

## 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://www.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.

**Experiment title:**

A 1s2p RIXS study of the oxygen evolving complex in PSII

**Experiment number:**

SC-3580

**Beamline:**

ID26

**Date of experiment:**

from: 28/11/2012 to: 12/12/2012

**Date of report:****Shifts:**36 in 16  
bunch  
mode**Local contact(s):**

Pieter Glatzel

*Received at ESRF:***Names and affiliations of applicants (\* indicates experimentalists):**

Laboratory Helmholtz Zentrum Berlin G-I2 Synchrotron Methods and Instrumentation Wilhelm-Conrad-Röntgen-Campus Albert-Einstein-Str. 15 D – 12489 BERLIN  
Name Dr. WERNET Philippe\*

Laboratory CEA Saclay iBiTec-S/SB2SM/LBSR Bât 144 F - 91191 GIF-SUR-YVETTE  
Name Dr. LASSALLE Benedikt\*

Laboratory ESRF 6 rue Jules Horowitz B.P 220 F - 38043 GRENOBLE Cedex  
Name Dr. GLATZEL Pieter\*

Laboratory Helmholtz-Zentrum Berlin (HZB) Albert Einstein Str 15 D - 12489 BERLIN-ADLERSHOF  
Name SCHROEDER Henning\*

Laboratory Lawrence Berkeley National Laboratory Physical Biosciences Division MS: 66-0325, 1 Cyclotron Rd. USA - 94720 BERKELEY  
Name Dr. YANO Junko\*

Laboratory MPI Solid State research Heisenbergstrasse 1 D - 70569 STUTTGART  
Name HAVERKORT Maurits W. Phone + 49 (0) 711 689 1666 Email [m.w.haverkort@fkf.mpg.de](mailto:m.w.haverkort@fkf.mpg.de)

Laboratory MPI fuer Bioanorganische Chemie Stiftstr. 34-36 D - D-45470 MUELHEIM AN DER RUHR  
Name Prof. Dr. DEBEER Serena\*

## Report:

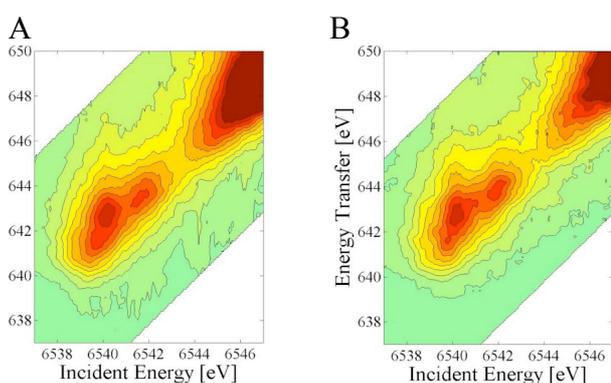
### Scientific background :

The oxygen-evolving complex (OEC) located in the PSII membrane-bound protein in plant, algae, and cyanobacteria catalyses the water-oxidation reaction. The OEC, with four Mn and one Ca, couples the 4-electron chemistry of water oxidation with the one-electron photochemistry of the reaction center by sequentially storing oxidizing equivalents through five intermediate S-states ( $S_i$ ,  $i = 0$  to 4), before one molecule of dioxygen is evolved (**Fig. 1**).<sup>1</sup> The  $Mn_4Ca$  cluster provides a high degree of redox and chemical flexibility so that several oxidizing equivalents can be stored during the S-state cycle. To understand the mechanism of water oxidation in detail, it is crucial to know whether the extracted electrons are directly derived from bound water, from the Mn atoms, or from any other parts of the OEC accompanying each S-state transition.<sup>2</sup>

Previously, we have used 1s2p direct resonant inelastic X-ray scattering (RIXS) to study the electronic structure of the  $Mn_4Ca$  cluster in the  $S_1$  and  $S_2$  states.<sup>3,4</sup> The result showed that Mn in the  $S_1$  state contains oxidation states III and IV; thus providing confirmation for the  $(III_2,IV_2)$  assignment in the  $S_1$  state. We also found strong covalency for the electronic configuration in the OEC and we conclude that the electron is transferred from a strongly delocalized orbital for the  $S_1$  to  $S_2$  transition.

