

THE IMPACT OF IN-RESERVOIR BIODEGRADATION PROCESSES ON NON GC-AMENABLE FRACTIONS OF CRUDE OIL AND ADVANCED THERMAL RECOVERY PROCESSES FOR HEAVY OIL

Steve LARTER¹, Barry BENNETT¹, Haiping HUANG¹, Jennifer ADAMS¹, Chunqing JIANG¹, Tamer KOKSALAN¹, Yuhong LIAO¹, Ryan P. RODGERS², Geoffrey C. KLEIN² and Alan G. MARSHALL²

1. *Petroleum Reservoir Group (PRG), Alberta Ingenuity Centre for Insitu Energy, Department of Geology and Geophysics, University of Calgary, 2500 University Drive NW, Calgary, Alberta, T2N 1N4 Canada.*
2. *National High Magnetic Field Lab, 1800 East Paul Dirac Dr
Tallahassee, Florida 32310 USA.*

Worldwide, heavy oil and oil sands bitumens dominate the oil inventory of the Earth with over 6 trillion barrels of petroleum. The average recovery of this immense resource is only 17% on average and due to the high viscosities often associated with these heavily and severely biodegraded oils, thermal recovery methods such as steam floods are often used to recover the material. This involves large expenditures of energy and associated emissions of carbon dioxide to simply recover the petroleum. Increasingly therefore researchers are looking at ways to chemically transform the petroleum insitu to decrease viscosities and reduce energy requirements during recovery. This process is termed insitu upgrading and typically involves thermal conversion of non-hydrocarbons to hydrocarbons at high temperatures (>250°C) in reservoirs, among other processes.

In this study we examine the impact of biodegradation on the non GC-amenable fractions of a series of biodegraded crude oil samples from two continuous reservoir sections covering the range of biodegradation, defined according to the Peters and Moldowan (PM) (1993) scale, from PM1 to PM8 and look at how the changes affect thermal conversion of the oils to lighter materials. We have investigated the use of 2D-GC and high resolution FT-ICR MS techniques for studying variations in crude oil composition at varying biodegradation levels and have used numerical models and mass balance processes to evaluate which components are being degraded. These approaches all have advantages and disadvantages. The advantages of the Fourier Transform mass spectrometry and modeling approach are that the entire material can be examined for degradation related changes and even GC unresolvable or GC immobile components, which are major fractions of heavy oils, can be studied while GC based methods remain very limited in this regard (Kim et al, 2005).

Numerical modeling (Larter et al, 2006) and mass balance studies of the changing oil composition in the well sections determined using classical geochemical methods suggests that loss of non-GC resolvable material through biodegradation represents up to 50% of the

mass loss from PM level 1 to PM level 5. Broadband negative ESI FT-ICR MS derived mass spectra of representative biodegraded oil samples show that the weight-average molecular weight of the whole oils increases with increasing biodegradation level that demonstrates not only the preferential degradation of the smaller components, but also the probable dealkylation of high molecular weight components such as asphaltenes. This hypothesis is confirmed by quantitative pyrolysis studies. The average resolving power of FT-ICR MS, ranging from $350,000 < m/\Delta m 50\% < 450,000$ for each spectrum, allowed molecular formulae for most oil components to be determined and facilitated the identification of material consumed and produced during degradation. Thus, for example, we see systematic changes in the proportions of acyclic and cyclic acids during biodegradation with acyclic material disappearing relative to the more resistant cyclic carboxylic acids, as seen by Kim et al (2005) and a general loss of alkylation in all fractions. We also see systematic changes in the molecular weight and distribution of nitrogen species in the oils.

The compositional changes of the heavy crude oils with increasing degradation result in a series of systematic changes as biodegradation proceeds that relates to increases in aromaticity and loss of alkylation. We describe and illustrate how these changes affect the ease by which thermal upgrading processes in reservoirs can proceed. This work was supported by the NSF National High Field Mass Spectrometry Facility (DMR 00-84173), Florida State University and the National High Magnetic Field Laboratory.

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NEW INSIGHTS INTO THE METABOLISM OF *n*-ALKENES AND *n*-ALKANES IN ANAEROBIC BACTERIA

Vincent GROSSI^{1,2}, Cristiana CRAVO-LAUREAU³, Danielle RAPHEL¹, Rémy GUYONEAUD³ and Agnès HIRSCHLER-REA⁴

1. *Laboratoire de Microbiologie, de Géochimie et d'Ecologie Marines, CNRS-UMR 6117, Centre d'Océanologie de Marseille, Campus de Luminy - Case 901, 13288 Marseille cedex 9, France*
2. *Present address: Paléoenvironnements et Paléobiosphère, CNRS-UMR 5125 PEPS, Université Lyon 1, Campus de la Doua - Bâtiment Géode, 69622 Villeurbanne cedex, France*
3. *Laboratoire d'Ecologie Moléculaire, IBEAS, EA 3525, Université de Pau et des Pays de l'Adour, BP1155, 64013 Pau cedex, France*
4. *Laboratoire de Microbiologie IRD, IFR-BAIM, Universités de Provence et de la Méditerranée, Campus de Luminy - case 925, 13288 Marseille cedex 9, France.*

A review of the actual knowledge of the anaerobic oxidation of *n*-alkenes and *n*-alkanes in anaerobic bacteria will be expanded with recent results giving new insights into the catabolism and the anabolism of these hydrocarbons in sulphate-reducing (SRB) and denitrifying bacteria.

The mechanism of the activation of hydrocarbons in the absence of oxygen is of particular environmental and geochemical interest. Different works during the past decade have demonstrated the utilization of hydrocarbons under anoxic conditions, but still many gaps remain in the understanding of the anaerobic oxidation of these apolar molecules. In some early studies of alkane-degrading microorganisms, an oxygen-independent initial metabolism of alkanes via dehydrogenation to 1-alkenes and hydration to primary alcohols was suggested. In recent investigations, however, alkane dehydrogenation to 1-alkenes was viewed critically and two alternative pathways for the initial oxidation of alkanes could be described: addition of fumarate at C-2 or carboxylation at C-3 (e.g. Callaghan et al., 2006). Despite few indications that alkanes and alkenes are degraded differently in certain SRB, the initial reactions of *n*-alkenes activation in anaerobic bacteria still remain enigmatic.

We investigated the anaerobic biodegradation of C₁₄-C₁₈ *n*-alk-1-enes in a marine SRB (*Desulfatibacillum aliphaticivorans* strain CV2803^T) recently isolated from marine sediments and known to degrade *n*-alkanes by addition of fumarate (Cravo-Laureau et al., 2005). This strain predominantly transformed C-odd and C-even *n*-alk-1-enes to C-odd and C-even fatty acids, respectively. In addition to classical bacterial fatty acids, unusual 2- and 4-ethyl-branched fatty acids and saturated and mono-unsaturated 4-methyl-branched fatty acids with carbon chain-length related to that of the growth substrate were systematically identified. Except for saturated 2-Me- and 4-Me-branched fatty acids, specific metabolites produced during the metabolism of *n*-alkanes by addition of fumarate (i.e. alkyl-succinates and 6-Me-

OPTIMIZATION OF THE PALEOBIOMARKER APPLICATIONS OF ALKENONES

John K. VOLKMAN¹, Fredrick G. PRAHL², Patricia BONIN³, Ian D. JAMESON¹ and Jean-François RONTANI³

¹CSIRO Marine and Atmospheric Research, GPO Box 1538, Hobart, Tasmania 7001, Australia

²College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331-5503, USA.

³Laboratoire de Microbiologie de Géochimie et d'Ecologie Marines (UMR 6117), Centre d'Océanologie de Marseille, F-13288 Marseille, France

The alkenones are long-chain unsaturated methyl and ethyl ketones that are synthesized by a limited number of haptophyte microalgae. The proportion of the C₃₇ di- and tri-unsaturated ketones varies in a systematic way with the growth temperature experienced by these organisms and an index, called U_{37}^k and defined as being the ratio $[C_{37:2}] / ([C_{37:2}] + [C_{37:3}])$, was proposed as palaeo-indicator of sea surface temperatures (SST). For alkenones to be reliable measures of SST in the geological record, it is essential that: (1) their sources are correctly attributed (since temperature calibrations can vary from one species to another) and (2) that any diagenetic effects that might alter the original temperature signal established during their initial biosynthesis can be estimated.

We have re-examined the double bond positions of the diunsaturated alkenones of several haptophytes (Prahl et al., 2006; Rontani et al., 2006a). We have demonstrated that the double bond positions in C₃₇–C₄₀ homologues occur at a fixed carbon number from the carbonyl group, contrary to early speculations. These new data, complemented by analyses of Black Sea sediments, have allowed us to recognise 3 distinct “families” of alkenones for which we proposed different biosynthetic pathways (Rontani et al., 2006a). These data imply that alkenone sources in sediments include other species and genera in addition to the more familiar *Emiliana* and *Gephyrocapsa*.

We have studied the impact of bacterial degradation, autoxidation and thiyl radical-induced stereomutation processes on the alkenone unsaturation ratio (U_{37}^k) in order to determine under what conditions these processes could lead to a significant bias during the determination of palaeotemperatures and to identify biomarker products from these processes. We isolated from microbial mats (Camargue, France) a bacterial community able to degrade these compounds very efficiently under aerobic conditions (Rontani et al., 2005). During these incubations, we observed variable selectivity during the attack of alkenones (variations of the U_{37}^k index ranged up to +0.10). Aerobic bacteria able to degrade alkenones selectively appeared to be also associated with some strains of *E. huxleyi* and are thus not limited to particular environments such as microbial mats.

The autoxidative reactivity of alkenones was determined using *in vitro* simulations (Rontani et al., 2006b). Alkenones appeared to be more sensitive towards oxidative free radical processes than analogues of other common marine lipids and their oxidation rates increase in proportion to their number of double bonds. As the result of this increasing reactivity with degree of unsaturation, the $U_{37}^{K'}$ ratio increased significantly (up to 0.2) during the incubation. Autoxidative degradation of alkenones could also be demonstrated in cells of *E. huxleyi*. Free radical oxidation and aerobic bacterial degradation processes, which can act throughout the water column and in the oxic zone of the sediments, could explain the selective degradation of alkenones observed in some aerobic sediments and suspended particles. They are also consistent with the fact that $U_{37}^{K'}$ values recorded in sediments are often higher than those in the particles settling through the overlying water column.

