EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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 via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can 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:** Palladium mobility in hydrothermal systems: ground proofing MD approach	**Experiment number:** 30-02-1057
Beamline:	**Date of experiment:** from: 5 to: 11/Dec/2013	**Date of report:** 20/8/2014
Shifts: 18	**Local contact(s):** Denis Testemale	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

***Prof Joël Brugger**

***Dr. Denis Testemale**

***Dr. Barbara Etschmann**

***Dr Weihua Liu**

***Ms Yuan Mei**

Report:

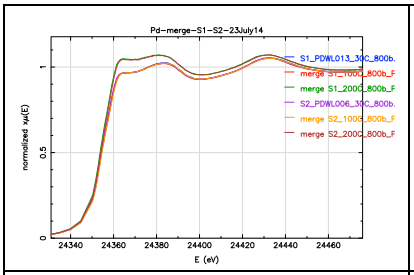
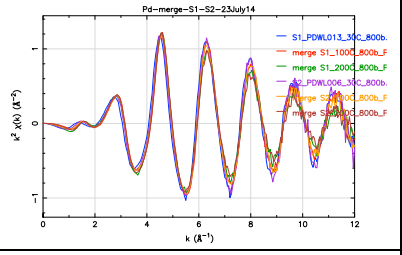
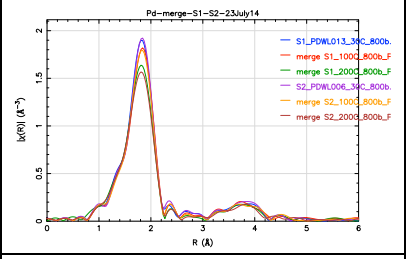
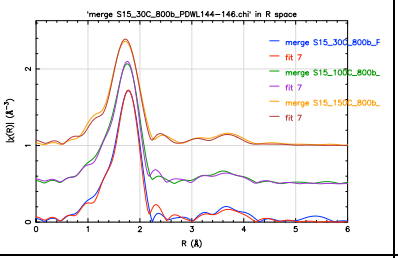
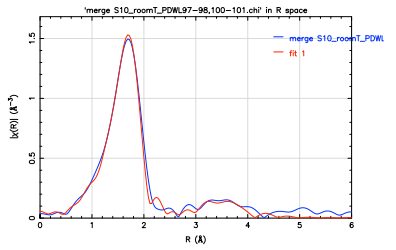
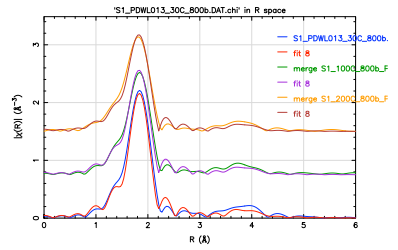
The aim of this experiment was to measure the speciation of Pd(II) chloride and bisulfide complexes and use this data as a bench mark for MD calculations. The work was presented at Goldschmidt (2014) and a manuscript is in progress for submission to GCA. That paper focuses on MD simulations, with the XAS data being used to groundproof the model predictions.

We failed to measure Pd-S complexes in solution as the solubility is incredibly low (lower than expected from thermodynamic calculations). We tried a number of times varying various parameters (eg solution composition), however, the only time we obtained lovely Pd-S spectra they remained unchaged over the entire temperature range, which is suspicious to say the least and led us to belive we were measuring scattering from the solid.

We had more luck with the Pd(II) chloride solutions. EXAFS were measured for the following solution compositions:

	H_2O	$PdCl_2$	HCl	NaCl	$HClO_4$
Sol1*	19.9948 g	0.2183 g	1.995 g		
Sol2*	20.0131 g	0.1988 g	0.0318 g	1.2007 g	
Sol3*	19.9254 g	0.2085 g		1.216 g	
Sol4*	8.04 g	2.01 g of Sol 2	2.81 g		
Sol 10	9.9758 g	0.0141 g			5.0755 g
Sol 15: $PdCl_2$ in 1 drop 37% HCl	10.0254 g	0.0188 g (not all dissolved)	0.0255 g		

* Concentration of Cl >> Pd

		
Energy space. NB: Change in XANES with temperature – this is not due to precipitation of Pd. Not due to normalisation.	k-space: there is no beat pattern, this is indicative of a single ligand type	R-space: Slight shoulder, but no real evidence for an O-peak (can fit ~0.3(3) O).
		
Sol 15: fit 30, 100 & 150 °C	Sol 10: fit 30 C	Sol 1: fit 30, 100 & 200 °C

The following fit parameters were refined:

Solution	**T,P**	**nO, rO (Å), ssO (Å^2)**	**nCl, rCl (Å), ssCl (Å^2)**	**GOF, E_0**
Sol1 2 ≤ k ≤ 12 1 ≤ R ≤ 5 2 ≤ k ≤ 12 1 ≤ R ≤ 5 2 ≤ k ≤ 10 1 ≤ R ≤ 5	30 °C, 800 bar 100 °C, 800 bar 200 °C, 800 bar	Max nO ~0.3(3), effectively no Pd-O.	nCl = 4 (fix) rCl = 2.305(2) Å ssCl = 0.0010(3) Å^2 nCl = 4 (fix) rCl = 2.305(2) Å ssCl = 0.0027(3) Å^2 nCl = 4 (fix) rCl = 2.305(2) Å ssCl = 0.0035(5) Å^2	χ^2_{red} = 138 Enot = 6.1(3)
Sol10 2 ≤ k ≤ 12 1 ≤ R ≤ 5	ambient	nO = 2* rO = 2.022(9) Å ssO§ = 0.0006(4) Å^2	nCl = 2* rCl = 2.274(5) Å ssCl = 0.0006(4) Å^2	χ^2_{red} = 295 Enot = 5.0(6)
Sol15 2 ≤ k ≤ 12 1 ≤ R ≤ 5 2 ≤ k ≤ 12 1 ≤ R ≤ 5 2 ≤ k ≤ 10 1 ≤ R ≤ 5	30 °C, 800 bar 100 °C, 800 bar 150 °C, 800 bar	nO = 1.3(2) rO = 2.04(1) Å ssO§ = 0.0010(4) Å^2 nO = 1.7(2) rO = 2.06(1) Å ssO§ = 0.0009(5) Å^2 nO = 1.7(3) rO = 2.07(2) Å ssO§ = 0.0020(8) Å^2	nCl = 2.7(2) rCl = 2.288(5) Å ssCl = 0.0010(4) Å^2 nCl = 2.3(2) rCl = 2.298(6) Å ssCl = 0.0009(5) Å^2 nCl = 2.3(3) rCl = 2.302(8) Å ssCl = 0.0020(8) Å^2	χ^2_{red} = 250 Enot = 7.5(9)

*Attempts to refine nO&nCl (with the constraint of a maximum nCl=2, determined from the composition of the solution) resulted in nO = nCl = 2.

§ ssO were constrained to be the same as ssCl.