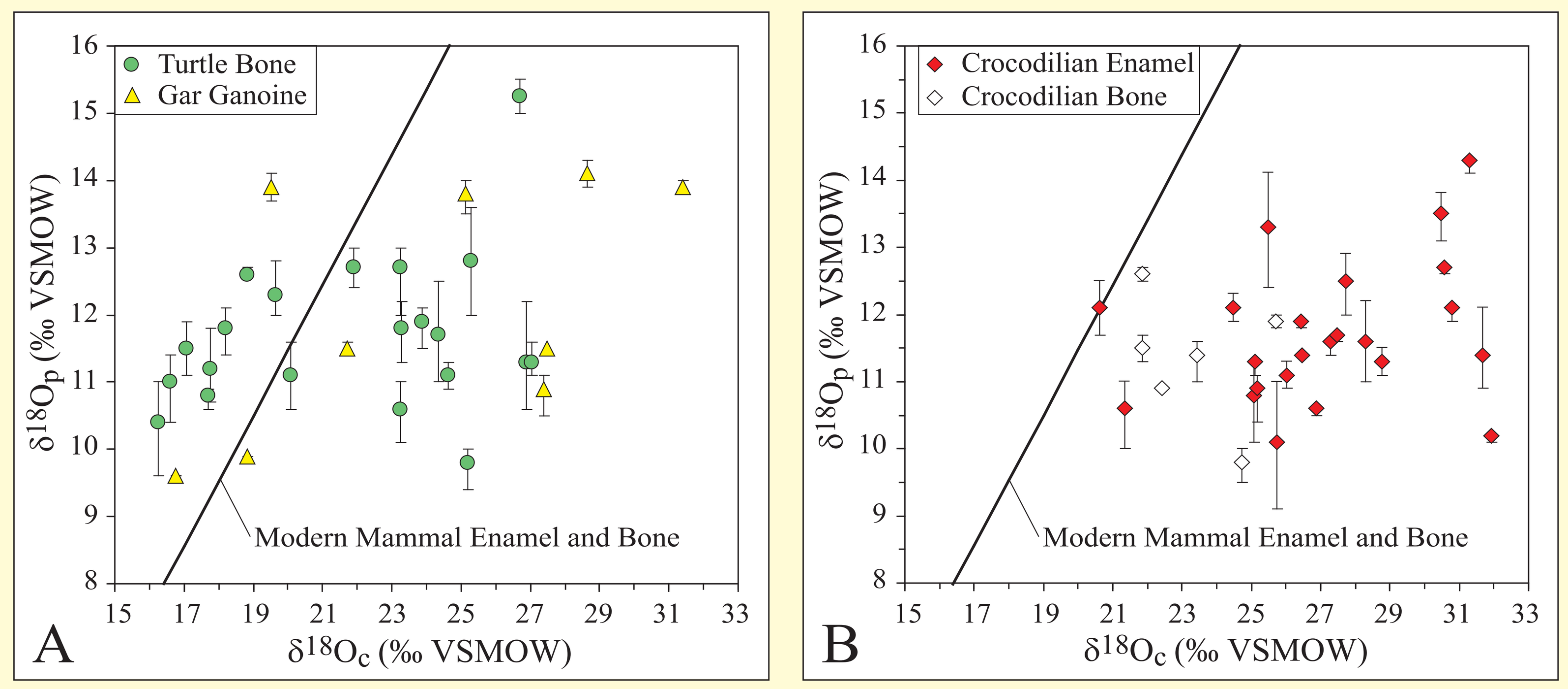


Figure 1: Unaltered bone and enamel from modern mammals exhibits a strong covariation ($r^2 = 0.98$) between $\delta^{18}O_c$ and $\delta^{18}O_p$ (Bryant et al., 1996; Iacumin et al. 1996). A lack of covariation between $\delta^{18}O_p$ and $\delta^{18}O_c$ for bone, enamel, and ganoine from this study suggests that carbonate or phosphate, or both, have been diagenetically altered.