Several *in vitro* experiments allowed us to demonstrate that alkenone stereomutation may be induced by thiyl radicals (Rontani et al., 2006c). Based on these results, the *cis-trans* alkenone isomerisation previously observed during bacterial incubations of *E. huxleyi* cells under sulphate-reducing conditions was attributable to the formation of thiyl radicals either from methanethiol produced by bacterial degradation of DMSP or from oxidation of thiolate ions by transition metals. This process, which can occur in many anoxic environments, may cause a significant increase (ranging from +0.05 to +0.10) in the measured value for the palaeotemperature proxy $U_{37}^{K'}$.

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THE LIFECYCLE OF DIAMOND CAGE HYDROCARBONS IN NATURE

Zhibin WEI¹, J. Michael MOLDOWAN¹, Jeremy DAHL¹, Dan JARVIE² and Ron HILL³

1. Department of Geological and Environmental Sciences, Stanford University, CA 94305-2115, USA

2. Humble Geochemical Services, Division of Humble Instruments & Services, Inc., P. O. Box 789, Humble, Texas 77347, USA

3. U.S. Geological Survey, Box 25046, Denver Federal Center, MS 939, Denver, CO 80225, USA

Diamondoids, also called “nanodiamonds”, can be regarded as extraordinary small fragments of a diamond lattice. They naturally occur in virtually all petroleum and are composed of fused cyclohexane rings all in chair conformation forming a cage structure. These nanodiamonds have shown potential in many research fields, e.g., nanotechnology, pharmacology, petroleum geochemistry. Although lower diamondoids (adamantanes, diamantanes and triamantanes) have been formed in laboratory experiments by super-acid rearrangement of a wide variety of isomeric precursor molecules, the origin of diamondoids in nature has puzzled organic geochemists for several decades.

In this study, we attempt to ascertain the organic precursors, formation mechanisms, and fate of diamondoids, which may shed light on the lifecycle of diamondoids in nature. The present work has clearly demonstrated that diamondoids in nature originate from petroleum or petroleum precursor molecules through molecular rearrangements involving numerous carbonium ion intermediates in the presence of acidic clays. The pattern of diamondoid formation follows carbonium ion mechanisms rather than free radical mechanisms, as supported by the findings that acidic clays largely facilitate the generation of diamondoids from kerogen compared with S^0 and other minerals (Wei et al., 2006a). Diamondoid analysis was performed on a large set of oil and condensate samples. Our results indicate that diamondoids become enriched in oil as oil cracking increases (Dahl et al., 1999). Despite their high stability, diamondoids are perishable in nature. Compelling evidence can be provided by thermal destruction of diamantane at high temperatures in the laboratory, by a dramatic drop in the abundance of diamondoids in the extracts of highly mature coals and sedimentary rocks (Wei et al., 2006b), and by the biodegradability of adamantane in petroleum reservoirs where microbial activities are evident. Therefore, diamondoid cage compounds have their lifecycle in nature: birth, enrichment and demise (Figure 1).

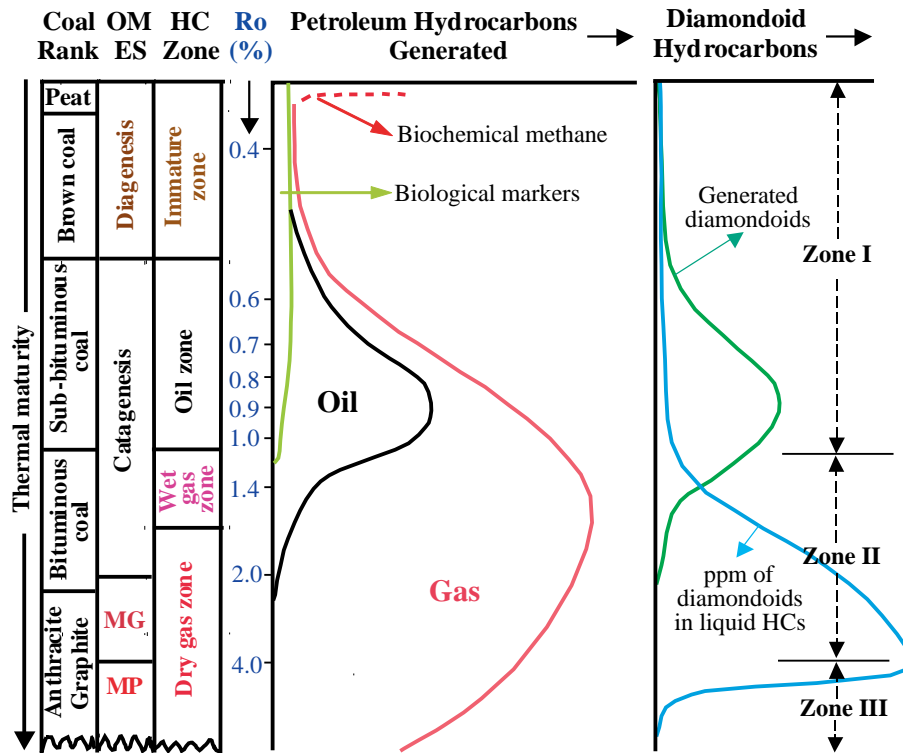


Figure 1. General schemes for formation of petroleum hydrocarbons and diamondoids, concentrations of diamondoids in liquid hydrocarbons, and stages of coal rank as a function of thermal maturity of the source rock, showing the “lifecycle” of diamondoids in nature. Coal Rank = stages of coal rank; OM ES = main stages of evolution of organic matter; HC Zone = main zones of hydrocarbon generation; MG = metagenesis; MP = metamorphism; Zone I = diamondoid birth/generation; Zone II = diamondoid generation and enrichment; Zone III = diamondoid destruction.

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**ASSESSING THE ROLE OF STEROL METHYLTRANSFERASE HOMOLOGUES
IN THE METHYLHOPANOID SYNTHESIS PATHWAY OF
METHYLOBACTERIUM EXTORQUENS AM-1**

Alexander S. BRADLEY¹, Christopher J. MARX² and Roger E. SUMMONS¹

1. Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology,
Cambridge, MA 02139 USA.

2. Department of Organismic and Evolutionary Biology, Harvard University, Cambridge, MA 02138 USA

Hopanoids are polycyclic triterpenoids that are abundant in the geological record and common in some bacteria. Among the classes of hopanoids, methylhopanoids have been of particular utility to organic geochemists. In this study we test the hypothesis that the gene responsible for hopanoid A-ring methylation is a bacterial homologue of eukaryotic S-adenosyl-L-methionine (SAM)-dependent sterol methyltransferase.

Several cyanobacteria and proteobacteria produce hopanoids methylated at the C-2 position (Summons *et al.*, 1999). In ancient sediments, the detection of 2 α -methylhomohopanes (derived from 2 β -methyl-bacteriohopanepolyols) in high amounts relative to desmethylhopanes is usually attributed to ancient cyanobacterial productivity. These compounds have been detected in rocks 2.7 billion years old; this has been interpreted as the earliest evidence for the evolution of oxygenic photosynthesis (Brocks *et al.*, 1999). Similarly, 3 β -methylhopanoids are produced by aerobic type I methanotrophs such as *Methylococcus* (Summons & Jahnke, 1992). The detection of their hydrocarbon derivatives in ancient rocks is usually interpreted as a proxy for aerobic methane cycling and used to infer paleoenvironmental conditions (e.g. Brocks *et al.*, 2005).

Despite the importance of these molecules to organic geochemists, very little is known regarding either the genetic basis for hopanoid methylation or the physiological function of hopanoids. Identification of the gene or genes responsible for hopanoid methylation would provide a basis with which to rapidly examine the potential distribution of methylhopanoids in microbes (via screening of genomic databases). Comparative sequence analysis of these genes may shed light on the evolution of this ancient pathway. Understanding the physiological role of these molecules would be a boon to investigations that make paleoenvironmental interpretations upon their detection.

The methyl group on the hopanoid A-ring is known to be derived from L-methionine, likely via SAM (Zundel & Rohmer, 1985). SAM is a methyl donor for a variety of methyltransferase enzymes, including the sterol methyltransferases (SMTs) that operate on the sterol side chain in some eukaryotes. Examination of genomic databases revealed the

presence of SMT homologues in the genomes of several methylhopanoid-synthesizing bacteria that lack sterols, including the cyanobacteria *Synechococcus* and *Nostoc*, the methanotroph *Methylococcus*, and the methylotroph *Methylobacterium*, among others. The translated amino acid sequences for these genes contain a highly conserved region that corresponds to the SAM-binding domain in SMT, but lack the sterol-binding region that is unique to SMT. Due to i) the presence of these genes in a wide variety of methylhopanoid synthesizing organisms, ii) the fact that these genes are homologous to SMT, which operates on triterpenoids, and iii) the likelihood that these genes are SAM-dependent, it has been hypothesized that these genes encode enzymes operating to methylate hopanoid A-rings (Summons *et al.*, 2006).

The α -proteobacterium *Methylobacterium extorquens* AM1 is a genetically tractable methylhopanoid producer in which we are conducting experiments to test this hypothesis. When grown on succinate, *Methylobacterium* produces C₃₀-methylhopanols. Its genome contains a SMT homologue with 35% identity to SMT1 of *Arabidopsis* and a conserved SAM-binding region. We are creating several mutant strains of *Methylobacterium*, each of which lacks a gene we suspect may be involved in hopanoid synthesis (such as squalene-hopene cyclase) or methylation. Examination of the hopanoid content of the mutant strain lacking the SMT homologue will test our hypothesis that this gene participates in A-ring methylation. Physiological characteristics of this and other mutant strains will be compared to wild-type *Methylobacterium*, in an attempt to gain insight into the physiological function of hopanoids and methylhopanoids.

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THE DEBITS PROJECT: INVESTIGATION OF DEEP MICROBIAL ECOSYSTEMS IN A TERRESTRIAL ENVIRONMENT

Kai MANGELSDORF¹, Klaus-G. ZINK^{1,2}, Andrea VIETH¹, Brian HORSFIELD¹,
Richard SYKES², Barry A. CRAGG³, Joachim RINNA³, Gwang T. KIM⁴
Andrew WEIGHTMAN⁴, R. John PARKES³ and John FRY⁴

1. GFZ Potsdam, Telegrafenberg, D-14473 Potsdam, Germany; e-mail: K.Mangelsdorf@gfz-potsdam.de.

2. GNS Science, PO Box 30-368, Lower Hutt, New Zealand

3. Cardiff School of Biosciences, PO Box 915, Cardiff CF10 3TL, UK

4. School of Earth, Ocean and Planetary Sciences, University of Cardiff, PO Box 914, Cardiff, CF10 3YE, UK

The investigation of the extent and dynamics of deep microbial ecosystems in sedimentary basins is a relatively young and intriguing topic in today's geoscience research. With the finding of ubiquitous deep microbial life on Earth, inevitably the question arises as to how microorganisms can survive in such ancient and, from a surface perspective, hostile habitats. In addition to elevated temperature and pressure conditions, nutrient limitation and limited porosity and permeability, deep microbial communities have to cope with a decrease in the available carbon and energy sources, because of the sedimentary organic matter becoming more recalcitrant with depth (Parkes *et al.*, 2000). The activation and usability of such food or substrate sources with increasing depth is, therefore, of specific interest when investigating deep microbial populations. There are relatively few investigations of the microbiology of sub-surface coal-bearing formations.

