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Other Collaborators:

Final Report (2017)

Procurement of a Tandem EDS/STEM Mapping, SEM and 3D-Rendering System for Chemical-Structural Analysis of Biological Composites

Agreement # W911NF-16-1-0208

PI: David Kisailus, UC Riverside

Agency: Army Research Office

Program Manager: Dr. Stephanie McElhinny, Biochemistry, Life Sciences Division

Abstract

After acquiring the Infrared Imaging Microscope with large area mapping capabilities for structure-function research and education in composite and semiconducting materials, we have been largely successful in obtaining high quality, high-resolution FTIR maps of multiple biological composites. This includes the chemical mapping of the radular teeth of *Cryptochiton stelleri* (chiton), the crush resistant exoskeleton from *Phloeodes diabolicus* (the Iron Clad beetle), and the hard and impact resistant dactyl club from the stomatopod *Odontodactylus scyllarus*.

The FTIR microscope has enabled us to make significant contributions in uncovering details about ultrastructural features of the various regions within these biological composites and has enabled us to begin deriving new design strategies for the synthesis of impact and abrasion-resistant composites.

Through the acquisition of this FTIR microscope, we have also enabled the training and education of post-doctoral researchers, graduate and undergraduate students. Personnel that have utilized this instrument include: Dr. Sourangsu Sarkar (post-doctoral researcher), Dr. Lessa Grunenfelder (post-doctoral researcher), Parawee Pumwongpitak (Ph.D. student), Nicholas Yaraghi (Ph.D. student), Steven Herrera (Ph.D. student, Hispanic minority), Jesus Rivera (Ph.D. student, Hispanic minority), Thomas Dugger (Ph.D. student), Ramya Mohan (Ph.D. student), Kanako Sato (visiting Ph.D. student), Brian Macdonald (undergraduate student) and Jeff Geiger (undergraduate student). In addition to training and education, this equipment has enabled our lab to collaborate with multiple PIs around the world, including: Dr. Joanna McKittrick (UCSD), Dr. Matthew Shawkey (Univ. Akron), Dr. Pablo Zavattieri (Purdue University), Dr. Dimitri Deheyn (Scripps, UCSD), Dr. Atsushi Arakaki (Tokyo University of Agriculture and Technology), Dr. Yoshiaki Maeda (Tokyo University of Agriculture and Technology), Dr. Hiroaki Imai (Keio University).

Finally, through the procurement of this instrument, the data we have acquired data that has lead to outreach events at the Riverside Metropolitan Museum (May, 2015). During this event, 8 of my 11 undergraduates working in the Biomimetics and Nanostructured Materials Lab have presented their research to a public audience.

Research objectives relevant to DoD

The proposed instrumentation has greatly enhanced the quality of research and research-related education currently funded by the DoD as well as established new research capabilities at the University of California, Riverside, for performing research potentially of interest to the DoD.

ARO's mission is to serve as the Army's premier extramural basic research agency in the engineering, physical, information and life sciences; developing and exploiting innovative advances to ensure the Nation's technological superiority. ARO enables its mission based on an aggressive basic science research program so that cutting-edge scientific discoveries and the general store of scientific knowledge will be optimally used to develop and improve weapons systems that establish land force dominance.

The Biochemistry program's main goals are to focus on fundamental studies in biochemistry, structural biology, cell biology, and biophysics that will facilitate the development of novel systems and processes to enhance Soldier protection and performance. The research areas include biomolecular self-assembly, molecular recognition, protein and nucleic acid structure-function relationships, enzymology, signal transduction, cell-cell communication, macromolecular structure, and synthetic biology. This program also supports basic research in structural studies of molecular and macromolecular organization for novel materials or surfaces. The Mechanical Behavior of Materials program seeks to establish the fundamental relationships between the structure of materials and their mechanical properties as influenced by composition, processing, environment, and loading conditions. The program emphasizes research to develop innovative new materials with unprecedented mechanical, and other complementary, properties. A primary research thrust area of this program to realize novel mechanisms of energy absorption and dissipation and identifying novel mechanisms for enhancing specific toughness, engineering and synthesizing new materials containing unique and specifically designed chemical and biological functionalities and activities while maintaining, and preferably enhancing, requisite mechanical properties. Finally, the Synthesis and Processing of Materials Program encourages basic research on innovative processing and synthesis of advanced high performance structural materials systems. The vision of the program is to discover and illuminate the scientific linkages between novel processing and resultant microstructures, which enable exceptional properties in structural materials. Research thrusts specific to this program include high specific-strength materials and hierarchical composites, the subject of the PI's current project with ARO. Since advances in this area are enabled by insights and scientific breakthroughs achieved through combinations of novel experimental tools, this instrumentation will help to achieve these goals.

In order to address the above ARO needs, the PI, a recently promoted professor at University of California, Riverside (UCR), Bourns College of Engineering, initiated several projects that investigate structure-function relationships of high-performance composites as well as developed synthetic strategies towards biologically inspired composites.

Our research touches all three of these program's objectives by (1) performing structural studies of molecular and macromolecular organization for novel materials or surfaces, (2) uncovering novel mechanisms of energy absorption and dissipation and identifying novel mechanisms for enhancing specific toughness through ultrastructural analyses combined with mechanical testing of this composite, and (3) discovering scientific linkages between biological processes and resultant microstructures. We aim to establish synthesis-structure-function relationships in mineralized and biologically inspired composite materials by overlaying ultrastructure, chemical and mechanical maps of regional features expanded on a global scale. This includes a detailed understanding of the underlying organic matrix, which is believed to exert control over the crystallization process that ultimately controls the function of the composite. We will interrelate these observations to identify dominant mechanisms at relevant scales and extract design strategies for mimetic syntheses of high performance materials.

