

Degradation of organic pollutants by metal coenzyme purified from organisms is a frontier research field in both environmental science and bioinorganic chemistry. Methanogens, which are widely distributed in nature, have been proved to be powerful in reductive dehalogenation, while F430 coenzyme has been proved to play a key role. However, the mechanism of reductive dehalogenation reaction by F430 coenzyme has not been revealed yet. This project aims to reveal the complex F430 dehalogenation mechanism through kinetic and analytical experiments, quantum chemical calculations and stable isotope fractionation technologies. Halogenated pollutants will be studied, including halogenated alkanes, and alkenes. The proposed studies merge experimental approach in which typical analytical and kinetic approaches will be combined with state-of-the-art methodology of isotope effects measurements by isotopic-ratio-mass-spectrometry, with theoretical calculations of the experimentally studies processes. This symbiotic experimental-theoretical approach should allow us to reliably determine isotope effects of carbon and chlorine on studied systems, interpret them in terms of actual mechanisms and build QSAR relationship that should prove predictive in assessment of F430 coenzyme catalytic activity toward other pollutants of environmental importance. The results can help us to understand the thermodynamic feasibility, conversion rate and product formation path of F430 dehalogenation. The implementation of this project will further expand the theory and practice of the dual element stable isotope fractionation as a "mechanism probe", and develop linear free energy relationship models for predicting the transformation of halogenated organic pollutants by F430 coenzyme, the results of which can be used to quickly evaluate the degradation and detoxification effect of the dehalogenation process by F430. The results will provide an important theoretical basis for the application of F430 coenzyme and its synthetic compounds in remediation of contaminated sites. Combining experimental work with theoretical predictions proved over the years to be ideal approach to studies of complex reactions since not all steps are usually amenable for experimental scrutiny and experimental data in such systems need theoretical support. The complementarity and practical collaborative skills between PIs of both sides has been recently demonstrated by the joint publication on isotope effects on a catalytic system which appeared last year in high quality journal (Li Ji, Chenchen Wang, Shujing Ji, Kasper P. Kepp, and Piotr Paneth. *ACS Catalysis*, 2017, 7, 5294–5307). The bilateral cooperation in this project will further promote the application of isotope fractionation studied by both experimental and theoretical methods in revealing complex biotransformation mechanisms of pollutants.