Biomineralization is a biologically mediated process by which available ions are extracted from the solution to produce a solid structure that offers an adaptive advantage to the producing organism, performing mechanical/structural or functional/defensive roles. Because of this wide range of essential functions, the biotechnological application of biominerals is extremely varied, making them a prime source of inspiration to biologists and chemists to create novel biomimetic materials [1]. Among their potential applications, biominerals can serve for environmental monitoring, specifically, marine bivalves are sensitive organisms that register environmental changes and they help in assessing pH variation in sea water [2], ii) the evolution of the watershed (depositional vs erosional processes) [3], iii) climate changes [4], and iii) the effect of metal dispersion caused by anthropogenic activities [5].

Bivalves build their shell by a biologically controlled process occurring at the interface between the organism cells and the environment, forming an organo-mineral hard tissue mainly made up of Ca-carbonate (aragonite and/or calcite) [6], and organic molecules (horny conchiolin in the external surface of the shell, chitin, polysaccharides, proteins and glycoproteins in the medium and inner layers) [7]. Bivalves incorporate actively trace elements via intracellular or intercellular transport ways [8]. In our study, we applied a multidisciplinary and multitechnique approach to investigate Zn incorporation into marine bivalve shells belonging to different genera (Donax, Glycymeris, Lentidium, and Chamelea) grown in mine-polluted seabed sediments (Zn up to 10 g/kg). Samples were investigated by X-ray diffraction (XRD), chemical analysis, soft X-ray microscopy combined with low-energy X-ray fluorescence (XRF) mapping, X-ray absorption spectroscopy (XAS), and transmission electron microscopy (TEM). These bivalves grew their shells producing aragonite as the main biomaterial, and they are able to incorporate up to 2.0–80 mg/kg of Zn. Zn is mainly located in the bulk of the aragonite crystal matrix but it is not hosted in the Ca-carbonate structure. We identified three main different Zn phases: Zn phosphate, Zn hydroxycarbonate (hydrozincite), and Zn cysteine whose relative content changes as a function of Zn concentration in the shell. Zn phosphate is the most abundant species in the shells with the lowest Zn content (Lentidium, with Zn concentration of 29 mg/kg and Zn$_{phosph}$ of 51%; Donax, with Zn concentration of 27 mg/kg and Zn$_{phosph}$ of 55%), whereas Zn cysteine becomes more relevant (up to 56% of the total species) in Chamelea, characterized by a higher Zn concentration (Zn 80 mg/kg).

Our findings show that investigated bivalves can synthesize different phases other than Ca-carbonate when exposed to high Zn concentrations, suggesting that the biomineralization process acts as a detoxification sink to remove Zn excess from the immediate environment. In addition to the elucidation of biomineralization processes, achieved results are relevant to develop quantitative biomonitoring techniques and paleoproxy tools. A deeper understanding will be achieved by XAS microbeam analyses at a micorscale on shell cross-sections to observe potential variations in Zn speciation inside the bivalve shell, and through the analysis of the soft tissues combined to shell analysis to observe if potential correlations between the metal content and Zn coordination environment occur.

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