Coordination of uranium(VI) with functional groups of bacterial lipopolysaccharide studied by EXAFS and FT-IR spectroscopy

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Electronic Supplementary Information

1. Description of the EXAFS analysis of minor scattering contributions

The doublet structure (small Fourier transform (FT) peaks at ~3.85 Å and at ~4.23 Å, Figure 2 in article) belongs to the following single scattering (SS) and multiple scattering (MS) paths (see Figure S1 and explanation below):

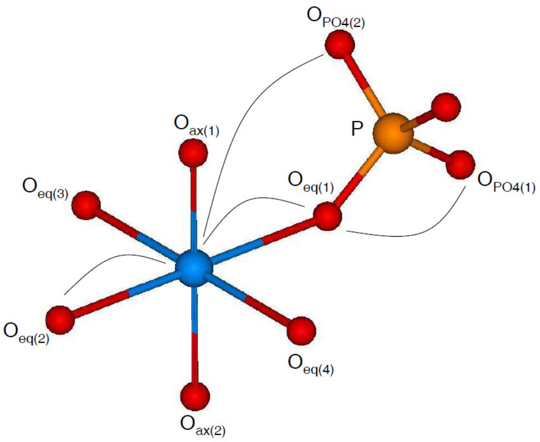

Figure S1. For clarity only one of the four coordinated PO_4 groups is shown. The lines show the possible scattering pathways which influence the mentioned FT feature.

In meta-autunite all U-$O_{eq(1,2,3,4)}$ distances are equal and the angles $O_{eq(1)}$-U-$O_{eq(2)}$ and $O_{eq(3)}$-U-$O_{eq(4)}$ are 180°. For all four PO_4 groups the angles U-$O_{eq(1,2,3,4)}$-$O_{PO4(1,2,3,4)}$ are 180°. For such angles for MS a focussing effect is expected which enhances the MS scattering amplitude in the measured signal. The scattering amplitude of the MS decreases if the angle decreases. In addition the scattering amplitude of the MS decreases as their effective path length R_{eff} increases. From these considerations the following SS and MS paths might influence the shape and the amplitude of the FT peaks at ~3.85 Å and ~4.23 Å:

SS:

8 x U-$O_{PO4(2)}$ at 4.07 Å

4 x U-$O_{PO4(1)}$ at 4.64 Å

MS:

8 x U-$O_{eq(1)}$-$O_{PO4(1)}$-U at 4.64 Å

4 x U-$O_{eq(1)}$-$O_{PO4(1)}$- $O_{eq(1)}$-U at 4.64 Å

4 x U-$O_{eq(1)}$-U-$O_{eq(2)}$-U 4.65 Å

(The R_{eff} are taken from the crystal structure of meta-autunite.)

Note that four of these paths are at a very similar R_{eff} (4.64 Å - 4.65 Å), hence their scattering signal sums up at the same position in the FT.

A crucial task for including these paths in the fit is the choice of the correct Debye-Waller (DW) factor for each path. Due to the strong overlapping of the paths and the small amplitude the DW's are strongly correlated, hence an independent fit of the DW's will cause large errors in determination. The DW's of the MS might be estimate from the DW's of the involved SS paths and then linked in a fit with the DW's of the SS paths in order to stabilize the fit. The problem in here is that also the DW's of the SS paths, especially for $O_{PO4(1)}$ and $O_{PO4(2)}$, are not known a-priory and that in turn they cannot be found due to the strong correlation with the unknown DW's of the MS paths. We used the mentioned paths for a fit of sample A (Table S1).

