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Carbon isotopes of enamel-bound organic matter – a new paleobiological archive

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Carbon isotopes of tissue or collagen extracted from dentin/bone are commonly used to reconstruct past ecosystems, particularly C3/C4 plant consumption in herbivores. $\delta^{13}C$ of structural carbonate within tooth enamel ($\delta^{13}C_{CO3}$) serves as a proxy for average dietary C, but with a variable ^{13}C enrichment of ~9-16‰. $\delta^{13}C_{collagen}$, in contrast, records the $\delta^{13}C$ of dietary protein more directly. The difference between these two values, $\Delta\delta^{13}C_{CO3\text{-}collagen}$, has been shown to differ significantly between groups of animals based on trophic level, dietary quality, and digestive physiology. Collagen preservation is limited to thousands of years, very rarely surviving up to 100 kA, limiting the application of $\Delta\delta^{13}C_{CO3\text{-}collagen}$. In deeper time contexts, $\delta^{13}C_{CO3}$ is still preserved, but it is challenging to determine the correct offset to calculate $\delta^{13}C_{diet}$ from $\delta^{13}C_{CO3}$. Additionally, concerns of secondary carbonate formation during diagenesis have led to uncertainty as to optimal sample preparation.

Primary organics exist in tooth enamel, though their low concentrations have traditionally precluded isotopic analysis. In this work, we present the first measurements of enamel-bound organic matter (EBOM) $\delta^{13}C$ measured on a modified EA-IRMS system capable of analyzing ~100 nmol C, requiring ~8 mg of enamel. We present a ground-truthing dataset of $\delta^{13}C_{EBOM}$ and $\delta^{13}C_{collagen}$ (extracted from tooth dentin) in modern cows from a farm in Pennsylvania. Both cow $\delta^{13}C_{EBOM}$ and $\delta^{13}C_{collagen}$ range from ~ -27 to -13‰ and closely correlate, covering the span of C3 to C4 feeding. Our results confirm that $\delta^{13}C_{EBOM}$ faithfully records the same information as $\delta^{13}C_{collagen,}$ while overcoming its preservation constraints. In that regard, we also present preliminary data from fossil tooth enamel confirming preservation of $\delta^{13}C_{EBOM}$ over geologic timescales. We propose the use of $\delta^{13}C_{EBOM}$ for (1) validating $\delta^{13}C_{CO3}$ records, and (2) extending the use of $\Delta\delta^{13}C_{CO3\text{-}collagen}$ into deep time.