## What are the thermodynamic controls on methanogenesis?

CHRISTINA M. SMEATON  $^{1,2^{\ast}}$  and Philippe Van Cappellen  $^{1,2}$ 

- <sup>1</sup> Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada
- <sup>2</sup> Water Institute, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

(\*correspondence: christina.smeaton@uwaterloo.ca)

For microorganisms such as methanogens, which operate close to the thermodynamic limit, metabolic activity and growth are closely controlled by the availability and allocation of energy. Here, we assess the role of enivronmentally relevant conditions, including temperature, pH, and aqueous composition on the thermodynamic favourability of acetotrophic and hydrogenotrophic methanogenesis, as well as the common precursor pathways of acetate production and oxidation. We further implement the calculated Gibbs energies of catabolism and anabolism under non-standard state conditions into our newly derived and validated semi-theoretical Gibbs Energy Dynamic Yield Method (GEDYM) to predict dynamic growth yields (Y) for each methanogenic and precursor pathway. We show that temperature (range 5-55°C) is expected to have a significant effect on the transition between acetate production and oxidation, with significant implications on their coupling to acetotrophic and hydrogenotrophic methanogenesis, respectively. By using GEDYM, we further show that acetotrophic methanogenesis may be thermodynamically inhibited at highly exergonic catabolic energy values. Overall, GEDYM extends beyond traditional catabolic energy threshold assessments and offers a theoretical framework to capture the role of dynamic geochemical conditions on microbial growth in order to improve the predictive modeling of methanogenesis in the environment.