

**C₈₀₋₈₂ ARCHAEBACTERIAL TETRAPROTIC ACIDS IN CRUDE OILS:
STRUCTURAL IDENTIFICATIONS, DISTRIBUTIONS AND IMPLICATIONS FOR
EXPLORATION AND PRODUCTION**

Ben SMITH^{1, 2}, Steve ROWLAND¹, Geoffry FOWLER³, Bjart LUTNAES⁴ and Jostein KRANE⁴

1. Petroleum & Environmental Geochemistry Group, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, United Kingdom.

2. Oil Plus Limited, Hambridge Road, Newbury, Berkshire RG14 5SS, United Kingdom.

3. BG Group, Thames Valley Park, Reading, Berkshire. RG6 1PT, United Kingdom.

4. Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, NO 7491, Norway.

Archaeal C₈₀ tetraprotic acids (TPAs; otherwise known as ‘ARN’ acids or high molecular weight naphthenic acids) have been reported in a few heavy immature crude oils (Baugh *et al.*, 2005) and a tentative structure has been reported for one C₈₀ acid based on analysis of mixtures (Lutnaes *et al.*, 2006). We now report the isolation and identification of a series of individual Archaeal C₈₀₋₈₂ TPAs, correction of the previous C₈₀ structure, quantitative analysis of the concentrations and distributions of the acids in a wide variety of crude oils and determination of the ¹³C isotopic signatures of the TPAs. The resulting information is important for oil exploration and for resolution of some oil production problems where deposition of metal salts of the acids causes pipeline blockages and corrosion difficulties.

TPAs were isolated from crude oils of North Sea and West African oilfields by ion exchange and other methods and converted to methyl esters as reported previously (Lutnaes *et al.*, 2006). Examination of the methyl esters by high temperature gas chromatography (HTGC) and High Performance Liquid Chromatography (HPLC) using an evaporative light scattering detector (ELSD), revealed the distributions of resolved 4-8 ring acids for the first time and electrospray ionisation mass spectrometry (ESI-MS) also revealed the presence of previously unreported C₈₁ and C₈₂ acids. Milligram quantities of several of the individual TPAs were isolated by HPLC and the structures (e.g. Figure 1) elucidated by nuclear magnetic resonance (NMR) spectroscopy. In some cases high field (900 MHz) spectroscopy was needed in order to differentiate between regioisomers. A previous tentatively assigned structure was found to be slightly in error but all of the acids contained a unique cross-linked bridge. This feature was previously only tentatively assigned in the tetraether membrane lipids of certain hyperthermophilic Archaea (Lutnaes *et al.*, 2006).

Use of weighed amounts of the individual isolated acids allowed calibration of the HPLC-ELSD response and hence the concentrations of each TPA in the crude oils to be

determined and measured. The distributions of 4-8 ring acids differed in the various oils, possibly reflecting the growth temperatures of the bacteria from which the acids are assumed to have originated. The ^{13}C isotopic signatures of some of the acids were consistent with such a hypothesis. It is possible that an index of palaeotemperature similar to that proposed for bacterial tetraethers, can now be constructed and examples are given. This will have important implications for exploration geochemistry, whilst the detailed knowledge of the TPA structures will be useful for guiding the production of chemicals to act as inhibitors of TPA salt deposition in pipelines.

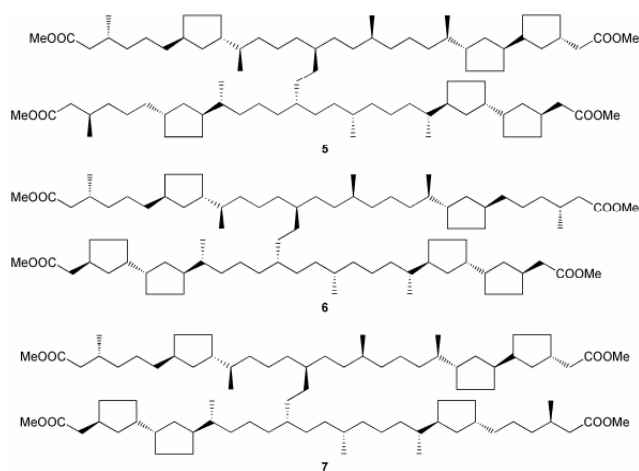


Figure 1. Structures of the regioisomers of some of the C₈₀ 6 ring Archaeal tetra protic acids (TPAs) as methyl esters assigned by NMR spectroscopy after isolation by HPLC. Structure 5 comprises the most abundant TPA in the oils studied to date (cf Lutnaes *et al.*, 2006).

