Recent advances in the search for new hydrocarbon biomarkers

CHRISTIAN HALLMANN[1,2]*, LENNART VAN MALDEGEM[1], KLAUS WOLKENSTEIN[3,4], PIERRE SANSJOFRE[5], CHRISTIAN GRIESINGER[4]

[1]Max-Planck-Institute for Biogeochemistry, Jena, Germany (*correspondence: challmann@bgc-jena.mpg.de)
[2]MARUM, University of Bremen, Germany.
[3]Geoscience Centre, University of Göttingen, Germany.
[4]Max Planck Institute for Biophysical Chemistry, Göttingen, Germany.
[5]Université de Bretagne Occidentale, Plouzane, France.

Biomarker hydrocarbons, i.e. the sedimentary remains of biological lipids that carry a high degree of taxonomic specificity [1], represent one of the most useful geochemical tools for the reconstruction of past organismic diversity—particularly in settings or periods, where morphological fossils are scarce, undiagnostic or absent [2]. But the biomarker concept relies on an unambiguous relationship of the sedimentary remnant to a precursor lipid with known biosynthetic origin. This in turn requires precise structural knowledge of the analyte.

Apart from established biomarkers the rock record also hosts 'orphan biomarkers' whose biological precursor has not yet been established, as well as components that carry different degrees of proven or hypothesized diagnosticity, but whose unknown structure—usually as a consequence of low concentrations or complex matrices—preclude establishing precursor-product relationships.

Significant analytical advances have taken place over the past years, e.g. in the sensitivity of NMR analyses through micro-cryo-NMR [3] and in the resolution of separation science. Here we present a case study of the isolation and identification of a novel gammaceroid biomarker that occurs sparsely but consistently throughout the last ~750 Myr of Earth history and which appears indicative for intense heterotrophy, as shown by carbon isotope systematics. We will discuss the advanced purification protocol that allowed us to recover the pentacyclic terpenoid from a large hump of unresolved complex matter (UCM) in ~98 % purity, as well as the subsequent complete structural identification of the molecule with only 20.6 μg of isolate. Our findings highlight the relevance of heterotrophy in the deep geological past and open new avenues in the search for novel molecular markers.

[1] Brocks & Summons (2003) *Treatise on Geochemistry* **8.03**, 63–115. [2] Hallmann et al. (2011) *Topics in Geobiology* **36**, 355–401. [3] Wolkenstein et al. (2015) *J Am Chem Soc* **137**, 13460–63.