ROBL-CRG	**Experiment title:** EXAFS investigations of uranium species formed by monocellular and polycellular algae	**Experiment number**: 20 - 01 - 656
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Report:

Experimental

The aim of this study is to determine the structural parameters of the formed uranyl complex species in inactive and active monocellular *Chlorella vulgaris* cells in the pH range from 3 to 7. The stored algal biomass was re-suspended in 0.9% $NaClO_4$ solution and contacted 72 h with $UO_2(ClO_4)_2$ (inactive cells). For the experiments with active algal cells the biomass was contacted 96 h with uranium containing mineral medium. After separation of the washed algal biomass by centrifugation the fresh samples were put into polyethylene sample holder surrounded with Kapton tape. The U L_{III}-edge spectra were measured in fluorescence mode at room temperature and at 30K using a closed-cycle He-cryostat. The EXAFS spectra were analyzed using the suite of program EXAFSPAK /1/. The theoretical scattering phases and amplitudes were calculated by using x-ray structural data of meta-autunite with the scattering code FEFF8 /2/.

Results

Figure 1 shows the raw U L_{III}-edge k^3-weighted EXAFS spectra and their corresponding Fourier transforms (FT) of uranium containing inactive algal cells (samples A-C) measured at room temperature and at 30 K after shock freezing of the samples as examples. The spectra of algal cells contaminated at pH 3, 5 and 6 and measured at RT (A1, B1, C1) are well reproduced by taking only backscattering of O atoms into account. In the case of U(VI)-algae species formed at pH 3 we obtained for the axial

oxygen a radial U-O_{ax} distance of 1.77 Å and for the equatorial oxygen a radial U-O_{eq} distance of 2.38 Å. At pH 5 and 6 the U-O_{eq} signal is splitted in two different U-O_{eq} distances (U-$O_{eq(1)}$= 2.27 or 2.28 Å and U-$O_{eq(2)}$= 2.45 Å). But no significant uranyl-phosphate interactions were found in these samples.

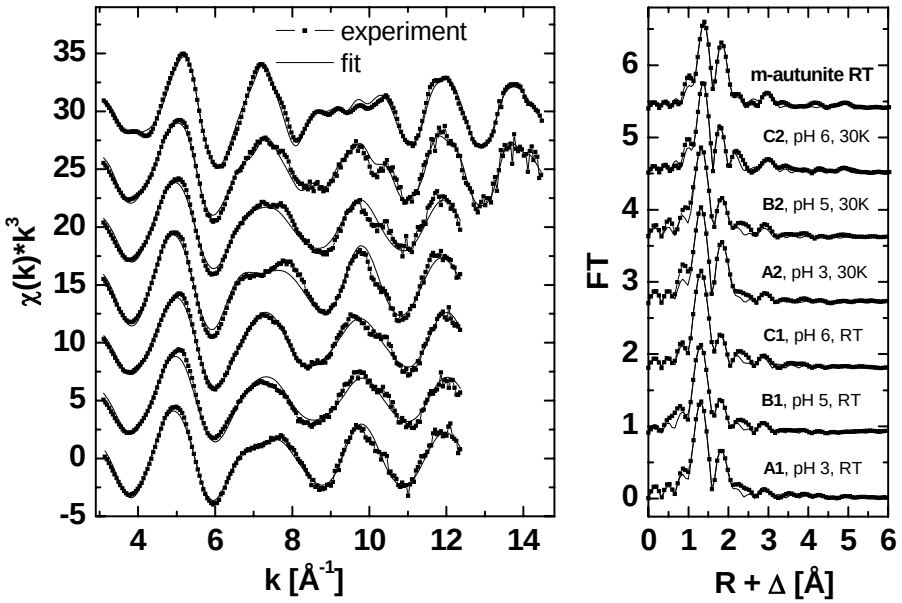

Fig. 1. Raw U L_{III}-edge k^3-weighted EXAFS spectra (left) and corresponding Fourier transform (right) of different algal samples [Algae] = 0.75g $_{dry\ mass}$ / L [U(VI)] = $1 \cdot 10^{-4}$ M

After shock freezing of the algal samples (A2, B2, C2) four phosphate groups coordinate in a bidentate fashion with four O_{eq} at 2.31 Å, four P at 3.59 Å and four U atoms at a U-U distance of 5.21 Å according to the XRD of m-autunite were obtained at pH 6. The long U-O_{eq1} distance of 2.45 Å - 2.50 Å in the complex species in all samples is similar to those observed for bidentate coordinated carboxylic groups. Factor analysis of the EXAFS spectra shows that two principal chemical environments coexist. This is also supported by the fact that in both cases (RT, 30K) the spectra of the sample at pH 5 can be reproduced by a linear combination of the spectra of the samples at pH 3 and pH 6. Therefore, we conclude that at pH 3 U(VI) is coordinated mostly by carboxylic groups, at pH 5 by carboxylic and phosphate groups, while at pH 6 U(VI) mostly interacts with phosphate groups. Currently, the corresponding analyses of the spectra of uranyl complex species formed with active *Chlorella* cells are performed.

References

/1/ George, G. N., Pickering, I. J.: EXAFSPAK A Suite of Computer Programs for Analysis of X-Ray Absorption Spectra. Stanford Synchrotron Radiation Laboratory, Stanford, CA. USA. (1995)

/2/ Ankudinov et al.: Real-space multiple scattering calculation and interpretation of x-ray absorption near-edge structure, Phys. Rev. B 58 (1998), 7565-7576