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# Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF**.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

*http://193.49.43.2:8080/smis/servlet/UserUtils?start*

***Reports supporting requests for additional beam time***

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

## Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

## Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

| ESRF | **Experiment title:** Interaction between microorganisms and metals using EXAFS | **Experiment number**: 20_01_625 |
|---|---|---|
| **Beamline**: BM 20 | **Date of experiment**: from: 10.06.2003 to: 12.06.03 | Date of report 26-08-03 |
| **Shifts:** 6 | **Local contact(s)**: Andreas Scheinost | *Received at ESRF:* |

**Names and affiliations of applicants** (* indicates experimentalists):

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## Report:

Nanoclusters –near monodispersed metal particles that are generally less than 10 nm (100Å) in diameter- have attracted intense over the past decade. On reason of this is the belief that nanoclusters will have unique properties, derived in part from the fact that these particles and their properties lie somewhere between those of the bulk and single-particle species. These strange "morsels of matter" have fascinating potential uses; nanoclusters have significant potential especially for catalysis as new types of high activity and selectivity catalysts.Palladium metal is one of the most promising catalysts. It has been used for removing nitrate ion from drinking water, hydrogenation and for combustion reactions. In this work the formation of Pd nanoclusters by the cells and S-layers of *B. sphaericus* JG-A12 and 9602 in anaerobic conditions are studied using EXAFS spectroscopy.

Pd K–edge X-ray absorption spectra were collected at low temperature in fluorescence mode at the Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility, Grenoble (France) using the Si(111) double-crystal monochromator. The energy was calibrated by measuring the Pd K-edge transmission spectrum of a palladium foil and defining the first inflection point as 24350 eV. Eight spectra for each sample were recorded. The EXAFS oscillations were isolated from the raw, averaged data by removal of the pre-edge background, approximated by a first-order polynomial, followed by $\square_0$-removal *via* spline fitting techniques and normalization using a Victoreen function. Deadtime correction was applied. The EXAFS spectra were analyzed according to the standard procedures using the program EXAFSPAK. The theoretical scattering phase and amplitude functions used in data analysis were calculated using FEFF8.

Throughout this section, FT peak distances are reported in units of Å, uncorrected for phase shift (i.e., $R + \Delta R$). In contrast, when referring to neighboring atoms, we report actual distances.
The $k^3$-weighted $\chi$ spectra determined using extended X-ray absorption spectroscopy (EXAFS) analyses of the palladium clusters and Pd complexes formed by the cells *B. sphaericus* JG-A12 and the S-layer protein of the latter bacterium are presented in Figure 1, 2 and Figure 3, respectively along with the best fits obtained from the fitting procedure.