Aiming to address the above ARO needs, the PI has initiated several projects in the past year that investigate structure-function relationships of high-performance composites as well as develop synthetic strategies towards biologically inspired composites and nanostructured materials. This includes the PI's previous and current research with ARO: Organic Matrix Templating and Function in an Ultrahard Biological Composite, award #W911NF12-1-0257 and Organic-mediated Mineral Transport and Force Transduction in an Ultrahard Biological Composite, award #W911NF-15-1-0306.

One major focus area of the Kisailus lab at UCR is to develop new structural materials that have high strength and durability, and are light-weight and damage-tolerant. Biomineralized tissues are used as model systems for the understanding of structure-function relationships that serve as templates for biologically inspired systems. These biological systems demonstrate the ability to control nano- and microstructural features that significantly improve mechanical performance of otherwise brittle materials. By investigating the structure-function relationships of these mineralized structures using modern chemical, morphological, and mechanical characterization techniques, we will develop the necessary synthetic tools for the design and fabrication of light-weight, ultrahard and tough composites that mimic the various design elements and performance properties present in the biological systems.

Much of our work relies the elucidation of the primary mechanisms of organic mediated templating and toughening within these unique composite materials through the following investigations:

1. A detailed study of the chemical and ultrastructural features of the fully mineralized composites with a complementary mechanical investigation (combined modeling and experimental) of the mineralized structures.
2. A thorough investigation of the underlying organic framework (structural and chemical) that provides templating for mineral growth as well as scaffolding for the composite.
3. Synthesis of biomimetic materials through in-vitro mineralization studies to understand organic-inorganic interactions and growth mechanisms, which provide architectural features that enhance performance and enable biomimetic syntheses.

The acquisition of the FTIR microscope has enabled us to significantly enhance our research capabilities towards all of these investigations by uncovering key elements in different composites that provide them with such remarkable ability to control interfacial elements which affects their performance.

<u>Accomplishments based on acquisition of the FTIR microscope:</u>
The following are overviews of results that have been attained based on acquisition of the FTIR microscope from Agilent (Figure 1).

Figure 1. Agilent CARY 680/620 FTIR microscope with 128x128 Focal Plane Array detector.

Numerous ongoing research projects in the Kisailus lab are investigating structure-function relationships in a wide range of self-sharpening, abrasion-resistant, and impact tolerant biological structures.

Current major research projects that would significantly benefit from this set of instruments focus on investigating structure-function relationships in three distinct types of impact tolerant biological composites; the exoskeletons from the terrestrial diabolical iron clad beetle and a flying beetle from Japan, the dactyl clubs of stomatopod crustaceans, and the ultrahard, mineralized teeth in Chitons. Another project, was performed in collaboration with Professor Hiroaki Imai at Keio University in Tokyo, investigates micro-and nano-features of abrasion resistant rice plants, which contain silica in their plant walls. Beyond this, many additional projects that need FTIR microscope analyses have been initiated as part of the PI's new MURI grant.

Initiated through the analysis of biologically-based composite materials, the results obtained from these studies will provide bio-mimetic / inspired tools for the design and fabrication of ultra-hard, abrasion and impact resistant materials.

Project 1: AFOSR funded "*MURI: Convergent Evolution to Engineering: Multiscale Structures and Mechanics in Damage Tolerant Functional Bio-composite and Biomimetic Materials*".

The PI and his collaborators from Purdue, UC Berkeley, Northwestern, and UCSD have initiated this work through AFOSR (Program Manager: Hugh DeLong, Deputy Director, Mathematics, Information and Life Sciences Directorate) for the development of ultra-tough, impact resistant composites. The project involves investigating multiple organisms to determine new design concepts for light-weight, tough, strong and impact resistant materials. The involvement of a new start up company, Nature Inspired Industries, will provide a pathway to eventual commercialization of the technologies in products of value to the DOD.

The following show some examples of structures being investigated, which utilized the FTIR microscope.

BEETLE: The goal of this project is to elucidate the toughening mechanisms of the exoskeleton from the terrestrial diabolical iron clad beetle (Figure 2), a non-mineralized biological composite, and apply the lessons learned from these studies toward the fabrication of synthetic high-performance composites.

Figure 2. The terrestrial diabolical iron clad beetle (*Phloeodes diabolicus*).

A major component of this research will be the ultrastructural analysis of the exoskeleton of this extremely impact and crush resistant beetle and compare it with other beetles designed for flying. Here, we will develop specific techniques for the fabrication of three-dimensional structures with the requisite micro- and nano-scale morphological features that may contribute to the bulk mechanical properties (Figure 3). One approach through which this will be accomplished is through the use of 3D printing or electrospinning of fiber reinforced composites.

