Molecular structure of crustacean exoskeletons and relationships to biomineral toughness and rigidity

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Animals in the Class Malacostraca include well-known species, such as crabs, isopods, shrimp, and the American lobster. Their exoskeletons are comprised of calcite and/or amorphous calcium carbonate, as well as chitin and proteins such as present in other arthropods, the insects and arachnids. These structures are unique biominerals that provide protection, locomotion, and stability.

This study was designed to determine the mechanical and structural properties of exoskeletons from three Malacostraca species— two crabs and the American lobster (Mergelsberg et al., in advanced prep). Using high-energy synchrotron x-rays and PDF, we found the crystallinity of chitin (% Cr_{130}) and $CaCO_3$ (calcite/total $CaCO_3$) is covariant between the body parts of the crab species. Crab claws have greater crystallinity than the main body as expected per the biological function of these body parts. In contrast, the crystallinity of the claws and main body of the lobster are similar and parts contain little calcite relative to amorphous $CaCO_3$. Parallel Raman spectroscopic analyses of exoskeleton cross-sections independently confirm the covariant crystallinities. Crystallinity *within* the cross-section is highly variable in the lobster exoskeleton.

The findings led us to test the hypothesis that chitin crystallinity, not mineral crystallinity, is the primary control on exoskeleton toughness and rigidity. By determining the stress-strain relationship for exoskeleton samples, we found that greater rigidity in the exoskeleton is correlated with chitin crystallinity. That is, lower crystallinity correlates with more flexible structures. There is no relationship between exoskeleton strength and % calcite, but strength is correlated with exoskeleton thickness. The measurements suggest chitin is the primary contributor to exoskeleton reinforcement for these crustaceans and challenge the long-standing assumption that $CaCO_3$ contributes strength to the exoskeleton. Rather, the data suggest chitin is the key structural component that confers toughness and rigidity to the exoskeletons of all arthropods, including crustaceans.