Analysis of an ultra hard magnetic biomineral in chiton radular teeth

Recent analyses of the ultrastructural and mechanical properties of mineralized biological materials have demonstrated some common architectural features that can help explain their observed damage tolerance. Nature has accomplished this feat through the precise control of anisotropic crystal nucleation and growth processes in conjunction with nanoscale control over the self-assembly of spatially distinct organic and inorganic phases, resulting in effective inhibition of crack propagation through these materials. One such example is found in the hyper-mineralized and abrasion resistant radular teeth of the chitons, a group of herbivorous marine mollusks who have the surprising capacity to erode away the rocky substrates on which they graze\(^1\)-\(^4\). Through the use of modern microscopy and nanomechanical characterization techniques, we describe the architectural and mechanical properties of the radular teeth from \textit{Cryptochiton stelleri}. Chiton teeth are shown to exhibit the largest hardness and stiffness of any biominerals reported to date, being notably as much as three-fold harder than human enamel and the calcium carbonate-based shells of mollusks. We explain how the unique multi-phasic design of these materials contributes not only to their functionality, but also highlights some interesting design principles that might be applied to the fabrication of synthetic composites.

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Ever since early humans first used antler to shape stone tools via lithic reduction, we have been fascinated by the structural complexity and mechanical robustness of biominerals. The 19th century saw an explosion in the interest to catalog global biodiversity and through the course of these expeditions, many new species were discovered and the details of their skeletal systems were documented in exquisite detail (Fig. 1). It was these detailed ultrastructural studies\textsuperscript{5-7} that helped lay the groundwork for the modern field of biomineralization\textsuperscript{2}. In more recent times, the availability of advanced instrumentation such as synchrotron X-ray diffraction and high resolution transmission electron and scanning probe microscopy in conjunction with the latest advances in genomics and proteomics have permitted significant progress into not only the nanoscale characterization of these materials, but also the factors regulating their controlled fabrication.

These biominerals display similar, and frequently superior, mechanical robustness to those exhibited by many engineering materials with similar chemical composition, such as structural ceramics. Biological systems have accomplished this feat through the demonstrated ability to control size, morphology, crystallinity, phase, and orientation of the mineral under benign processing conditions (i.e., near-neutral pH, room temperature, etc.). They utilize organic-inorganic interactions and carefully controlled microenvironments that enable kinetic control during the synthesis of inorganic structures\textsuperscript{4}.

In these biomineralized systems, minerals and organic macromolecules exist in close proximity and at nanoscale dimensions. Interactions at these interfaces are vital to the functions of structural materials found in nature such as shells, teeth, and bone\textsuperscript{4}. Although the organic constituents of these biological composite materials are present in relatively small quantities\textsuperscript{4}, they significantly alter

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Fig. 1 Evolution of the field of biomineralization through time. 19th Century: Gross morphological skeletal anatomy of Caryophyllia profunda (a), Cassis sp. (b), and Euplectella aspergillum (c) collected during the Challenger expedition between 1873 and 1876. 20th Century: Electron microscopy studies of the aragonitic spherulites from Aphrocallistes vastus (d), mineralized tablets of nacre from Haliotis rufescens (e), and fused hexactine siliceous spicules from Aphrocallistes vastus (f). 21st Century: TEM image of a focused-ion beam milled sclerite from Corallium rubrum (g), High resolution TEM and associated electron diffraction pattern of a single nacre tablet from Haliotis rufescens (h), and atomic force micrograph of the concentric lamellae of consolidated silica nanoparticles of a spicule from Tethya aurantia (i). (a-c) adapted from\textsuperscript{5-7} and (g) adapted from\textsuperscript{8}. 

the mechanical behavior of the bulk structures. In organic-inorganic composites, the existence of the organic phase leads to significant energy dissipation at the interfaces during loading, resulting in a combination of properties that may well improve the abrasion and wear resistance of the structure in comparison to monolithic materials with equivalent chemical composition. One such example are the hypermineralized teeth of chitons, which are shown to be harder and stiffer than any other known biomineral as discussed in detail below.