The international DEBITS (Deep Biosphere In Terrestrial Systems) project was started in February 2004 in the Waikato coal area on the North Island of New Zealand and is especially dedicated to terrestrial deep microbial ecosystems. The aim of the project is the investigation of the indigenous microbial populations and the characterisation of their habitats using biogeochemical, organic-geochemical and microbiological approaches.

The Waikato coal area represents a perfect natural laboratory for terrestrial deep biosphere research, because in this area organic carbon-rich lithologies are intercalated with coarser grained sediments. While the coaly seams are potential substrate providers (feeder lithologies), the coarser grained lithologies might act as habitats for microorganisms (carrier lithologies), having enough permeability to enable sufficient supply of respiratory compounds and hence for effective metabolism. Within the DEBITS project a 148 m deep well was drilled at Ohinewai in the Waikare Coalfield, taking strict precautions to prevent or at least to control any contamination of the core material by surface microorganisms. The DEBITS-1 well penetrates a complex succession of interbedded organic carbon-rich layers and coarser grained mudstones, siltstones and sandstones. At a depth of about 76 m the core intersected an

unconformity. Sediments below the unconformity were previously buried to more than 2000 m and therefore have experienced significantly higher temperatures, resulting in sub-bituminous coal rank, compared to the organic carbon-rich lithologies above the unconformity, of lignite rank.

Microbial *life markers (cell membrane phospholipids)* and intact and viable prokaryotic cells were detected above and below the unconformity, indicating either that sediments below this boundary have not been sterilized by increased burial and heating or that these sediments have been re-colonized after uplift. The phospholipid *life marker* profile decreases from the top to the base of the DEBITS-1 core. In contrast, the prokaryotic cell counts show no overall decrease with depth. An explanation for this discrepancy might be that microorganisms in deeper parts of the DEBITS-1 core are not necessarily smaller in number but in size due to the more extreme environmental conditions. There is a high molecular prokaryotic diversity, with some groups of *Bacteria* and *Archaea* similar to the marine deep biosphere. Methanogens (methane-producing microorganisms) were also detected and methane production occurred in long term slurry incubations.

Comparing the phospholipid (PL) abundances with the organo- and lithofacies in selected transects from organic carbon-rich to coarser grained organic carbon-poor lithologies, distinct trends can be recognized. While the organic carbon rich lithologies contain almost no PLs, the highest PL signals are generally detected at or near the transition zones, decreasing into the adjacent clay/silt/sand layers. The PL *life marker* distribution points to better conditions for the deep microbial populations in the coarser grained sediments close to the organic carbon-rich lithologies. Water extraction experiments show highest amounts of small fatty acid anions (e.g. acetate) near the transition zones (Vieth et al., this volume). A release of substrate from the organic carbon-rich seams into the adjacent sediments is suggested. Thus, the distribution of the microbial populations appears to be the result of sufficient substrate supply (most likely from the coaly layers) and sufficient pore space and permeability for metabolic exchange processes within the pore water.

Most reference samples far away from organic carbon-rich sediments contain no PLs. However, there are several exceptions with reference samples having PLs and transect samples with no PLs, which shows that there is still much to learn about deep microbial feeding processes and optimal life habitats for deeply buried microorganisms.

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ANALYSIS OF SPORE DIPICOLONIC ACID CONTENTS FOR ESTIMATING THE NUMBER OF ENDOSPORES IN SEDIMENTS

Jörg FICHTEL¹, Jürgen KÖSTER¹, Jürgen RULLKÖTTER¹ and Henrik SASS²

1. Institute of Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, P.O. Box 2503, D-26111 Oldenburg, Germany

2. School of Earth, Ocean and Planetary Sciences, Cardiff University, Cardiff, CF10 3YE, Wales, U.K.

Endospores are bacterial resting stages being able to remain viable for long periods of time. Consequently, they can be expected to accumulate in sediments during burial. Since they can be stained with fluorescent dyes they may contribute significantly to total cell counts emphasizing the need for a method for the estimation of endospores in sediments.

In the present study, dipicolinic acid (DPA), which is accumulated in the endospore core, was used to quantify spores in sediment samples from the backbarrier tidal flat of the island of Spiekeroog in the southern North Sea. For converting sediment DPA contents into endospore numbers, ten bacterial strains were examined for their DPA content per endospore. Six strains (*Bacillus* sp. G50II, *Bacillus* sp. G400 I, *Bacillus* sp. N300I, *Bacillus* sp. NA402, *Oceanibacillus* sp. NC301 and *Clostridiales* bacterium strain G100XIII) were isolated from the sediment sampling location. The other four strains comprised two well described *Bacillus* species from a culture collection (*B. megaterium* DSM 32^T and *B. subtilis* ssp. *subtilis* DSM 10^T) and two sulphate-reducing bacteria *Desulfosporosinus orientis* DSM 765^T and *Desulfotomaculum* sp. B2T (Sass & Cypionka, 2004). DPA contents of endospores ranged from 1.4×10^{-16} mol (*Bacillus* sp. G400I) to 1.3×10^{-15} mol (*Desulfosporosinus orientis* DSM 765^T). The observed differences in spore DPA content of the different strains apparently corresponded well with variations in spore volume (Fig. 1). Average spore volumes determined for the different strains ranged from $0.40 \mu\text{m}^3$ to $2.43 \mu\text{m}^3$, with spores of *Desulfotomaculum* sp. B2T being largest and having six times the volume determined for *Oceanibacillus* sp. NC301 spores. A rough correlation of DPA content and volume was indicated by linear regression using all data points, resulting in a DPA concentration of $0.46 \text{ mol DPA l}^{-1}$ which fits well to all strains with the exception of *Desulfosporosinus orientis* DSM 765^T. The spores of the tidal flat isolates showed little variation in size and DPA content and generally contained less DPA than endospores of the two sulphate reducers or of *Bacillus megaterium*^T. For the tidal flat strains, an average of 2.2×10^{-16} mol DPA per spore was determined and used for conversion of sediment DPA contents into spore numbers. Estimated endospore numbers were in a range of 10^6 to 10^7 endospores g^{-1} sediment and exceeded viable counts of spores determined after oxidic incubation in pasteurized MPN series

(Köpke et al., 2005) by at least three orders of magnitude, indicating that only a minor fraction of the endospores in the sediment can be detected by cultivation-dependent approaches. Since quantification on the basis of dipicolinic acid contents does neither discriminate between viable and non-viable spores nor between different physiological groups, it apparently provides a more realistic estimate of the contribution of endospores to the microbial community. For this reason, we suggest the use of DPA for determination of endospore numbers as a valuable amendment to total cell counts to reveal the importance of endospores in sedimentary microbial communities.

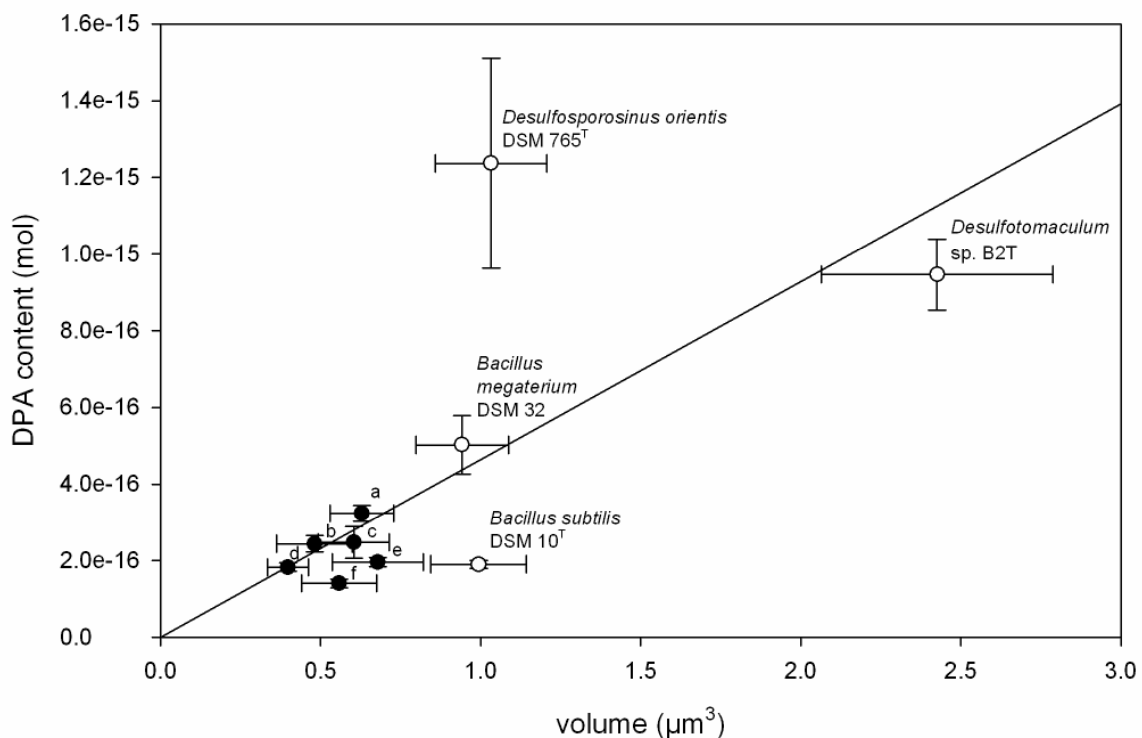


Figure 1. Plot of DPA content versus volume of the endospores analyzed in this study. The regression line (including all data points) represents $0.46 \text{ mol DPA l}^{-1}$ spore volume and fits well to most of the strains. Black dots: tidal flat isolates a) *Bacillus* sp. NA402 b) Strain G100XIII c) *Bacillus* sp. N300I d) *Oceanibacillus* sp. NC301 e) *Bacillus* G50II f) *Bacillus* G400I. White dots: sulphate reducers and aerobic freshwater bacilli.