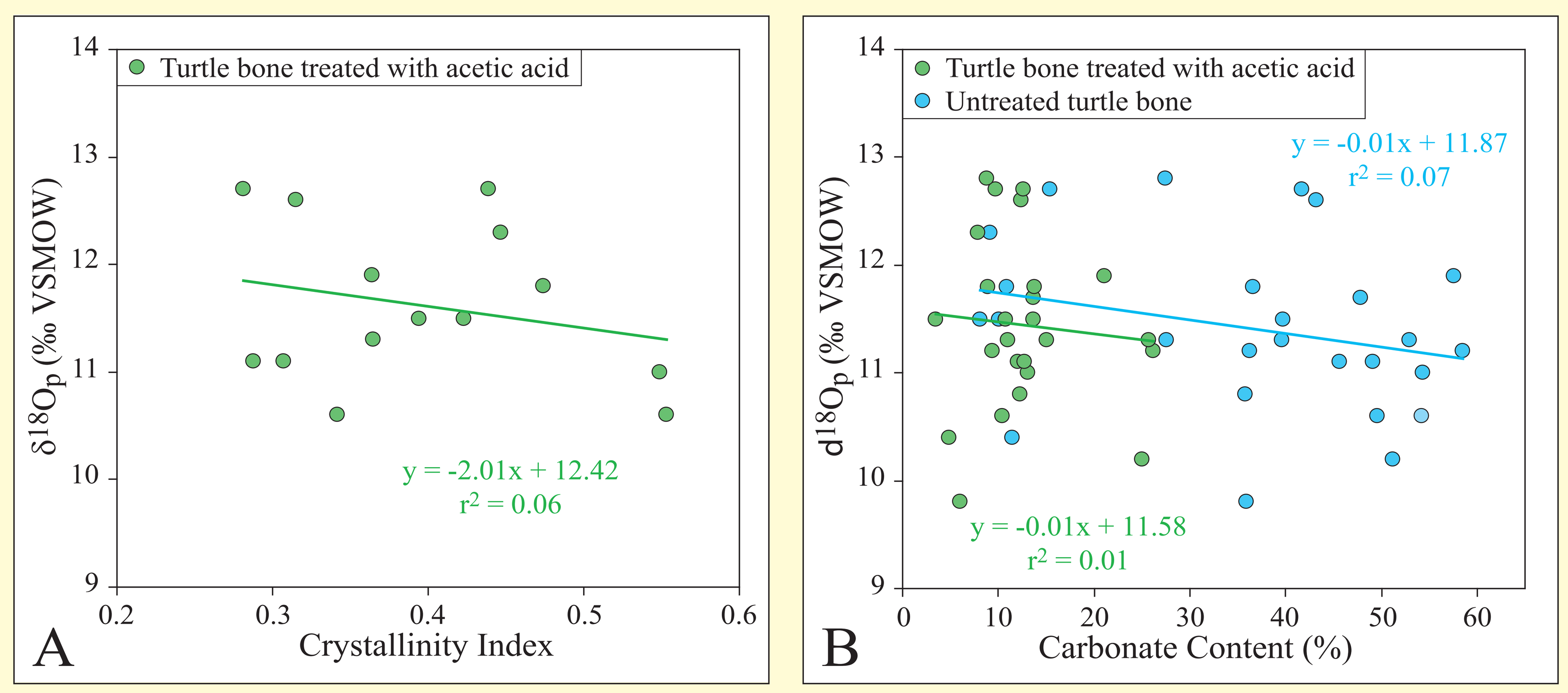


Figure 2: Both high crystallinity and low carbonate content are thought to be indicative of recrystallization or replacement of primary HA (Person et al., 1995). Furthermore, diagenetically altered HA is generally ^{18}O-depleted relative to unaltered HA (Zazzo et al, 2004), and previous studies suggest ^{18}O-depleted waters in the P-E Bighorn Basin (Koch et al., 2003). However, neither high crystallinity (A) nor low carbonate content (B) is a good predictor of low $\delta^{18}O_p$ values for turtle bone from this study.