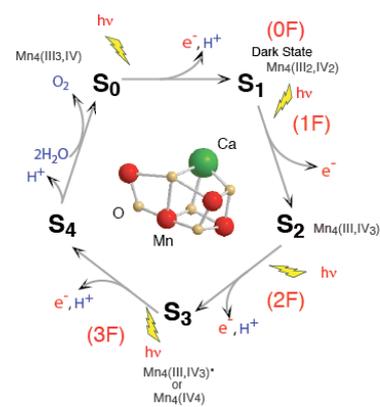
### Results :

During the last beamtime (Dec 2012) at ID26, we measured 1s2p RIXS data on all S-states of PSII that are accessible using the flash (F)-freeze technique (0F (dark state), 1F, 2F, and 3F; cf. **Fig. 1**) with higher energy resolution ( $\sim 0.6$  eV) than previously used ( $\sim 1.2$  eV) to gain a comprehensive picture of the Mn electronic structure and its changes during the catalytic cycle in PSII. Great care was taken to monitor the



**Fig. 2:** K absorption pre-edge 1s2p RIXS plane for PSII (A)  $S_1$  and (B)  $S_2$  states.

The  $S_1$  and  $S_2$  spectra are shown in **Fig. 2**. Deconvolution of flash-induced spectra (1F, 2F, and 3F) to get pure S-state spectra is in progress based on the EPR (electron paramagnetic resonance spectroscopy) data which was collected prior to the beamtime. We find very similar spectral shapes for all S-states confirming the highly covalent character of Mn in the OEC. The higher spectral resolution achieved on ID26 allows identification of three prominent spectral features. Full theoretical calculations of 1s2p RIXS in such complex systems is currently not possible. Therefore, we have to rely on comparison with model systems.

