

SLS Symposium on Environmental Science

Tuesday, March 1, 2011

10:00 to 12:15, WBGB/019

10:00 Interaction of Halogenated Pesticides with Site-Specific Mutants of Cytochrome P450cam

Guillaume Pompidor, Saptaswa Sen, Soumen Kanti Manna, Juan C. Fontecilla-Camps, Shyamalava Mazumdar

10:30 Studying the formation of Ni₃C from CO and metallic Ni at T=265°C in situ using Ni K-edge X-ray absorption spectroscopy.

Rudolf Struis, D. Bachelin, Chr. Ludwig, and A. Wokaun

11:00 Coffee

11:15 Microbial Metabolism and Biogeochemical Cycles: Synchrotron Spectromicroscopy Studies

Luca Quaroni, Heide Schulz-Vogt, Ken Wilson

11:45 Relevance of Arsenic Binding to Humic Acid in the Presence of Copper Ions

Xiaolan Liu, M. Nachtgeal, Ch. Ludwig, M. Harfouche and E. Kleymenov

Interaction of Halogenated Pesticides with Site-specific Mutants of Cytochrome P450cam

Guillaume Pompidor¹, Saptaswa Sen², Soumen Kanti Manna², Juan C. Fontecilla-Camps³, Shyamalava Mazumdar²

¹Swiss Light Source at the Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

² Department of Chemical Sciences, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India ³Institut de Biologie Structurale Jean-Pierre Ebel, CEA/CNRS, 41, rue Jules Horowitz, 38027 Grenoble Cedex 1, France

ABSTRACT

Cytochrome P450 forms a super-family of b-type heme proteins found in organisms in all domains of life, which are major catalysts in the oxidative biotransformation related to body detoxification, steroid hormone biosynthesis, drug metabolism, etc.[1]

P450cam from *Pseudomonas Putida* is a monooxygenase which catalyzes the hydroxylation of its natural substrate, camphor, into 5-*exo*-hydroxy-camphor. Nevertheless this enzyme has been shown to catalyze multiple reactions including dehalogenation of organochlorine compounds. Taking advantage of the non-specificity of the enzyme, bio-engineering has been carried out to perform the biodegradation of several halogenated insecticides.

The X-ray structures of two mutants (Y96F and Y96F/T101V) crystallized with three different insecticides (aldrin, endrin and dieldrin) show the binding mode in the active site. In combination with enzymatic assays and mass spectroscopy, these results allow to propose a mechanism for the dehalogenation of these insecticides and open up the possibility of soil depollution by P450cam enzyme.

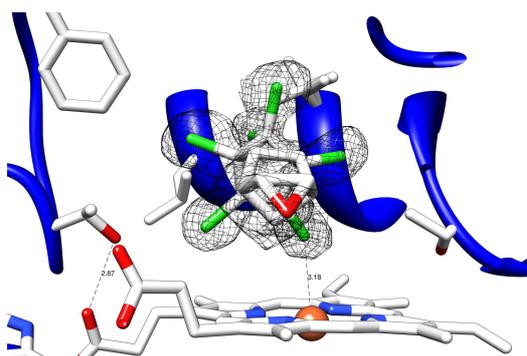


Figure 1: Electron density of the dieldrin bound in the active site of the Y96F of P450cam.

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Studying the formation of Ni₃C from CO and metallic Ni at T=265°C *in situ* using Ni K-edge X-ray absorption spectroscopy.

R. Struis^{1,2}, D. Bachelin¹, Chr. Ludwig^{1,2}, and A. Wokaun¹

¹ Paul Scherrer Institut, General Energy Research Department, CH-5232 Villigen PSI, Switzerland.

² Swiss Federal Institute of Technology at Lausanne (EPFL), School of Architecture, Civil and Environmental Engineering (ENAC-III), CH-1015 Lausanne, Switzerland.

