ESRF	**Experiment title:** X-ray emission spectroscopy for paleoclimatology: Studies of the trace element distribution in fossil mussel shells	**Experiment number**: EC-571
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Abstract

We investigated 7 different freshwater bivalve shells by means of spin-resolved x-ray absorption near edge spectroscopy (XANES) and x-ray emission spectrocopy (XES). These shells, which are used for paleoclimate reconstructions of continental areas, are composed of aragonite ($CaCO_3$) and less than 5-3% of organic materials. The aim of the experiments was to clarify whether or not Mn is replacing the Ca^{2+} ion within the carbonate structure, or within the shell organic membranes (inter- or intra-crystalline). The obtained data shows that the former is indeed the case, implying that Mn in these shells provides an excellent climate proxy.

Materials and Methods

The bivalve shells used here were recent specimens of *Hyriopsis cumingii*, *Margaritifera margaritifera*, *Margaritifera falcata*, *Anodonta Cygnea*, *Anodonta Anatina* and *Unio tumidus as well as* recent and archaelogical specimens of *Diplodon ch. Patagonicus* from two different Patagonian lakes (El Trébol and Escondido). Powdered shell nacre of the internal region of the ventral margin was extracted with a diamond-covered drill bit. The reference compounds comprised organic and inorganic reference substances as well as geological crystals. In addition. the outermost layer (periostracum) of a recent *Diplodon* shell was analized as reference for organic shell material. After homogenization in an agate mill the samples were mixed 1:1 with BN, pressing pellets of 5 mm diameter and aproximatly 1-2 mm thickness. XANES and XES spectra were normalized to an absorption intensity of 1 at the maximum of the white line and to an emission intensity of 1 at the maximum of the Mn-K$\beta_{1,3}$ peak, respectively.

Results

All spectra (Fig 1A) of the different bivalve shells studied here (independent of the bivalve type, its provenance, or if recent or archaeological) show the same absorption features, coinciding exactly in the position of the Mn *K-edge* (6.548 keV) and the white line (6.552 keV), and in the position (6.540 keV) and intensity of the pre-edge peak. Signs of damage due to irradiation were observed in some of the bivalve

spectra after 20-30 minutes in the beam. The shell average spectrum is compared to that of Mn-bearing $CaCO_3$ (calcite) and $MnCO_3$ (rhodochrosite) in Fig 1B.The Mn *pre-edge* feature is a result of quadrupole 1s→3d transitions and is present at the same energy in all 3 cases. In addition the spin-resolved XANES shows that the electronic configuration of Mn in these materials in largely $3d^5$ corresponding to Mn^{2+} (cf. Fig 1C). This result is further supported by the data provided in Fig 1D, showing that the pre-edge of the shells agrees well with the Mn^{2+} reference materials.