The chitons (Mollusca, Polyplacophora; Fig. 2a) are an ancient group of mollusks with a fossil record dating back nearly half a billion years. Despite their long and successful history and their ecological importance in rocky coastal habitats they are a comparatively small group with about 650 modern species. Chitons are flattened and usually elongated mollusks that are protected dorsally by a shell consisting of eight overlapping plates. The foot is broad and powerful, well adapted for clinging tightly to the hard surfaces on which the animal grazes for algae. Like most other groups of mollusks, the chitons have a radula (Fig. 2b, c), a rasping, toothed conveyor belt-like structure, which is used for feeding. The composition and morphology of the radular teeth vary from group to group and depend to a large extent on the dietary specifics and the mechanical properties of the substrates on which they feed.

Cryptochiton stelleri is native to the temperate Northern Pacific and is the world's largest species of chiton, reaching a maximum length of up to 33 cm, thus making it an ideal research system for investigating radular tooth architecture and mechanics. Despite its large size, the meat of this mollusk has no commercial value and is generally not considered palatable. This is exemplified in an account by Ricketts and Calvin who wrote, “After one experiment the writers decided to reserve the animals for times of famine; one tough, paper-thin steak was all that could be obtained from a large Cryptochiton, and it radiated such a penetrating fishy odor that it was discarded before it reached the frying pan.”

New radular teeth are continually secreted and shaped inside a specialized secretory organ, the radular sack, where they are fused with the underlying radular cuticle that maintains tooth alignment with respect to one another. Slow migration of the cuticle strip brings the newly formed teeth forward until they are in a functional position, at the anterior-most region of the radula. Because every stage of tooth development is contained on a single radula, it represents an ideal model system for investigating the dynamic processes of biomineralization. Our present study reports a detailed investigation of the unique properties of the radular teeth of C. stelleri. Lowenstam's initial investigations into the architecture of the radular teeth from C. stelleri revealed that the tricuspid mineralized cap is a multi-component system consisting predominantly of an amorphous phosphatic core covered with a hard veneer of magnetite. Although mineralogical analyses by Raman and EDS have been performed previously at various locations on radular tooth cross-sections, detailed elemental and mechanical maps during the tooth maturation process have not been reported.

In this work, we present a more detailed understanding of the mineralized radular teeth via nano-mechanical and elemental mapping in order to provide insight into the important structural gradients that
contribute to the unique impact and abrasion-resistant properties of this material.

**Results and discussion:**

The mature radular teeth are each composed of a mineralized tricuspid cap with a stalk-like flexible attachment to the base of the radula (Fig. 2d-f). When examined by optical microscopy, the second row of lateral teeth appears black and lustrous (Fig. 2c), and synchrotron X-ray transmission studies reveal the nature of the electron density distribution of this material (Fig. 2e). These observations are also supported by backscattered electron microscopy studies\(^{13}\) where the tooth caps are significantly brighter compared to the background material of the stalk and basal supporting membrane (Fig. 2d-f).