Rudolf.Struis@psi.ch

Nowadays, sustainability and CO₂-neutrality are motivations to produce methane (CH₄) from the H₂ and CO rich synthesis gas resulting from wood gasification.[1] Methanation uses a Ni metal (Ni⁰)-based catalyst that is also easily deactivated in the presence of wood-native contaminants (sulphur, tars, alkalis) or by parallel reactions (coking, carburization).[2, 3] Many fundamental studies have been made over time on carbon poisoning of Ni-based catalysts under different conditions of industrial interest, but a detailed understanding of the poisoning mechanism is still missing due to the complexity of the poisoning problem and the lack in careful fundamental studies under reaction relevant conditions. [4] Therefore, we studied the carburization reaction ($2\text{CO}+3\text{Ni}^0\rightarrow\text{Ni}_3\text{C}+\text{CO}_2$, T=265°C) with Ni⁰ nanoparticles *in situ* using synchrotron-based X-ray absorption spectroscopy (XAS) at the Ni K-edge. The study showed that the interpretational uncertainties expected from the fact that the bulk structure of Ni⁰ and Ni₃C are very alike (but not identical) can be overcome by using a modified version of the difference file method, by employing complementary tools like wavelet transform analysis, and by exploiting the destructive interference effect between oscillatory signals from Ni atoms in slightly different environments.

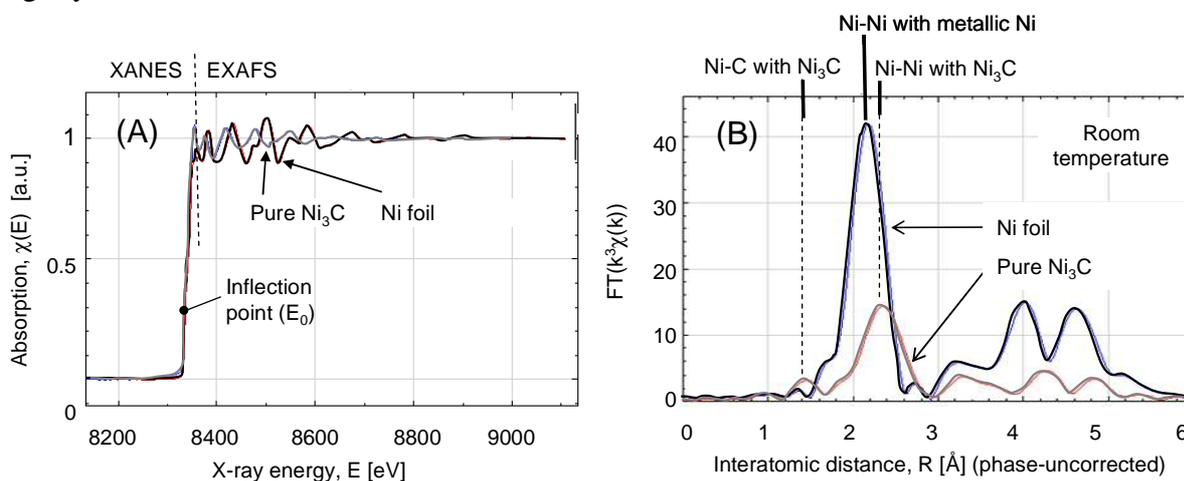


Fig. 1 (A) Background-corrected, normalized Ni K-edge transmission spectra of Ni⁰ foil and pure Ni₃C as a function of the X-ray energy. (B) Fourier transform of $k^3\chi(k)$ data derived from the spectra shown under (A).

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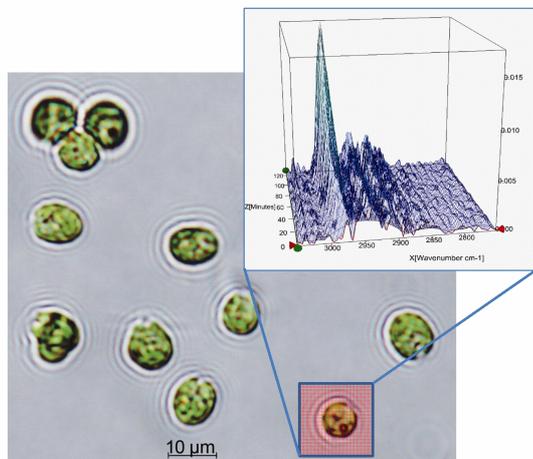
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Microbial Metabolism and Biogeochemical Cycles: Synchrotron Spectromicroscopy Studies