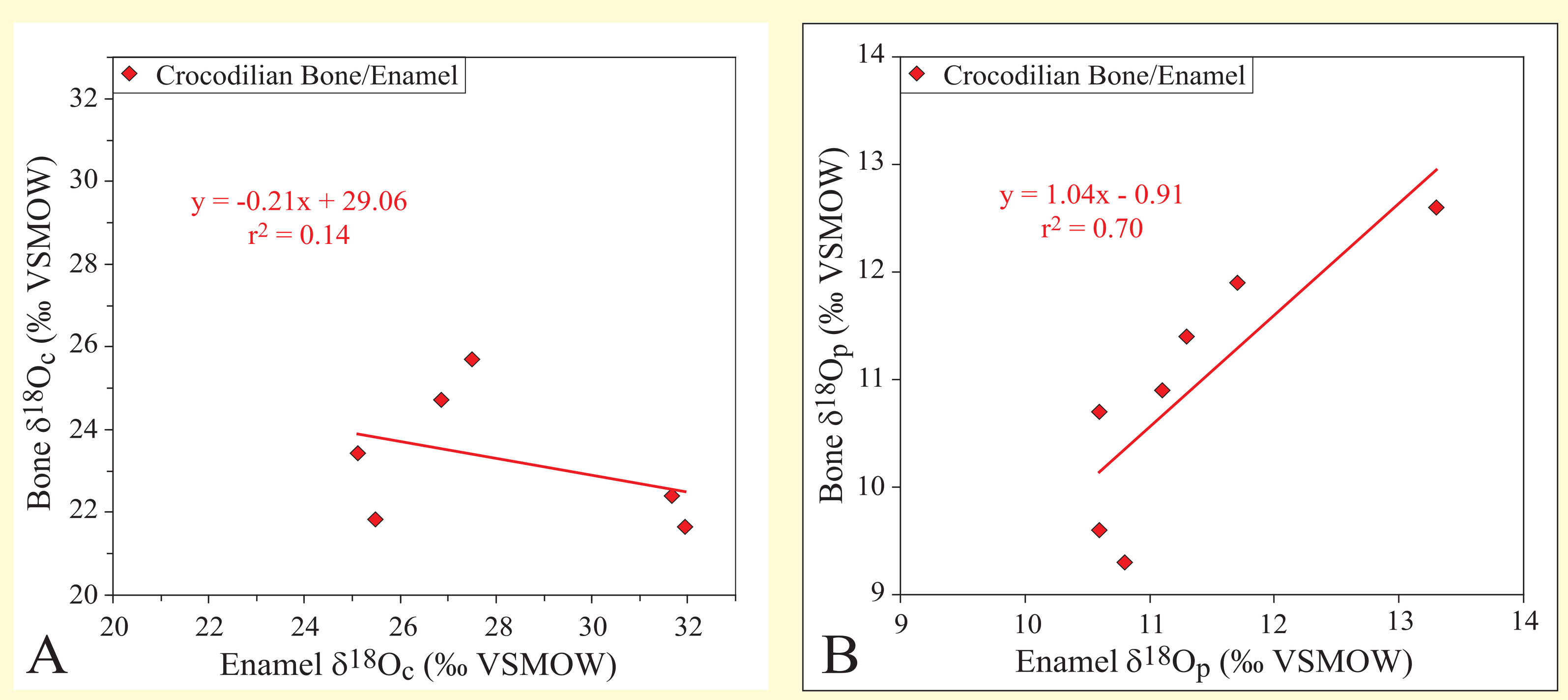


Figure 3: Unaltered enamel and bone $\delta^{18}O$ from within an individual animal should be in equilibrium, and should therefore covary strongly. While intra-individual samples of crocodilian bone and enamel taken from jaw fragments with teeth preserved *in situ* exhibit a poor correlation for $\delta^{18}O_c$ (A), they exhibit a strong positive correlation for $\delta^{18}O_p$ (B).

Estimates of mean annual temperature for the P-E Clarks Fork Basin are made by using two equations. First, the $\delta^{18}O$ of P-E meteoric/surface water ($\delta^{18}O_w$) is predicted from

$$\delta^{18}O_w = \delta^{18}O_p - 22.6$$

Next, estimates of $\delta^{18}O_w$ are used along with heterotherm (crocodilian or gar) $\delta^{18}O_p$ in the phophate-water temperature equation of Longinelli and Nuti (1973) to predict MAT:

