

# Nanoscale investigation of hydroxylapatite formation in Alligator Gar fish scale

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Alligator Gar (*Atractosteus spatula*) is a modern armored fish thought to be descended from Mesozoic aged ray-finned bony fish (palaeoniscoids). Its scales are dermal denticles consisting of a bony core and a ganoid enamel-like (ganoine) cap. SEM and  $\mu$ CT imaging revealed that the ganoine cap was a dense layer of apatite anchored to the underlying bone by circumferential ridges. The bone beneath the ganoine was, in places, a dense and highly textured composite of hydroxylapatite (HAp) and type I collagen (Col) similar to bone of other vertebrates. The ganoine HAp was enriched in Na and depleted in Mg relative to the bone HAp. Ca/P ratios from EPMA tended to be higher in the bone relative to the ganoine. FTIR analyses indicated the presence of  $\text{CO}_3^{2-}$  in both the ganoine and bone HAp, but the spectra showed different absorption bands for Col in the amide region (1100 to 1800  $\text{cm}^{-1}$ ). At the nanoscale, TEM tomography and STEM imaging of partially demineralized bone identified two types of HAp, one intracollagenous and roughly centered on what may be the “gap” zone of Col, and another extracollagenous and larger than the banding repeat of Col. Both HAp crystal types were thin and oriented at an angle to the Col long axis, which implies an interpenetration of HAp and Col at the nanoscale. HAp<sub>(bone)</sub> separated from Col had the form of thin  $\sim 50 \times 50 \times 5 \text{ nm}^3$  sheets that were interconnected at corners to form a structure similar to an open “Granny Square” crochet quilt. TEM EDX analyses of bone separates had a lower Ca/P than EPMA of HAp<sub>(bone)</sub>+Col, a result indicating a possible third component in gar scale bone. The physical properties of this HAp/Col interpenetration model would be greatly different from a parallel HAp/Col model.