Luca Quaroni, Heide Schulz-Vogt, Ken Wilson

Microorganisms play a significant role in the processing of organic and inorganic compounds in the environment. These transformations range from the decay of biological matter to the global cycling of such elements as sulfur and phosphorus. Understanding the detailed biochemical processes that mediate microbial transformation of the surrounding medium is a key issue in microbiology, environmental studies and biotechnology. Many of the processes develop in a heterogeneous environment and need to be resolved in space on the scale of a few micrometers. Particularly advantageous in this context is the use of spectromicroscopy techniques, which allow the study of structure and reactivity inside selected individual cells and in their immediate proximity. In this presentation we discuss the use of synchrotron FTIR spectromicroscopy, also coupled to other synchrotron techniques, to investigate microbial metabolism. The technique provides information on composition, concentration and time evolution of chemical processes. Most importantly, it allows the study of living samples. We present specific applications to the investigation of the fermentative metabolism of unicellular algae and sulfur metabolizing bacteria.



*Time resolved synchrotron FTIR absorption spectra recorded on a single cell of *Chlamydomonas reinhardtii*, showing evolution of ethanol from its fermentative metabolism.*

Relevance of Arsenic Binding to Humic Acid in the Presence of Copper Ions

X. Liu^{1,2}, M. Nachtegaal¹, Ch. Ludwig^{1,2}, M. Harfouche¹ and E. Klymenov¹

1. Paul Scherrer Institute (PSI), 5232 Villigen PSI, Switzerland

2. Swiss Federal Institute of Technology (EPFL), CH-1015 Lausanne, Switzerland

Xiaolan.liu@psi.ch

It was estimated that more than 100 million people are at risk due to consumption of harmful arsenic-enriched groundwater [1]. Understanding the mechanism controlling arsenic speciation and mobility in groundwater is therefore essential to assess its bioavailability. Recent studies indicated that soluble arsenic (As) concentrations in groundwater often correlate with high amounts of dissolved organic carbon [2]. This suggests that dissolved organic matter (DOM) may play a major role in mobilizing As oxyanions by forming As-DOM complexes. The binding of As oxyanions to negatively charged DOM via metal cation (Me) is generally considered as the major reaction mechanism among all the possible reaction pathways for As-DOM complexation [3]. However, no direct evidence of this reaction was ever found since till now, most of the studies were conducted by means of solution chemistry. In this context, XAS is a very valuable tool since it can provide direct structural information and consequently elucidate the interactions and correlation between arsenic and organic matter in natural systems.

Using a combination of chemical methods and normal/HERFD XAS spectroscopy, we were able to prove the occurrence of humic acid-copper-arsenate ternary complex under environmentally relevant neutral pH conditions and investigate their coordination environment. We found that arsenate tetrahedron is linked to the copper octahedron after the release of water molecules in bidentate, mono or binuclear forms. The findings of our study imply that arsenic complexation with humic acid bridged by Cu^{2+} can directly affect arsenic mobility in the environment.

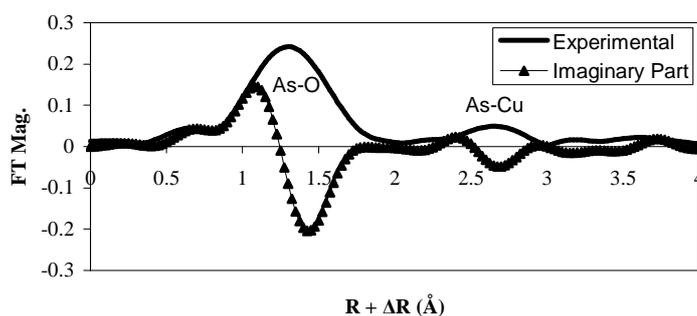


Fig.1 Fourier transform of k^3 -weighted As k-edge experimental and simulated EXAFS spectra of the ternary complex

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