$$MAT(^{\circ}C) = 111.4 - 4.3(\delta^{18}O_p - \delta^{18}O_w)$$

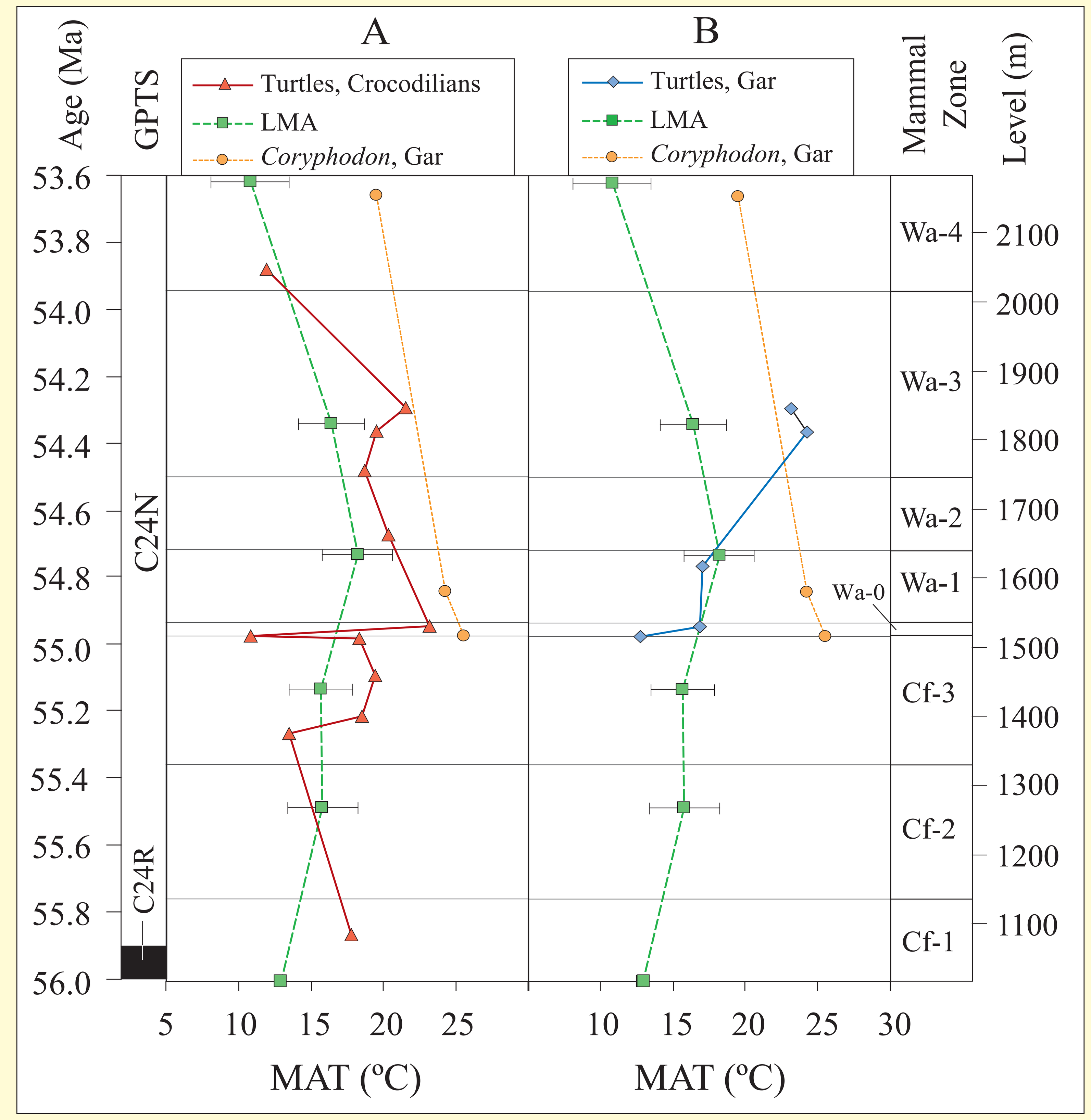


Figure 4: Estimates of terrestrial Paleocene-Eocene MAT made from emydids and crocodilians (A) and from emydids and gar (B) reconstruct two primary patterns predicted by previous MAT estimates based on leaf-margin analysis (LMA) (Wing et al., 1999) and $\delta^{18}O_p$ from gar and the mammal *Coryphodon* (Fricke and Wing, 2004). First, a rapid warming event is recorded at the Paleocene-Eocene boundary (Wa-0 Mammal Zone). Second, an early Eocene cooling trend on the order of 6 to 8ºC is observed from approximately 54.7 to 53.8 Ma.

CONCLUSIONS

The results of this study generally support the hypothesis of Barrick et al. (1999) that suggests the primary $\delta^{18}O_p$ of fossil emydid turtle bone may be preserved, and can be used along $\delta^{18}O_p$ from co-occurring heterotherms to quantify terrestrial paleotemperatures. This conclusion is supported by several observations. First, bone $\delta^{18}O_p$ values generally fall within the range of $\delta^{18}O$ values of presumably unaltered mammal tooth enamel from previous studies of the same localities. Second, in contrast to $\delta^{18}O_c$, intra-individual samples of crocodilian bone and enamel $\delta^{18}O_p$ exhibit a fairly strong positive correlation. Finally, MAT estimates based on bone, enamel and ganoine $\delta^{18}O_p$ from this study are in general agreement with independent estimates based on LMA. This result testifies to the utility of both $\delta^{18}O$ and LMA approaches to estimating terrestrial paleotemperature, since each method provides an independent estimate through entirely different sample materials, assumptions, and taphonomic biases.

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