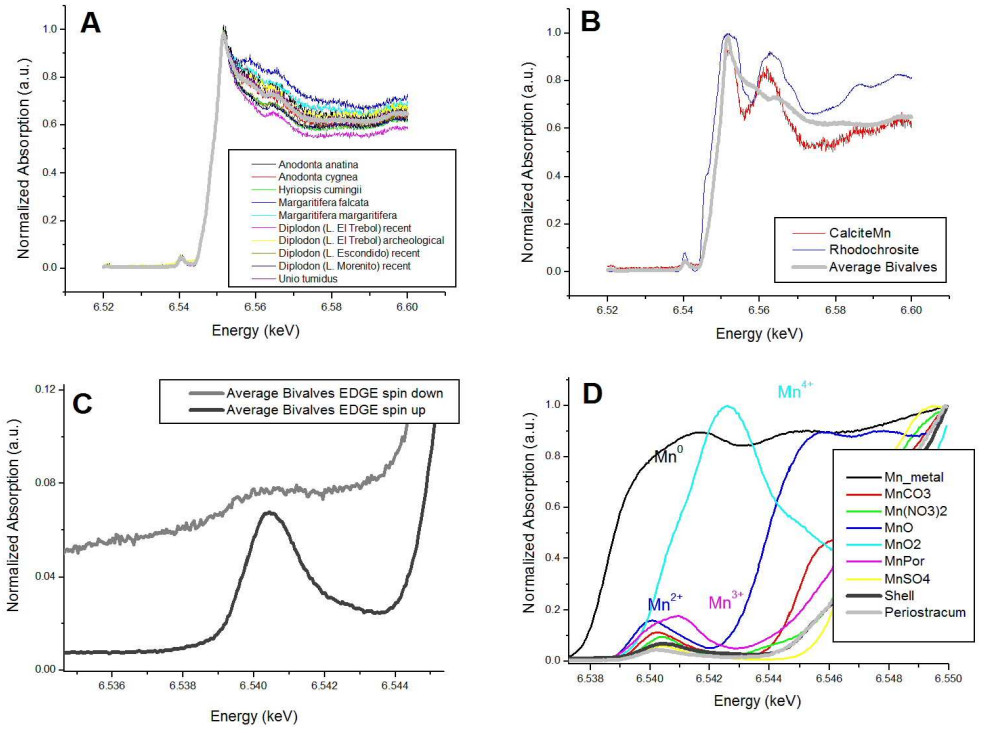
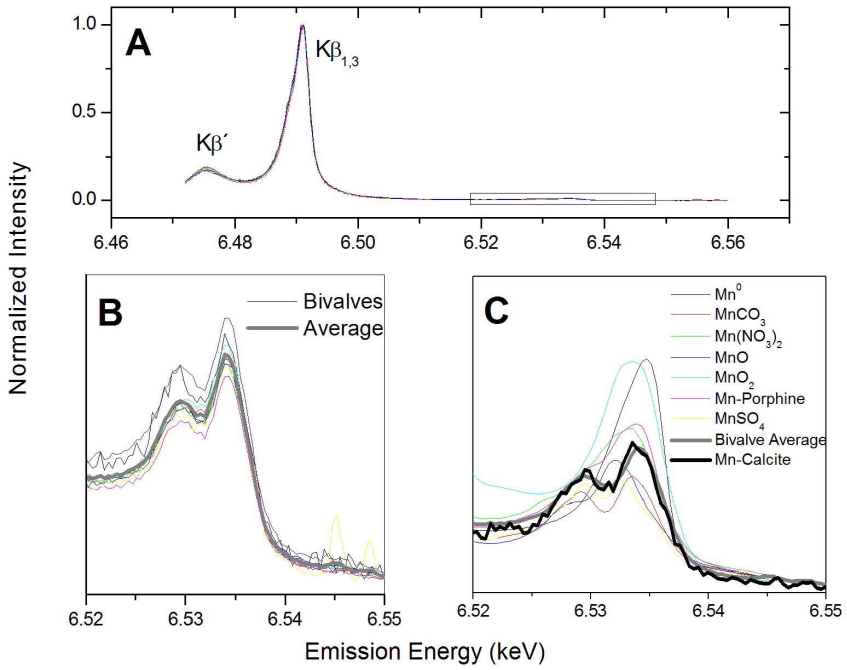


Fig1: (A) Mn K-edge absorption spectra of bivalves shell powder; average in gray.(B) Average bivalve absorption spectrum compared to Mn-containing carbonate crystals. (C) Average bivalve absorption pre-edge feature by spin polarized measurement. (D) pre-edge peak of the shell average curve (dark gray) and *Diplodon* shell periostracum (light gray) compared to different reference Mn compounds. Spectra are normatized to the white line.

Mn-Kβ emission spectra, which provide detailed information regarding the chemical environment, are shown in Fig.2. All bivalves show the same Kβ´ and $K\beta_{1,3}$ main (Fig 2A) and $K\beta_{2,5}$ satellite lines (Fig 2B). Most importantly, the "bivalve" average spectrum (Fig 2A) shows the same features as the emission of a Mn-bearing calcite crystal and $MnCO_3$ (Fig 2C), while it clearly differs from the reference compounds containing Mn in other environments. This data therefore reveals that Mn in the shell material is in a calcite microenvironment.

Fig 2: (A) bivalves Mn Kβ emission spectra. (B) zoom at the $K\beta_{2,5}$ satellite lines in (A) showing the "average" spectrum. (C) Emission spectra of different compounds compared to the bivalve aveage.



Conclusion

XES and spin-resolved XANES measurements allowed determining the Mn oxidation state in the internal nacre of seven freshwater bivalves with potential as climate proxy. The results for all the studied species show the presence of Mn^{2+} in a rombohedral structure, similar to that observed for Mn^{2+} replacing the Ca^{2+} ion in geological calcite. Possible contributions of other Mn bering phases (as Mn organically bound) remained undetected. Thus, Mn concentration patterns in these kind of shells seems to be an excellent proxy to reconstruct the present and past water chemistry at seasonal resolution in river and lacustrine environments.