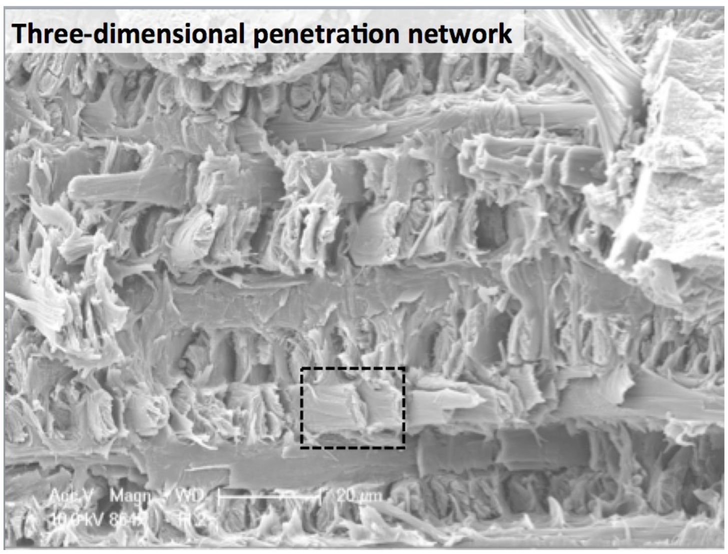

Figure 3: Micro- and nano-scale morphological features that may contribute to the bulk mechanical properties of the beetle exoskeleton. The fiber and matrix components, as well as their interfaces within this structure are being investigated to develop biomimetic composites.

Initial analyses of this structure using the new FTIR microscope (Figure 4), in conjunction with XRD, have indicated that it consists primarily of alpha-chitin fibrils that are dispersed within an organic matrix. Additional analyses have indicated this matrix is proteinaceous. However, further analyses are needed using the FTIR microscope to pinpoint the region-specificity of these proteins, which is critical to understanding fundamental structure-mechanical property relationships as well as the design of new biomimetic composites with controlled interfaces.

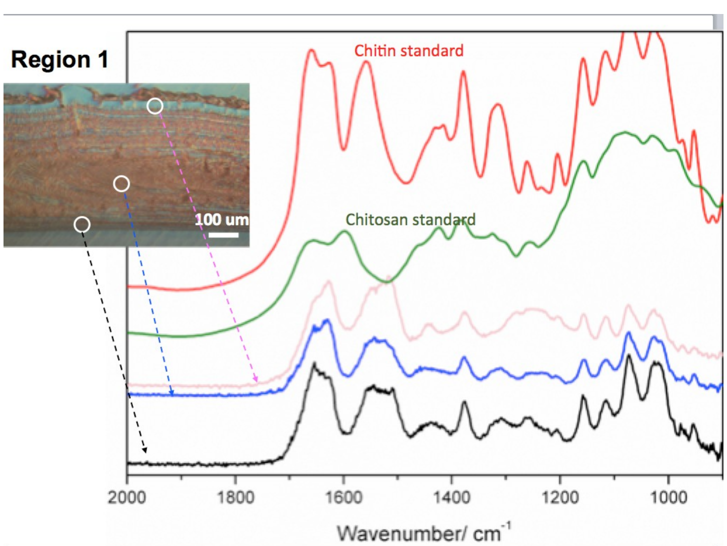

Figure 4. FTIR reflectance spectra of different regions within the cross-section from the elytra (top half of beetle exoskeleton).

In addition, we are comparing the structures within the terrestrial beetle to a flying beetle found in Japan (*Trypoxylus dichotomus*). Here, we investigate region-specific domains within the exo- and endo-cuticle regions of the elytra from this species. Figure 5 show FTIR mapping of different bands from regions within the exo- and endo-cuticle regions.

