2013B 期 採択長期利用課題の事後評価について - 1 -

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利用推進部

2013B 期に採択された長期利用課題について、2016A 期に 3 年間の実施期間が終了したことを受け、第 59 回 SPring-8 利用研究課題審査委員会長期利用分科会（2016 年 12 月 13 日開催）において、事後評価が行われました。

事後評価は、長期利用分科会が実験責任者に対しヒアリングを行った後、評価を行うという形式で実施し、SPring-8 利用研究課題審査委員会で評価結果を取りまとめました。以下に対象となる長期利用課題 2 課題の評価結果を示します。研究内容については本誌 104 ページの「最近の研究から」に実験責任者による紹介記事を掲載しています。

なお、2013B 期に採択された長期利用課題 3 課題のうち残り 1 課題の評価結果は「SPring-8/SACLA 利用者情報」Vol.22 No.4（2017 年 11 月号）に掲載する予定です。

－ 課題 1 －

課題名	Application Development of Nuclear Resonance Vibrational Spectroscopy (NRVS) and Synchrotron Mössbauer Spectroscopy of Multinuclear Iron Proteins
実験責任者(所属)	Stephen Cramer (University of California, Davis)
採択時課題番号	2013B0103
ビームライン	BL09XU
利用期間／配分総シフト	2013B～2016A／99 シフト

［評価結果］

The principal investigator developed the technique of NRVS (Nuclear Resonance Vibrational Spectroscopy) to study vibrational modes of an iron atom in proteins. His group focused on Fe-S proteins in this project. They worked on intermediate states in enzymatic reactions of hydrogenase and nitrogenase which play important roles in hydrogen catalysis and nitrogen fixation, respectively. DFT models were used to analyze the NRVS spectra to discuss the mechanisms of enzymatic reactions. This is undoubtedly a leading-edge biochemistry as shown by more than ten publications since 2013 in high-profile journals such as *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.*, and *Nature Comm.*. Thus, the committee judges that this project was completed successfully. There are some unresolved technical issues in the experimental techniques, which should be considered in the next Long-Term project.

［成果リスト］

（査読付き論文）

[1] SPring-8 publication ID = 27050
H. Wang *et al.*: "A Practical Guide for Nuclear Resonance Vibrational Spectroscopy (NRVS) of Biochemical Samples and Model Compounds" *Methods in Molecular Biology* **1122** (2014) 125-137.

[2] SPring-8 publication ID = 27816
L. Lars *et al.*: "Nuclear Resonance Vibrational Spectroscopy Reveals the FeS Cluster Composition and Active Site Vibrational Properties of an O_2-tolerant NAD^+-reducing [NiFe] Hydrogenase" *Chemical Science* **6** (2015) 1055-1060.

[3] SPring-8 publication ID = 28326
A. Scott *et al.*: "Structural Characterization of CO-Inhibited Mo-Nitrogenase by Combined Application of Nuclear Resonance Vibrational Spectroscopy, Extended X-ray Absorption Fine Structure, and Density Functional Theory: New Insights into the Effects of CO Binding and the Role of the Interstitial Atom" *Journal of American Chemical Society* **136** (2014) 15942-15954.

[4] SPring-8 publication ID = 32563
M. Maiuri *et al.*: "Low Frequency Dynamics of the Nitrogenase MoFe Protein via Femtosecond Pump Probe Spectroscopy － Observation of a Candidate Promoting Vibration" *Journal of Inorganic*

Biochemistry **153** (2015) 128-135.

[5] SPring-8 publication ID = 32565
P. Serrano *et al*.: "Nitrosylation of Nitric-Oxide-Sensing Regulatory Proteins Containing [4Fe-4S] Clusters Gives Rise to Multiple Iron–Nitrosyl Complexes" *Angewandte Chemie International Edition* **55** (2016) 14575-14579.

[6] SPring-8 publication ID = 32566
H. Ogata *et al*.: "Hydride Bridge in [NiFe]-hydrogenase Observed by Nuclear Resonance Vibrational Spectroscopy" *Nature Cimmunications* **6** (2015) 7890.

[7] SPring-8 publication ID = 32619
L. Gee *et al*.: "Docking and Migration of Carbon Monoxide in Nitrogenase: The Case for Gated Pockets from IR Spectroscopy and Molecular Dynamics" *Biochemistry* **54** (2015) 3314-3319.

[8] SPring-8 publication ID = 33468
L. Gee *et al*.: "Synchrotron-based Nickel Mössbauer Spectroscopy" *Inorganic chemistry* **55** (2016) 6866-6872.

－ 課題２ －

課題名	NRVS of mononuclear and binuclear non-heme iron enzyme intermediates and related model complexes
実験責任者(所属)	Edward Solomon (Stanford University)
採択時課題番号	2013B0105
ビームライン	BL09XU
利用期間／配分総シフト	2013B～2016A／135 シフト

［評価結果］

The Long-Term project aims at understanding the molecular mechanism of non-heme iron (NHFe) enzyme intermediates and related model complexes using nuclear resonance vibrational spectroscopy (NRVS) and density functional theory (DFT) calculations. In 2013B through 2016A oxygen-activated intermediates have been investigated, which include the selective halogenation of Fe(IV)=O NHFe intermediate, the low/high-spin chemistry of NHFe Fe^{III}-OOH intermediates, the oxidative chemistry of extradiol dioxygenases, and the geometric and electronic structures of peroxy intermediates and high valent intermediates. The qualities of these results are high because of its unique approach to the local structure around iron ions in biologically relevant materials.

Besides for the results, the Long-Term project also has contributed to the development of a new methodology for investigating molecular systems with iron atoms, based on a combination of NRVS experiment and DFT computation. The series of studies have shown that the NRVS data are well reproduced by experimentally-calibrated DFT calculations, indicating that the methodology can provide reliable information on the reaction coordinate for catalysis and other molecular systems.

Therefore, the committee evaluates the Long-Term project as a successful one, although their publications are delayed. The results should be published in major journals as early as possible.

［成果リスト］

（査読付き論文）

[1] SPring-8 publication ID = 32555
K. Sutherlin *et al*.: "Nuclear Resonance Vibrational Spectroscopic Definition of Peroxy Intermediates in Nonheme Iron Sites" *Journal of American Chemical Society* **138** (2016) 14294-14302.

[2] SPring-8 publication ID = 33479
E. Solomon *et al*.: "O_2 Activation by Non-Heme Iron Enzymes" *Biochemistry* **55** (2016) 6363-6374.

[3] SPring-8 publication ID = 33480
K. Park and E. Solomon: "Modeling nuclear resonance vibrational spectroscopic data of binuclear nonheme iron enzymes using density functional theory" *Canadian Journal of Chemistry* **92** (2014) 975-978.