Re-Equilibration of Enamel Carbonate During Maturation

ROBIN B. TRAYLER[1,*] AND MATTHEW J. KOHN[1]

[1]Boise State University, Boise, ID 83725
(*correspondence: robintrayler@boisestate.edu)

Mammalian tooth enamel consists of ~96% carbonate-apatite. Enamel forms in two stages, apposition and maturation. During apposition, a mineral-poor, protein-rich matrix is deposited. Although this matrix contains only ~25% of the total mineral content of mature enamel, crucially, it contains ~50% of the final CO_3 content (i.e. concentration of CO_3 is ~2x higher than in mature enamel). During maturation, enamel crystallites coarsen and infill, and this stage dominates the PO_4 wt% of the mature enamel [1]. Both the CO_3 and PO_4 components of enamel are commonly analyzed for $\delta^{18}O$. If apatite that forms during apposition never equilibrates during maturation, $\delta^{18}O$ values from the CO_3 component should be biased towards appositional values relative to PO_4. Using a simple model of enamel formation [2] we predict that, for a sinusoidal input signal, $\delta^{18}O$ values of CO_3 should show the same period but a higher amplitude and a positive phase shift relative to PO_4 values. This also implies a non-constant offset between CO_3 and PO_4 $\delta^{18}O$.

To test whether CO_3 isotopes are biased towards apposition, we collected 36 serial samples along the growth axis of an *Equus ferus caballus* (horse) tooth and analyzed them for $\delta^{18}O$ values from both CO_3 and PO_4. The cross-correlation between smoothed profiles for each component shows no discernable lag (r = 0.94). Similarly, the root mean squared error between the PO_4 and CO_3 profiles shows a minimum error at zero lag, although lags up to –2mm are feasible. Likewise, the amplitude of the CO_3 component is dampened relative to PO_4. These results differ from previous predictions leading to two possible interpretations: 1) During enamel formation a portion of the CO_3 component partially re-equilibrates during maturation while the PO_4 does not. 2) Both components re-equilibrate during maturation and the contribution from the initial matrix is lost. Both options would explain the absence of a time-lag between CO_3 and PO_4 but neither explains well the greater dampening of the CO_3 profile relative to PO_4. Disparities in CO_3 vs. PO_4 equilibration during enamel formation help explain scatter in $\Delta^{18}O(CO_3\text{-}PO_4)$ observed in modern and fossil teeth.

[1] Sydney-Zax, Mayer, & Deutsch (1991) *Journal of Dental Research*, 913-916 [2] Passey & Cerling (2002), *Geochimica et Cosmochimica Acta*, 3225-3234