EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** **Uptake mechanisms of the europium actinide surrogate by marine organisms**	**Experiment number**: CH4206
Beamline: BM08	**Date of experiment**: from: 03/07/2014 to: 08/07/2014	**Date of report**: 05/03/2015
Shifts: 15	**Local contact(s)**: Simona Torrengo	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
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Context of the experiment

Non-negligible quantities of radionuclides (RNs) have been released in the environment in the past decades (nuclear tests, accidents etc). Although the inventory of radionuclides and in particular actinide elements has been widely studied in the hydro- and geosphere, speciation and transfer mechanisms are more difficult to assess, mostly because those elements are present at the ultra-trace scale. This proposal focuses on the description of actinide species in seawater for future understanding of possible transfer mechanisms from the hydrosphere to the marine biotope. (far below the ppb level, generally speaking). Those inventories have been generally achieved with alpha and gamma nuclear radiometry or analytical techniques. Among the environmental compartment, seawater is the most abundant and one of the most complex systems. For actinides in seawater, an approach based on complexation constants and predictive speciation diagrams has been reported.[1] This approach is a useful guide to better describe the molecular speciation but lacks experimental data. We have started to explore the speciation of Eu(III), U(VI) and Np(V) in seawater on the MARS beam line of SOLEIL.[2] Eu(III) is used here as a non radioactive surrogate of Am(III) and Cm(III) that are both representative of the heavy actinide sub-family with essentially +III oxidation state and low hydrolysis tendency (therefore very mobile).
In seawater, bioaccumulation of inorganic contaminant has already been described to occur with algae, mussels, fishes and sponges that can serve as biomonitors of a metallic pollution. Among these organisms, sponges as sessile active filter feeders and have been identified as hyper accumulators of several heavy metals. Sponges are ubiquitous in the Mediterranean sea and some species have been selected as bio accumulator to better understand the accumulation mechanisms of actinides in marine organisms.

Results

Experiments carried out in collaboration with the International Atomic Energy Agency (IAEA) in Monaco demonstrated the hyper-accumulation of $^{152}Eu/^{153}Eu$ (^{152}Eu is a gamma emitter used here to follow the uptake rate) by *Aplysina cavernicola*. This data clearly indicates that after 15 days, limits in terms of concentration factors have not been achieved. The accumulation mechanisms are of course unknown but we have observed the presence of 200 nm scale particles localized preferentially far from the osculum (Figure 1, data obtained at the STXM beam line 11-0-2 of ALS, Berkeley).

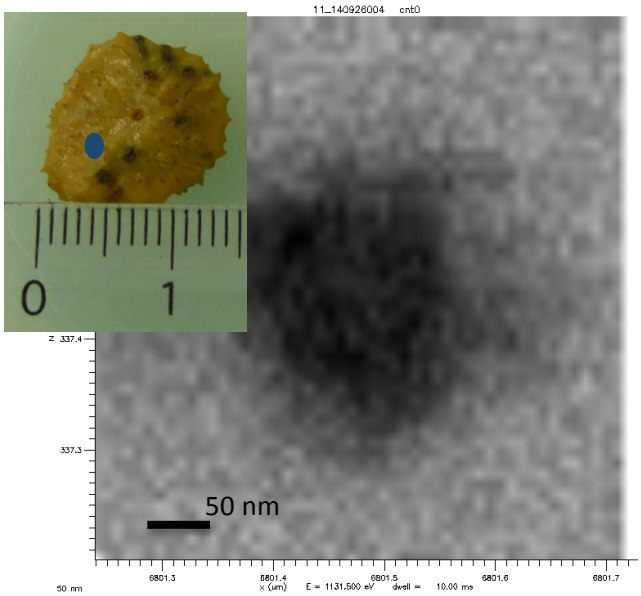

Fig. 1 : Contrast X ray image (Eu $M_{IV,V}$ edges) of a transversal cut of the sponge. Insert : the blue point in the cut represents the zone of the X ray image. In the center, the osculum (scale in cm).