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INTACT POLAR LIPIDS IN THE MARINE DEEP BIOSPHERE – STRUCTURAL DIVERSITY AND QUANTITIES

Julius S. LIPP and Kai-Uwe HINRICHS

Organic Geochemistry Group, RCOM & Dept. of Geosciences, University of Bremen, 28334 Bremen, Germany.

The deep biosphere is thought to contain live biomass that represents up to 10% of the total carbon in live cells of our planet (Parkes et al., 2000). This vast ecosystem has become the research focus of microbiologists and geochemists to address key questions like: What types of microbes thrive in deeply buried sediments? And, what are the processes they are mediating? Recent studies have provided information on metabolic activities and quantities of deeply buried prokaryotic cells (Biddle et al., 2006; Inagaki et al., 2006; Schippers et al., 2005, 2006). However, some fundamental questions remain unresolved or even lead to highly controversial answers. For example, various techniques appear to disagree already at the domain level on WHO actually inhabits this ecosystem. Molecular biological methods like catalyzed reporter deposition - fluorescent in situ hybridization (CARD-FISH) and quantitative polymerase chain reaction (Q-PCR) suggest a predominance of bacterial over archaeal cells (Schippers et al., 2005; Inagaki et al., 2006). On the other hand FISH and intact polar lipids (IPL) suggest a predominance of archaea among live prokaryotes (Biddle et al., 2006).

Intact membrane lipids are considered to be markers for live subsurface cells (Sturt et al., 2004) since the polar headgroup is cleaved off the core lipid after cell death. Careful determination of response factors in calibration series with IPL standards shows no preferential detection of one compound class over the other. However, there are several principal difficulties that have to be overcome while analyzing environmental samples: general low abundance of target IPL compounds and the complex matrix with a high background of degraded material.

A robust analytical protocol based on high performance liquid chromatography coupled to ion trap multistage mass spectrometry (HPLC-IT-MSⁿ) was developed and applied to a set of samples from the Peru margin surface (RV Sonne SO147), ODP Legs 201, 204, 207, and IODP Expeditions 301 and 311. The major bacterial IPLs identified comprise phosphatidylglycerol (PG), phosphatidylethanolamine (PE) and phosphatidylcholine (PC) diacylglycerides with C₁₆ and C₁₈ acyl groups. The diversity in archaeal IPLs is limited to different core lipid structures, e.g. archaeol-based diether lipids vs. glycerol dibiphytanyl

glycerol tetraether (GDGT) lipids with various combinations of sugar headgroups. The composition of archaeal IPLs appears to be linked to the diversity of archaeal phylotypes.

The observed IPL concentrations were converted to cell concentrations for comparison to results from molecular biological approaches. Surface sediments are dominated by bacterial IPLs with possible admixtures of eukaryotic lipids while archaeal lipid concentrations are low. Concentrations of bacterial lipids decline rapidly to levels significantly lower than those of their archaeal counterparts. The analysis of ODP/IODP samples from deeply-buried horizons shows evidence for bacterial lipids in about 20% of samples analyzed to date. On the basis of these observations in combination with results of degradation experiments of archaeal and bacterial IPLs under typical anaerobic sedimentary conditions (Pamela Rossel et al., unpubl. data), we interpret the predominance of archaeal IPLs as evidence for a far more important role than suggested by other techniques. A composite view comprised of ~ 60 samples from both surface and deeply buried sediments on the abundance of total prokaryotic lipids in subsurface environments provides an interesting comparison to corresponding data on intact cells (cf. Parkes et al., 2000): concentrations of IPLs decline more rapidly with depth than the counts of intact cells from a global data set.

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**MATURATION CHARACTERISTICS OF THE NEW ZEALAND COAL BAND:
PART 2 – KEROGEN RESTRUCTURING AND IMPLICATIONS FOR MODELLING
PETROLEUM FORMATION**

Richard SYKES¹, Volker DIECKMANN^{2,3}, Brian HORSFIELD², Tiem T.A. VU² and
Per Erling JOHANSEN⁴

1. GNS Science, PO Box 30368, Lower Hutt 5040, New Zealand

2. GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, Germany

3. Shell International Exploration and Production, Kessler Park 1, 2288 GS Rijswijk, Netherlands

4. Applied Petroleum Technology, Instituttveien 18, PO Box 123, 2027 Kjeller, Norway

The maturation characteristics of humic (i.e. vitrinite-rich) coals and coaly mudstones are fundamentally different to those of classic marine and lacustrine source rocks and, thus, for basin modelling purposes, require separate study. The unique maturation characteristics of coaly kerogen are well exemplified by the New Zealand Coal Band (Cretaceous–Cenozoic), which displays an unexpected, rank-related increase in HI of up to 150 mg HC/g TOC prior to the onset of oil expulsion (Sykes and Snowdon, 2002). This increase has been attributed primarily to kerogen restructuring (Killops et al., 2002; Sykes and Snowdon, 2002), which is thought to involve mainly aromatisation and polycondensation reactions reincorporating bitumen into the kerogen macromolecular structure and in the process, creating new, higher energy bonds (Schenk and Horsfield, 1998; Dieckmann et al., 2006). In this study, we have used Soxhlet extraction, TLC and open-system pyrolysis techniques to investigate evidence for progressive kerogen restructuring along the NZ Coal Band and to assess its implications for kinetics-based modelling of petroleum formation.

Thirteen well-characterised, rank series coals [Rank(S_r) 5.4–18.9, R_o 0.39–2.61%] of relatively uniform kerogen type from the NZ Coal Band were Soxhlet-extracted using an azeotropic solvent mixture for 72 hrs. The extracts are dominated by asphaltene and polar compounds. HI values of the extracted coals are up to c. 100 mg HC/g TOC less than those of the non-extracted counterparts (Fig. 1). Indeed, for coals of Rank(S_r) 12.6 (R_o 0.87%) or less, up to c. 30% of their S_2 hydrocarbon yields is heavy bitumen-derived. Significantly, however, the extracted coals display the same rank-related increase in HI up to the onset of oil expulsion, confirming that the increase is indeed linked to the kerogen fraction.

For both the extracted and non-extracted sample sets, plots of the S_2 hydrocarbon generation rate curves (normalised to mg HC/g initial $C/^\circ C$) against Rock-Eval temperature reveal nesting of the curves for the three least mature samples [Rank(S_r) 5.4–6.6, R_o 0.39–0.45%), followed by progressive offset of curves to higher temperatures for successively more mature samples; i.e. each curve extends beyond the envelope of the preceding sample in the

rank series. This distribution is consistent with the neo-formation of more refractory kerogen with progressive maturation – kerogen that is expected to generate late-stage, high-maturity gas (Dieckmann et al., 2006).

To further test this theory, hydrocarbon generation rate curves were obtained for the non-extracted coals at laboratory heating rates of 0.7, 2, 5 and 15 K/min and discrete activation energy and frequency factor distributions derived following the enhanced kinetics approach of Dieckmann (2005). Initial results are equivocal, probably because of the significant heavy bitumen component of many of the samples. However, irrespective of the kinetics results, the progressive offset of the S2 hydrocarbon generation rate curves beyond the immature envelopes indicates that hydrocarbon generation kinetics obtained from immature samples would likely result in erroneous predictions of petroleum formation histories at geological heating rates (Schenk and Horsfield, 1998).

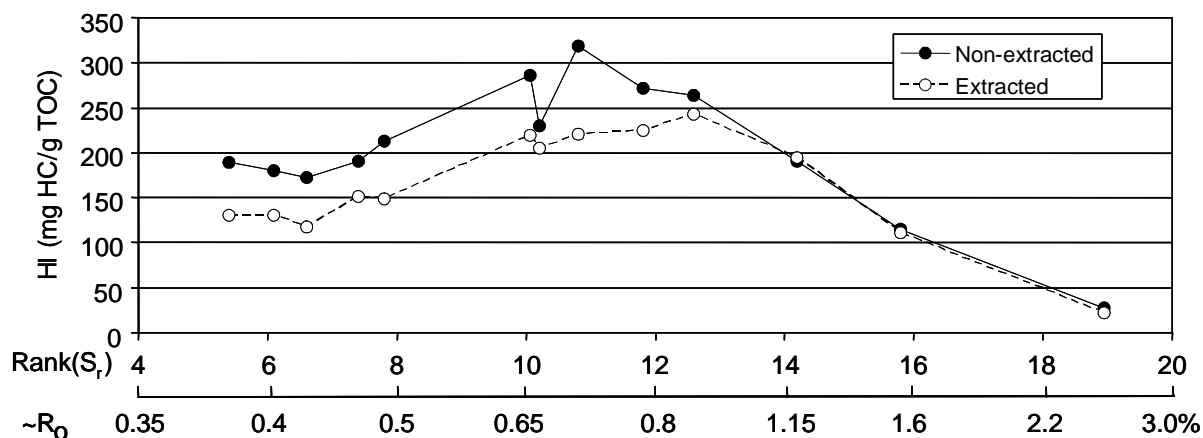


Figure 1. Plot of HI versus Rank(S_r) and equivalent R_o for selected coals from the NZ Coal Band, pre- and post-extraction.

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BIOMARKER AND CARBON ISOTOPE SYSTEMATIC IN CENOZOIC COAL AND FOSSIL WOOD OF CENTRAL EUROPE

Achim BECHTEL^{1,2}, Reinhard F. SACHSENHOFER², Reinhard GRATZER², Andreas LÜCKE³ and Wilhelm PÜTTMANN⁴

1. Department of Mineralogy & Petrology, University of Bonn, Poppelsdorfer Schloss, D-53115 Bonn, Germany

2. Department of Applied Geosciences & Geophysics, University of Leoben, Peter-Tunner-Str. 5, A-8700 Leoben, Austria

3. Institute for Chemistry and Dynamic of the Geosphere V: Sedimentary Systems (ICG V), Research Center Jülich, D-52425 Jülich, Germany

4. Institute of Atmospheric and Environmental Sciences, Department of Analytical Environmental Chemistry, J. W. Goethe-University, Georg-Voigt-Str. 14, D-60054 Frankfurt a.M., Germany

In the light of recent findings, biomarker and carbon isotope systematic in coal and fossil wood are expected to provide valuable information for the reconstruction of floral assemblages and paleoenvironmental changes during the Cenozoic. Carbon isotope analyses of terrigenous organic matter have been used to reconstruct changes in the isotopic composition of upper ocean and atmospheric carbon reservoirs (Arens et al., 2000). Carbon isotope values of cellulose from tree-rings and fossil wood have also been related to climatic change (e.g. temperature, humidity) via water-use efficiency of land plants.