Table S1: Shell fit of sample A (without UU interactions). Bold letters – additional included paths for description of the FT features at ~3.85 Å and ~4.23 Å

Path	CN	R (Å)	DWx10^3 (Å^2)
SS U-Oax	2*	1.783(2)	1.8(1)
MS U-O_{ax1}-U-O_{ax2}-U	/2	/3.566	/3.6
SS U-O_{eq}	3.7(1)	2.285(2)	1.9(2)
MS U- $O_{eq(1)}$-U-$O_{eq(2)}$-U	**/3.7**	**/4.570**	**/3.8**
SS U-P	/3.7	3.587(4)	3.0(5)
MS U-$O_{eq(1)}$-P-U	/7.4	/3.687	3(1)
SS U-$O_{PO4(2)}$	**/7.4**	**4.09(9)**	**45(2)**
SS U-$O_{PO4(1)}$	**/3.7**	**4.78(2)**	**9(2)**
MS U-$O_{eq(1)}$- $O_{PO4(1)}$-U	**/7.4**	**/4.78**	**/9**
MS U-$O_{eq(1)}$- $O_{PO4(1)}$-$O_{eq(1)}$-U	**/3.7**	**/4.78**	**/9**

/ - parameter linked proportional to the parameter in the row above, * - fixed parameter. Numbers in parenthesis gives the estimated standard deviation of the free parameter as calculated by EXAFSPAK.

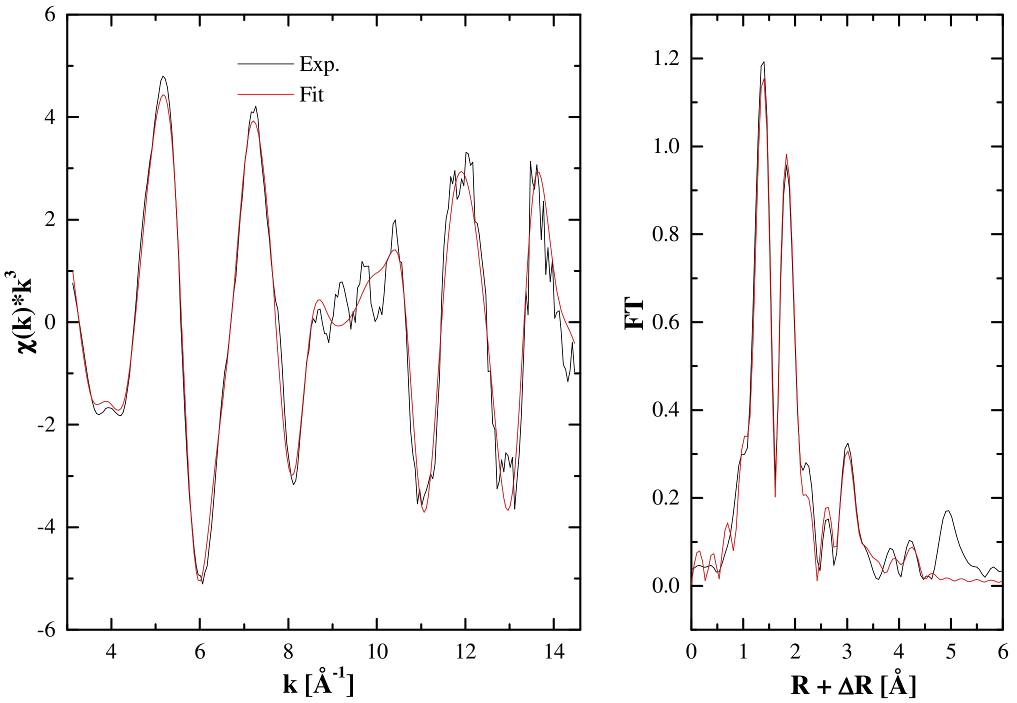

Figure S2. Best fit of sample A including the SS and MS paths for the description of the FT features at ~3.85 Å and ~4.23 Å.

For the MS U-$O_{eq(1)}$-U-$O_{eq(2)}$-U we assumed that the DW is twice the DW of the SS path U-$O_{eq(1)}$. For the MS U-$O_{eq(1)}$-$O_{PO4(1)}$-U and U-$O_{eq(1)}$-$O_{PO4(1)}$-$O_{eq(1)}$-U we assumed that the DW is equal to the DW of the SS path U-$O_{PO4(1)}$. The DW of $O_{PO4(2)}$ is very high (45 Å^2) with a standard deviation of 2 Å^2 (see Table S1) and the standard deviation in distance is also very high (0.09 Å). The feature at ~4.23 Å is well reproduced and the ~3.85 Å a bit less. On the other hand after this fit the FT residual (experiment-fit) in the region at ~3.85 Å and ~4.23 Å is equal to the experimental error, hence there is no need to explore further the origin of this resulting residual.