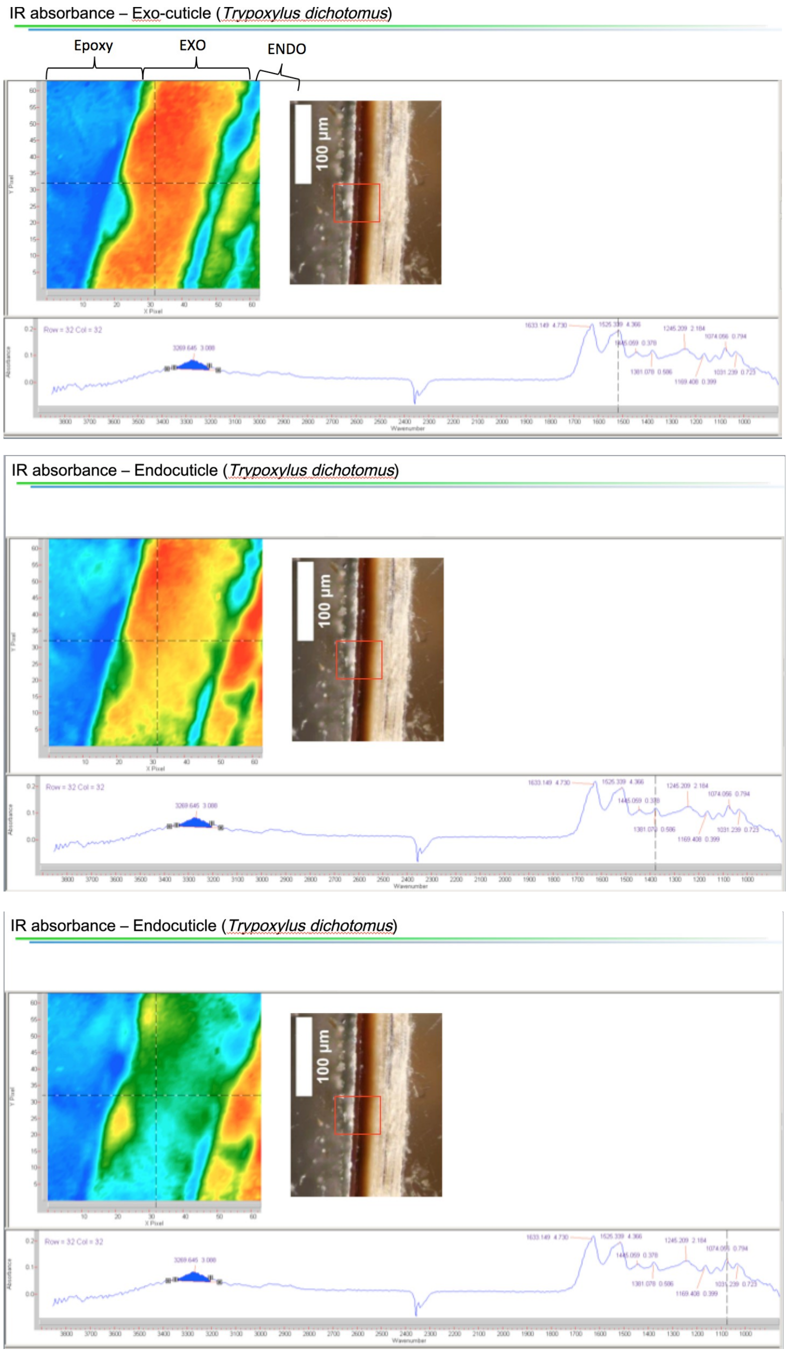

Figure 5. FTIR maps of different regions within the cross-section from the cuticle (bottom half of exoskeleton) from the Japanese flying beetle (*Trypoxylus dichotomus*).

MANTIS SHRIMP (STOMATOPOD): Here, we are studying the structure-function relationships in damage-tolerant impact/shock-resistant stomatopod (Figure 6) dactyl club while addressing the ongoing quest to develop the new generation of scalable high-performance *biologically-inspired* multifunctional materials. This ultrahard organic-inorganic composite structure is capable of inflicting significant damage following impact with a wide variety of biomineralized structures (e.g., mollusk shells, crab exoskeletons, the skulls of small fish, and the occasional weary fisherman).

Figure 6: Dactyl modifications in stomatopods that that either hunt by impaling their prey with spear-like structures (left) or those that smash them with a powerful blow from a heavily mineralized club (right) stomatopods. (Illustrations adapted from Brooks, 1886). Species: *Neoanchisquilla sp.* (left) and *Odontodactylus scyllarus* (right).

In fact, these formidable structures are capable of accelerations to 10,400 g and speeds of 23 m/s from a standing start. Because of their rapid strike, they can generate cavitation bubbles between the appendage and the striking surface. The collapse of these cavitation bubbles produces significant forces on their prey in addition to the instantaneous forces of 1,500 N that are caused by the direct impact of the dactyl club. Despite these significant forces, the dactyl clubs are extremely fracture-resistant and are able to tolerate thousands of highly energetic blows, a characteristic that can be directly linked to their ultrastructural features. This research model is quite different from others due to its multi-phasic architecture and in the fact that it performs primarily an offensive, rather than a defensive function. The ultimate goal of this project will be to not only understand the structure-function relationship in this unique impact tolerant biological structure, but to ultimately develop synthetic engineering analogs that exhibit equally impressive mechanical properties.

We have acquired a new nanoindentation system that was used to perform depth-sensing nanoindentation experiments on the polished longitudinal and cross-sectional specimens of the dactyl clubs to create the multi-sectional modulus maps and line scans. Multiple indentations (at 1mN) were performed at different locations (from the impact surface to the club interior) on the dactyl club to obtain the depth and region dependent mechanical properties. Figure 7 shows a nanoindentation map (modulus) of the cross section of the dactyl club.

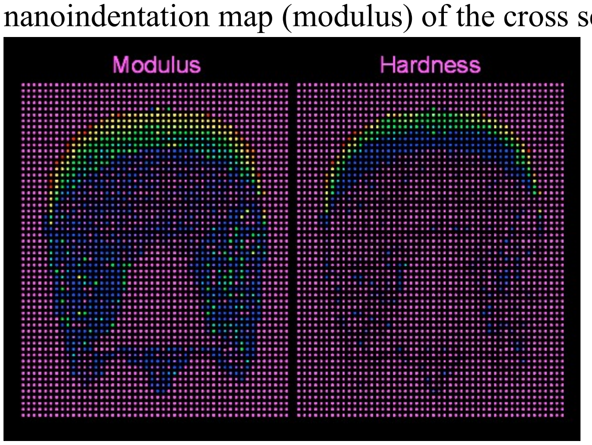

Figure 7. Nanoindentation map depicting the elastic modulus and hardness of regions within the dactyl club. The modulus was highest in the exocuticle, reaching up to 80 GPa, while the less mineralized endocuticle had a modulus of 5 GPa. Similarly, the hardness ranged from ca. 3.5 GPa in the exocuticle to ca. 0.8 GPa in the endocuticle.

The regions within the club display different mechanical properties. Note the large differences in modulus across two interfaces (i.e., 5 GPa – 30 GPa – 65 GPa), similar to what is observed in a human tooth from dentin – dentin/enamel junction – enamel.

Based on these results, an understanding of organic – mineral interfaces will be important to derive not only structure-functional relationships, but also synthesis-structural interplay. Figure 8 shows some initial results of FTIR mapping of a cross section of the dactyl club. Further analysis will include the investigation of partially molted clubs to understand region-specific organics that guide the crystallization of hydroxylapatite on the outer region of the club as well as those that stabilize amorphous mineral deep inside the club.

