

Bacterial Hopanoids as Environmental Markers

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Hopanoids are an abundant group of biomarker molecules that are widespread in the geosphere, and have a record back to at least 2,500 Myr (Summons et al., 1999). They are mainly derived from bacteriohopanepolyols, which are produced as membrane lipids by many different bacteria (Rohmer et al., 1984; Farrimond et al., 1998). Significantly, different bacteria can produce distinctive bacteriohopanepolyol compositions, affording these compounds potential as markers for past bacterial populations. Here we report the findings of a study within which we have applied an analytical approach targeted specifically at determining the abundance and composition of these bacteriohopanepolyols, and their diagenetic products, in Recent sediments from a broad range of sedimentary environments. Briefly, sediments were freeze-dried prior to solvent extraction. The extracts were divided into three aliquots, each of which was treated differently to optimise for the analysis of bacteriohopanepolyols, hopanols (including diols, triols and bacteriohopanetetrol) and hopanoic acids by gas chromatography-mass spectrometry (Innes et al., 1997).

Prior to our work, bacteriohopanetetrol was the only bacteriohopanepolyol reported in Recent sediments, and the compound routinely cited as the main precursor of the hopanes in geological samples. It is now clear that this commonly held view is a misconception. Although we found this compound in all the sediments analysed, it often accounted for only a relatively small proportion of the bacteriohopanepolyols. In many cases the dominant bacteriohopanepolyols are those with a more complex functional group at the end of the side chain (so-called "composite" hopanoids) or compounds with six functional groups on the side chain. This newly recognised complexity in the sedimentary hopanoid composition demonstrates the potential of the hopanoids as marker compounds.

Our data show considerable variation in the composition of bacteriohopanepolyols in modern sediments, in terms of the relative abundance of compounds with four, five or six functional groups on the hopanoid side chain (tetra-, penta- and hexafunctionalised hopanoids). We interpret this feature to be the result of different bacterial populations producing hopanoids of distinct compositions in the different environments. It is particularly notable that sediments from the small, highly productive lakes contain a greater proportion of hexafunction-

alised hopanoids, these being derived from Type I methanotrophic bacteria, which occur around the chemocline in these stratified water bodies (Farrimond et al., in press).

Results from an HPLC-based method for the analysis of bacteriohopanepolyols show that still further compositional detail may be obtained through the determination of individual composite hopanoids (which cannot be distinguished by the GC-MS approach outlined above).

Although the hydrocarbon skeletons of the hopanoids are relatively stable, a variety of reactions convert bacteriohopanepolyols to more simple products during sediment diagenesis (hopanols, hopanoic acids, hopanes, and ultimately, the hopane biomarkers which are routinely employed in petroleum geochemistry). Although part of the polyfunctionalised side chain is lost during these reactions, the resulting products may still preserve information about the number and position of the original functional groups, and thus some of the bacterial source signal. For example, C₃₂ and C₃₄ hopanediols (Rodier et al., 1999) and novel compounds (C₃₃ hopanediol and C₃₂ hopanetriol; reported in this presentation) can be related to a restricted number of bacteriohopanepolyol precursors. However, these functionalised geohopanoids will not survive deep burial in the geosphere, and for longer-term preservation of information we must look to the hopanoids in macromolecular sedimentary organic matter; these are bound through the sites of original functionality, and may thus preserve source-specific information.

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