The additional inclusion of these minor scattering contributions has no effect on the fitted structural parameters of the major components as fitted in the article (Table 2). Moreover, due to the necessary linking of the minor scattering contributions to the major scattering contributions no additional information which would influence our structural interpretation in the article can be gathered.

2. Luminescence spectroscopy - Experimental

U-LPS suspensions identical to the EXAFS samples A, B and C and additional $UO_2(ClO_4)_2$ and UO_2^{2+}/PO_4^{3+} (U:P = 1:3, pH 4.6) were prepared for luminescence measurements.

The spectra of the suspensions were recorded at room temperature using a pulsed Nd:YAG laser system (Continuum Minilite Electro-Optics, Inc., Santa Clara, USA) with a fast pulse generator (FPG/05, EG&G Princeton Instruments, NJ, USA), and a digital delay generator (model 9650, EG&G Princeton Instruments, NJ, USA). The excitation wavelength of the uranyl luminescence was 266 nm with pulse energy of 0.3 mJ. The spectra were measured with a diffraction grating of 100 mm^{-1} from 371 to 674 nm, averaging three spectra with 50 laser pulses each, and a gate time of 2 μs. The luminescence emission was detected using an iHR 550 spectrograph (Horiba Jobin Yvon, Germany), controlled by the accompanying software LabSpec5 (Horiba Jobin Yvon, Germany).

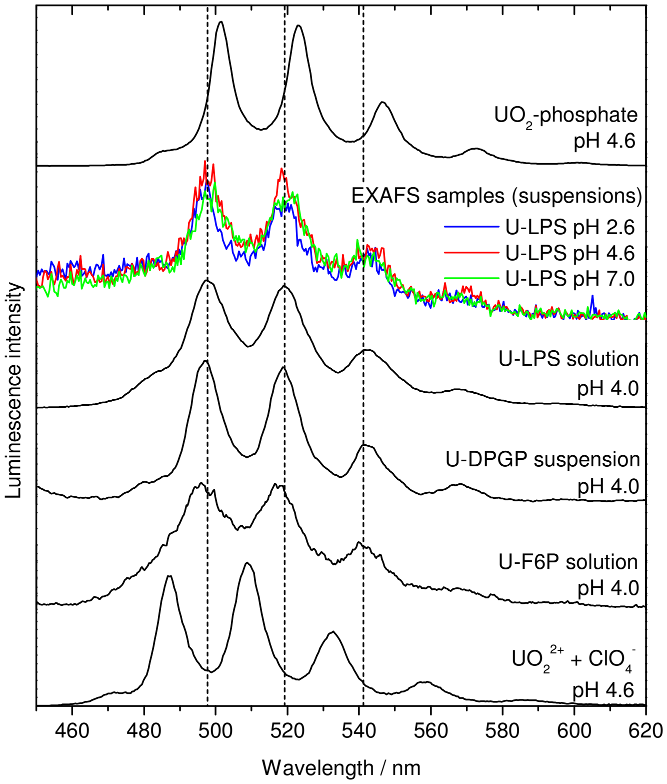

Figure S3. Luminescence spectra of U-LPS EXAFS samples A, B, and C (blue, red and green lines; U:P = 1:3). For comparison, UO_2-phosphate (top; U:P = 1:3), UO_2-perchlorate (bottom)and some U(VI) organic phosphate compounds are added.[1,2,3]
DPGP: 1,2-dipalmitoyl-sn-glycero-3-phosphate
F6P: fructose-6-phosphate

References

1 A. Barkleit, H. Moll and G. Bernhard, *Dalton Trans.*, 2008, 2879-2886.
2 A. Koban and G. Bernhard, *J. Inorg. Biochem.*, 2007, **101**, 750-757.
3 A. Koban, G. Geipel, A. Rossberg and G. Bernhard, *Radiochim. Acta*, 2004, **92**, 903-908.