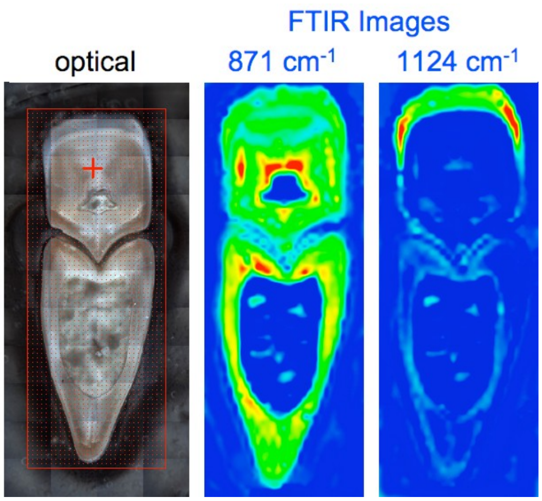

Figure 8. FTIR mapping of cross-sections within the club of the smashing mantis shrimp. Regio-specificity is highlighted at different wavenumbers.

Project 2: ARO-funded "<u>Organic Matrix Templating and Function in an Ultrahard Biological Composite</u>" and "<u>Organic-mediated Mineral Transport and Force Transduction in an Ultrahard Biological Composite</u>"

The chitons (Mollusca, Polyplacophora) 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, 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.

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) exhibit distinct mechanical properties (Figure 9). 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. 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, 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. 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 scrapping edge of the tooth and establishes a self-sharpening condition, an observation consistent with radula structural studies on other species.

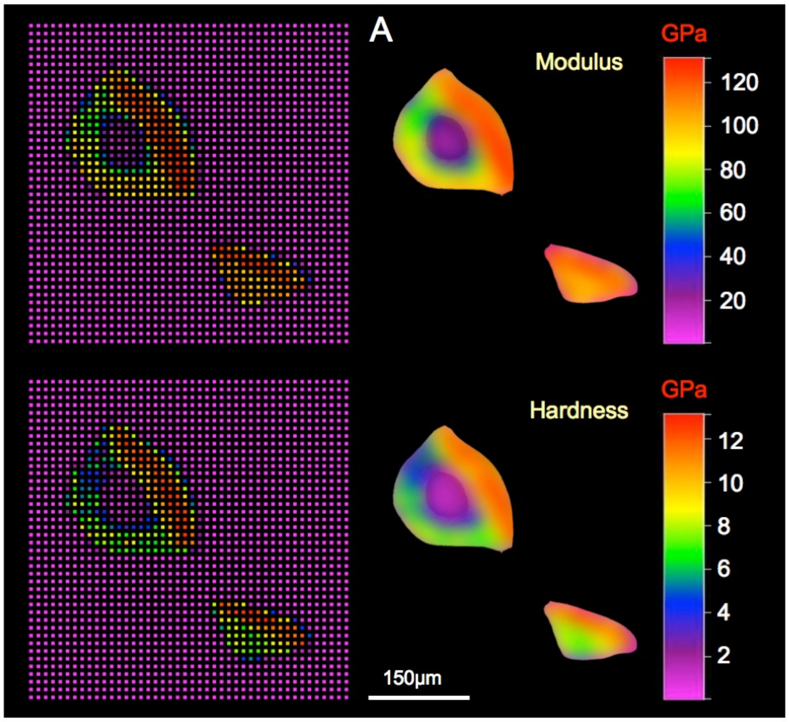

Figure 9: Nanomechanical testing of radular tooth cross-sections from *C. stelleri*. (A) Indentation (left) and the corresponding gradient (right) maps of modulus (upper) and hardness (lower) through a tooth tip and mid-region reveal that the leading edge of the tooth has a higher modulus and hardness than the trailing edge.

Over the past year, we initiated testing of the organic stylus, which supports the ultrahard magnetic teeth. At the macroscale, an ultrahard tooth is attached to softer and flexible stylus (Figure 10). From our preliminary studies, we find that the organic interface between this ultrahard tooth and flexible stylus undergoes some chemical and mechanical changes as a function of maturation (Figure 10, middle). We have also performed some initial elemental analyses of the stylus and have found large, but differing concentrations of sulfur within its leading and trailing edges (Figure 10, right).

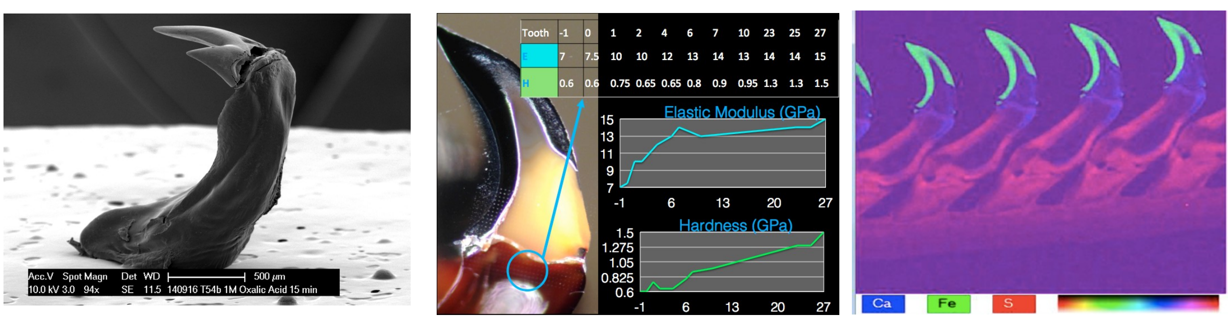

Figure 10. SEM micrograph (left) of a fully mineralized tooth attached to its stylus. Nanoindentation modulus and hardness (middle), as a function of tooth number, at the organic interface between the tooth and stylus demonstrating significant increases with mineralization. Elemental mapping of Ca, Fe, S (right) of the longitundinal sections of teeth plus styli highlighting the presence of sulfur (red) along the leading and trailing edges of the stylus and likely enhancing stiffness of the organic.

