Mineralogy of Hypermineralized bone

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The mineral, bioapatite, is a form of carbonated hydroxylapatite, which makes up over 50 wt.% of bone. However, normal bone contains much collagen, which is interlaced with mineral crystallites at the nanometer and micrometer scale, making the study of bioapatite very difficult. Hypermineralized bone with extremely high mineral contents (>80 wt.%) fortunately allows the application of many analytical techniques to investigate the mineralogy of bioapatite with very little interference from collagen.

The hypermineralized whale rostrum was used to investigate the chemistry of bioapatite. Electron microprobe analyses of the rostrum's bioapatite show an average CO_3^{2-} of ~8 wt% and an average Ca/P atomic ratio of 1.7. It shows a homogenous distribution of the mineral content, except around a few vascular holes and vessels. Hydroxyl depletion in the bioapatite is coupled with carbonate substitution and Ca can be substituted by Na and Mg in mineralization. Bulk analysis by X-ray fluorescence shows that the bioapatite in the rostrum has an average composition of

$(Ca_{8.40}Mg_{0.20}Na_{0.54})[(PO_4)_{4.87}(CO_3)_{1.13}](OH)_{0.87}$.

Compared to human tooth enamel, heterogeneity occurs in the chemistry and mechanical properties of the rostrum: the mineral prisms in enamel show extreme homogeneity of orientation, i.e., *c* axis of the crystals parallel the longitudinal direction, whereas there is some amount of variation in orientation in the crystals of the rostrum. In biomedical tests, the bioapatite in the rostrum also shows higher deviations in indentation depth than the enamel.

The mineralogical changes in bioapatite were investigated using dolphins' bullae. During aging, the abundant pores in the edge areas become filled with densely mineralized tissue whereas organic matter is reduced. These changes yield greater homogeneity in mineral content throughout the adult bullae. Ca/P atomic ratios with Mg, S, and other minor/trace elements, otherwise, are almost constant in the central areas over time. Enhancement of the coupled substitutions of CO_3^{2-} for PO_4^{3-} and Na for Ca during aging yield a carbonate content up to ~10 wt.% in the adult bulla. Remarkably, the degree of crystallinity of the bioapatite remains approximately constant with age despite the increase in carbonate contents.