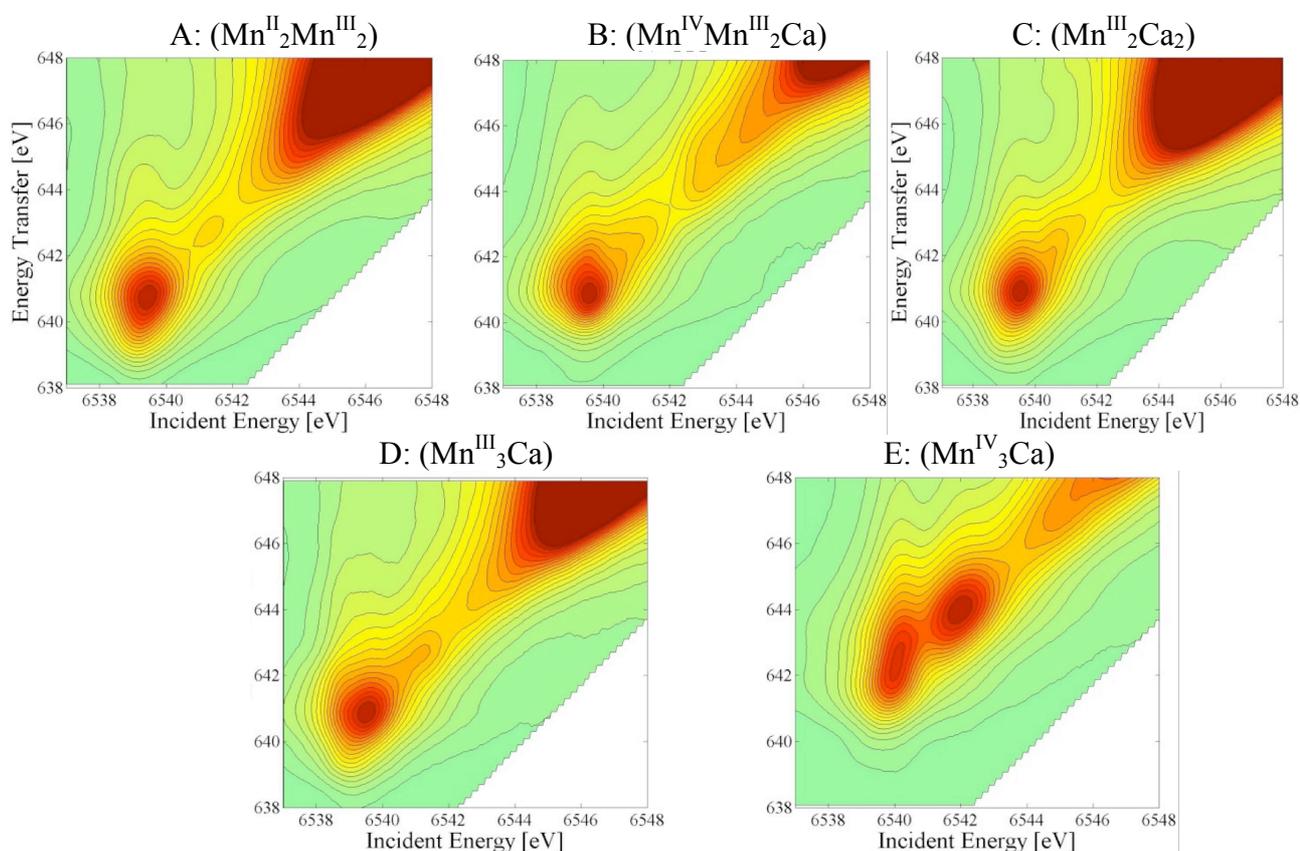


**Fig. 1:** Kok Cycle for water splitting reaction in PSII.

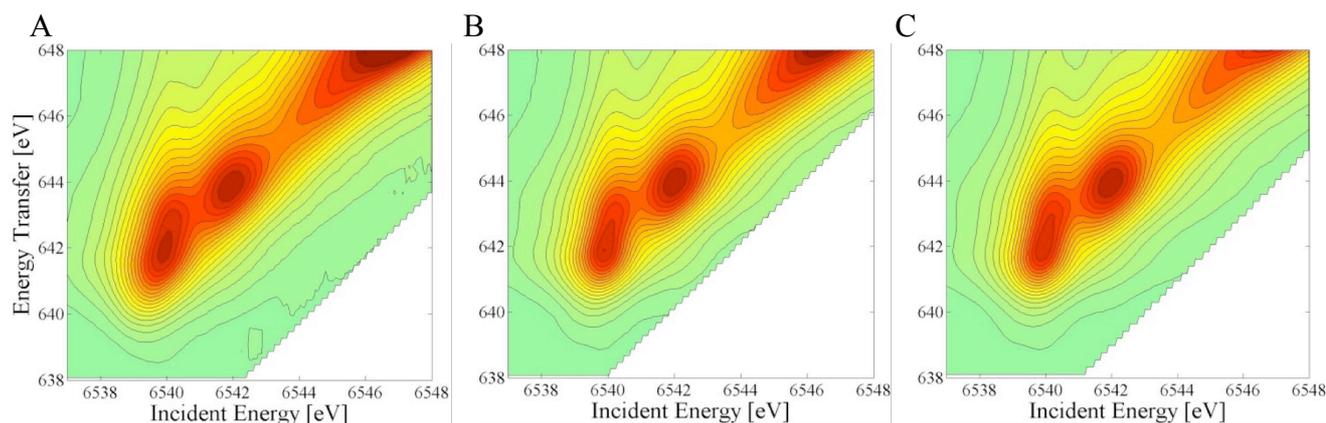
modification of the electronic structure induced by the X-ray beam. The maximum acceptable X-ray exposure time was determined to 5s and the samples thus had to be frequently moved under the beam. Furthermore, a large number of PSII samples was measured to obtain sufficient statistics (Mn concentration  $\sim 1$  mM). The RIXS planes are constructed by recording several line scans, each spot with 5s exposure time. In order to obtain the RIXS plane with correct normalization, the Mn concentration had to be determined for each spot. A set of macros was written by the BL staff and ESRF software groups to deal with this problem.

