 ROBL-CRG	<b>Experiment title:</b> Molecular scale studies on the speciation of U(VI) bound to cells and S-layers of Archaea	<b>Experiment number:</b> 20-01-688
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 24/06 to: 29/06/10	<b>Date of report:</b> 20/04/11
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## Experimental

This study aimed to characterize at molecular scale the local coordination of U(VI) associated with the marine bacterium, *Idiomarina loihiensis* MAH1, in seawater using X-ray absorption spectroscopy. The strain MAH1 was isolated from the Alboran Sea in the west side of the Mediterranean Sea, and their cells were able in the absence of U(VI) to precipitate minerals including phosphates (e.g. struvite,  $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) and carbonates (Ca–Mg kutnahorite,  $\text{CaMg}(\text{CO}_3)_2$ ) in sea water (González-Muñoz et al. 2008).

The speciation of U(VI), at environmentally relevant concentrations ranging between  $10^{-6}$  and  $10^{-4}$  M, associated with the cells of the strain MAH1 was studied in sea water system, the natural habitat of this bacterium using TRLFS spectroscopy and transmission electron microscope (TEM). TRLFS analysis indicated that the cells of the studied bacterium precipitate U(VI) as U calcium carbonate mineral phases with fluorescence properties similar to those of liebigite  $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 11(\text{H}_2\text{O})$ . In addition, a second mineral phase, uranyl phosphates (meta-autunite), could be implicated in the biomineralization of this radionuclide. High Resolution Transmission Electron Microscope (HRTEM) analysis indicated that the mineral phases precipitated were localized on the cell wall. However, these techniques were not able to determine the structural parameters of the U(VI) species precipitated by the marine bacterium.

The results of this study will help to understand the role of microbial process on the transport and mobility of radionuclides in the Alboran Sea as it is the only connection between the Mediterranean Sea and the Atlantic Ocean, and where the transportation of radioactive wastes and the traffic of nuclear submarines are very intense.

## Results

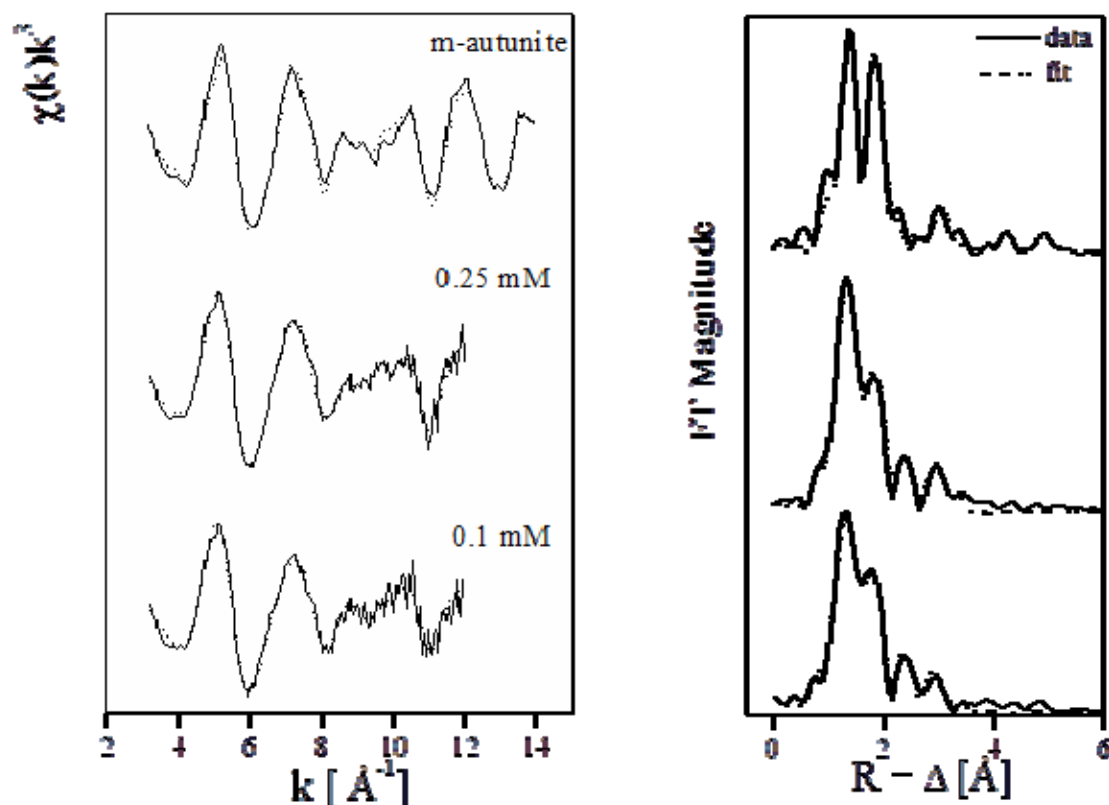


Fig1. Uranium L<sub>III</sub>-edge k<sup>3</sup>-weighted EXAFS spectra (left) and the corresponding Fourier transforms (FT) (right) of the uranium complexes formed by the cells of the strain MAH1 at U(VI) concentration of 0.1 and 0.25 mM and reference compound (m-autunite).

A visual comparison of the XANES fingerprints for the reference samples U(VI) and U(IV) indicated the presence of U(VI) in the two samples studied in this work (data not shown). The presence of U(VI) in the XANES spectra is evidenced by the display of a characteristic shoulder at 17.188 eV, which is consistent with U(VI) oxidation state.

The uranium L<sub>III</sub>-edge EXAFS spectra and their corresponding Fourier transforms (FT) for the uranium species formed by the cells of the strain MAH1 in seawater at U(VI) concentrations of 0.1 and 0.25 mM are presented in Fig. 1. The FT represents a pseudo-radial distribution function of the uranium near-neighbor environment. The EXAFS spectra of the U-treated bacterial cell samples are similar to m-autunite spectrum with regard to the U-O<sub>eq</sub>, U-P and U-U distances. These findings suggest the precipitation of an inorganic m-autunite-like uranyl phosphate phase by the bacterial cells in seawater.

## REFERENCES

1. González-Muñoz et al. (2008) Chemosphere 72 (3), 465-472.