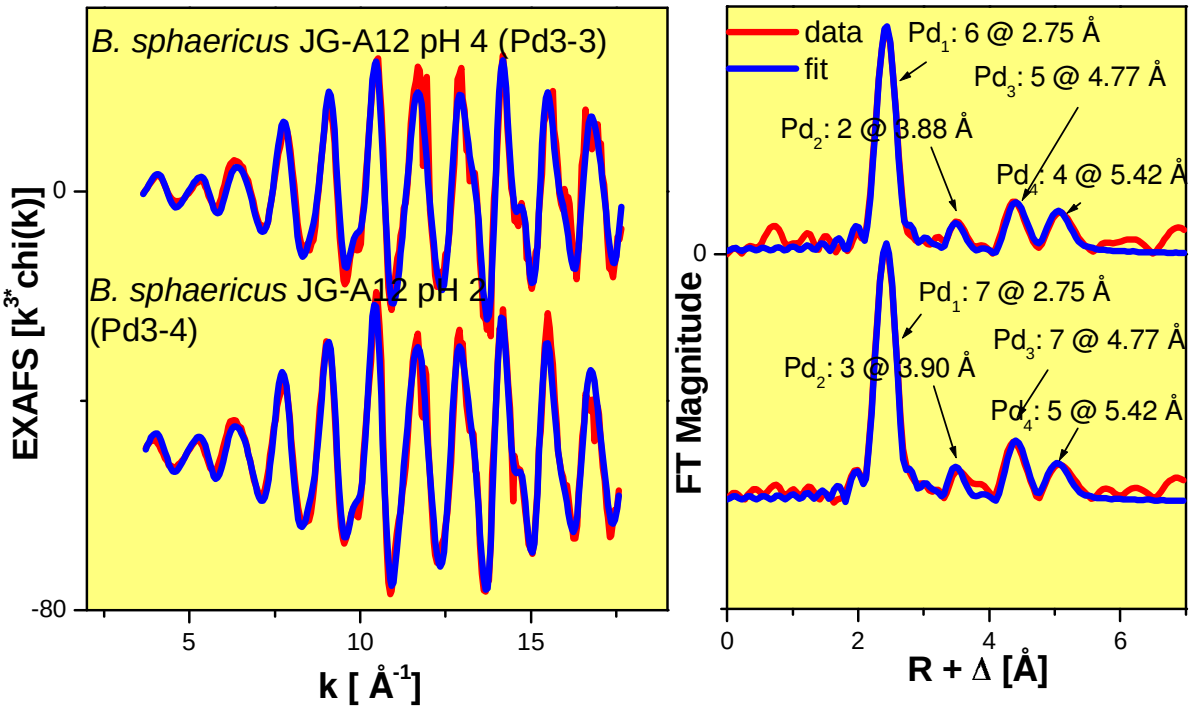


**Fig. 1.** Pd K-edge $k^3$–weighted EXAFS spectra (left) and corresponding FT (right) of the Pd clusters formed by the cells of *B. sphaericus* JG-A12 at pH 2 and 4 .

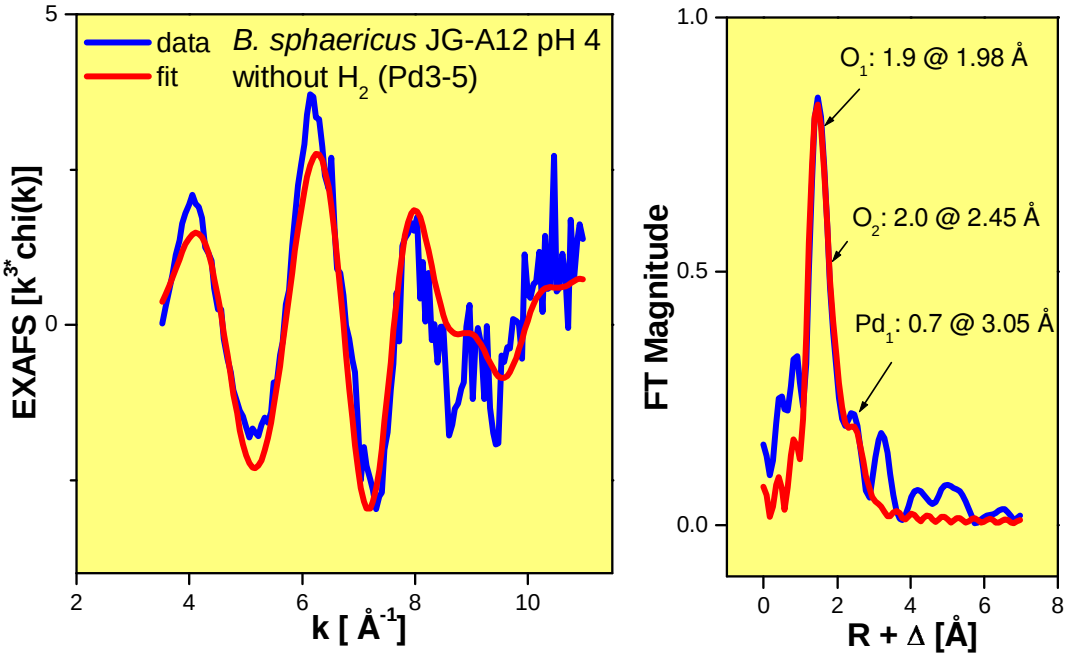


**Fig. 2.** Pd K-edge $k^3$–weighted EXAFS spectra (left) and corresponding FT (right) of the Pd complexes formed by the cells of *B. sphaericus* JG-A12 at pH 4 without presence of reducing agent.