In this study, we report on biomarker and carbon isotope analyses of coal, resinates, woody macrofossils, and extracted cellulose obtained from lignite deposits of Central Europe (Austria, Bulgaria, Germany, Hungary, Slovenia) covering the time interval from Early Eocene to Pliocene. The concentration of diterpenoid biomarkers (including abietane-, pimarane-, isopimarane-, beyerane-, kaurane-, and phyllocladane-type hydrocarbons) relative to the sum of diterpenoids plus triterpenoid hydrocarbons, containing the structures typical of the oleanane-, the ursane-, or the lupane-skeleton, are used as proxies for the contribution of gymnosperms versus angiosperms to peat formation. Our results demonstrate that bulk organic matter of coal and coaly sediments is influenced by varying contributions of angiosperms and gymnosperms, by different isotopic composition of land plant tissue (e.g. leaves, wood, bark), as well as by microbial activity. The concentration ratios of terpenoid biomarkers in coal seams indicate the predominance of angiosperms in the peat-forming vegetation during Eocene and Early Oligocene, whereas Late Oligocene to Pliocene coals are derived from gymnosperm-dominated (i.e. coniferous) sources. The results are in general agreement with paleobotanical records and demonstrate the potential of biomarker analyses in paleoecological studies.

The $\delta^{13}\text{C}$ variations found in resinites, fossil wood and wood cellulose support their capability to trace paleoenvironmental conditions. In contrast to fossil wood, $\delta^{13}\text{C}$ values of cellulose from woody macrofossils are only negligibly influenced during decomposition. The carbon isotope analyses demonstrate isotopic trends of land plants parallel to the marine record during the Tertiary (Zachos et al., 2001). Furthermore, co-variations of $\delta^{13}\text{C}$ of coals, fossil wood from gymnosperms, and wood cellulose with climatic changes (i.e. mean annual temperature, mean annual precipitation) reconstructed from paleobotanical data from eastern Germany are noticed (Krutzsich et al., 1992; Eissmann, 1994; Krutzsich, 2000). We propose that the observed patterns were primarily produced by variations of the isotope ratios of oceanic and atmospheric carbon reservoirs, and additionally modified by climatic changes due to their influence on plant physiology. Thus, the terrestrial carbon isotope record indicates changing $\delta^{13}\text{C}$ values of atmospheric CO_2 associated with atmospheric $p\text{CO}_2$ and paleoclimate. Carbon isotope studies on fossil wood of known taxa and on their cellulose provide a powerful tool in reconstructing the isotopic record of land plants and its implication for environmental changes during the Earth's history.

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OILS SOURCED FROM PERMIAN COALS - GEOCHEMICAL EVIDENCE FROM SYDNEY BASIN OIL SEEPS AND SHOWS

Manzur AHMED¹, Herbert VOLK¹, Simon C. GEORGE², Mohinudeen FAIZ¹ and Linda STALKER³

1. CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia

2. Australian Centre for Astrobiology, Macquarie University, Sydney, NSW 2109, Australia

3. CSIRO Petroleum, PO Box 1130, Bentley, WA 6102, Australia

Oil from coal is still the subject of considerable debate, with unambiguous examples of commercial petroleum accumulations due to coal source rocks largely limited to Late Mesozoic and Cenozoic southern hemisphere examples (Wilkins and George, 2002). Petersen and Nytoft (2006) suggested that this may be due to floral control on oil generation potential, linked to the evolution of land plants. These authors also reported on some Permian coals from the Australian Cooper and Sydney Basins that may have marginal oil generation potential. In the coal-rich Sydney Basin (Australia), the presence of a petroleum system has been known for decades from the occurrences of numerous oil seeps and oil shows encountered during coal mining and the drilling of coal exploration wells (e.g. Philp and Gilbert, 1986). Nevertheless, whether these oils were sourced from coals or from other shaly source-rocks interbedded within the Coal Measures is not yet clearly established. This study assesses the organic geochemical and petrological characteristics of selected coal samples from the Late Permian Illawarra Coal Measures, fine-grained sediment samples from above and within the Coal Measures, and oil samples from the Early Triassic sandstones overlying the Coal Measures, in order to investigate if these oils are related to the coals.

Organic geochemical and petrological data demonstrate that the Sydney Basin coals (vitrinite reflectance values from 1.0 to 1.4 %) have higher hydrogen indices, higher liptinite contents and much higher organic matter extractabilities than the fine-grained sediments in the section. Biomarker evidence such as the high relative abundances of pristane, C₁₉ and C₂₀ tricyclic terpanes, C₂₄ tetracyclic terpane and C₂₉ steranes and diasteranes indicates that the oil shows and seeps were sourced from higher plant dominated organic matter deposited in an oxic environment. This is corroborated by the low abundances of dibenzothiophenes, and the absence of extended tricyclic terpanes and gammacerane in these samples. The source and maturity-specific biomarkers and aromatic hydrocarbon distributions of the oils exhibit notable affinities to those of the coals (Fig. 1). The affinity of the oils to the coals is also demonstrated by the similarities in bulk carbon isotopic compositions of the total oils and the coal extracts ($\delta^{13}\text{C}_{\text{Oil}} = -24.7$ to -23.1 ‰ and $\delta^{13}\text{C}_{\text{Extract}} = -26.3$ to -25.3 ‰) and carbon

isotopic compositions of their individual *n*-alkanes ($\delta^{13}\text{C}_{n\text{-Alkanes of oil}} = -25.7$ to -23.4 ‰ and $\delta^{13}\text{C}_{n\text{-Alkanes of Extract}} = -25.6$ to -24.6 ‰), with the exception of the heavier bulk isotopic composition of Metropolitan oil seep and the compound specific isotopic composition of Metropolitan coal extract. Permo-Triassic fine-grained sediments have relatively higher abundances of C_{14} and C_{15} bicyclic sesquiterpanes, C_{23} tricyclics terpane, C_{29} $\alpha\beta$ hopane, 2α -methylhopanes, C_{30} 30-norhopane, 29,30-bisnorhopane, C_{27} steranes, C_{27} diasteranes and dibenzothiophenes. These distributions suggest a mixed terrestrial and calcareous organic matter input to the fine-grained sediments, which is significantly different from both the oils and the coals (Fig 1).

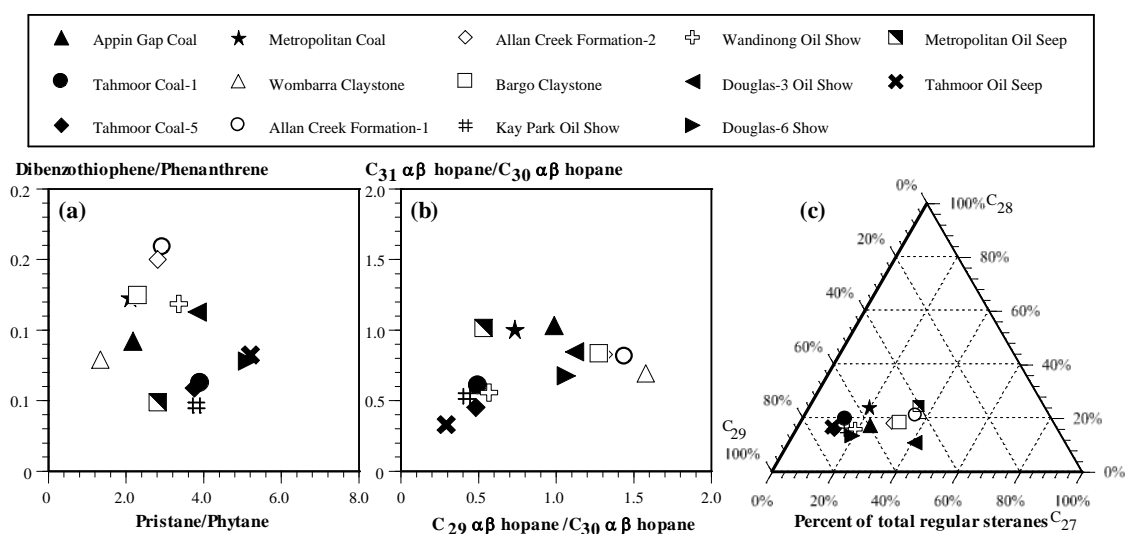


Figure 1. Cross plots of (a) Pristane/Phytane versus Dibenzo[thiophene]/Phenanthrene, (b) $\text{C}_{29} \alpha\beta$ hopane/ $\text{C}_{30} \alpha\beta$ hopane versus $\text{C}_{31} \alpha\beta$ hopane/ $\text{C}_{30} \alpha\beta$ hopane and ternary diagram of (c) C_{27} , C_{28} and C_{29} regular steranes showing the genetic relationship of the oils and coals.

The similar biomarker features, bulk/compound specific carbon isotopic compositions and molecular maturities of the oils and the coals indicate that they are genetically related. This new evidence for generation and expulsion of oil from Permian Coals in the Sydney Basin indicates that this basin may have the potential for commercial oil accumulations in Permian or Early Triassic sandstones.

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PHYSIOLOGY OF PHOTOAUTOTROPHS AND PALEOENVIRONMENT DURING THE CRETACEOUS OCEAN ANOXIC EVENTS BASED ON NITROGEN AND CARBON ISOTOPE ANALYSES OF INDIVIDUAL SEDIMENTARY PORPHYRINS

Yuichiro KASHIYAMA^{1,2}, Nanako O. OGAWA¹, Yoshito CHIKARAISHI¹, Jun'ichiro KURODA¹, Hiroshi KITAZATO¹ and Naohiko OHKOUCHI¹

1. *Institute for Research on Earth Evolution, Japan Agency for Marine-Earth Science and Technology.*

2. *Department of Earth and Planetary Science, The University of Tokyo.*

Sedimentary porphyrins are tetrapyrrole molecules with alkyl chains derived from chlorophylls, heme, and other biomolecules (e.g., Treibs, 1936; Baker and Louda, 1986; Callot and Ocampo, 2000). In particular, structures of deoxophylloerythroetioporphyrin (DPEP) and its analogues strongly suggest them to be originated from chloropigments. Thus, stable isotopic compositions of nitrogen and carbon of these porphyrins should directly reflect those of the chloropigments (e.g., Hayes et al., 1987; Chicarelli et al., 1993). We analysed nitrogen and carbon isotopes of various individual porphyrins extracted from sequential samples from the Livello Bonarelli black shale (uppermost Cenomanian, Italy) to elucidate the physiology of photoautotrophs and paleoenvironment during the Cretaceous OAE.