Cross-sectional examinations by scanning electron microscopy (Fig. 2f, \(\alpha\)) and energy dispersive spectroscopy (EDS) of the radular teeth of *C. stelleri* reveal that they are composed of two distinct mineral phases\(^{2,4}\) (Fig. 3a). The core region of the teeth is enriched in iron phosphate and the exterior of the teeth in iron oxide (Fig. 3a, b). EDS analysis also reveals a significantly higher C content in the tooth core as well as small amounts of Ca, K, Na, Mg, and Si (Fig. 3b). X-ray and electron diffraction (Figs. 3c, 5d) of the tooth exterior region reveal that it is composed of ferromagnetic iron oxide (magnetite)\(^{2,4,15}\), while EDS, Raman spectroscopy\(^{11,12,16}\) and dark-field transmission electron microscopy of the tooth core material suggest the presence of weakly crystalline hydrated iron phosphate (Figs. 3b, d; 5e)\(^{2,4}\). The iron phosphate rich core region of the radular teeth exhibits two intense Raman bands at 1050 and 1010 cm\(^{-1}\) along with weak bands at 1110 cm\(^{-1}\) and in the range of 400 – 700 cm\(^{-1}\) (Fig. 3d). It is generally accepted that the stretching and bending vibrations of phosphate groups occur at 1000 – 1200 and 400 – 700 cm\(^{-1}\), respectively. The Raman peaks of crystalline materials are typically sharp and well separated in the regions of 900 – 1200 cm\(^{-1}\) and 100 – 400 cm\(^{-1}\).\(^{17,18}\) In contrast, the Raman peaks of amorphous/nanocrystalline materials are wider, weaker and typically not well resolved for the vibrations from the phosphate or iron-oxygen moieties, which is consistent with our analyses of the core region of the radular teeth (Fig. 3d). The raman spectra also suggest a large \(\alpha\)-chitin component in the core material (Fig. 3d) and TEM studies reveal the presence of abundant chitin fibers throughout this region (Fig. 5e)\(^{19,20}\). In addition, EDS point scans across focused ion beam milled samples of the tooth core material reveal the presence of isolated domains of silica. These siliceous domains appear more electron transparent in TEM studies compared to the comparatively electron dense surrounding hydrated iron phosphate (Supplemental Fig. 2)\(^{2,4}\).

Nanomechanical analyses of polished cross-sections through both the tooth tip and mid-region reveal that the two mineral phases (the magnetite veneer and the core of weakly crystalline hydrated iron phosphate – see Fig. 2f) exhibit distinct mechanical properties (Fig. 4a). The magnetite veneer has a modulus ranging from 90 to 125 GPa and a corresponding hardness ranging from 9 to 12 GPa. To the best of our knowledge, these values represent the highest modulus yet reported for a biomineral\(^{22}\). The hardness is notably about 3 times higher than that of enamel and nacre, which exhibit indentation hardness and modulus of 3 – 4 GPa and 65 – 75 GPa\(^{22}\), respectively, making this material exceptionally well suited for the continuous scraping activity of the radular teeth. In contrast, the weakly crystalline core region has a modulus of ca. 25 GPa and a hardness of ca. 2 GPa. Mechanical mapping of cross-sections through these two regions of the teeth reveals a distinct gradient in mechanical properties with the modulus of the leading edge of the tooth ca. 15% higher than that on the trailing edge. This design strategy results in an uneven wear pattern along the scraping edge of the tooth and establishes a self-sharpening condition (Fig. 4b), an observation consistent with radula structural studies on other species\(^{23}\).

Indentation fracture studies of the magnetite veneer reveal that cracks propagating through this material usually travel parallel to the long axis of the tooth rather than perpendicular to it (Fig. 5b). In contrast, cracks propagating through the tooth core are largely isotropic and lack any defined directionality (Fig. 5a). In addition, as a propagating crack crosses the boundary between the core material and the outer magnetite shell, significant crack deflection occurs at this interface (Fig. 5a) because of the stress redistribution occurring either from small-scale yielding of the thin organic layers, or from debonding at the organic/mineral interface, with the latter mechanism being more efficient in protecting the uncracked material across the interface\(^{24}\) (Fig. 5a). This strategy of crack deflection is very effective at maintaining the tooth structural integrity and preventing catastrophic failure of the material. Examination of fractured tooth cross-sections reveals how the organization of the magnetite crystallites facilitates this mechanical response (Fig. 5c).

Scanning electron microscopy of these fractured surfaces reveals that the magnetite is organized into ca. 250 nm wide bundles of crystallites that are oriented parallel to the long axis of the teeth, each of which is surrounded by a thin organic layer\(^4\). Transmission electron microscopy analysis of focused ion beam-milled samples from both the core region (Fig. 5e) and the outer magnetite shell region (Fig. 5d) confirm both the rod-like orientation of the magnetite crystallites and the weakly crystalline, organic rich nature of the core material. Selected area electron diffraction and dark-field imaging of the outer magnetite shell also reveal that although the magnetite crystallites (each of which measure ca. 30 nm in diameter) are organized into aligned rod-like columns, there is no preferred orientation of the constituent crystallites (Fig. 5d). In contrast, the diffuse electron diffraction pattern of the tooth core material clearly demonstrates the weakly crystalline form of the iron phosphate phase.

