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Evaluating aridity using triple oxygen isotopes in tooth enamel

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Aridification is hypothesized to have a key effect on human evolution. While there are numerous proxy records that help determine water balance, there are few that record the specific environments in which hominins lived. The $\delta^{18}O$ values of herbivore teeth have been used to assess aridity, but this proxy is limited because it cannot separate the effects of aridity from other factors including rainfall amount and moisture source. The determination of $\delta^{17}O$ values along with $\delta^{18}O$ values can provide additional constraints on the factors that influence oxygen isotopes in biogenic carbonates and apatites and in the waters from which they form. This is because the relationship between $\delta^{18}O$ and $\delta^{17}O$ is distinct for kinetic processes (e.g., evaporation) and equilibrium processes. $\Delta^{17}O$ is the deviation from an expected relationship between $\delta^{18}O$ and $\delta^{17}O$ by which the $\Delta^{17}O$ values of waters (e.g., meteoric waters and leaf waters) become more negative as evaporation increases.

We analyzed $\delta^{18}O$ and $\delta^{17}O$ values of tooth enamel from mammalian herbivores with different water use strategies (giraffe, hippo, elephant, rhino, wildebeest, hartebeest, and oryx) from eastern and southern Africa to explore how $\Delta^{17}O$ varies with both taxon and environmental conditions. Our results indicate that the $\Delta^{17}O$ value of enamel is a function of both the species and aridity with the range of the $\Delta^{17}O$ values being similar to the range in plant waters (> 300 per meg, where 1 per meg is 0.001‰) and much greater than that of the range of local waters (< 100 per meg). While the use of $\delta^{18}O$ values of enamel to evaluate aridity is limited by the heterogeneity of $\delta^{18}O$ of meteoric water, variation in $\Delta^{17}O$ values of enamel were independent of the $\delta^{18}O$ values of meteoric water. For example, while giraffe enamel from Kgalagadi, South Africa (~180 mm mean annual precipitation (MAP)) and Garamba National Park, Democratic Republic of the Congo (~1250 mm MAP) have $\delta^{18}O$ values that are within 1‰ of each other, the $\Delta^{17}O$ values of the enamel indicate that the Kgalagadi giraffe (-301±27 per meg) has experienced more arid conditions than the Garamba giraffe (-208±22 per meg) because more negative $\Delta^{17}O$ values are related to increased evaporation of waters.

The $\Delta^{17}O$ values of enamel samples can be used to evaluate the diagenetic alteration of enamel carbonate by directly targeting the oxygen isotopic composition of teeth. Enamel samples that have not been altered will have $\Delta^{17}O$ values reflective of the low $\Delta^{17}O$ value of O_2 (~ -500 per meg) in the $\Delta^{17}O$ values of animal body water (i.e., the water from which tooth enamel has formed). Therefore, all tooth enamel, regardless of environment, will have $\Delta^{17}O$ values that are lower than would be expected than if they have precipitated from body water influenced by meteoric waters and plant waters alone. In comparison, we expect that enamel samples that have been diagenetically altered will have $\Delta^{17}O$ values similar to meteoric water (i.e., the digenetic fluid from which carbonate has reprecipitated) rather than that of plant water. We expect this concept to hold true for other biogenic carbonates and apatites.

The $\Delta^{17}O$ value of enamel has the potential to be a powerful aridity proxy because it enables us to use the oxygen isotope records of enamel to compare degree of aridity regardless of geographical, latitudinal and hydrological setting and the $\delta^{18}O$ values of input water, allowing the evaluation of aridity across time and between different regions. Furthermore, this method proves a self-check for the diagenetic alteration of the primary oxygen isotopic composition of the enamel carbonate. The $\Delta^{17}O$ values of enamel (and other biogenic carbonate and apatites) can be applied across geologic periods and is relevant to active fields of study in which aridity is thought to have varied.