# 2017A 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

2017A 期に採択された長期利用課題について、2018B 期に 2 年間の実施期間が終了したことを受け、第 64 回 SPring-8 利用研究課題審査委員会長期利用分科会（2018 年 12 月 13 日および 14 日開催）による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。以下に評価を受けた課題の評価結果を示します。研究内容については本誌の「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、2017A 期に採択された長期利用課題 4 課題のうち残り 2 課題の評価結果は次号以降に掲載する予定です。

― 課題 1 ―

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| 課題名 | NRVS of mononuclear and binuclear non-heme iron enzyme intermediates and related model complexes |
| 実験責任者（所属） | Solomon Edward（Stanford University） |
| 採択時課題番号 | 2017A0137 |
| ビームライン | BL09XU |
| 利用期間／配分総シフト | 2017A～2018B／93 シフト |

［評価結果］

This program was conducted as a renewal of the long-term project performed previously in 2013B - 2016A. The applicant defined the goal of the research project as to understand the geometric and electronic structure of mononuclear and binuclear non-heme irons in enzymes. The applicant is working with general interests on the enzymes but also focuses on the interaction of oxygens with the irons, which is quite informative to understand its biologically important roles in human health, catalysis and bioremediation, and so on.

During the period of the program, the applicant and his colleagues have established and polished the powerful combination of NRVS and DFT, and routinely collected high-quality NRVS spectra to determine and analyze accurate structures of the metal centers. In particular, they revealed the reaction intermediates of an extradiol dioxygenase, homoprotocatechuate 2,3-deoxygenase using a freeze trap method. Furthermore, its NRVS structure can correct the relevant crystal structure determined previously. These results have expanded the experimental applicability and reliability of NRVS for iron proteins, and led to 7 articles published in major journals.

As described above, the committee concluded that this long-term project was successfully conducted.

［成果リスト］

（査読付き論文）

[ 1 ] SPring-8 publication ID = 37162
K. Sutherlin *et al*.: “NRVS Studies of the Peroxide Shunt Intermediate in a Rieske Dioxygenase and Its Relation to the Native $Fe^{II}$ $O_2$ Reaction” *Journal of the American Chemical Society* **140** (2018) 5544-5559.

[ 2 ] SPring-8 publication ID = 37163
K. Sutherlin *et al*.: “Nuclear Resonance Vibrational Spectroscopy Definition of $O_2$ Intermediates in an Extradiol Dioxygenase: Correlation to Crystallography and Reactivity” *Journal of the American Chemical Society* **140** (2018) 16495-16513.

― 課題 2 ―

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| 課題名 | Application & Development of Nuclear Resonance Vibrational Spectroscopy (NRVS) and Synchrotron Mössbauer Spectroscopy of Iron-Hydrogen Interactions in Hydrogenases, Nitrogenases, and Model Complexes |
| 実験責任者（所属） | Stephen Cramer（University of California, Davis） |

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| 採択時課題番号 | 2017A0141 |
| ビームライン | BL09XU |
| 利用期間/配分総シフト | 2017A～2018B／84 シフト |

［評価結果］

The principal investigator focused on the investigation of the chemistry of hydrogen combined with metals, especially the nature of Fe-H bonds in enzymes which are important for the future energy and environment issues. In order to analyze the active site structures of the enzymes with organometallic transition metals, he introduced the NRVS (Nuclear Resonance Vibrational Spectroscopy) technique with the DFT calculations.

Although it is regrettable that technical developments to reduce measurement time were not carried out extensively, the committee recognizes the scientific achievements and appreciates that the PI published many high-impact original and review papers, and delivered several invited talks.

［成果リスト］

(査読付き論文)

[ 1 ] SPring-8 publication ID = 37054
E. Reijerse *et al*.: "Direct Observation of an Iron-Bound Terminal Hydride in [FeFe]-Hydrogenase by Nuclear Resonance Vibrational Spectroscopy" *Journal of the American Chemical Society* **139** (2017) 4306-4309.

[ 2 ] SPring-8 publication ID = 37058
V. Pelmenschikov *et al*.: "Reaction Coordinate Leading to H2 Production in [FeFe]-Hydrogenase Identified by Nuclear Resonance Vibrational Spectroscopy and Density Functional Theory" *Journal of the American Chemical Society* **139** (2017) 16894-16902.

[ 3 ] SPring-8 publication ID = 37071
M. Carlson *et al*.: "Sterically Stabilized Terminal Hydride of a Diiron Dithiolate" *Inorganic Chemistry* **57** (2018) 1988-2001.

[ 4 ] SPring-8 publication ID = 37072
L. Gee *et al*.: "NRVS for Fe in Biology: Experiment and Basic Interpretation" *Methods in Enzymology* **599** (2018) 409-425.

[ 5 ] SPring-8 publication ID = 37073
C. Pham *et al*.: "Terminal Hydride Species in [FeFe]-Hydrogenases Are Vibrationally Coupled to the Active Site Environment" *Angewandte Chemie International Edition* **57** (2018) 10605-10609.

[ 6 ] SPring-8 publication ID = 37074
V. Pelmenschikov *et al*.: "High-Frequency Fe-H Vibrations in a Bridging Hydride Complex Characterized by NRVS and DFT" *Angewandte Chemie International Edition* **57** (2018) 9367-9371.