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OIL-SOURCE ROCK CORRELATIONS – HOW DO WE MEASURE SUCCESS?

Joseph CURIALE¹

1. Chevron Corporation, 14141 Southwest Freeway, Sugar Land, Texas 77479 USA

A rigorous, defensible and causal oil-source rock correlation definitively ties an individual source rock sample to an individual crude oil using genetically-based, internally consistent parameter matches. Given the importance of these correlations as risk reduction tools in exploration of both frontier and mature sedimentary basins, it is surprising how few rigorous oil-rock correlations can be found in the open literature (Waples and Curiale, 1999), and how many published correlations are indefensible. Indeed, although petroleum geochemists can cite several “accepted” oil-source rock pairs, the invoked chemically and geologically consistent correlative relationship is subjective to an extent that would be unacceptable in other areas of organic geochemistry. My objectives here are to outline the reasons for the inherent subjectivity of oil-source correlations, and to recommend conceptual and practical approaches for improving them as an approach toward reducing exploration risk.

An oil-source rock correlation is a causal relationship established between the two components which is consistent with all known chemical, geochemical and geological information -- a definition originally established implicitly by Hunt et al. (1954). Specifically: (a) the relationship must be *causal* -- the oil must arise (at least in part), from the specified source rock; (b) chemical data used in the correlation must be *comparable* -- the elemental, molecular and isotopic data derived from the source rock must be of the same type as that derived from the oil; and (c) all available geological data must be *supportive* -- clear geological evidence must exist which *allows* the proposed source rock to have sourced the oil. The presence of all three points is required before declaring a correlation to be successful.

The three points of this definition will be satisfied if we address one analytical and three geological aspects of the problem. Natural extraction of crude oil from its source rock – i.e., “expulsion” – differs mechanically and temporally from laboratory extraction, leading to a correlation problem referred to here as “extraction differences”, and representing the single greatest analytical uncertainty in correlation efforts. Geologically, three aspects confound oil-source correlations: occurrence of multiple source units; lateral and vertical variation in source unit(s) organic matter; and lateral and vertical variation in reservoir unit(s) organic matter. Since the seminal work on multiple source units by Seifert et al. (1979), numerous authors have demonstrated the pervasive occurrence of multiple source input, and new

examples will be presented here. Lateral and vertical source variability has also been demonstrated extensively, with cm-scale variations shown to be commonplace. Lateral and temporal changes in conduit and reservoir organic matter, accompanied by compositional differences due to migration-induced phase changes, are extensive in many petroleum systems. Several examples of these natural geological variations will be presented, including multiple sourcing in Alaska and China, intra-source unit organic differences in Brazil, Thailand and West Africa (e.g., $\delta^{13}\text{C}_{\text{OM}}$ ranges > 10 o/oo), and migration-induced compositional differences in the USA and elsewhere (e.g., substantial differences in molecular ratios previously thought to be source-defined). Emphasis is placed on the difficulty, and importance, of identifying the original source signature from the composition of the crude oil, in the face of post-source compositional changes caused by these multiple geological influences.

Five recommendations are forwarded as part of a unified approach to deal with oil-source rock correlation concerns, and examples of applying these actions are presented. (1) Select representative samples using statistically defensible methods. (2) Establish the inherent compositional variability – laterally and temporally – in each prospective source unit. (3) Assess the extent of migration-induced changes in oil composition. (4) Support each correlation with migration histories derived from 4d models. (5) Iterate correlation results with new data gathered from ongoing exploration efforts. These recommendations are designed (a) to allow correlation success to be measured more objectively, (b) to establish risking parameters for direct use in basin assessment, and (c) to provide baseline criteria for use in reviewing oil-source rock correlations prior to publication.

