

Nanoscale distribution of Zn in foraminifera shell: a multi-scale/multi-technique investigation

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Foraminifera are unicellular organisms widespread in marine ecosystems that, building Ca-carbonate shells, may incorporate trace metals present in the ocean waters because of natural or anthropogenic supply. The distribution and chemical speciation of these elements across the foraminifera shell is a research topic relevant for defining proxies in ocean and environmental sciences. Here we focus on Zn, being an abundant trace element in contaminated as well as clean waters. We reveal peculiar differences in Zn concentration and chemical speciation at the micro and nanometric scale with the formation of independent mineral phases, in particular hydrozincite and sphalerite. These differences appear to be related to the cellular mechanisms involved in the calcite shell biosynthesis: the Ca-carbonate synthesis in foraminifera can be either in extracellular or intracellular space, implying some diversity in physiology and cation transport process. Independent mineral phases of Zn dispersed in biogenic calcite material are likely due to an unravelled detoxification mechanism. Their formation is shown to be species dependent and is a tool for a deeper understanding of environmental processes, past ocean circulation and biogeochemical cycling. Combined use of state of art complementary probes (synchrotron radiation and laboratory set up) was crucial to achieve a reliable detailed multi-scale characterization.