DOES INTACT COENZYME F430 ACCUMULATE?: IMPLICATION FOR ITS USE AS PROXIES FOR METHANE PRODUCTION AND CONSUMPTION

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Introduction

Coenzyme F430 is a hydrocorphinoid nickel complex, which catalyzes the last step of methanogenesis (Thauer, 1998). Since this last step is a common step in all methanogenic pathways including hydrogenotrophic, aceticlastic and methylotrophic methanogenesis, coenzyme F430 can be a robust biomarker for all methanogens including unknown methanogens. Recent study suggested that ANME archaea also utilize coenzyme F430 for reversed methanogenesis (Scheller et al., 2010). Thus, coenzyme F430 should be useful tool to investigate quantitative distributions and/or activities of methanogens and ANMEs in natural environments (Inagaki et al., 2015; Kaneko et al., 2014).

In the application of F430 analysis to biogeochemical studies, the effect of F430 accumulation should be considered because it would prevent us from precisely detecting modern microbial signal. In general, it is believed that coenzyme F430 does not accumulate in environmental conditions. So far, degradation experiments have been conducted only once, which reported that 96% of coenzyme F430 is epimerized within 2h at 100°C (Diekert et al., 1981). Thus, quantitative data for the rate of degradation are limited and the accumulation effect at milder environmental conditions is still unknown. In this study, we investigated the rate of epimerization of coenzyme F430, the first degradation process of coenzyme F430, in a range of temperature and pH conditions.

Results and Discussion

Coenzyme F430 was converted to 12,13-diepi-F430 via 13-epi-F430 during epimerization (Figure 1-a). The concentration of coenzyme F430 exponentially decreased, which indicates pseudo-first order reaction (Figure 1-b). Determined rate constant (k) based on the curve fitting varied from 0.0017 to 0.082 at pH7 in the temperature range of 15-60°C, hence its half-life ranged from 0.5 to 17 days. Arrhenius plot showed a strong correlation ($R^2 = 0.99$) between k and temperature. Predicted half-life at 2°C that simulates the condition of sediment-seawater interface was 59 days.

Our results demonstrate that coenzyme F430 is readily converted to its epimers and does not accumulate even in low temperature environments such as near-surface marine sediments. The epimerization is not the only pathway of degradation: other degradation processes including dehydrogenation etc should simultaneously occur depending on redox, temperature and pH conditions (Pfaltz et al., 1985). We therefore conclude that coenzyme F430 is a promising proxy for the living cells of methanogens and methanotrophs to investigate modern methane production and consumption processes. Combination with carbon isotopic analysis of coenzyme F430 enables us to discriminate and quantify methanogenesis and anaerobic oxidation of methane (Goldschmidt2015: Kaneko et al., 2015).

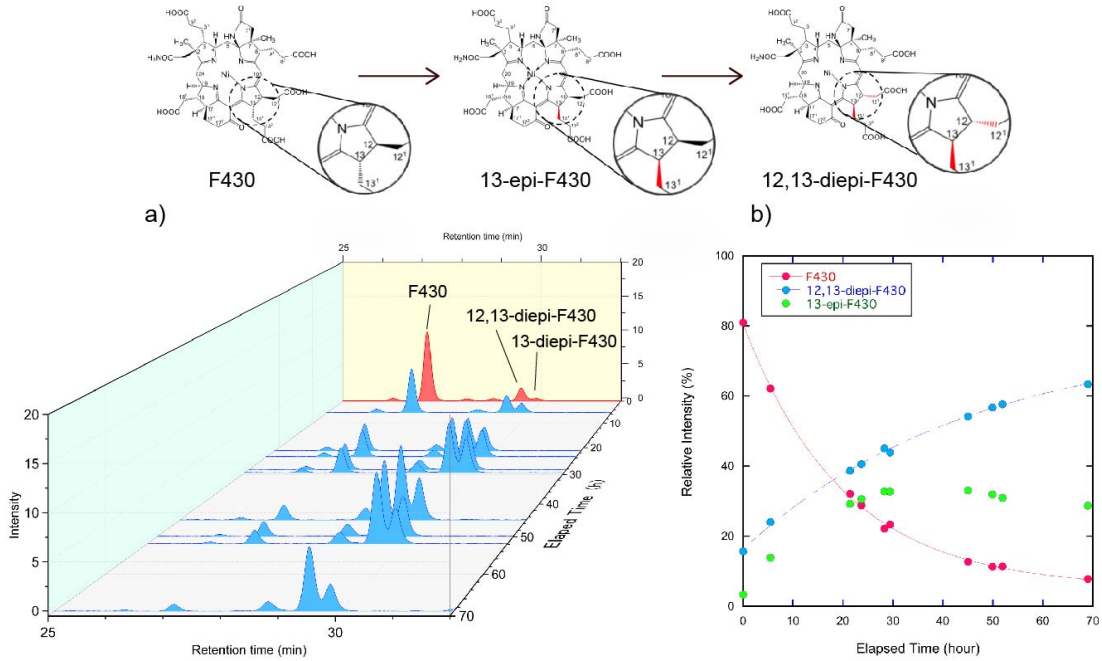

***Figure 1**. Changes in LC-chromatogram of coenzyme F430 and its epimers (a) and degradation curve (b)*

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