Based on the isotopic relationship between tetrapyrrole portion of chlorophylls and cells of the photoautotroph (the former 4.8‰ depleted in ¹⁵N and 1.8‰ enriched in ¹³C relative to the latter; Ohkouchi et al., 2006; Ohkouchi et al., in prep.), nitrogen isotopic compositions of the entire photoautotrophic community is estimated to be -2 to 0‰ based on δ¹⁵N of Ni DPEP (-6.6 to -4.8‰) and Cu DPEP (-5.7 to -5.1‰). These values strongly suggest that the nitrogen assimilated during phototrophic primary production was largely supplied *via* N₂-fixation. Meanwhile, carbon isotopic compositions of Ni DPEP (-20.5 to -17.9‰) and Cu DPEP (-20.1 to -16.3‰) suggest that of the entire photoautotrophic community being approximately -22 to -18‰. Thus, the estimated isotopic fractionation associated with carbon fixation in the Bonarelli paleoenvironment was strikingly small (-15 to -13‰) compared to those of the simulated *ordinary* photoautotrophic community in each paleoenvironments, namely, -20 to -14‰ and -23 to -20‰, respectively. The result suggests rapid growth rates for these photoautotrophs in an intense bloom conditions that perhaps had associated active transport of carbon substrates and/or a significant rate of β-carboxylation. Therefore, both nitrogen and carbon isotopic signatures of the porphyrins suggest considerable contribution of diazotrophic cyanobacteria in the primary production.

Moreover, all samples from the Livello Bonarelli black shale contain trace amounts of porphyrins with more than 34 carbon atoms that should have derived from

bacteriochlorophylls *c*, *d*, and *e* of the obligate anaerobic photoautotroph, green sulfur bacteria. It thus suggests presence of reduced, anaerobic water mass within the photic zone ($0 < 200\text{m}$) in a strongly stratified water column. In fact, the dominance of diazotrophic cyanobacteria in primary production should be an inevitable consequence of water column stratification due to diminished supply of dissolved inorganic nitrogen to the surface water.

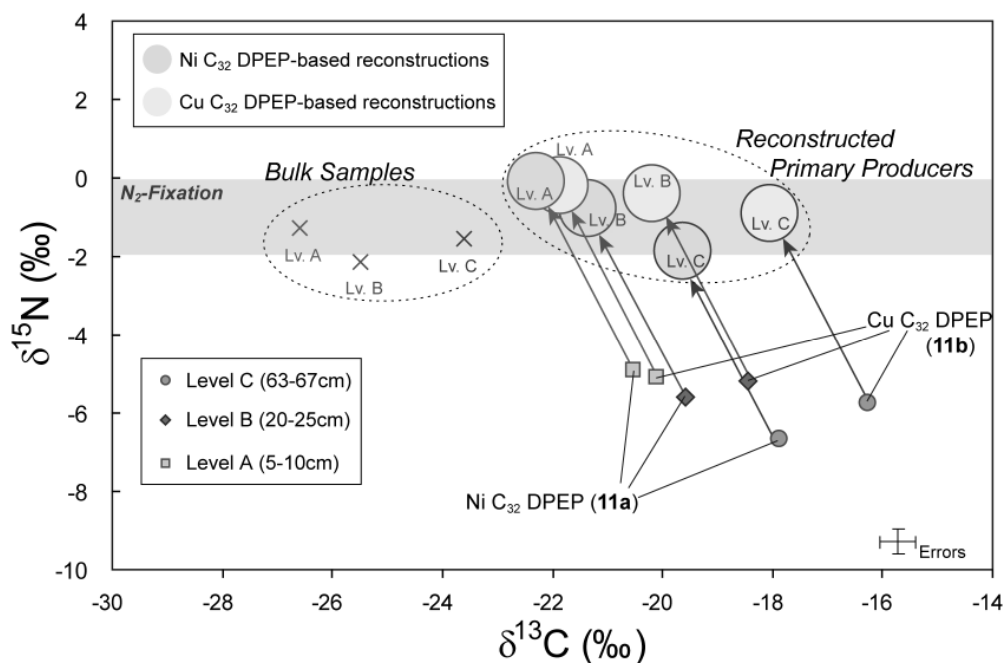


Figure 1. Reconstructed $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ values of photoautotrophic cells from the Livello Bonarelli black shale. Circles indicate approximate ranges of mean isotopic compositions for the photoautotrophic community reconstructed from by Ni and Cu C_{32} DPEPs for each stratigraphic level. $\delta^{15}\text{N}$ for diazotrophic photoautotrophs is expected to be -2 to 0 ‰. Isotopic compositions of bulk organic matters are plotted as well.

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HOW LARGE WAS THE “TRUE” CARBON ISOTOPE EXCURSIONS AT THE PETM?

Francesca A. SMITH¹, Katherine H. FREEMAN² and Scott L. WING³

1. *Department of Earth and Planetary Sciences, Northwestern University, 1850 Campus Drive, Evanston, IL, 60208, USA, cesca@earth.northwestern.edu*

2. *Department of Geosciences, The Pennsylvania State University, 235 Deike Building, University Park, PA 16802*

3. *Department of Paleobiology, National Museum of Natural History, Smithsonian Institution, Washington, D.C., USA.*

The Paleocene-Eocene Thermal Maximum (PETM) is a period of extreme and abrupt global warming that coincides with a pronounced negative carbon isotope excursion (CIE) in both terrestrial and marine carbonate and organic matter. Although the cause of the CIE is debated, all proposed mechanisms call for the rapid addition of ¹³C-depleted carbon to the ocean-atmosphere-biosphere system. If processes that fractionate carbon isotopes operated in the same way during the PETM as before and after, then terrestrial and marine reservoirs should show a uniform shift in values of the same magnitude. Instead, terrestrial leaf wax lipids demonstrate a CIE of 5-6‰ or more, whereas the marine carbonate CIE is only 3-4‰.

One hypothesis is that the marine carbonates have been isotopically altered, and that the leaf wax lipid record demonstrates the true magnitude of the CIE (5-6‰) (Pagani et al., 2006). Ocean acidification during the PETM would have led to non-deposition and dissolution of carbonate preventing the accumulation of marine carbonate at the base of the PETM (Zachos et al., 2005). In addition, reduced pH and carbonate concentrations at the base of the PETM would have led to more positive carbon isotope ratios of marine carbonate, reducing the magnitude of the excursion by up to 0.5‰ until pH rebounded (Bowen *et al.*, 2004).

Here we examine this hypothesis by assuming that our leaf wax lipid record from the Bighorn Basin, WY, USA, represents the true magnitude of the CIE (5‰). We estimate the expected marine carbonate CIE by first calculating the carbon isotope signature of atmospheric CO₂ and then calculating the δ¹³C values for calcite in equilibrium with atmospheric CO₂ (via dissolved inorganic carbon). Because the equilibrium fractionation factor between calcite and CO₂ is temperature-dependant, the warmer PETM causes the estimated marine carbonate CIE to be 6‰, even larger than that observed in leaf waxes. The largest CIE observed in marine carbonate is 4‰ (Fig. 1). If the leaf wax CIE represents the true CIE, the marine record would have to be enriched in ¹³C by 2‰ throughout the entire PETM.

To date, no mechanism has been presented that can cause a sustained 2‰ enrichment in marine carbonates throughout the PETM. The effects of ocean carbonate and acidification would be concentrated at the beginning of the PETM and are estimated at 0.5‰. Therefore, we support the alternative hypothesis, that the leaf wax CIE is amplified relative to the true CIE through changes in carbon isotope discrimination by plants. Although the true CIE, meaning the net isotopic change in the combined ocean-atmosphere-biosphere reservoir, need not be that of marine carbonates (3-4‰), we have shown that it is even less likely to be that of leaf wax lipids (5-6‰) and is most likely somewhere in-between.

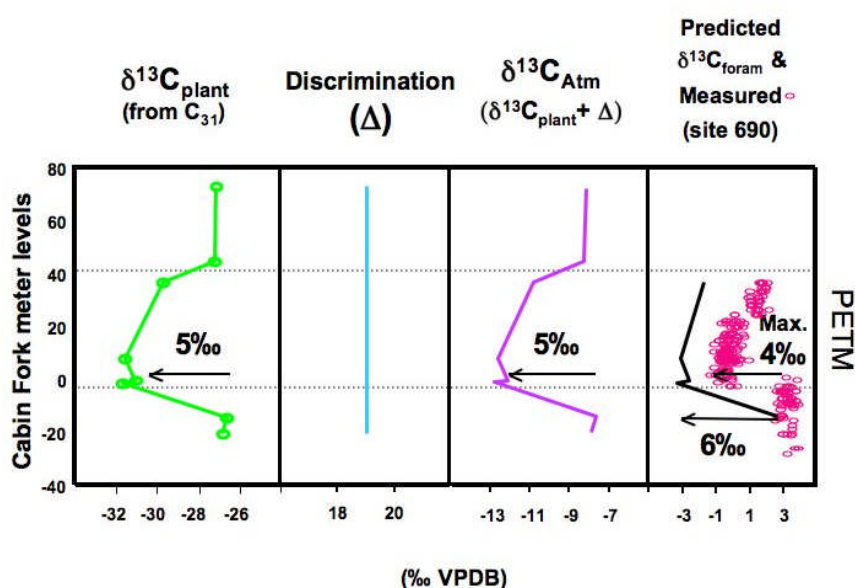


Figure 1 A) $\delta^{13}\text{C}$ of total plant tissue calculated from C_{31} n -alkane measured in the Bighorn Basin, WY, USA using $\epsilon = 4.94$ ‰. B) ^{13}C -discrimination assumed. C) Predicted atmospheric CO_2 $\delta^{13}\text{C}$. D) Predicted $\delta^{13}\text{C}$ values for marine calcite (solid line) precipitated in equilibrium with atmospheric CO_2 following. Measured values from planktonic forams from site 690 (ovals) (Thomas et al., 2002). CIE magnitude indicated by arrows.