While the hardness and modulus of the teeth are directly related to the intrinsic mechanical properties of the constituent mineral phases, indentation fracture measurements of sodium hypochlorite-treated
Fig. 3 Elemental and phase analysis of the radular teeth from C. stelleri. EDS analysis of the mature radular teeth (a,b) reveal an iron phosphate core surrounded by a thick veneer of iron oxide. Powder XRD (c) suggests the presence of α-chitin and magnetite as the dominant crystalline phases. A chitin reference pattern is shown in orange and the crystal structure of magnetite is shown to the right of the diffraction pattern. Raman Spectroscopy (d) identifies the two likely mineral phases in the shell and core regions as magnetite and hydrated iron phosphate, respectively. A Raman linescan (d-left) through the region highlighted in the backscattered SEM image illustrates the transition zone between the two mineral phases. The dominant peak in the blue spectrum at 670 cm⁻¹ corresponds to the νFe-O vibration of magnetite while the dominant peak in the pink spectrum at 1010 cm⁻¹ corresponds to the νP-O vibration of iron phosphate. A higher resolution raman spectrum of the radular tooth core material with the labeled peaks corresponding to α-chitin, phosphate and water is shown in 2D-right. See Supplemental Fig.3 for more details.
teeth reveal that following destruction of the tooth organic matrix, the fracture toughness drops precipitously, while the modulus and hardness remain largely unaffected (<15% reduction, unpublished work). This illustrates the important point that structural integrity can be attained only in the presence of the organic matrix that facilitates the anisotropic organization of the magnetite crystallites, binds them into a composite structure, and plays a critical role in crack blunting and deflection at interfaces. The highly mineralized nature of the external magnetite region of the radular teeth is exemplified by its low organic content (ca. 2%) compared to the core iron phosphate region (ca. 8%).

To gain additional insight into the abrasion resistance of the radular teeth from *C. stelleri*, we plotted the $E/H$ combination on an Ashby-type plot that compares the abrasion tolerance of a wide range of materials (Fig. 6a). Here the guidelines correspond to abrasion damage by localized plastic deformation against a blunt and rigid contact (Fig. 6b), for which the critical normal load for yielding $P_y$ (according to Hertzian contact mechanics) is proportional to the materials property group $P_y \propto H^{3/2}E^2$. Hence by plotting $E$ vs. $H$ values on a log-log plot, materials lying on lines with a slope of $2/3$ are predicted to perform equivalently against yield damage at the contact.

Based on these criteria, we predict that the radular teeth of *C. stelleri* perform better against wear damage than the hardest known biominerals: enamel and nacre. Perhaps even more remarkable, the predicted abrasion resistance against a blunt contact exceeds that of zirconia (a common ceramic used in load-bearing applications) and is equivalent to the hardest structural ceramics such as silicon carbide (SiC) and boron carbide (B$_4$C). For reference, a geological magnetite mineral standard is also shown on the plot. Interestingly, the latter exhibits hardness values (10.5 ± 0.2 GPa) equivalent to the radular teeth of *C. stelleri*, but is significantly stiffer (175 GPa), i.e. 1.6 to 1.9 more stiff than the radular teeth. Small-scale sliding at the mineral/organic interfaces during external loading is a plausible cause to explain the larger compliance of radular tooth magnetite. From the materials selection plot, one expects the radular tooth magnetite to exhibit a higher tolerance to abrasion, here expressed in terms of residual indentation depth after contact loading, i.e. the smaller the residual depth, the better abrasion resistance. We performed indentation curves with a spherical tip (nominal tip radius 1 μm) on the two materials to verify this assertion up to normal peak load of 1 mN. Representative curves are presented in Fig. 6c, together with the predicted curves from the elastic Hertzian solution (with the actual radius tip calibrated from indentation curves on fused quartz in the elastic domain). Since deviation from the elastic solution corresponds to the onset of yielding, comparison between the elastic solution and the obtained experimental data allows detection of the critical load at yielding $P_y$.

