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Tooth enamel maturation reequilibrates oxygen isotope compositions and supports simple sampling methods

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Abstract

Oxygen isotope and major element zoning patterns of several disparate ungulate teeth were collected to evaluate the timing and geometry of enamel formation, records of isotope zoning, and tooth enamel sampling strategies. Isotopic zoning in mammalian tooth enamel encodes a sub-annual time series of isotopic variation of an animal's body water composition, with a damping factor that depends on the specifics of how enamel mineralizes. Enamel formation comprises two stages: precipitation of appositional enamel with a high CO_3:PO_4 ratio, followed by precipitation of maturational enamel with a lower CO_3:PO_4. If appositional and maturational enamel both contribute to isotope compositions (but with different CO_3:PO_4), and if isotope compositions vary seasonally, paired $\delta^{18}O$ values from CO_3 and PO_4 profiles should show a spatial separation. CO_3 isotope patterns should be shifted earlier seasonally than PO_4 isotope patterns. Such paired profiles for new and published data show no resolvable shifts, i.e. CO_3 and PO_4 $\delta^{18}O$ profiles show coincident maxima and minima. This coincidence suggests that enamel maturation reequilibrates appositional isotope compositions. If enamel maturation establishes enamel isotope compositions, the geometry of maturation, not apposition, should be considered when devising sampling protocols. X-ray maps of Ca zoning show that the majority of enamel (inner and middle layers) mineralizes heavily at a high angle to the external tooth surface and the enamel-dentine junction over length scales of 2–4 mm, while the outer enamel surface mineralizes more slowly. These data suggest that isotopic sampling strategies should parallel maturational geometry and focus on interior enamel to improve data fidelity. The magnitude of isotopic damping is also smaller than implied in previous studies, so tooth enamel zoning more closely reflects original body water isotopic variations than previously assumed.
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Keywords: Stable isotopes; Enamel mineralization; Tooth growth; Maturation

1. INTRODUCTION

Stable isotopes in mammalian tooth enamel are commonly used to address a variety of ecological and climatological questions (e.g., see Koch, 1998, 2007; Kohn and Cerling, 2002; Clementz, 2012). Unlike bone and dentine, enamel is not strongly susceptible to diagenetic alteration, so it faithfully preserves biogenic isotope compositions over millions of years. Teeth also mineralize progressively from tooth tip to root and are not remodeled after formation, so they encode and preserve a sub-annual times series of isotopic variations in the animal. Subsampling to extract these variations has become a well established technique to investigate sub-annual fluctuations in climate and feeding ecology (e.g., Fricke and O'Neil, 1996; Fricke et al., 1998; Kohn et al., 1998; Balasse, 2002). However, because enamel formation consists of multiple discontinuous stages of mineralization, isotopic zoning within a tooth does not perfectly record the instantaneous isotope composition of an animal or environment, rather the record is damped relative to this variation (Passey and Cerling, 2002). Several authors have proposed approaches to minimize this

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problem, either by subsampling strategies (Hoppe et al., 2004; Zazzo et al., 2012; Blumenthal et al., 2014; Holroyd et al., 2014) or by numerical modeling and inversion (Passey et al., 2002, 2005). Both these approaches rely on accurate understanding of the timing and geometry of enamel formation.

In this paper, we examine chemical and isotopic systematics in tooth enamel to critically evaluate how it forms and encodes its isotope composition. In the first part of the paper we show that while enamel forms via a two-stage process, only second stage mineralization appears to contribute to the isotope compositions recorded in teeth – compositions essentially reequilibrate during maturation so that the physical and isotopic character of first-stage mineralization appears inconsequential to isotope studies. In the second part we use X-ray composition mapping of several developing teeth to investigate the complexities of second-stage mineralization and its relationship to existing subsampling strategies. The geometry of second-stage mineralization bears little to no resemblance to first-stage mineralization. Consequently, even if apposition-stage isotopic compositions were partially preserved, proposed sampling strategies based on first-stage microstructure alone should be avoided.

2. ENAMEL MINERALOGY AND FORMATION

Enamel is the most highly mineralized tissue in mammals, and contains nearly 100% bioapatite mineral. Chemically, bioapatite is $Ca(PO_4)_3OH$ with carbonate (CO_3) substitutions in the phosphate (PO_4) and hydroxyl (OH) sites (Elliott, 2002). Both the carbonate and phosphate components are commonly analyzed for their stable isotope compositions. Of the two, carbonate analysis is more common, both because it archives two isotope systems, carbon and oxygen, and because analysis is simpler. Enamel phosphate is thought to be more resistant to diagenesis, leading to its use primarily on geologically older fossils (Kohn and Cerling, 2002).

