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References

DELLWIG, O., HINRICHS, J., TERJUNG, F., REUTER, R. & BRUMSACK, H.-J. (2003). Tidal and seasonal variations of a backbarrier intertidal system near Spiekeroog Island and the adjoining German Bight, in prep.

DETERMANN, S., REUTER, R., WAGNER, P. & WILLKOMM, R. (1994) Fluorescent matter in the eastern Atlantic Ocean: Part 1. Method of measurement and near-surface distribution. Deep-Sea Res., **41**, 659-675.

MOFFETT, J. W. (1994). A radiotracer study of cerium and manganese uptake onto suspended particles in Chesapeake Bay. Geochim. Cosmochim. Acta, **58**, 695-703.

NICO, P. S., ANASTASIO, C. & ZASOSKI, J. (2002). Rapid photo-oxidation of Mn(II) mediated by humic substances. Geochim. Cosmochim. Acta, **66**, 4047-4056.

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METHANOGENESIS FROM METHYLAMINE AND METHANOL AT CHANGING HYDROGEN CONCENTRATIONS

Niko Finke, Tori M. Hoehler & Bo B. Jørgensen

Methylotrophic methanogens in pure culture metabolize methylated substrates (e. g. methanol, methylamine, acetate) to CH_4 and CO_2 in a predictable ratio (KELTJENS & VOGELS, 1993). Detailed studies revealed, that the proportion of the two products can deviate from the predicted stoichiometry. PHELPS *et al.* (1985) showed that methanogenesis from acetate yielded more CO_2, if the methanogen was cocultured with a sulfate reducer oxidizing the hydrogen produced by the methanogen. The continuous leakage of reducing power (as H_2) from the methanogen, as a result of sulfate reducing activity, allows the methanogen to oxidize a greater proportion of the carbon to CO_2. We hypothesized that natural variations in H_2 concentrations in aquatic sediments might affect the degree to which H_2 liberation and oxidative metabolism of methylotrophic substrates occurs (Fig. 1). To test this hypothesis, we performed incubation experiments using methanogenic sediment in which H_2 concentrations were caused to vary as a function of temperature and sulfate concentration (HOEHLER *et al*., 1998). In an additional experiment, lactate was added to the sediment to increase the hydrogen concentration due to increased fermentation activity. The conversion of methanol and methylamine to CH_4 and CO_2 in these treatments was quantified using radiotracer techniques. Increasing temperatures and decreasing sulfate concentrations both resulted in increasing H_2 concentrations, as well as the addition of lactate (Figs. 2, 3). With increasing H_2 concentrations, methanogenesis yielded less oxidized carbon (Fig. 4, Table 1). At the lowest H_2 concentrations, the fraction of electrons lost to H_2 leakage significantly exceeded that channeled into methane production. This was true even in the absence of sulfate (e. g., for the lowest temperatures). Thus, dependent on the hydrogen concentration, protons can represent a more important electron acceptor than the methyl carbon for methylotrophic methanogenesis.

Marine sediments are spatially separated according to the electron acceptor used for terminal oxidation. The decreasing

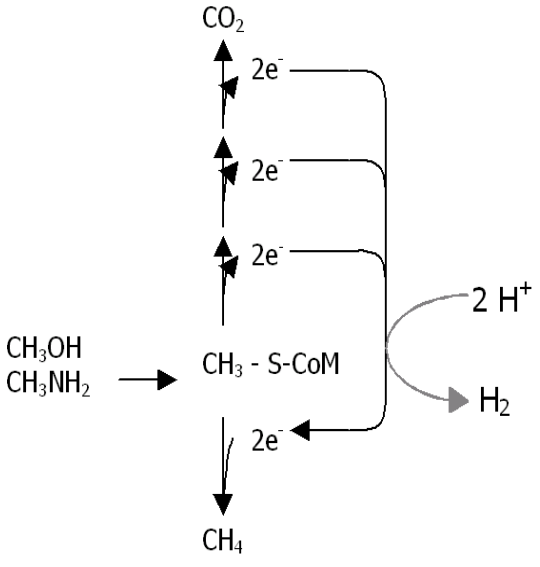

Fig. 1. Pathway of methanogensis from methanol and methylamine. Dependent on the surrounding hydrogen concentration the methanogens can transfer more or less electrons to hydrogen instead of methane.