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BIOMARKERS AND ISOTOPIC RECORDS OF CLIMATE CHANGE ACROSS THE PALEOCENE-EOCENE THERMAL MAXIMUM

Luke HANDLEY¹, Richard D. PANCOST¹, Elizabeth A. HAWKINS¹, Catherine M. BENNET¹, Paul N. PEARSON², Erica M. CROUCH³ and Paul R. BOWN⁴

1. *Organic Geochemistry Unit, Bristol Biogeochemistry Research Centre, School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK*

2. *School of Earth, Ocean and Planetary Sciences, Cardiff University, Park Place, Cardiff CF10 3YE, UK*

3. *Geological Time Section, GNS Science, PO Box 30368, Lower Hutt, NZ*

4. *Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK*

The Paleocene-Eocene Thermal Maximum (PETM), a period of abrupt and significant global warming, is one of the most dramatic climate events in the history of our planet. It is characterised by a rapid negative shift in the $\delta^{13}\text{C}$ values of marine and terrestrial carbon, a change attributed to a massive release of methane from gas hydrates. Carbon isotopic records have been obtained from terrestrial settings and used to estimate the magnitude of the shift in atmospheric CO_2 $\delta^{13}\text{C}$ values. Unfortunately, such records are limited in number and resolution. In an attempt to address this issue, we have studied two PETM sedimentary sequences dominated by terrestrial organic matter: a Kumara section (New Zealand), deposited in deltaic to nearshore marine sediments and one from Tanzanian continental margin sediments. Analyses of the distribution of higher plant and bacterial biomarkers and their carbon isotopic composition provide direct records of changes in higher plant vegetation, sedimentary redox conditions and atmospheric CO_2 .

In the Kumara section, the organic matter is dominated by terrestrial biomarkers derived from either higher plants (e.g. *n*-alkanes with a strong odd-over-even predominance) or bacteria (hopanes), consistent with deposition in a riverine or deltaic setting. *N*-alkane $\delta^{13}\text{C}$ values were measured and a 4.5‰ negative shift recorded, suggesting the studied interval spans the PETM. Interestingly, the negative isotope excursion is associated with a remarkable change in biomarker assemblages over this interval. First, pristane and phytane (derived from algal chlorophyll) and low-molecular-weight *n*-alkanes become more abundant, indicating a shift to marine dominated conditions. Second, a variety of biomarker proxies suggest that bottom waters and sediments became more reducing. Third, the abundance of oleananes, angiosperm biomarkers, increases dramatically, possibly reflecting a dramatic change in the higher plant assemblage. These shifts in depositional setting coincide with a lithologic transition and provide direct evidence for sea level rise associated with the PETM.

In the Tanzania section, similar terrestrial biomarkers abound, but in addition to *n*-alkanes and hopanes other functionalised biomolecules were also identified: *n*-alkanols and *n*-alkanoic acids (with an even-over-odd predominance) derived from higher plants and bacterially-derived hopanoids. Hopane and hopanoid abundances and distributions vary through the section, with a significant decrease in the abundances of all hopanoids just below the PETM boundary, whereas the *n*-alkanoic acid distribution switches from a short-over-long-chain predominance to a predominance of long chain components at the PETM and then back again after the event. Lower molecular weight *n*-alkanoic acids are typically derived from bacteria whereas higher plants are the primary source for their higher molecular weight homologues; therefore, these trends suggest a change in the organic matter source during the PETM, possibly driven by an increase in terrestrial runoff. The $\delta^{13}\text{C}$ values derived from *n*-alkanes reveal a negative shift of $\sim 6.5\text{‰}$ over the PETM interval. The magnitude of this shift is much greater than the value of 3‰ quoted in most of the existing literature and based on planktonic foraminifera¹.

Although these large terrestrial shifts could be the result of changes in humidity or plant distribution, it is also possible that these terrestrial records better represent the true magnitude of the carbon isotope excursion. This has implications for the quantity and source of the ^{13}C -depleted carbon, and other sources, besides methane hydrates, should be considered.

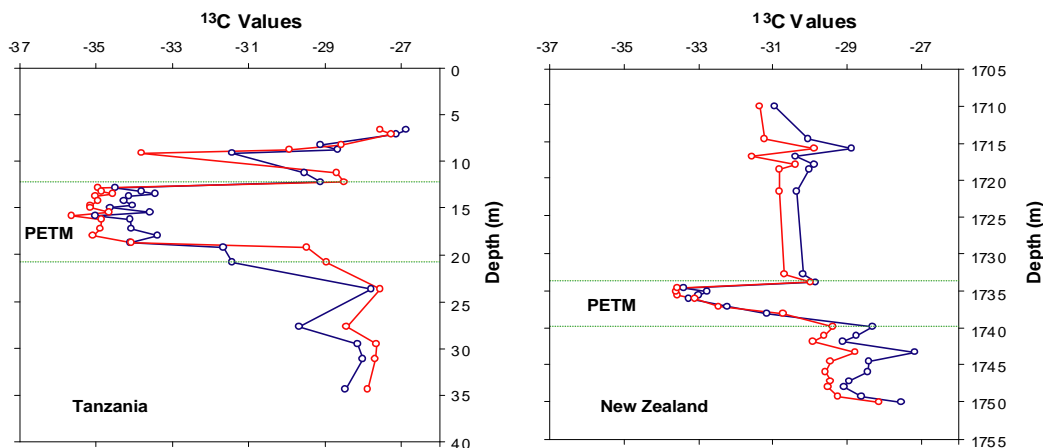


Figure 1. $\delta^{13}\text{C}$ values of higher plant derived C_{27} and C_{29} *n*-alkanes through the PETM, blue and red data points respectively. The Tanzanian setting yields a CIE of $\sim 6.5\text{‰}$, whilst the New Zealand section shows a 4.5‰ negative shift. Both values are larger than the traditional 3‰ marine excursion.

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IMPROVED UNDERSTANDING OF TERTIARY DELTAIC PETROLEUM SYSTEMS BASED ON CSIA: AN EXAMPLE FROM THE NIGER DELTA, NIGERIA

OluKayode J. SAMUEL¹, Chris CORNFORD², Martin JONES¹, Lisa PRATT³, Arndt SCHIMMELMANN³ and Chidi ENEOGWE⁴

1. CEG, Drummond Building, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK

2. Integrated Geochemical Interpretation Ltd., (IGI), Hallsannery, Bideford, EX39 5HE, UK

3. Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA

4. Geochemistry Laboratory, Mobil Producing Nigeria, QIT, Eket, Akwa Ibom, Nigeria

Recent developments in hydrocarbon exploration focus on processes and efficiencies contributing to petroleum systems. Arguably, this statement is least true for Tertiary deltas in general and the Niger Delta in particular. Despite more than four decades of active exploration, the petroleum systems operating in the Niger Delta still remain controversial. Notable is the fact that some oil accumulations reservoired within Tertiary sands show poor molecular and isotopic correlations with alleged delta source rocks.

Several studies of source rocks and oils of the Niger Delta have provided the foundations of our current understanding (e.g. Ekweozor and Okoye, 1980; Bustin, 1988; Haack et al., 2000; Eneogwe and Ekundayo, 2003). Kerogens of the deltaic source rocks have been described as terrigenous in terms of organic matter provenance with vitrinite being the most abundant maceral ($\geq 80\%$; Ekweozor and Okoye, 1980; Bustin, 1988). Most studies of Niger Delta crude oils rely on physical properties of oils and stable carbon isotope ratios of hydrocarbon fractions, in combination with molecular ratios from gas chromatography separation of gasolines and heavier hydrocarbons. However, molecular information can be misleading, where long distance migration increases the chance of leaching molecules from organic-rich rocks leading to migration contamination (Curiale, 2002). Deltaic sedimentary geometries, with multiple distal sands combining proximally, promote both leaching and the mixing of end-member oils, which confuses oil-source rock correlations based on both organofacies and expulsion maturity as measured by biological marker (biomarker) parameters.

Compound specific stable carbon isotopes analyses (CSIA) of individual compounds, particularly *n*-alkanes, in combination with a range of biomarkers, arguably offer a more reliable definition of organo-facies and hence approach to correlation. Despite successful application of CSIA in a number of basins such as the North Sea (e.g. Bjorøy et al., 1993), this technique has not been widely applied as a complementary tool to better assess the Niger Delta oil systems. CSIA data can on its own merit help to unravel and quantify the degree of oil mixing, (e.g. Rooney et al., 1998).

In this work, CSIA data are combined with high resolution biomarker and light hydrocarbon data on a suite of oils from twenty-three fields from the west, central and eastern shallow water of the delta, together with three deepwater fields. No source rocks were analysed. Based on these data, at least two petroleum systems are present in the Niger Delta, the first being a terrigenous system that is pervasive and characterized by negatively sloping $\delta^{13}\text{C}$ *n*-alkane stable carbon isotope profiles, dominant C_{29} steranes (~ 51%), indicating expulsion from a source rock deposited under oxic (Pr/Ph >2.5) and non-stratified conditions (lack of gammacerane). The second petroleum system shows evidence of generation from a source rock of marine organofacies (detection of C_{30} *n*-propyl cholestane and high % C_{27} steranes, ~ 30 %) deposited under sub-oxic (Pr/Ph ratios <2.5) and stratified (presence of gammacerane) conditions as well as positive to flat $\delta^{13}\text{C}$ *n*-alkane isotope profiles. The marine system comprises deepwater oils and some shallow water oils from the west and east. Oils of intermediate properties could reflect expulsion from an intermediate organofacies, leaching during migration or mixing. The marine system is thought to indicate expulsion from discrete *sub-delta* source rocks envisaged to have been laid down during the early opening of the central South Atlantic (mid-late Cretaceous) prior to the delta build-up, and hence are now underneath the main delta prograde. The terrigenous oils are sourced from *intra-delta* source rocks, either delta top coals or large volumes of leaner shales containing land plant exinites.

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PITFALLS AND POTENTIAL REMEDIES OF THE CURRENT OIL-SOURCE CORRELATION APPROACH: CASE STUDIES IN TWO OF THE WORLD'S LARGEST TERTIARY DELTAIC SYSTEMS

Maowen LI¹, Shuichang ZHANG², Lloyd SNOWDON¹ and Dale ISSLER¹

1. Geological Survey of Canada, 3303-33 Street NW Calgary, Alberta T2L 2A7, Canada

2. PetroChina Research Institute of Petroleum Exploration & Development, Beijing 100083, China

Biomarkers are used routinely by the oil industry to group genetically related oils, to correlate discovered oils with source rocks and to postulate the probable source rock depositional environments of migrated oils of uncertain origin. Dahl et al. (1994) suggested that biomarker distributions in reservoir oil could be used to monitor lateral facies changes in the underlying source rocks in vertically drained basins. Several case studies showed that this biomarker approach could allow petroleum geologists to constrain source rock quality, one of the key variables in petroleum systems, even when the source rock has not been penetrated. The present study uses geological and geochemical data from two of the world's largest Tertiary deltaic systems to demonstrate the common pitfall of the current oil-source correlation approach and to suggest potential remedies for addressing the problem.