Here, we utilized the FTIR microscope to start to locate specific chemical features within the stylus (Figure 11).

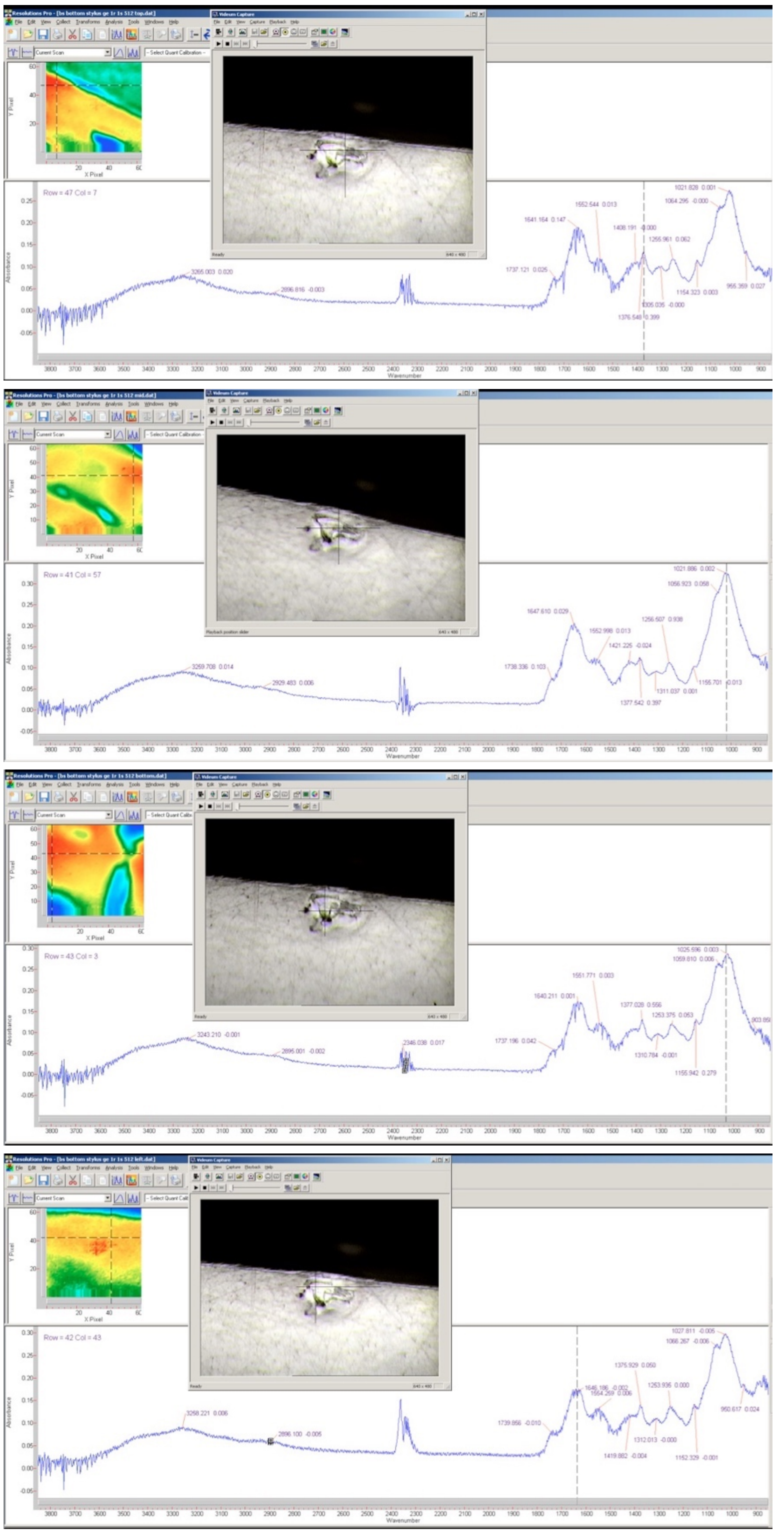

Figure 11. FTIR maps from the bottom of the Chiton stylus. Different maps represent selected wavenumbers.

Project 3: Collaborative project with Keio University (Prof. Hiroaki Imai and Ms. Kanako Sato): "Structure-function relationships in mineralized rice plants":

In this project, our collaborator, Prof. Hiroaki Imai and his student who visited my lab, Ms. Kanako Sato were interested in studying structure-function relationships in mineralized rice plants. These plants have silica plates and particles embedded in their plant walls that serve two functions: (i) anti-predation and (ii) redistributing light to enable more efficient photosynthesis. Here, we hosted Ms. Sato in our lab, who brought samples with her. In this study, we investigated 4 different silica mineralized regions within the plant: projections, flat areas, boundaries and stoma. Our initial investigations with the FTIR microscope has shown that only the projection regions showed differences from the others (Figures 12 and 13). However, we did observe the presence of N-H and C-H bonds within all silica. This suggests the presence of poly-lysines that enable condensation reactions of SiO_2. Further investigations will attempt to differentiate between poly-lysines and their locations relative to the mineral.