The data and analysis confirm that (1) the critical load at yielding is indeed higher for the radular teeth as predicted from the index $P_y \propto H^{3/2}E^2$, and (2) the residual indentation depth $h_r$ of the radular teeth after incursion at a peak load of 1 mN is smaller, resulting in a better tolerance to abrasion than geological magnetite (in the absence of friction).

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*Fig. 4 Nanomechanical testing of radular tooth cross-sections from C. stelleri. (a) Indentation (left) and the corresponding gradient (right) maps of modulus (upper) and hardness (lower) through a tooth tip and mid-region reveal that the leading edge of the tooth has a higher modulus and hardness than the trailing edge, thus establishing the self-sharpening condition illustrated in (b). The direction of tooth movement against the substrate is indicated by the blue arrow. (c) adapted from*.

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When abrasion is produced by sharp stiff particles, plastic deformation initially occurs at the contact and the abrasion resistance approximately scales with the hardness\[^{25}\]. In such a case, the radular teeth from *C. stelleri* again outperform all other known biominerals. But yielding can be quickly followed by cracking at the contact in brittle materials\[^{25,28-30}\], and microcracking becomes the dominant wear mechanism. It can be shown that abrasion damage is then proportional to the material property group $K_{IC}^4 / H^2$ where $K_{IC}$ is the fracture toughness\[^{31}\]. Hence, a moderate increment of fracture toughness significantly improves the abrasion resistance (power-law exponent of 4). While $K_{IC}$ of radular tooth

![Fig. 5 SEM and TEM analysis of failure modes in the radular teeth of *C. stelleri*. While crack propagation through the tooth core is isotropic (a), those propagating through the outer magnetite shell travel parallel to the long axis of the teeth (b). SEM analysis of a fractured tooth (c) reveals its closely packed rod-like ultrastructure. TEM bright-field, dark-field, and selected area electron diffraction studies of focused ion beam milled tooth sections through the magnetite shell region (d) and the core region (e) show the highly parallel nature of the magnetite crystallite bundles (d), the organic-rich fibrous core material, and the weakly crystalline nature of the associated mineral phase (e).]
magnetite still awaits experimental determination, it is anticipated that its complex hierarchical microstructure toughens the structure against catastrophic fracture in comparison to monolithic magnetite, much to what has been established for the hierarchical calcium carbonate microstructures of nacre and conch shells. Additionally, tolerance to abrasion is proportional to the factor $1/E^2$. Supplemental Table 1 compares this index (as well as those discussed earlier) with literature values for various biominerals and engineering ceramics. These data suggest that the radular teeth from *C. stelleri* perform as well as hard ceramics, but appear less tolerant to microcracking from a sharp abrasive than enamel or mollusk shells. Knowledge of the radular tooth’s fracture toughness, however, will be necessary to confirm this prediction. These results emphasize the importance of the geometry of the contact in defining the abrasion tolerance of biominerals. A comprehensive experimental study of wear at the micro-scale is the topic of an on-going investigation.

The results obtained from the investigations outlined above have the potential to enable progress in the emerging fields of nanotechnology and nanomanufacturing, exploiting control mechanisms established by nature to make novel materials and devices exhibiting unique properties. For example, the graded modulus design of the radular teeth and their anisotropic rod-like substructure provides design cues that could be used in the fabrication of ultrahard materials for precision cutting or wear-resistant components. The graded modulus design would be particularly useful for creating a self-sharpening condition in instances where location or situation would not permit regular replacement or sharpening of the cutting blades. In addition to understanding the structure function relationships in these unique abrasion- and impact-tolerant materials, the high abundance of crystalline magnetite also make them an ideal model system for elucidating the synthesis mechanisms of magnetic materials at ambient temperatures and pressures and near-neutral pH. Toward this endeavor, future investigation of the structure and composition of the tooth organic matrix could ultimately lead to the identification of specific chemical functionalities that play a critical role in controlling magnetite nucleation and growth.

