Spectroscopic study of the role of Br and Sr in colored parts of the *Callinectes* sapidus crab claw

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Abstract: The exoskeleton of crustaceans comprises of a composite material consisting of chitin biopolymers and inorganic biominerals, mainly calcium carbonate, that determine their mechanical properties. Crabs accumulate Sr with the Sr/Ca ratio being directly related to the concentration of Sr in the water. Br is another element that is accumulated by crustaceans though feeding with algae. The claw of the *Callinectes sapidus* crab exhibits vivid coloration (white and blue in the palm and orange in the fingers), caused by the presence of chromo-proteins that trap the astaxanthin (AXT) carotenoid chromophore. X-ray Fluorescence (XRF), Raman, visible light Reflectance, and Br- and Sr-K-edge X-ray Absorption Fine Structure (XAFS) spectroscopies were applied for the study of the color variations along the claw. The macroscopic color at different regions is consistent with the reflectance spectra that exhibit variations related to the selective absorption caused by the electronic transitions of the conjugated polyene chain of AXT. The interaction of the protein with the chromophore molecule modifies its light absorption properties giving rise to different colors. Combination of the XRF and Raman spectra indicate that Br is present only in the stained parts of the claw (orange and blue) where the chromo-protein is also detected. Analysis of the Br-K-edge EXAFS spectra recorded from the stained parts reveals that Br is bonded to benzene rings most probably of the chromo-protein amino acid residues. Combined Sr-K-edge XAFS and Raman analysis discloses that Sr substitutes for Ca in the calcium carbonate. Nano-crystalline calcite and aragonite phases prevail in the finger and the palm of the claw, respectively. In the latter case, an amorphous phase was found to coexist with the nano-crystalline one. The variations in the biomineralization in the fingers of the claw are attributed to the necessity for improved mechanical properties at its end.

