Manganese speciation in Diplodon chilensis patagonicus shells: a XANES study

A.L. Soldati (1), V. Vicente-Vilas (2), J. Goettlicher (3), and D.E. Jacob (1)

(1) Johannes Gutenberg University of Mainz, Geosciences, Mainz, Germany (soldatia@uni-mainz.de, +4961313923070), (2) Catholic University of Valencia, Faculty of Medicine, Valencia, Spain, (3) Institute for Synchrotron Radiation ISS, Forschungszentrum Karlsruhe, Germany

In addition to other types of climate archives, biogenic skeletons of a variety of different organisms (i.e. shells of bivalves, skeletal hard parts of corals or sponges) are increasingly used for high-resolution climate reconstructions. Bivalves are particularly suited for such analyses because they are geographically broadly distributed and have been shown to record climate and environmental information reliably and over long time intervals. Variation of environmental parameters such as food supply, substratum type, salinity, illumination, temperature, concentration of dissolved oxygen or oxygen/carbon dioxide ratio, among others, may affect growth pattern, shell structure, mineralogy, isotopic fractionation and chemistry. Thus, shell features, minor and trace element composition patterns and isotopic signals may serve as an archive of environmental history.

In turn, palaeoclimatic parameters such as ambient temperature, precipitation gradients, seawater salinity and primary production can be reconstructed from the shells by means of sclerochronological and geochemical methods. However, the distribution of minor and trace elements in the biominerals is not only influenced by the environment or vital effects, but also by intrinsic biomineralisation parameters like the carbonate polymorphism and the mineral habit (Soldati et al., 2008a). Generally, it is assumed that the X^{2+} ions are replacing the Ca^{2+} ion in the calcium carbonate ($CaCO_3$) structure, but newest findings show that amorphous (or disordered) phases may play a role in hosting some of the elements use as proxies (Meibom et al., 2008; and Finch and Allison, 2007).

In this work we focused on the freshwater clam *Diplodon chilensis patagonicus*, a widely distributed inhabitant of lakes and rivers in southern South America. Thanks to its long life span and seasonal growth *Diplodon* mussels exhibit excellent characteristics to construct an accurate chronological archive, with time windows of up to around a century, resolving the environmental signal annually and even seasonally (Soldati et al., 2008b). High resolution trace elemental analysis by LA-ICPMS and EPMA in the shells show that elements like Mg and Mn are related to the seasonal pattern and can be enriched along the organic-rich annual shell growth lines. Thus, these elements could possibly be bound organically instead of occupying a defined site in the crystal lattice of the calcium carbonate phase.

LA-ICP-MS results show that Mn concentrations in these *Diplodon* shells range between 1000-300 μg/g and 100-10 μg/g and that the areas of enrichment are in the micrometer range. Raman and XRD measurements at high spatial resolution failed in recognizing whether the Mn is in carbonate solid solution or not. Therefore, speciation techniques like X-ray absorption fine structure (XAFS) spectroscopy with a high lateral resolution are required to address this question. Prior to XAFS spectroscopy the samples were mapped with the intensity of the Mn Kα fluorescence emission line in order to locate the Mn rich areas of interest. Because of the Mn concentrations in the sub % range the XAFS spectra at the positions of interest have been recorded in fluorescence mode using a 7 element Si(Li) detector. This study focuses on the near edge (XANES: X-ray absorption near edge structure) part of the spectra. For data evaluation, XANES spectra of reference substances were additionally measured in order to get first hints to Mn valence and bonding. As standards were used Mn and Mn rich carbonates, Mn oxides with Mn in different oxidation states, and Mn in organic compounds (Mn-porphyrin and Mn-acetate). The XAFS measurements have been carried out at the SUL-X beamline of the synchrotron radiation source ANKA of the Forschungszentrum Karlsruhe. Data evaluation is ongoing.

References

MEIBOM, A., CUIF, J.P., HOULBREQUE, F., MOSTEFAOUI, S., DAUPHIN, Y., MEIBOM; K.L. & DUNBAR, R. (2008). Compositional variations at ultra-structure length scales in coral skeleton. *Geochimica et Cosmochimica Acta* 72: 1555-1569.

FINCH, A.A. & ALLISON, N. (2007). Coordination of Sr and Mg in calcite and aragonite. *Mineralogical Magazine* 71: 539-552.

SOLDATI A.L., JACOB D.E., WEHRMEISTER, U. & HOFMEISTER, W. (2008a). Structural characterization and chemical composition of aragonite and vaterite in freshwater cultured pearls. *Mineralogical Magazine* 72: 577-590.

SOLDATI A.L., JACOB D., SCHÖNE B.R., BIANCHI M.M. & HAJDUK A. (2008b). Seasonal periodicity of growth and composition in valves of Diplodon chilensis patagonicus (D'Orbigny, 1835). *Journal of Molluscan Studies*, doi:10.1093/mollus/eyn044.