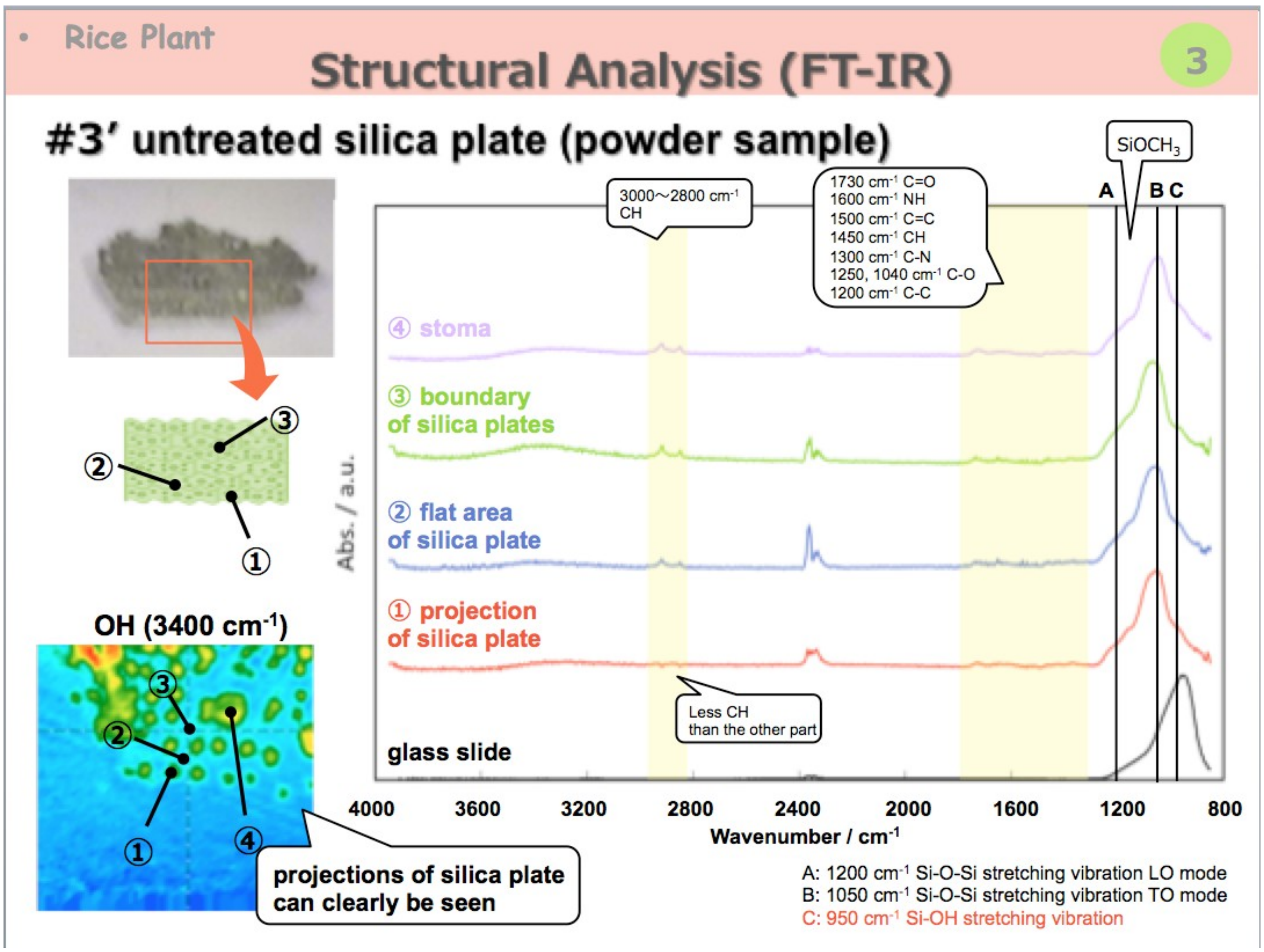

Figure 12. FTIR maps from different structural features from within a rice plant.

