Thermodynamic Constraints on the Biosynthesis and Diagenesis of Bacteriohopanepolyol Lipid Biomarkers in Active Hydrothermal Systems and the Geologic Record. G. M. Boyer[1], E. L. Shock[1,2], J. Woods[1], [1]GEOPIG, Department of Chemistry and Biochemistry, Arizona State University, [2]School of Earth and Space Exploration, Arizona State University.

The goal of many biogeochemical studies is to link the synthesis of microbial biomolecules, such as lipids, to the environment where the biomolecules are found. The approach we are taking is to evaluate the relative energetic costs of producing certain lipid structures, and assess how these costs affect the environmental distribution of biomarkers assuming that cells are attempting to minimize the energetic cost of their lipids while maintaining membrane function. Bacteriohopanepolyols (BHPs) are bacterially-synthesized lipids commonly used as biomarkers due to their ubiquity in nature and their wide variety of possible side-chain structures [1, 2, 3, 4, 5, 6, 7], although the specific purpose of each structure is poorly understood.

For this reason, we used BHP lipids to test the theory that individual structures will be more abundant in environments where energetic costs to produce them are minimized, and that relative abundance of these lipids can be predicted quantitatively. As a starting point, the partial molal thermodynamic properties of two commonly-occurring BHP side-chain structures, bacteriohopanetetrol (BHT) and nitrogen-containing bacteriohopaneaminotriol (BHA) were estimated from group-contribution theory using experimentally-obtained thermodynamic properties of small molecules reported in the literature. Relative abundances of BHA:BHT were then predicted assuming metastable equilibrium between the two structures, and these predictions were then compared to observed BHA:BHT abundances extracted from 36 sediments or microbial mats of geochemically diverse hot springs in Yellowstone National Park, USA and Fluðir, Iceland. Predicted and observed ratios of BHA:BHT show similar trends, though a systematic shift from predicted equilibrium ratios suggests that bacteria are spending energy to acquire the nitrogen necessary to explain observed abundances of nitrogen-containing BHP structures. This energetic cost is generally highest (chemical affinity estimated between 15-30 kJ mol^{-1}) in locations where dissolved inorganic nitrogen abundance is low, such as in siliceous alkaline hot springs, and lowest (about 2-3 kJ mol^{-1}) in environments where both nitrogen-containing BHPs and dissolved inorganic nitrogen are extremely abundant.

Lastly, we have applied the same thermodynamic estimations of BHA:BHT in living systems to track energetic distance from equilibrium of BHT to one of its major digenesis products, anhydrobacteriohopanetetrol (anhydroBHT), along the depth of a Baltic Sea sediment core reported in the literature [3]. At the surface of the core where the sediments are most recent, the ratios of BHT:anhydroBHT are energetically furthest from equilibrium (chemical affinity ~ 21.5 kJ mol^{-1} at 0 cm depth) and move toward equilibrium with increasing depth (chemical affinity ~12.0 kJ mol^{-1} at 1000 cm depth), reflecting the transformation of a less-stable biomolecule, BHT, to more-stable degradation structure, anhydroBHT, in sediments over the course of thousands of years. By understanding the thermodynamics behind the diagenesis of BHPs, we are closer to predicting how environmental conditions affect the preservation or alteration of these biomarkers, and quantifying the underlying energetic parameters that influence the rate of this process.

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