![Fig. 6 Abrasion performance of the radular teeth from *C. stelleri* against a blunt contact.](a) Property map resistance of yield damage (stiff abrasive) for various materials (adapted from) predicts that the radular teeth perform better than known biominerals against a spherical contact and approaches that of the hardest engineering ceramics. (b) Schematic description of yield initiation beneath the contact during a normal loading/unloading cycle. (c) Representative indentation curves with a spherical tip on the radular teeth and a geological magnetite control: deviation from the elastic Hertzian solution corresponds to incipient yielding and confirms that the radular teeth have a higher critical load (in agreement with $P_c \propto H^2/E^2$), while its residual impression, $h_r$, is smaller at that peak load.
Materials and methods

Research specimens
Live specimens of Cryptochiton stelleri were collected from Vancouver, British Columbia between October 2008 and March 2009 and maintained live in a recirculating seawater system until ready for use. The radulae were dissected from these specimens and rinsed in fresh seawater to remove any organic debris and immediately dehydrated through a graded series of ethanol treatments. Following complete dehydration to 100% ethanol, the anterior-most region of each radula (containing the fully mature teeth) was removed and embedded in Spurrs resin. The resin blocks obtained were polished to P1200 with progressively finer grades of silicon carbide paper and then with diamond lapping films of particles sizes down to 0.25 μm to obtain a smooth finish.

The resulting samples were examined either by nanoindentation, Raman spectroscopy, back-scattered and secondary scanning electron microscopy, or focused ion beam milled for transmission electron microscopy as described below:

Nanoindentation
Full-map indentation tests were performed on cross-sections through the tip and mid-region of the mature radular teeth from C. stelleri in ambient air using a Triboindenter nanomechanical testing system (Hysitron, Minneapolis, MN, USA) with either a Berkovich or a cube corner tip at a peak force of 5 mN. The load function consisted of a 5-second loading to 5 mN, followed by a 5-second hold at that force, and then a 5-second unloading. The resulting indents in a grid-array measured ca. 12.5 μm apart and the hardness and reduced modulus were calculated from the unloading curve of each, using the Oliver-Pharr method. Similar indentation measurements were also performed on the same tooth samples that had been hydrated with deionized water using rows of intents that crossed from the outer magnetite shell region into the iron phosphate core region. The measurements were performed to investigate the possible influence that sample dehydration might have on the measured mechanical properties. These results revealed that due to the highly mineralized nature of the teeth, there was on average only a ca. 15% reduction in both modulus and hardness within both mineral phases of the teeth in the hydrated vs. the dry state. For this reason, and to standardize measurements from sample to sample, all subsequent measurements were performed with dry samples.

The resulting modulus and hardness data were plotted using XYZPlot (Hysitron) and the corresponding gradient maps were created by applying a Gaussian blur function to the resulting indentation maps which were superimposed on the corresponding back-scattered electron micrographs. For comparative purposes, a profile of indents was also performed on polished sections of conch shells (Strombus gigas) using the procedures described above. Indents were also performed with a spherical tip (nominal radius 1 μm) on both the polished radula sections and a geological magnetite control at prescribed peak loads of 1 mN (0.1 mN/sec. loading rate) with a 5 second hold. Calibration of the tip radius was done by performing a series of indents on fused quartz (reduced modulus 69 GPa) in the elastic domain and fitting the loading curves with the Hertzian’s solution. Best fit gave an actual radius of curvature of 400 nm.

Scanning electron microscopy and Energy dispersive spectroscopy
Polished tooth samples were gold coated and examined with a FEI XL-40 or a Tescan VEGA TS-S3130MM scanning electron microscope equipped with an IXRF systems energy dispersive spectrometer. In addition to the polished sections, whole fractured teeth were also analyzed by SEM to identify their failure modes. Additional teeth were soaked overnight in a 5.25% sodium hypochlorite (NaOCl) solution to remove the organic phase. The resulting samples were then soaked overnight in DI water, mechanically fractured, rinsed briefly with ethanol and air dried for examination by SEM. Additional NaOCl-treated teeth were prepared, embedded and polished for nanomechanical testing as described above.