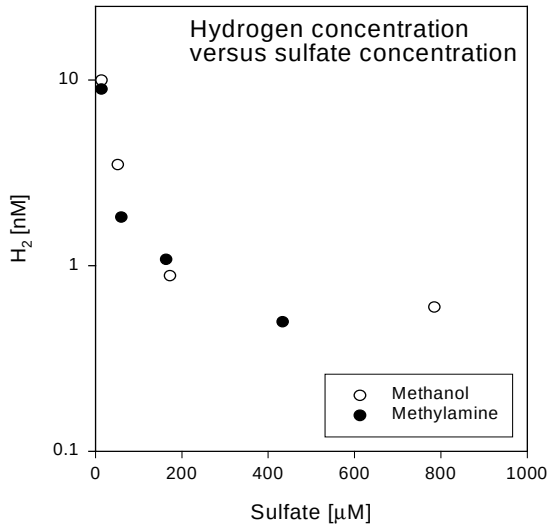

Fig. 2. Hydrogen concentration in dependence of the sulfate concentration in incubations with sediment from Dangast, Wadden Sea Germany

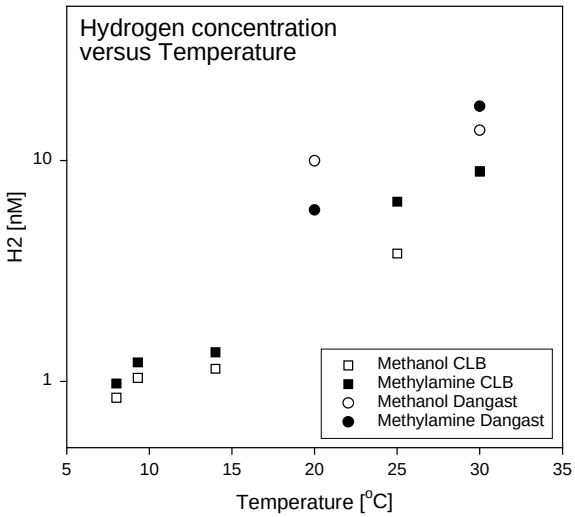

Fig. 3. Hydrogen concentrations as a function of the incubation temperature in sediments from Dangast, Wadden Sea Germany, and Cape Lookout Bight, USA.

energy yield of the terminal oxidation processes has been used to explain this finding. But the energy yield itself cannot be responsible for the exclusion. The control of reducing power in the cells by external hydrogen concentration can help understand the exclusion of the different electron accepting processes. By controlling the reducing power of the microbial cells, hydrogen concentrations influence the redox chemistry of the energy conserving reactions. In the sulfate reducing zone, hydrogen concentrations are kept low, thus prohibiting methane production from either competitive or uncompetitive substrates.

Table 1. Hydrogen concentration and fraction of $^{14}CO_2$ as a percentage of the total methanogenesis products (CO_2 + CH_4) as a result of lactate addition.

	hydrogen [nM]	%CO_2
no addition	14	44
approx. 500 µM lactate	3200	36

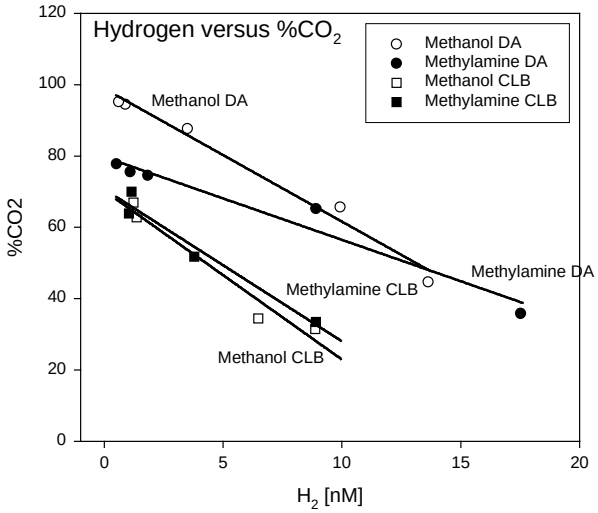

Fig. 4. Fraction of $^{14}CO_2$ as percentage of the total methanogenesis products (CO_2 + CH_4) in the sulfate and temperature treatment. Regression lines for the incubations with methanol and metylamine are shown for the different locations (r^2 >0.95)

References

HOEHLER, T. M., ALPERIN, M. J., ALBERT, D. B. & MARTENS, C. S. (1998) Thermodynamic control on hydrogen concentrations in anoxic sediments. Geochim. Cosmochim. Acta, **52**, 1745-1756.

KELTJENS, J. T., VOGELS, G. D. (1993) Conversion of methanol and methylamines to methane and carbon dioxide. In: FERRY, J. G. (ed.), Methanogenesis. Chapman & Hall, New York London, 253-303.

Phelbs, T. J., Conrad, R. & Zeikus, J. .G (1985) Sulfate-dependent interspecies H_2 transfer between *Methanosarcina barkeri* and *Desulfovibrio vulgaris* during coculture metabolism of acetate or methanol. Appl. Environm. Microbiol., **50**, 589-594.

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