

# Experiment title (EV-95): Understanding heavy metals bioavailability during biomineralization processes in foraminifera

Authors: G. De Giudici, P. Lattanzi, D. Medas, F. Podda, C. Meneghini

## Report

Understanding mechanisms of heavy metals incorporation during biomineralization processes is a fundamental key for interpretation of the geological record and for developing efficient environmental technologies. Specifically, in Sardinia extreme pollution in Zn, Fe, Co and other heavy metals, due to industrial activity, is known to affect the SW coast due to past mine activity and anomalous geochemical background for heavy metals (Medas et al 2012). In previous works we found that foraminifera are suitable bioindicators of heavy metal pollution; in fact, in presence of heavy metals, foraminifera shells undergo shape deformation, accumulate heavy metals into the carbonate polycrystalline structure, and show intense bioerosion by bacteria (Cherchi et al. 2012).

Benthic foraminifera are unicellular organisms that have a few-days-long lifetime. In this timespan, they produce a  $\text{CaCO}_3$  shell having generally a maximum millimetric size. Foraminifera taxa comprise many species, and each of them produces different shapes and respond differently to environmental stress (see Figure 1). In addition, many different organic ligands can be used to transport cations in the body of the unicellular organism (Erez et al, 2003); these molecules are typically specie dependent.

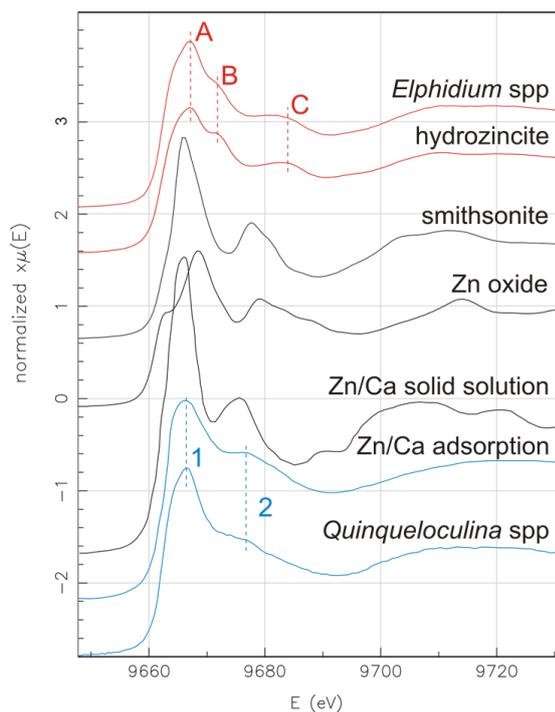


Figure 1. Normalized absorption spectra in the Zn K-edge XANES collected on reference compounds and foraminifera samples. Spectra of Zn/calcite solid solution and Zn adsorbed on calcite from Elzinga and Reeeder (2002), modified. Spectra are vertically shifted for the sake of clarity. Similar features between hydrozincite standard and Elphidium spp samples (A,B,C), and between Zn adsorbed on calcite and Quinqueloculina spp samples (1,2) are highlighted

In the XAS experiment EV-95 the Zn speciation in foraminifera shell, was investigated for different low-Mg and high-Mg foraminifera species, affects significantly the nature of Zn containing phases. During experiment EV 95, we unexpectedly found hydrozincite-like phase  $[\text{Zn}_5(\text{CO}_3)(\text{OH})_6]$  in the shells of the so called low Mg foraminifera (*Elphidium spp.*, Fig. 1), while, in the so called high-Mg foraminifera (*Quinqueloculina spp.*, Fig. 1), Zn seems likely randomly dispersed in the  $\text{CaCO}_3$  lattice or adsorbed on  $\text{CaCO}_3$  crystallites. In general, Mg substitution in  $\text{CaCO}_3$  crystals implies an increase in the lattice constants, and this can affect Zn bioavailability and speciation in the foraminifera shells. These results were obtained also in a previous Zn-K edge XAFS investigation undertaken at BM23, carried either grinding hundreds of individuals into cellulose pellets, and is confirmed by using  $\mu\text{XAFS}$  facility to map the Zn distribution into the foraminifera shells of different species. Moreover,  $\mu\text{XAFS}$  mapping has also put in evidence the presence of other 3d metals, in particular Co and Fe, having peculiar distribution as a function of the foraminifera species (unshown).

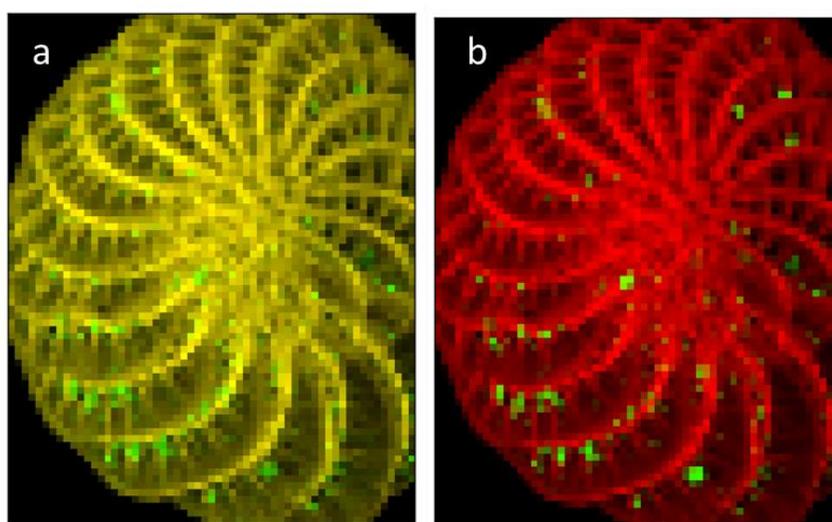


Figure 2 shows images of an *Elphidium spp.* individual. 2a and 2b are the two images from micro XRF collected with a beam of  $4 \mu\text{m}$  and a pixel of  $8.4 \mu\text{m}$ . In 2a Ca (yellow) and Mg (green) are shown, the intensities varies from 219 to 189.000 cps from Ca, and from 45 to 3300 for Mg, Ca and Mg are shown to be co-located. 2b shows location of Ca (red) and Zn (green), the intensity of Zn XRF signal varies from 30 to 104000 cps, indicating a great variability in Zn concentration

The results obtained during experiment EV95 are relevant to both the understanding of the geological record and developing effective bio-monitoring techniques. A paper is going to be submitted, and additional beamtime will be required for investigating Fe and Co speciation in the foraminifera shells.

## References

- Cherchi et al. (2012) Biogeosciences, 9: 4607-4620.  
 Medas et al. (2012). Bio-Geo-Interactions in Metal Contaminated Soils, Soil Biology 31, Springer, 113-130.  
 Erez (2003). Rev. Mineral. Geochem., 54: 1-31.