

Coenzyme F430 as a biomarker for methanogenesis and anoxic methane oxidation

*Masanori Kaneko¹, Yoshinori Takano², Naohiko Ohkouchi²

1.National Institute of Advanced Industrial Science and Technology, 2.Japan Agency for Marine-Earth Science and Technology

Coenzyme factor (F430) is a prosthetic group of a key enzyme for methanogenesis, methyl coenzyme M reductase (MCR) [e.g. Ellefson et al., 1982]. Coenzyme F430 should be a practical biomarker to investigate distribution of methanogens and methanogenic potential in natural environments for the following reasons: 1) it should be common in all methanogens, 2) it has a potential to reflect only modern methanogenic activity due to its unstable nature, 3) it is clear proxy because other source organisms are highly restricted (only anaerobic methane oxidizing archaea [Krüger et al., 2003; Mayr et al., 2008]).

Recently we developed quantitative analysis of coenzyme F430 by triple quadrupole mass spectrometry coupled with liquid chromatography, which allow to detect coenzyme F430 in environmental samples including marine sediment with fmol level concentration [Kaneko et al., 2014].

The major concerns in application of the coenzyme F430 analysis as a biomarker tool are stability of coenzyme F430 and discrimination of source archaea (methanogens vs. ANMEs). Previous studies reported that free (not bound to MCR) coenzyme F430 changed to epimers in hour scale at 200C and hour to day scale at room temperature [e.g. Diekert et al., 1981]. However, it is still ambiguous how the epimerization is observed in environmental conditions. In general marine setting, methanogenesis occurs after sulfate reduction and the habitats of methanogens and ANME are clearly controlled by sulfate concentrations. On the other hands, these archaeal sources should be discriminable by compound specific isotope analysis of coenzyme F430 because isotope effects involved with their metabolic pathways are quite deferent [Hinrichs et al., 1999].

In this talk, we will show distribution of coenzyme F430 in environmental samples including paddy soils, ANME microbial mats and marine sediments, and carbon isotopic composition of coenzyme F430 from ANME archaea to address stability of coenzyme F430 and discrimination of source archaea.

[References]

Diekert et al., 1981. Nickel Requirement and Factor F-430 Content of Methanogenic Bacteria. *Journal of Bacteriology*, 148(2): 459-464.

Ellefson et al., 1982. Nickel-Containing Factor-F430 - Chromophore of the Methylreductase of *Methanobacterium*. *Proceedings of the National Academy of Sciences of the United States of America*, 79(12): 3707-3710.

Hinrichs et al., 1999. Methane-consuming archaeobacteria in marine sediment. *Nature*, 398: 802-805.

Kaneko et al., 2014. Quantitative Analysis of Coenzyme F430 in Environmental Samples: A New Diagnostic Tool for Methanogenesis and Anaerobic Methane Oxidation. *Analytical Chemistry*, 86(7): 3633-3638.

Krüger et al., 2003. A conspicuous nickel protein in microbial mats that oxidize methane anaerobically. *Nature*, 426(6968): 878-881.

Mayr et al., 2008. Structure of an F430 variant from archaea associated with anaerobic oxidation of methane. *Journal of the American Chemical Society*, 130(32): 10758-10767.

Keywords: Coenzyme F430, function specific biomarker, methanogenesis