

## Element profile and chemical environment of sulfur in clam shell: insights from micro-XRF and XANES

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Element profiles of sulfur and strontium in the inner layer of a clam shell (*Hippopus hippopus*) were investigated by means of micro X-ray fluorescence, and sulfur *K*-edge X-ray absorption near-edge structure (XANES) were used to evaluate the local environment of sulfur in aragonitic and calcitic bivalve shells. The spectra of S *K*-edge XANES collected from bivalve shells and S-bearing organic and inorganic reference materials indicated that inorganic sulfate was present in calcitic bivalve shells. However, XANES results did not permit us to discriminate between organic and inorganic sulfate in aragonitic shells. Strontium fluctuations and thin section observations suggested that Sr was incorporated into the shells at high growth rates during warm seasons. The first-order fluctuations of sulfur in the inner shell layer showed clear annual fluctuations, with sulfur concentrations being lower during periods of faster growth. Bivalve shells consist of well-crystallized CaCO<sub>3</sub> and amorphous CaCO<sub>3</sub> containing organic matter, and the proportion of crystalline CaCO<sub>3</sub> increases during the high growth season. Our results suggest that trace sulfur profiles in aragonitic shells could be the result of cyclic changes of shell crystallization related to bivalve physiology and environmental factors.

Keywords: Sulfur, micro-XRF, Synchrotron radiation, XANES, Strontium