We collected 1s2p RIXS spectra of a series of model compounds ( $\text{Mn}_x\text{Ca}_y$  compounds synthesized by G. Christou's group in U. Florida, and different structural models of the  $\text{CaMn}_3$  subsite of the OEC, and tetranuclear heterometallic trimanganese dioxo clusters where the cation is varied  $[\text{Mn}_3\text{M}(\mu_4\text{-O})(\mu_2\text{-O})]$  (M: redox-inactive cation such as Ca, Sr, Zn, Sc) synthesized by T. Agapie's group in Caltech, USA (a total of 22 model systems; examples are given in **Fig. 3** and **Fig. 4**).<sup>5,6,7</sup> A detailed analysis is currently under way. We are furthermore pursuing theoretical calculations using these model complexes to understand the electronic structure of the  $\text{Mn}_4\text{Ca}$  cluster and its changes during the catalytic reaction. Since the full RIXS process cannot be simulated, such calculations have to rationalize the concept of "formal oxidation state" and enable to extract quantities that can be set in context with experiment, e.g. spin and charge density on Mn.

We consider our beamtime on ID26 a success and an excellent set of data was obtained. We note that such experiments are very challenging due to the radiation sensitivity of the samples and the low Mn concentration.



**Fig. 3:** K absorption pre-edge RIXS plane for (A)  $\text{LMn}^{\text{II}}_2\text{Mn}^{\text{III}}_2\text{O}_1(\text{OAc})_3(\text{OTf})_2$ ; (B)  $[\text{LMn}^{\text{IV}}\text{Mn}^{\text{III}}_2\text{CaO}_2(\text{OAc})_2(\text{OTf})(\text{DME})](\text{OTf})_2$ ; (C)  $(\text{Mn}^{\text{III}})_2(\text{Ca}^{\text{II}})_2\text{HMP}$ ; (D)  $[\text{LMn}^{\text{III}}_3\text{CaO}_2(\text{OAc})_2(\text{OTf})(\text{DME})](\text{OTf})$ ; (E)  $\text{LMn}^{\text{IV}}_3\text{CaO}_4(\text{OAc})_3\text{THF}$ .



**Fig. 4:** K absorption pre-edge RIXS plane for a series of heteronuclear  $\text{Mn}^{\text{IV}}_3\text{MO}_4(\text{OAc})_3$  (M: Sr, Sc, Y) complexes; (A)  $[\text{LMn}^{\text{IV}}_3\text{SrO}_4(\text{OAc})_3\text{DMF}]_2$  (B)  $[\text{LMn}^{\text{IV}}_3\text{ScO}_4(\text{OAc})_3](\text{OTf})$  and (C)  $[\text{LMn}^{\text{IV}}_3\text{YO}_4(\text{OAc})_3(\text{DMF})_2](\text{OTf})$ .

## References:

- (1) Wydrzynski, T. & Satoh, S. (eds). (2005) *Photosystem II* Springer, Dordrecht.
- (2) Messinger, J. (2004) *Phys Chem Chem Phys* **6**, 4764.
- (3) Glatzel, P.; Bergmann, U.; Yano, J.; Visser, H.; Robblee, J. H.; Gu, W. W.; de Groot, F. M. F.; Christou, G.; Pecoraro, V. L.; Cramer, S. P.; Yachandra, V. K. (2004) *J. Am. Chem. Soc.* **126**, 9946.
- (4) Glatzel, P., Yano, J., Bergmann, U., Visser, H., Robblee, J. H., Gu, W., de Groot, F. M. F., Cramer, S. P., and Yachandra, V. K. (2005) *J. Phys. Chem. Solid.* **66**, 2163.
- (5) Mukherjee, S.; Stull, J. A.; Yano, J.; Stamatatos, T. C.; Pringouri, K.; Stich, T. A.; Abboud, K. A.; Britt, R. D.; Yachandra, V. K.; Christou, G. (2012) *Proc. Nat. Acad. Sci. U.S.A.* **109**, 2257.
- (6) Kanady, J. S., Tsui, E. Y., Day, M. W.; Agapie, T. (2011) *Science* **333**, 733.
- (7) Tsui, E. Y., Tran, R.; Yano, J.; Agapie, T. (2013) *Nat. Chem.* **5**, 293.