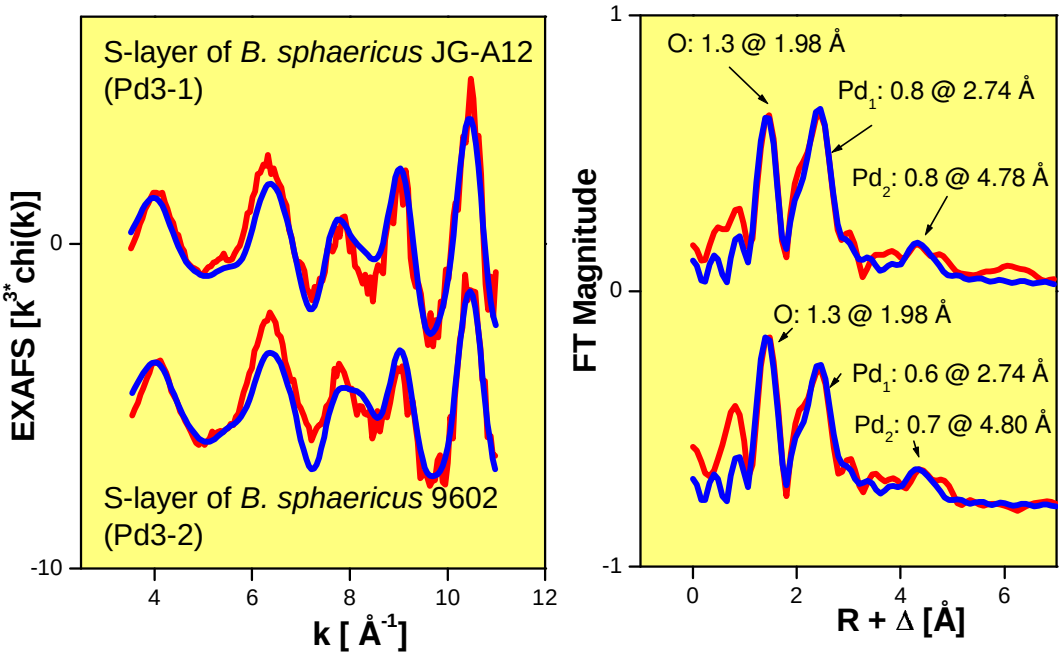


Fig. 3. Pd K-edge $k^3$–weighted EXAFS spectra (left) and corresponding FT (right) of the Pd complexes formed by the S-layers of B. sphaericus JG-A12 and 9602

**I. Interaction of palladium with cells of *B. sphaericus* JG-A12**

The FT of the EXAFS spectra of the palladium clusters formed by the cells of *B. sphaericus* JG-A12 in presence of $H_2$ (reducing agent) at pH 2 and 4 (Fig. 1) are similar and presented 4 peaks. Using Pd-Pd phase and amplitude functions form a palladium foil, these FT give distance of 2.75, 3.88, 4.77 and 5.42 ± 0.02 Å. These results confirmed the formation of palladium nanoclusters by the cells of the mentioned bacterium at pH 2 and 4 in the presence of $H_2$.

However in the absence of reducing agent ($H_2$) (Fig. 2) the FT of the EXAFS spectra are completely different from those obtained in the presence of $H_2$. The preliminary fit of the first 2 main shells using the Pd-O amplitude and phase functions giving a distances of 1.98 and 2.45 ± 0.02 Å. The third FT peak was modeled to a Pd-Pd contribution giving a distance of 3.06 ± 0.02 Å which is in good agreement with the Pd-Pd distance in PdO (R=3.03 ± 0.02 Å).

**II. Interaction of palladium with S-layer of *B. sphaericus* JG-A12 and 9602**

In these 2 samples, the first peak was modelled to a contribution of a oxygen backscatter at a distance of 1.98 ± 0.02 Å which is in good agreement with the Pd-O1 distance in PdO (R=2.018 ± 0.02 Å). The 2 and 3 peaks are arising from contribution of palladium backscatter giving distances of 2.74 and 4.78 ± 0.02 Å.

**Future working**

1. Calculation of the Pd-nanocluster size using TEM and EXAFS spectroscopy
2. In situ monitoring of Pd nanoclusters formed by the cells and S-layers of *B. sphaericus* by energy dispersive EXAFS at Beamline ID (ESRF, France).