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Interfacial Structure and Damage Mitigation from the Radular Teeth of *Cryptochiton stelleri*

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Abstract: There is an increasing need for the development of multifunctional lightweight structural materials with high strength that are both flexible and durable. Natural systems have evolved efficient strategies, exemplified in the biological tissues of numerous animal and plant species, to synthesize and construct composites from a limited selection of available starting materials that often exhibit exceptional mechanical properties that are similar, and frequently superior to, mechanical properties exhibited by many engineering materials. These biological systems have accomplished this feat by establishing controlled synthesis and hierarchical assembly of nano- to micro-scaled building blocks. This controlled synthesis and assembly require organic that is used to transport mineral precursors to organic scaffolds, which not only precisely guide the formation and phase development of minerals, but also significantly improve the mechanical performance of otherwise brittle materials.

One such example is found in the tongue-like feeding apparatus (radula) of the chiton, a marine snail that produces one of the most abrasion-resistant structures (Figure 1) in the animal kingdom [1-3]. The chiton exhibits selective biomineralization, with shell plates consisting of aragonitic $CaCO_3$ [2] and radular teeth mineralized by iron oxides and iron phosphates [2-6].

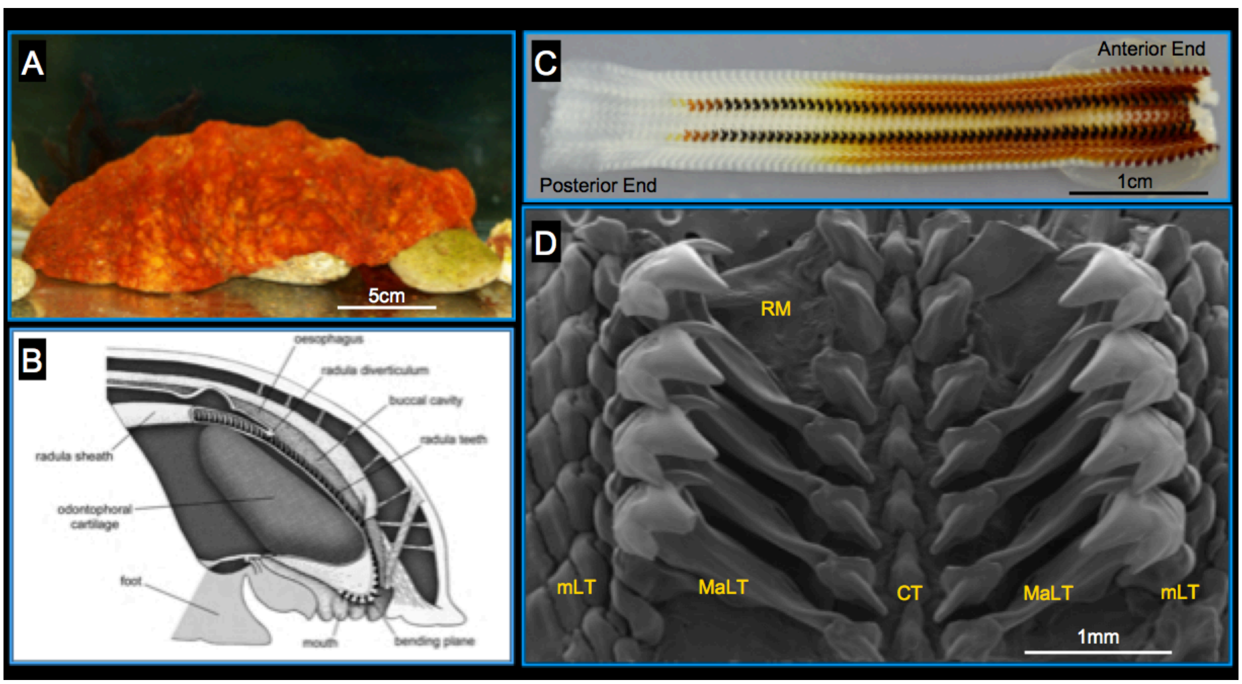

Figure 1. (A) *Cryptochiton stelleri*, the gumboot chiton, is the largest known species of polyplacophora, commonly growing more than 30cm in length. (B) These marine mollusks graze on algae and microflora using buccal musculature to manipulate a flexoglossan radula across rocky substrates in the inter- and subtidal regions. (C) The radula is tongue-like organ that contains 80 rows of teeth at different stages of maturation and mineralization. The posterior end of the radular belt contains completely unmineralized teeth that consist of translucent, fibrous α-chitin scaffolds. The anterior end contains teeth that are fully matured and ready for use. (D) Each row of teeth contains central teeth (CT), two major lateral teeth (MaLT), and sixteen marginal lateral teeth (mLT). The radula is

symmetric about the mid plane. The two major lateral teeth of the radula are mineralized and are more protrusive than the other types of teeth. The tooth is capped by a hard layer of magnetite and is connected to the soft radula by a curved tubular stylus. The interface between the hard tooth and soft stylus is strong enough to withstand thousands of rasping events without de-bonding at the junction.

The radular teeth are heavily mineralized in order to prevent abrasion during feeding on epilithic and endolithic algae on intertidal rocks. To fulfill this function, chiton teeth must be tough and wear-resistant. The teeth of gumboot chitons, *Cryptochiton stelleri*, are composed of the world's hardest biologically synthesized mineral [4, 5, 7]. Impressive mechanical properties are achieved in the chiton tooth through a hierarchically-arranged composite structure consisting of a hard shell of organic-encased and highly oriented nanostructured magnetite rods that surround a soft core of organic-rich iron phosphate [4, 7]. Microscopic and spectroscopic analyses combined with finite element simulations are used to probe the ultrastructural features and uncover structure – mechanical property relationships in the fully mineralized teeth of the gumboot chiton *Cryptochiton stelleri* [4, 7 – 9].

While the abrasion resistance of the chiton's hierarchically arranged magnetite capped tooth has properties comparable to alumina and zirconia, the mechanical properties of the stylus, the curved tubular structure that supports the teeth and braces them during rasping events, is relatively unknown. The styli of major lateral teeth act as non-jointed arms that connect the teeth to the radular belt, transfer force during feeding, and provide channels for fluid transport. The stylus is selectively reinforced by regionally controlling composition, varying cross sectional area, and controlling fiber orientation throughout the structure. The combination of these elements work to control the bending and torsional stiffness along the length of mature styli in *Cryptochiton stelleri* and reduce stress at the interface between the flexible radular membrane and the ultrahard tooth. Understanding the controlled regionalized mechanics along a contoured fiber structure is applicable to industries that require lightweight materials with custom physical and chemical properties within a single component part.

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