 ROBL-CRG	Experiment title: Interaction of uranium with bioligands produced by soil bacteria and with related model compounds using X-ray absorption spectroscopy	Experiment number: 20-01-661
Beamline: BM 20	Date of experiment: from: 02.07. to: 04.07.2008 17.11. to: 17.11.2008	Date of report: 08.06.2009
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Report: Synchrotron-based EXAFS is a powerful technique to obtain structural information on radionuclide bioligand species. Within this proposal we explore structural parameter of U(VI) species with natural bioligands (e.g., pyoverdins), simple molecules simulating their functionalities and also microbial cell wall compartments simulating the binding properties of microbial cell envelopes. The focus here is on lipopolysaccharide (LPS: main part of the outer membrane of Gram-negative bacteria) and peptidoglycan (PG: main part of the outer membrane of Gram-positive bacteria). The present report is focussed on the last topic: structural characteristics of U(VI) species with LPS and PG.

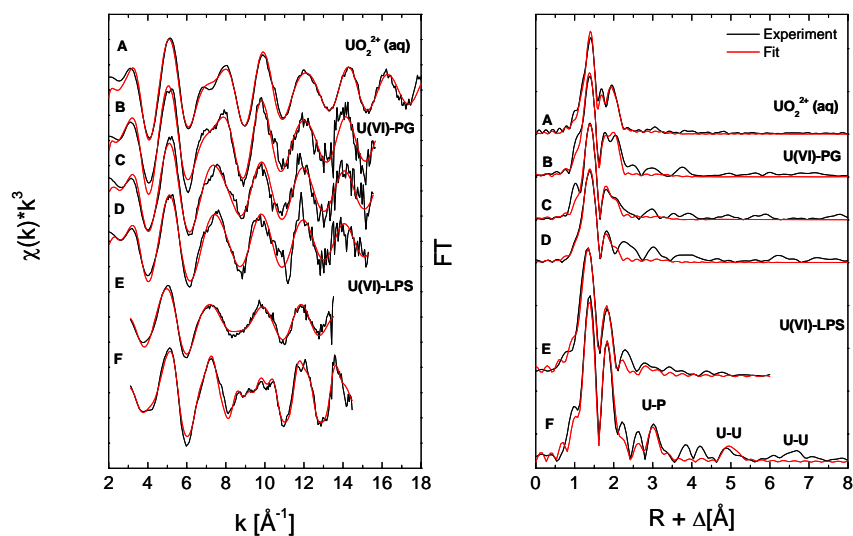


Fig. 1: U L_{III} -edge k^3 -weighted EXAFS spectra (left) and the corresponding Fourier transforms (right) and the theoretical fits (red line).

Experimental. U L_{III}-edge EXAFS measurements were carried out with wet pastes of LPS and PG after contact with concentrated UO₂²⁺ solutions with a fixed pH (see Table 1). These samples were measured at 15 K either in fluorescence or in transmission mode. For comparison a solution containing only UO₂²⁺ (0.05 M at pH 2.0) was measured at room temperature.

Results. A selection of the measured EXAFS oscillations and corresponding Fourier transforms are presented in Fig. 1. The extracted structural parameters are summarized in Table 1.

Table 1: Summary of the determined structural parameters.

Sample	Shell	N	R (Å)	σ ² (Å ²)	ΔE ₀ (eV)
A: 0.05 M UO ₂ ²⁺ , pH = 2.0	U=O	2	1.77	0.0015	12.5
	U-O _{eq}	4.9	2.41	0.0067	
B: 20 mg PG, 42 μmol UO ₂ ²⁺ , pH = 2.8	U=O	2.3	1.78	0.0018	13.6
	U-O _{eq}	4.8	2.43	0.0068	
C: 20 mg PG, 42 μmol UO ₂ ²⁺ , pH = 4.6	U=O	2.1	1.79	0.0017	11.5
	U-O _{eq}	6.0	2.40	0.0164	
D: 20 mg PG, 42 μmol UO ₂ ²⁺ , pH = 6.2	U=O	2.3	1.79	0.0022	11.9
	U-O _{eq}	6*	2.38	0.0176	
E: 100 mg LPS, 50 μmol UO ₂ ²⁺ , pH = 3.9	U=O	2*	1.79	0.0034	1.8
	U-O _{eq1}	2.7	2.33	0.0043	
	U-O _{eq2}	0.9	2.52	/0.0043	
F: 100 mg LPS, 10 μmol UO ₂ ²⁺ , pH = 4.6	U=O	2*	1.79	0.0017	1.0
	U-O _{eq}	3.2	2.29	0.0019	
	U-P	2.4	3.58	0.0025*	
	U-O _{eq-P}	/4.8	/3.68	0.0021*	
	U1	/2.4	5.20	0.0055*	
	U2		visible		

* fixed parameter, / linked parameter.

The changes in the U-O_{eq} distance reflect the pH-dependent speciation of the U(VI)-PG system. Between pH 3 and 5 uranyl coordinates to carboxyl groups whereas at pH values greater than 6 a mixed species is formed involving both carboxyl and amino or hydroxyl groups /1/. So the U-O_{eq} distance of 2.43 Å (B) points to preferred bidentate uranyl coordination to carboxyl groups. The decrease in U-O_{eq} detected (C and D) indicates a change in the coordination mode of U(VI) and possibly more functional groups could be involved due to the increased Debye-Waller factor. The EXAFS spectra measured in the U(VI)-LPS system are different. At an excess of LPS (F), uranyl is mainly bound through monodentate coordinated phosphoryl groups /2/. At equimolar ratios of uranyl and functional groups of LPS (E) additional carboxyl coordination in a bidentate manner becomes important.

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Reference

/1/ Barkleit, A. et al. (2009) Dalton Trans., published online DOI: 10.1039/b818702a.

/2/ Barkleit, A. et al. (2009) manuscript in preparation.