

BALANCING FUNCTION AND BIOENERGETIC COST: LIPID OXIDATION STATE IN THE CONTEXT OF HOT SPRING TEMPERATURE AND REDOX CHEMISTRY. G. M. Boyer¹, J. Woods¹, and E. L. Shock^{1,2}, ¹School of Molecular Sciences, Arizona State University, gmboyer@asu.edu ²School of Earth and Space Exploration, Arizona State University, eshock@asu.edu.

Introduction: The dry weight of cellular biomass is comprised primarily of macromolecules such as polypeptides, polynucleotides, polysaccharides, and lipids. Together, these macromolecules provide cellular function, and, as long as that functionality continues to suit the needs of the host, microorganisms adapt biomolecules to meet alternate strategies for survival and advantages when competing with other organisms.

In one such strategy, life may adapt its bulk chemical composition to increase stability while minimizing energetic cost. For instance, proteins encoded in metagenomes of extremophilic microbial communities within the outflow channel of a hot spring in Yellowstone National Park (YNP), showed an increase in the average oxidation state of carbon (Z_C), coinciding with increasingly oxidizing conditions [1], with the implication that oxidized amino acids are more thermodynamically stable, and therefore more cost-effective, to synthesize in increasingly oxic conditions [2].

Lipids and Redox: While proteins comprise a higher weight percentage of cellular biomass, there are more lipid molecules per cell, outnumbering proteins six to seven times in *E. coli* [3]. Lipids, like proteins, undergo a great variety of structural modifications to fulfill necessary functions, such as forming membranes, storing energy, accommodating and assisting membrane-bound proteins, and more, yet the full extent to which environmental redox conditions influence the Z_C of lipid composition of microorganisms at the community level is still unknown.

In this study, we calculated the abundance-weighted Z_C of intact polar lipids (IPLs) extracted from microbial biomass collected along the outflow channels of four hot springs in YNP and compared the results to redox conditions measured at each sample site. In addition to the full lipid structure, we sought to determine which of the following part(s) of IPL structure, if any, have a Z_C that correlates with environmental redox conditions: 1. aliphatic chains that form the nonpolar interior of cellular membranes, 2. ester, ether, or amide linkage of aliphatic chains to the lipid backbone, 3. the backbone, commonly glycerol, connecting the headgroup and aliphatic chains and 4. the polar headgroup, which includes many possible structures such as phosphates, sugars, amino acids, and more.

Results: We found that the bulk composition of IPLs in microbial communities becomes more oxidized along the hot spring outflow channels, coinciding with

decreasing water temperature and increasing concentration of dissolved oxygen. At the hottest spring source, $Z_C = -1.7$ (more reduced), which gradually increases to $Z_C = -1.2$ (more oxidized) at the coolest outflow site. This increase in Z_C of polar lipids is primarily attributed to membrane adaptations to decreasing temperature [4]; namely, an increase in the average degree of unsaturation of alkyl chains, a shift from ether-linked to ester-linked chains, and a decrease in overall chain length. Considering only the contribution of the IPL hydrophilic region to Z_C (i.e. headgroup, backbone, and alkyl-backbone linkage), while ignoring chain length and degree of unsaturation, lipid composition still becomes more oxidized with decreasing temperature, with Z_C ranging from -0.8 at the hottest (most reduced) site to $+0.2$ at the coolest (most oxic) site.

In contrast, Z_C of IPL headgroups alone does not correlate strongly with temperature or environmental redox conditions, suggesting that biosynthetic costs may be higher for this portion of the structure. However, when placed in the context of bulk lipid composition, microbes may still “win” bioenergetically by making up the difference elsewhere in the molecule.

Implications: In all four hot spring outflow channels, microbial communities have modified their lipid composition to maintain membrane homeostasis in response to changing temperature, although these same modifications may also correspond to increased energetic cost-effectiveness with increasing concentrations of dissolved oxygen. Certain lipid modification pathways that would alter the Z_C of an individual lipid while also regulating membrane fluidity, such as those responsible for synthesizing unsaturated fatty acids, have been shown to be aerobic or anaerobic [5], suggesting that evolutionary solutions arose to satisfy membrane homeostasis with respect to both temperature and exposure to environmental redox conditions.

References:

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