Transmission electron microscopy
Polished tooth cross-sections were prepared for TEM using a focused ion beam milling machine (Leo Gemini, 1540XB) to obtain thin sections measuring ca 100nm thick. The resulting foils were examined using a FEI-PHILIPS CM300 transmission electron microscope at 300 kV accelerating voltage.

Raman spectroscopy
Polished tooth samples prepared as described above were investigated using Raman spectroscopy (λ = 780 nm) under low laser power conditions (6 mW) to minimize sample heating. Raman linescans were performed with mineral standards to help identify the various inorganic phases present in the different regions of the teeth using a Thermofisher DXR dispersive Raman microscope.

X-ray transmission and diffraction
For X-ray diffraction, the mineralized caps from the mature teeth of C. stelleri were individually mechanically separated from the supporting chitinous stalk, ground into a fine powder, and examined using a Philips X’PERT Powder Diffractometer with Cu Kα radiation.

Synchrotron X-ray transmission imaging was performed at beamline X13B at the National Synchrotron Light Source, Brookhaven National Laboratory, using 19 keV X-rays (λ = 0.65 Å) and a beam spot focused to ~10 μm x 10 μm. Specimens consisting of several radular teeth still attached to their basal membrane were mounted in the beam and scanned in 25 μm steps both parallel and perpendicular to the basal plane. Transmitted intensity was recorded using a photodiode detector fixed beyond the sample and normalized by incident intensity measured with an ion chamber.
Acknowledgements:
We thank Philip Bruecker and Shane Anderson for help with specimen acquisition, Sara Krause for the illustration in Fig. 1b, and Dr. Kenneth Evans-Lutterodt of the National Synchrotron Light Source for contributing his expertise at the microdiffraction endstation X13B. The NSLS is supported under USDOE Contract DE-AC02-98CH10886. This work made use of the Scanning Electron Microscopy facilities in the laboratory of D. Morse at UCSB. Professor Kisailus acknowledges support from his initial complement at U. C. Riverside.

Author Contributions:

Supplemental Information

Table S1 Materials property group of various biominerals and structural ceramics. Yield damage from a blunt contact is proportional to \( H^3/E^2 \); yield from a sharp contact mostly depends on \( H \), while microcracking from a sharp abrasive depends on the index \( K^2_{IC}/H^2 \). \( K_{IC} \) of the radular teeth is unknown, hence only the factor \( 1/H \) \( E^2 \) is presented and used for comparison.

<table>
<thead>
<tr>
<th>Material</th>
<th>( H ) [GPa]</th>
<th>( E ) [GPa]</th>
<th>( H^3/E^2 ) [GPa]</th>
<th>( 1/H ) ( E^2 ) [GPa(^{-2})]</th>
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<td>Radular teeth from ( C. stelleri )</td>
<td>9 – 12</td>
<td>90 - 125</td>
<td>0.10 – 0.14</td>
<td>7\cdot10^{-6} – 1.4\cdot10^{-5}</td>
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<td>Magnetite</td>
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<td>175</td>
<td>0.03</td>
<td>7\cdot10^{-6}</td>
<td>This study</td>
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<td>Enamel</td>
<td>3.5 – 4.5</td>
<td>65 – 75</td>
<td>0.01 – 0.02</td>
<td>4\cdot10^{-5} – 6.8\cdot10^{-5}</td>
<td>35-37</td>
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<tr>
<td>Aragonite (Abalone and Conch shells)</td>
<td>3 – 4</td>
<td>70 – 75</td>
<td>0.01</td>
<td>6.3\cdot10^{-5}</td>
<td>This study, 38,39</td>
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<td>0.02</td>
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<td>40</td>
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<td>140 – 240</td>
<td>0.05 – 0.06</td>
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<td>0.05 – 0.12</td>
<td>1.5\cdot10^{-7} – 3\cdot10^{-7}</td>
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<td>430 – 480</td>
<td>0.13</td>
<td>1.6\cdot10^{-7}</td>
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Fig. S3 Detailed analysis of the Raman data obtained from the core region of the radular teeth of C. stelleri. The specific vibrations corresponding to specific peak locations are listed to the right of the figure.

REFERENCES