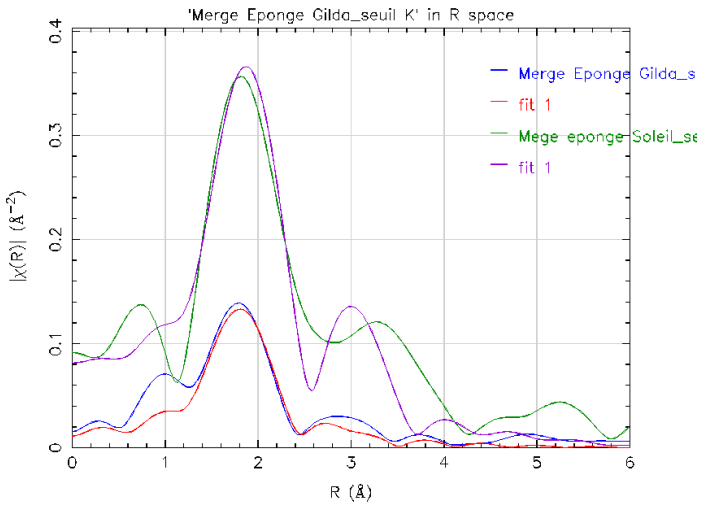

Fig. 2 : Combined fit (Fourier transform, FT) at both Eu K and L_{II} edges of doped *A. Cavernicola*. The K edge (blue) has been recorded at GILDA and the L_{II} edge (green) at MARS.
Combined fit :
- 8 O at 2.43(2) Å, σ^2 = 00060 Å^2
- triple (4 degenerate) and quadruple (2 degenerate) scattering paths for Eu...C-O have been added.
S_0^2 = 1.3, e0 = 1.46 eV (K), -0.53 eV (L_{II}), R factor = 5.7%.

We prepared a sponge doped with 200 ppm of ^{153}Eu (stable). First tests to record the XAS spectrum of Eu in the doped sponge revealed a very high contend of Fe in the sponge. This obliged us to work at the Eu L_{II} edge but the signal is highly affected by Fe fluorescence and data with a very low signal to noise ratio (noise in k = 16 E^{-3}) has been obtained. The only possibility to obtain better EXAFS data was therefore to work at the Eu K edge. Unfortunately, due to monochromator problems during the run, only one sample (the entire dehydrated sponge, grounded, pellet) could be recorded and not the fractional centrifugation samples.
Because of the low doping concentration, the spectral noise at the K edge is important, but an order of magnitude less than at the L_{II} edge : noise in k = 1.2 E^{-3}. Consequently, the spectral ranges had to be reduced to k = 8 (K edge) and 7 (L_{II} edge) Å^{-1}. In order to gain independent data points, we have performed a combined fit using both edges at the same time (number of independent point = 19). Figure 2 shows the FTs of the EXAFS spectra at both K and L_{II} edges and the corresponding fit (performed in kχ(k)). This preliminary result has been obtained with an Eu atom surrounded by 2 bidentate carbonates and complementary (4) water molecules. Coordination numbers have not been fitted (total fixed to 8) because this would have been meaningless with this noise level. The presence of at least one bidentate carbonate is deduced from the necessity to include multiple scattering paths that correspond to the distal carbonate oxygen. Figure 2 shows the fit performed with 2 bidentate carbonate and 4 water molecules. However other ratio with fixed total coordination numbers are also possible.
In parallel, TRFLS data has been recorded on the same sample. Although fluorescence data is more difficult to obtained on such solids than on liquids, the energy position (wavelength) and lifetime of the emission peak is also in agreement with an Eu carbonate complex.
Quantum chemical models of Eu carbonate complexes are being performed. Those models, combined with the XAS data, will help to further define the form of the Eu particles that have been observed in the X ray image.

1 G. Choppin, *Marine Chem.* (2006), **99**, 83.
2 M. Maloubier, P. Lorenzo Solari, P. Moisy, M. Monfort, C. Den Auwer, C. Moulin, *Dalton Trans. (*2015), accepted