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# Crystal Structure and Chemistry of Enamel and Enameloid Bioapatite from across the Tree of Life

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Using Rietveld refinements of powder X-ray diffraction data, we modelled unit cell parameters of enamel and enameloid bioapatite from a variety of cartilaginous and bony fishes, mammals, and reptiles across the phylogenetic tree of life. Biologically derived apatite [$Ca_5(PO_4, CO_3)_3(OH, F, CO_3)$], known as bioapatite, is the primary phase that makes up the highly mineralized outer layer of teeth. In mammals and reptiles, this layer is known as enamel and is almost completely hydroxylated. In fishes, this mineralized layer is referred to as enameloid, and is more fluorinated (2-5 wt%). Previous studies have found differences in the unit cell parameters of enamel and enameloid in individual organisms, but this study is the first to present a systematic dataset of basal and evolved fishes, mammals, and reptiles to assess differences in unit cell parameters. The results of our Rietveld refinements indicate that some fish enameloid (e.g., shark, parrotfish) have unit cell parameters close to that of fluorapatite; however, other fishes (e.g., piranha, pacu) have unit cells that resemble a hydroxylapatite unit cell. Furthermore, mammals and reptiles consistently have unit cell parameters close to that of hydroxylapatite, but variation exists in *a*- and *c*-axis unit cell lengths, unit cell volume, and unit cell density for all analyzed organisms. These variations can be attributed to systematic differences in the concentrations of defects like coupled substitutions (e.g., $Na^+ + CO_3^{2-} = Ca^{2+} + PO_4^{3-}$), especially for carbonate which is most commonly substituted for phosphate (type-B substitution), but can also substitute in the channel anion site (e.g., $CO_3$ = 2OH, type-A substitution). Chemical data from attenuated total reflectance infrared spectroscopy (ATR-FTIR) and X-ray energy dispersive spectroscopy (EDS) confirm variations among enamel with respect to cation and carbonate substitution types. The ensemble of structural and chemical data indicates that there is a phylogenetic relationship between enamel and enameloid crystal structure and chemistry. This work has not only implications for the identification of taxa at higher orders, but also for the susceptibility of tooth enamel to undergo diagenetic alteration *post mortem.*