Understanding Isotope Fractionation in Microbial Methanogenesis

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During microbial production of CH_4 (methanogenesis), the CH_4 product is typically depleted in ^{13}C relative to the substrate CO_2, with fractionations between ~20 and ~90‰. The dependence of C isotope fractionation on the energy available to methanogens and on the rate of methanogenesis has been studied in experiments and related to the reversibility of the enzymatically-catalysed steps in the pathway. However, mechanistic understanding of this behaviour is incomplete.

We developed a mechanistic model describing cell physiology and C isotope fractionation during hydrogenotrophic methanogenesis. Using kinetic and thermodynamic parameters, we numerically solved this model to yield metabolite concentrations and reversibilities of the enzyme reactions in the pathway at a steady state. We used these reversibilities, together with a novel set of equilibrium fractionation factors calculated by density functional theory, and estimates of kinetic fractionation factors, to calculate the net C isotope fractionation as a function of the energy available to the methanogens.

The model reproduces observed relationships between the Gibbs free energy of the overall reaction (ΔG_r) and C isotope fractionation, and its solutions illustrate a dual control of reaction reversibility on C isotope fractionation. Specifically, where ΔG_r departs from zero (at approximately –20 kJ mol^{-1}), a peak in net fractionation (~80-90‰) arises from the departure from equilibrium of the last two steps in the pathway (catalysed by Mcr and Mtr). At increasingly negative ΔG_r, gradual departure from equilibrium of the first step (catalysed by Fmd) leads to a decrease in net fractionation to ~20-40‰. Thus, we mechanistically explain the relation between ΔG_r and C isotope fractionation, further elucidating the factors governing the isotopic composition of CH_4 in the environment.