

ABSTRACT

Stable carbon (δ^{13} C) and oxygen (δ^{18} O) isotopes in tooth enamel bioapatite are frequently used for paleoclimate and paleoenvironmental reconstructions, although substantially more information can be gathered via further material characterization. The thermal stability of biologic (Pleistocene mastodon) samples were preliminarily assessed via step-heating dehydration-dehydroxylationdecarbonation experiments on a high-vacuum extraction line. H₂ and CO₂ gases were extracted at 150°C, 400°C, 850°C, and 1000°C. δD values for tooth enamel bioapatite show progressively more negative values upon heating to higher temperatures ranging from -39 to -127‰ with a mean hydroxyl δD of -77‰, while mean $\delta^{13}C$ values of carbonate A-type substitution is -11.9‰. Weight percent H₂O and CO₃ from these thermal experiments are 3.3% and 2.1%, respectively. Separate aliquots of biologic apatite were also subject to traditional step-wise, incremental reaction experiments in 100% orthophosphoric acid at 25°C to produce CO₂. The mean δ^{13} C and δ^{18} O values for standard, calcite-type reactions are -10.8‰ and -4.4‰, respectively, with an average weight percent CO₃ of 3.1%. The results show important differences from calcite reaction patterns, and may correspond to differences in A-type and B-type carbonate substitution in bioapatite compared with calcite. This work successfully separates A-type from B-type carbonate substitution in bioapatite and could offer a promising proxy for paleoenvironmental reconstruction, even in fossilized and altered bioapatites.



Apatite crystal model and chemical formula. Note that carbonate anion may substitute for phosphate oxygen (B-type) and hydroxyl group (Atype).



Pleistocene age mastodon tooth from Trinity River terrace near Dallas, TX was donated from the Shuler Museum at Southern Methodist University for this work.

MATERIALS CHARACTERIZATION AND THERMAL BREAKDOWN OF TOOTH ENAMEL BIOAPATITE Mariah Holloway and Neil Tabor

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LAB METHODS

Tooth enamel was physically separated from dentin *via* a rotary drill. The enamel was then ground into powder and separated into three size fractions: <88 μ m, 88-125 μ m, and >125 μ m. All analyses were conducted with the $< 88 \ \mu m$ size fraction.

- 0.1 M acetic acid
- 30% H₂O₂
- X-ray powder diffraction analysis
- Incremental dehydration-dehydroxylation-decarbonation experiments
- 100% H₃PO₄ reaction experiments at 25°C
- δD , $\delta^{13}C$, $\delta^{18}O$ analyses of H₂ and CO₂ gas using IRMS at SMU





X-ray diffraction patterns of treated tooth enamel bioapatite. The dominant peaks represent carbonated hydroxylapatite (HAp) and carbonated fluorapatite (FAp).

REACTION RATE OF BIOAPATITE WITH 100% ORTHO-PHOSPHORIC ACID

RESULTS



Reaction rate of carbonate minerals (left) and bioapatite (right) with 100% H₃PO₄ at 25°C. 100% of the CO₂ in bioapatite was not obtained until a minimum of 73 hours of reaction. Note that for bioapatite, there is an inflection point near a reaction time of 4 hours. This indicates a change in the reaction rate, possibly reflecting a transition from CO_2 liberated from B-type to A-type carbonate substitution.

DEHYDRATION-DEHYDROXYLATION-DECARBONATION EXPERIMENTS

Incremental dehydrationdehydroxylationdecarbonation spectra. A) ratios of CO_2 yield to H_2O yield are recorded as F values. Dehydration is the prominent process until carbonate begins to break down between 400°C and 850°C. Large yields of H_2 during the 150°C and 400°C heating steps are presumed to be adsorbed and lattice-bound H₂O, respectively. Hydrogen from the hydroxyl groups may begin to break down prior to 850°C. B) δD values from extracted H₂ gas become progressively more negative upon heating, with a mean δD value of -77‰.

ment	Wt % CO ₃	Wt % H₂O	Mean δD (‰)	Mean δ ¹³ C (‰)	Mean δ ¹⁸ Ο (‰)
mal	2.1	3.3	-77*	-11.9	N/A
<3.5 hrs)	3.1	N/A	N/A	-10.8	-4.4
>3.5 hrs)		N/A	N/A	-11.2	-4.3
acid rxn**	N/A	N/A	N/A	-11.2	N/A

*Mean δD value is the weighted mean of H₂ yields and corresponding stable hydrogen isotope values from the 400, 850, and 1000°C steps.

MOVING FORWARD

DEHYDRATION-DEHYDROXYLATION-DECARBONATION

• Further constrain the parameters of the thermal breakdown of carbonate by adding additional heating steps (e.g., 600°C)

REACTION RATE EXPERIMENTS

• Inform how size fraction changes the reaction rate with 100%

MODERN BIOAPATITE ASSESSMENT

• Assess how the characterization of fossilized bioapatite compares to that of modern animals

SCANNING ELECTRON MICROSCOPE ANALYSIS

• Determine the chemical composition and crystalline structure

FOURIER TRANSFORM INFRARED SPECTRA ANALYSIS

• Inform how A-type and B-type carbonate substitutions individually break down after step-heating

FOR MORE INFORMATION

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