

## Biological methane production and anaerobic oxidation of methane

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Approximately 140 Gt of biomass are formed globally each year from CO<sub>2</sub> via oxygenic photosynthesis (net primary production). Of this amount, 2-3% end up in anaerobic environments such as freshwater sediments, landfills, the intestinal tract of ruminants and termites, and deeper layers of marine sediments. In these methanogenic environments, the biomass is fermented to methane, yielding approximately 1 Gt CH<sub>4</sub> per year. In such environments, methanogenic archaea produce methane from H<sub>2</sub> and CO<sub>2</sub>, and other substrates in an energy gaining process. The methanogenic pathways involve unique enzymes, which use novel cofactors and coenzymes to catalyze the reactions needed for methane production. Methyl-coenzyme M reductase (MCR), which contains the Ni porphyrinoid F430 as prosthetic group, is a key enzyme of methane formation in methanogenic archaea (1). It catalyzes the reduction of methyl-coenzyme M with coenzyme B to methane and the heterodisulfide of coenzyme M and coenzyme B. For the activation of H<sub>2</sub>, methanogens use different types of hydrogenase enzymes, namely [NiFe]-hydrogenases and [Fe]-hydrogenase, which are not phylogenetically related each other (2). The [Fe]-hydrogenase harbors a unique iron-guanylylpyridinol cofactor (FeGP cofactor). Anaerobic oxidation of methane (AOM) with sulfate is accomplished by consortia of methanotrophic archaea and sulfate reducing bacteria. Indirect evidence suggests that AOM with sulfate functions at least in part as the reverse of methanogenesis from CO<sub>2</sub>. Accordingly, the enzyme activating methane should be a methyl-coenzyme M reductase (MCR) (3). Recently, we solved the crystal structure of MCR from methanotrophic archaea in complex with coenzyme M and coenzyme B, which indicates that the same substrates for MCR from methanotrophic and methanogenic archaea are used (4). I will present our most recent results on the biochemistry of methanogenesis and anaerobic oxidation of methane.

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