## Relating geochemical signatures to the metabolic state of cells

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Microbes respond to changes in environmental conditions by adjusting their metabolism. Metabolic adjustments involve perturbations to complex biochemical pathways. Biogeochemical proxies rely on understanding how these perturbations produce information-containing chemical signatures that can be preserved in the geological record. Experiments aimed at relating chemical information (e.g. isotope ratios) to metabolic parameters of microbial populations can improve understanding of the geological record.

We report experimental results that investigate this relationship. We have performed controlled experiments in which some aspect of microbial metabolism was perturbed, either by altering the electron donor, the growth rate, or using a mutant strain to alter a biochemical pathway. We have measured metabolic information on microbial populations, using proteomics and metabolomics to address how the response of biochemical machinery results in differential geochemical fingerprints.

Using *Methylobacterium* and *Desulfovibrio* as model systems we investigated the relationship of cellular metabolic state to i) the apparent fractionation of hydrogen isotopes between growth medium water and the biomass lipids (all strains), and ii) the fractionation between sulfate and sulfide during sulfate reduction (*Desulfovibrio*).

In *Methylobacterium*, lipid D/H-isotope ratios are strongly influenced by the production of intracellular metabolites such as NAD(P)H, and electron flow through central metabolism or the transhydrogenase PntAB [1]. In *Desulfovibrio*, the electron-bifurcating transhydrogenase (NfnAB) may play an important role, but D/H fractionation is also strongly correlated with growth rate [2] similar to sulfur isotope fractionation patterns [3,4]. Proteomic and metabolomic results from *Desulfovibrio* grown at fast and slow growth rates in electron-donor limited continuous culture may shed light on these results.

[1] Bradley *et al.* (2014). AGU Fall Meeting. [2] Leavitt (submitted) Frontiers in Microbiology. [3] Leavitt *et al.* (2013) PNAS 110, 11244–49. [4] Sim *et al* (2012) GCA 75, 75, 4244-4259.