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**MASSIVE SULFIDES FROM A HYDROTHERMAL FIELD HOST
CHEMOLITHOAUTOTROPHIC COMMUNITIES WITH UNUSUAL LIPID
BIOMARKERS**

Martin BLUMENBERG¹, Walter MICHAELIS¹, Sven PETERSEN² and Richard SEIFERT¹

*1. Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Bundesstrasse 55, 20146
Hamburg, Germany*

2. IFM-GEOMAR, Wischhofstrasse 1-3, 24148 Kiel, Germany.

Mid-ocean spreading and accompanying hydrothermal activities result in huge areas with exposure of minerals rich in reduced chemical species – basaltic and peridotitic rocks as well as metal sulphide precipitates – to the oxygenated sea water. These metal sulphides harbour microorganisms able to grow chemolithoautotrophically on reduced iron and sulphur compounds (e.g. Edwards *et al.*, 2005).

Studies of the biomarker interior and their carbon isotope signatures of a massive sulphide sampled from an inactive area at the western flank of the Turtle Pits hydrothermal field (Mid-Atlantic Ridge, 5°S) revealed a unique biomarker distribution. The microbial fauna is dominated by bacteria with a lipid composition mainly comprising of hydroxylated and *iso*-branched fatty acids but especially non-isoprenoidal dialkyl glycerol diethers partially with macrocyclic cores (including methyl branched hydrocarbons with 30 to 35 carbon atoms; Fig. 1). Structural homologues with yet unknown source were recently also found in hydrothermal sinter deposits from New Zealand (Pancost *et al.*, 2006). Similar to the bacterial lipids the archaea in the sulphide predominantly consist of macrocyclic ether lipids including a common C40 isoprenoid and an uncommon compound with an additional methyl group (Fig. 1) for which structural homologues are only reported from a methanogenic archaeum (Galliker, 1990) and a Pleistocene sulphur deposit (Burhan *et al.*, 2002). Compound specific analyses of the stable isotope signatures revealed $\delta^{13}\text{C}$ values for the majority of bacterial and archaeal lipid components of about 0‰ (versus VPDB), indicative of chemolithoautotrophs using carbon fixation pathways with only negligible isotopic fractionations. However, methanogens are also entrapped in the sulphide, demonstrated by ^{13}C -depleted isoprenoidal lipids with a $\delta^{13}\text{C}$ of about -50‰ (characteristic for CO_2 -reducing archaea synthesising lipids *via* the acetyl CoA-pathway).

Our work shows that sulphides deposited at a hydrothermal field represent suitable environments for uncommon microbiological communities with mostly chemolithoautotrophic organisms. Future studies have to reveal if the widely distributed ϵ -proteobacteria – known to be key-playing in sulphide bioleaching – are the source of the

unique glycerol diether composition, especially since recent genomic studies revealed that the ϵ -proteobacteria are phylogenetically closer related to the deeply branching, ether-lipid containing Aquificales than to other proteobacterial lineages (Sheridan *et al.*, 2003).

Nevertheless, massive sulphides at the Mid-Atlantic Ridge contain microbial communities not known from any other milieu on Earth and thus possibly represent a window into ancient microbial communities and thus into the early evolution of life.

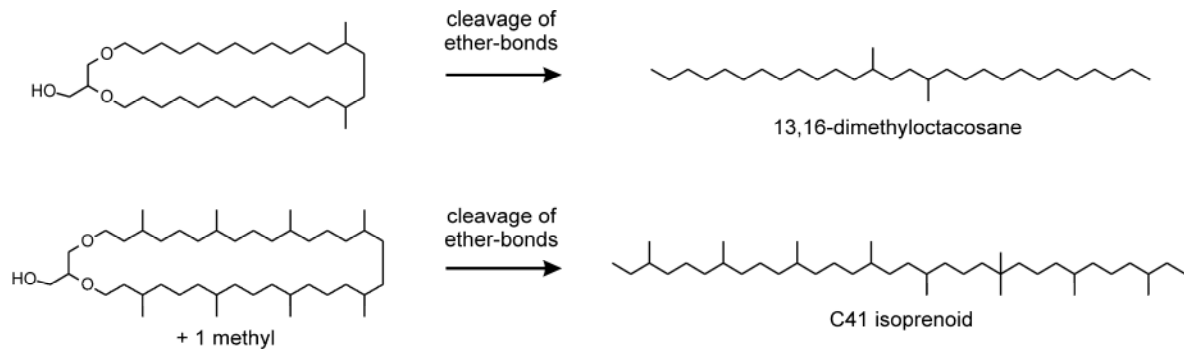


Figure 1. Examples of lipid biomarker series and their ether cleavage products present in a massive sulphide – tentatively identified from their mass spectra.

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