Influence of energy availability on the carbon isotopes of methane and biomarkers during hydrogenotrophic methanogenesis

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The isotopic signatures of organic molecules in the environment are widely used to identify microbial metabolic processes and to track the cycling of carbon. The lipid biomarkers of methane cycling archaea are of particular interest as they are unique, preserved over geologic time scales, and reflect processes that impact an important greenhouse gas. Their isotopic compositions have been used to distinguish regions where archaea produce and anaerobically consume methane. Previous work has demonstrated a direct relationship between energy availability and the stable carbon isotopes of methane during microbial synthesis from H_2 and CO_2 [1, 2]. A similar relationship has been suggested for lipid biomarkers [3]. Here, we cultured methanogens under precisely controlled energy conditions to further investigate the effect on the stable isotope signatures of amino acids and lipid biomarkers.

The isotopic distributions of carbon metabolized and synthesized by the hyperthermophile *Methanocaldococcus jannaschii* were quantified following growth at 82°C in a chemostat with high (~80 μM) and low (15 – 27 μM) H_2 concentrations. As expected, the stable carbon isotope fractionation factors for CH_4 were >15‰ larger in low H_2 experiments than in high H_2 experiments. Lipid biomarkers and amino acids were similarly impacted, with approximately 10‰ larger fractionation factors under low H_2 conditions. Simultaneously, substantial changes were observed with the relative amounts of carbon shunted to catabolic (CH_4) versus anabolic (amino acids, lipids, biomass) pathways. These data are being used to build a carbon and isotope model of methanogens that responds to energy availability.

[1] Valentine et al. (2004) *Geochim. Cosmochim. Acta.* 68: 1571-1590 [2] Penning et al. (2005) *Global Change Biology* 11: 2103-2113 [3] Londry et al. (2008) *Organic Geochemistry* 39: 608-621