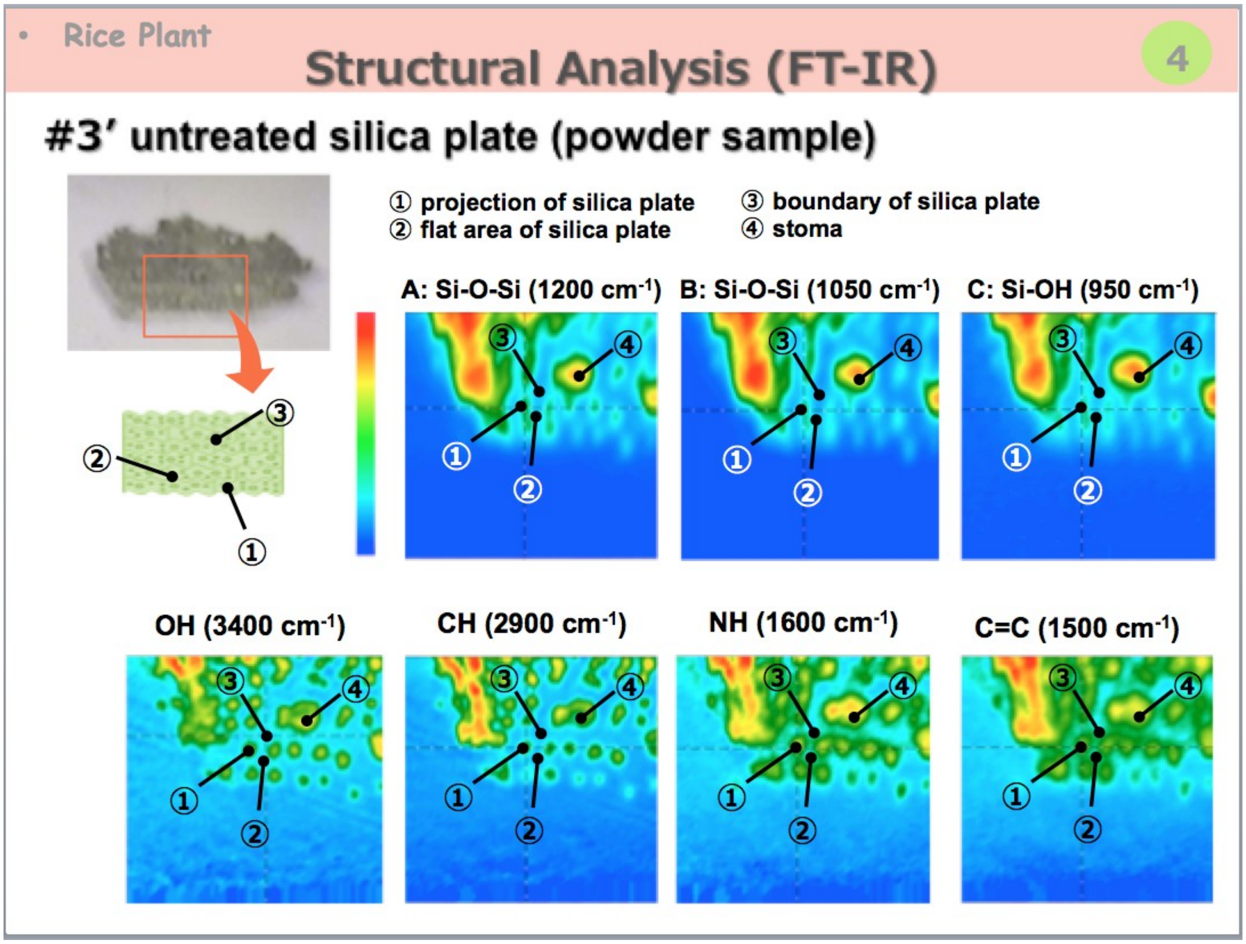

Figure 13. FTIR maps from silica plates highlighting different wavenumbers.

Supported Personnel and Collaborations:
<u>Training, Education, and Outreach Achievements</u>

Besides providing scientific knowledge on multiple projects, acquisition of the FTIR microscope has enabled training, education, and outreach.

Through the acquisition of this nanoindenter, we have also enabled the training and education of post-doctoral researchers, graduate and undergraduate students. Personnel that have utilized this instrument include: Dr. Sourangsu Sarkar (post-doctoral researcher), Dr. Lessa Grunenfelder (post-doctoral researcher), Parawee Pumwongpitak (Ph.D. student), Nicholas Yaraghi (Ph.D. student), Steven Herrera (Ph.D. student, Hispanic minority), Jesus Rivera (Ph.D. student, Hispanic minority), Thomas Dugger (Ph.D. student), Ramya Mohan (Ph.D. student), Kanako Sato (visiting Ph.D. student), Brian Macdonald (undergraduate student) and Jeff Geiger (undergraduate student). In addition to training and education, this equipment has enabled our lab to collaborate with multiple PIs around the world, including: Dr. Joanna McKittrick (UCSD), Dr. Matthew Shawkey (Univ. Akron), Dr. Pablo Zavattieri (Purdue University), Dr. Dimitri

Deheyn (Scripps, UCSD), Dr. Atsushi Arakaki (Tokyo University of Agriculture and Technology), Dr. Yoshiaki Maeda (Tokyo University of Agriculture and Technology), Dr. Hiroaki Imai (Keio University).

Finally, through the procurement of this instrument, the data we have acquired data that has lead to outreach events at the Riverside Metropolitan Museum (May, 2015). During this event, 8 of my 11 undergraduates working in the Biomimetics and Nanostructured Materials Lab have presented their research to a public audience.

The program for this event is shown below:

Publications:

Two publications have resulted since the acquisition of this equipment and at least six additional manuscripts are in preparation.

Interactions/Transitions:

We have established relationships with We have established relationships with Airbus, Boeing, DOT, TALOS (to initiate collaborations); Acquired new fiber and composite mechanical testing unit, electrospinner, muffle furnace (AFOSR); Acquired new 300W laser sintering 3D printer (open source, ceramic and metals). I have organized conferences: Symposium Organizer, MRS, Spring 2016, chairing a session on Multifunctional Materials at 20th Int'l Conference on

Composite Materials (July 2015), the conference chair for the American Association for Crystal Growth, 2014. I am now on the executive committee of the American Association for Crystal Growth (2015-2018).

Conclusions: The acquisition of this system has not only greatly enhanced our capability to carry out research activities related to composite structure-function, but has also benefited the PI's and other researchers' overall capabilities in materials research. By understanding structure-function relationships and developing synthesis strategies to biomimetic composite materials, which have proved to be important for DoD applications, we have aligned our research activities with multiple DoD missions.