2-METHYLHOPANOIDS: BIOMARKERS FOR CYANOBACTERIA AND FOR OXYGENIC PHOTOSYNTHESIS

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Summary: This paper reports new biomarker and carbon isotopic data for cultured cyanobacteria, cyanobacterially-dominated ecosystems and ancient sediments and petroleum. We found that cyanobacteria are the predominant source of a distinctive membrane lipid biomarker, namely 2-methylbacteriohopanepolyol (2-Me-BHP). We then sought evidence for a geochemical record of the fossil hydrocarbon analogues of these compounds (2-methylhopanes) and found a trend toward their increased relative abundance in marine sediments going back through geological time to 2500 Ma. We conclude that cyanobacteria were the dominant form of phytoplankton and source of molecular oxygen in the Proterozoic ocean. Extending the geological record of cyanobacteria further to Archean times is now a matter of finding a suitably preserved rock record.

Results and Discussion: Samples of cultured cyanobacteria and naturally occurring cyanobacterial mats were analysed using an established protocol[1] illustrated in Figure 1. Approximately 43% of the cultured samples contain 2-Me analogues (6 and 8). Four of five mats from the Yellowstone National Park hydrothermal environment had significant contents of 2-Me-BHP although none of five samples from hypersaline environments of Shark Bay did. While our present sample set represents a limited number of modern environments, the cultured organisms were a taxonomically diverse suite.

When hopanoids from bacteria enter the sediments, they undergo diagenetic and catagenetic conversion to the C_{27}-C_{35} geohopane series (3 in Fig. 1). The burial fate of 2-Me-BHP is virtually identical to BHP except that the 2β-methyl configuration of the original biochemicals (2 in Fig. 1) is progressively converted to more thermodynamically stable 2α-Me configuration (4 in Fig. 1) in the 2-Me geohopane series. Our study of the relative abundances of 2-methylhopanes in sediments, bitumen and oil reveals patterns connected to source rock lithology, maturity, and palaeoenvironmental setting. Higher relative abundances of 2-methylhopanes, expressed as a 2-methylhopane index, are a distinctive feature of oils and bitumens derived from carbonate rocks. Moreover, there are higher relative abundances of 2-methylhopanes in Proterozoic sediments of all lithologies compared to their Phanerozoic counterparts.

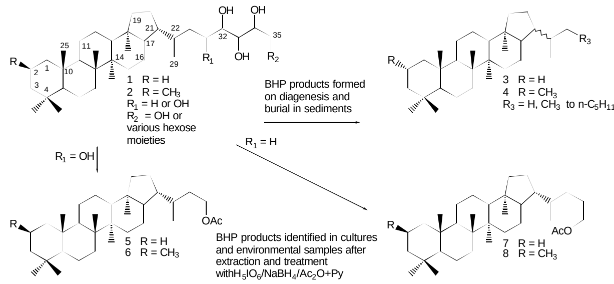

Figure 1. Structures of bacteriohopanepolyols (1, 2) typical of those found in cyanobacteria and their geohopane analogues recognised in sediments and petroleum (3, 4). The studies of biological samples were conducted using a procedure first developed by Rohmer and co-workers[1]. Periodic acid oxidation cleaves the hydrophilic portion of the molecule at the first gem-diol to yield tractable and volatile hopanol acetates of the type 5-8 and which are amenable to routine GC and GC-MS analysis. BHP lacking a gem-diol function evade detection.

Environmental studies: Analyses of various microbial mats from Yellowstone National Park reveal relatively simple patterns of lipid biomarkers that are appropriate for isotopic analyses at the molecular level. These data can be used to understand which compounds are produced by cyanobacteria, by *Chloroflexus* and by other groups. They also allow some delineation of how environmental parameters such as pCO_2 and growth temperature influence the biosynthesis of certain types of lipid. The history of oxygen and cyanbacteria are intimately linked. This is the only group of prokaryotes capable of oxygenic photosynthesis, that is, using the energy of sunlight to release the reducing power of water for fixation of CO_2 and O_2 production. Although debate still exists as to the timing and sequence of evolutionary events that led to oxygenic photosynthesis, and consequent oxygenation of the atmosphere and oceans, it is clear that the appearance `of the cyanobacteria is a crucial event that could be followed using their distinctive hydrocarbon biomarkers[2].

References: [1] Rohmer M., Bouvier-Navé, P. & Ourisson, G. (1984) *J. Gen. Microbiol.* **130**, 1137-1150. [2] Summons R.E. Jahnke L.L., Hope J.M. & Logan G.A. (1999) *Nature*, In Press.