Enamel microtexture in mammals is broken into two broad categories, radial and decussate enamel, distributed in three regions of enamel – outer, central, and inner regions – from the outer enamel surface (OES) to the enamel-dentine junction (EDJ). Radial enamel commonly forms the outer and inner enamel layers, although the inner layer varies in thickness (Pfretzschner, 1992; Koeingswald et al., 1993). In radial enamel, enamel prisms are oriented perpendicular to either the OES or EDJ. Decussate enamel prisms intersect and cross at shallow to high angles (crisscross) and bundle together to form optically distinct, macroscopically visible bands called Hunter-Schreger bands. Decussate enamel makes up the central and sometimes inner layers of enamel, and therefore, the majority of enamel volume in large mammals (Koenigswald and Sander, 1997; Moss-Salentijn et al., 1997).

Enamel mineralization takes place in two distinct stages, apposition (first-stage) and maturation (second-stage; Fig. 1; Robinson et al., 1978, 1979; Suga, 1979, 1982). Here we refer to the two correspondingly distinct mineral components as appositional and maturational bioapatite. During apposition, mineralization initiates at the occlusal or wear surface of the tooth and progresses toward the root. A protein matrix forms and is seeded with diffuse enamel crystallites (Fig. 1A). The surface of new apposition forms a low angle relative to the EDJ, such that sequential appositional layers imbricate. In fully mineralized enamel, incremental growth bands called striae of Retzius record the orientation of the appositional front (Hillson, 1986). The angle of apposition for several groups of ungulates is commonly ~5–15° relative to dentine (Kierdorf and Kierdorf, 1997; Hoppe et al., 2004; Kierdorf et al., 2006, 2012, 2013). The appositional matrix is mineral poor, with only ~25 wt% bioapatite (Moss-Salentijn et al., 1997; Passey and Cerling, 2002). While the total mineral content of the appositional matrix is low, however, appositional bioapatite within is carbonate rich, containing twice as much CO_3 as fully mature enamel (Robinson et al., 1979; Sydney-Zax et al., 1991). This difference in mineral content vs. CO_3 content is crucial to our study – if appositional bioapatite is retained in the final enamel, it contributes ~25% of the total mineral (PO_4) but ~50% of total CO_3. The innermost enamel layer, a 10–20 μm band along the EDJ, differs from this pattern of mineralization because it is heavily mineralized – at least 50% – early in enamel formation (Suga, 1979, 1982; Tafforeau et al., 2007; Blumenthal et al., 2014). Because this layer is so thin and rarely isolated for analysis, we do not consider its isotope systematics.

After apposition, enamel undergoes a prolonged maturation stage. Similar to apposition, maturation progresses from occlusal surface to root, although not necessarily at the same rate or with the same geometry (Fig. 1B, D). Maturation occurs earlier and faster in the inner and central enamel layers, with the outer enamel layer mineralizing last. During this stage, crystallites coarsen and infill, reducing organic contents to final concentrations of $\leqslant$1 wt% (Robinson et al., 1979; Suga, 1979, 1982; Hillson, 1986, 1978) and depositing the remaining ~75 wt% mineral and ~50 wt% of carbonate (Robinson et al., 1979; Sydney-Zax et al., 1991). While bulk enamel has a carbonate content of 3–4 wt% it is heterogeneously distributed ranging from ~5 wt% near the EDJ to ~3 wt% at the OES (Zazzo et al., 2005).

3. MODELING ENAMEL ISOTOPE COMPOSITIONS

If bulk enamel represents contributions from both appositional and maturational bioapatite, a bulk isotope composition should represent an average of their respective compositions, weighted by the amount contributed during each stage:

$$\delta_{final} = \delta_{app} \times f_{app} + \delta_{mat} \times (1 - f_{app}) \quad (1)$$

where δ_{final} = the final isotope composition of mature enamel, δ_{app} and δ_{mat} are the isotope compositions of appositional and maturational bioapatite respectively, and f_{app} is the fraction of the isotope deposited during apposition (Fig. 1C, E).

Passey and Cerling (2002) modeled this concept using two equations (see Table 1 for model parameters):

$$\delta_{ei} = (f_{app} \times \delta_{mi}) + (1 - f_{app}) \times \frac{\sum_{n=i+1}^{i+1+l_m} \delta_{m_n}}{l_m} \quad (2)$$