The Beaufort-Mackenzie Basin is a Mesozoic-Cenozoic trough formed by the opening of the oceanic Canada Basin, with sediments prograding northwards across the continental margin from the Late Cretaceous and through the Tertiary period. Molecular, isotopic and elemental data for a set of over 150 oils from the Mackenzie Delta and Canadian Beaufort Sea have been evaluated, and the depositional environment and organic matter characteristics of the potential source units for these oils have been predicted. The deltaic sediments in the Paleogene Aklak, Taglu and Richards sequences of the Beaufort-Mackenzie Basin are molecularly distinctive, containing biomarkers indicative of a major land plant contribution. These include the high C₂₉ sterane abundance relative to other steranes, and high oleananes, 24-norlupanes, 24,28-bisnorlupanes relative to hopanes, and the presence of a battery of partially aromatized, angiosperm and gymnosperm derived polycyclic hydrocarbons. In contrast, biomarker signatures of the marine source rocks in the Upper Cretaceous Smoking Hills/Boundary Creek formations are characterized by little or no oleananoids/lupanoids, abundant C₃₀ 24-n-propylcholestanes, and an almost 1:1:1 ratio of the C₂₇:C₂₈:C₂₉ regular and rearranged steranes.

The Pearl River Mouth Basin also contains a large Tertiary deltaic system developed on the northern continental shelf of the South China Sea, with oils being produced mainly from deltaic-near shore sandstone reservoirs in the upper Oligocene Zhuhai Formation. The

likely source rocks for these oils include the lacustrine shales and mudstones of the Eocene Wenchang Formation and the shallow lacustrine-deltaic coal-bearing sequence of the Eocene-Oligocene Enping Formation. Oils derived from the lacustrine source rocks in the Wenchang Formation typically contain abundant C₃₀ 4-methylsteranes, whereas the deltaic source rocks in the Enping Formation are characterized commonly by high pristane/phytane ratios and significant amounts of C₁₉ tricyclic terpane and bicadinanes.

What is common in both Tertiary deltaic systems is that the chemical compositions across different molecular weight and polarity fractions of a large number of oils in the deltaic reservoirs do not conform to those of the known source rocks, though correlations using the routine m/z 191 and 217 mass fragmentograms would favour one particular source that contains higher biomarker concentrations. For example, the presence of abundant higher plant markers in the Paleogene oils of the Beaufort-Mackenzie Basin appears to suggest a dominant deltaic coaly source with relatively low thermal maturity for these oils. However, GC/MS/MS analyses of the saturate fractions of these oils reveal that the C₂₉ sterane dominance on the m/z 217 mass fragmentograms is in fact a mixture of a group of immature terrestrially-derived C₂₉ steranes superimposed on a group of C₂₆ to C₃₀ steranes with mature structural configurations likely from the Upper Cretaceous marine source. Mass balance calculations indicate that addition of only 5% of the immature intra-reservoir deltaic source rock extract to a mature oil originating from the Upper Cretaceous marine source rocks would turn the mixture into an “immature oil” with an apparent coaly source. This suggests that the presence of abundant higher plant markers in the oil is a necessary but not sufficient indicator for the Paleogene deltaic source. In the Pearl River Mouth Basin, in contrast, laboratory mixing experiments using selected end member oils indicate that even with 50-80% contribution from the deltaic source in the Enping Formation, the mixtures still display biomarker signatures diagnostic of the lacustrine source rocks in the Wenchang Formation. Thus, the presence of abundant 4-methylsteranes in the light oils is also a necessary but not sufficient indicator for the lacustrine source rock in this basin. As mixing is the norm in vertically drained petroleum systems and “source rock” samples are collected commonly from exactly the wrong locations for this purpose, the established paradigms of oil-source correlation in many of the world’s largest Tertiary deltas need to be re-examined.

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CHANGES IN THE BULK AND COMPOUND-SPECIFIC STABLE ISOTOPES ($^{13}\text{C}/^{12}\text{C}$ AND D/H) OF WESTERN AUSTRALIAN CRUDE OILS THROUGH TIME

Dianne S. EDWARDS¹, Chris J. BOREHAM¹, Janet M. HOPE¹, John E. ZUMBERGE² and Roger E. SUMMONS³

¹ *Geoscience Australia. GPO Box 378 Canberra, ACT 2601, Australia*

² *GeoMark Research Ltd., 9748 Whithorn Drive, Houston, Texas 77095, USA.*

³ *Department of Earth, Atmospheric and Planetary Sciences MIT, E34-246, 42-44 Carleton St, Cambridge MA 02139, USA.*

This study focuses on the changes in the stable carbon ($\delta^{13}\text{C}$) isotopic composition of the saturated and aromatic hydrocarbons in western Australian crude oils through time. From this extensive dataset, carbon and hydrogen (δD) isotopic compositions of individual C_{7+} *n*-alkanes were obtained for the major genetic oil families. The samples originate from the Arafura, Bonaparte, Browse, Canning and Perth basins, with source ages that span the Cambrian to the Cretaceous. Complementary biomarker analyses provide insights into the type of organisms preserved in the source rock, its lithology and depositional environment, as documented by Geoscience Australia and GeoMark (2005).

This study shows that the line used to separate a global set of marine and non-marine oils by Sofer (1984), is not particularly useful for western Australian oils (Figure 1). Using the combination of bulk and *n*-alkane-specific $\delta^{13}\text{C}$ isotopic profiles, oil families of Palaeozoic and Mesozoic age can be distinguished. From the Early to the Late Palaeozoic, Australian oils have become isotopically more enriched in ^{13}C . The most depleted $\delta^{13}\text{C}$ value of -32.0 ‰ is recorded for the saturated hydrocarbon fraction ($\delta^{13}\text{C}_{\text{sat}}$) of a Cambrian oil-stain in the Arafura Basin. $\delta^{13}\text{C}_{\text{sat}}$ values of about -31 ‰ are recorded for Ordovician oils from the Canning Basin, with slightly more enriched values (mean $\delta^{13}\text{C}_{\text{sat}} = -29.3$ ‰) being obtained for Late Devonian marine oils in this basin. Early Carboniferous marine oils from the Bonaparte and Canning basins have mean $\delta^{13}\text{C}_{\text{sat}}$ values in the order of -28 ‰. Permian terrestrially sourced wet gases/condensates are some of the most ^{13}C -enriched samples from western Australian, with values of around -24.6 ‰ being recorded in the Bonaparte Basin and -25.7 ‰ in the Perth Basin. Early Triassic Perth Basin oils have extremely depleted saturated hydrocarbon isotopic values of around -32 ‰ that are not as pronounced in the aromatic hydrocarbon fraction (mean $\delta^{13}\text{C}_{\text{arom}} = -29.9$ ‰), separating them from the Ordovician Canning Basin oils.

Jurassic oils from the Bonaparte, Browse and Carnarvon basins exhibit a range in their $\delta^{13}\text{C}_{\text{sat}}$ values from -26.1 to -27.8 ‰, due to generation from multiple source rocks

throughout the oil window. Their source rocks were deposited in fluvio-deltaic to marine systems and contain varying amounts of land-plant material. Early Cretaceous marine oils of the Bonaparte and Browse basins have depleted $\delta^{13}\text{C}_{\text{sat}}$ values in the order of -30.2 ‰ and -28.6 ‰ respectively, and can be differentiated from the Early Carboniferous oils on their *n*-alkane-specific isotope profiles.

The *n*-alkane-specific $\delta^{13}\text{C}$ isotopic profiles of the Palaeozoic and Mesozoic oils and condensates characteristically follow the same trend as the bulk $\delta^{13}\text{C}$ isotopic values. The *n*-alkane-specific δD isotopic profiles typically complement those of the carbon isotopic profiles for the oils derived from marine source rocks. The carbon and hydrogen profiles exhibit distinct differences in oils that originate from either non-marine systems, or, in the case of the Triassic aged Perth Basin oils, a restricted anoxic marine environment.

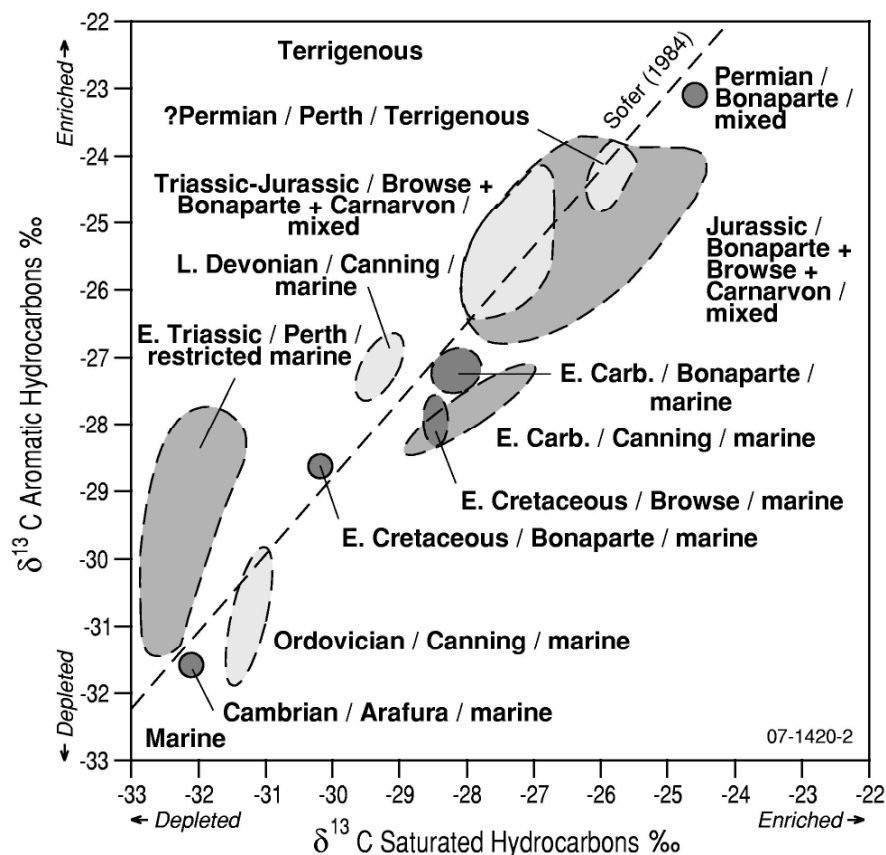


Figure 1. Stable carbon isotopic signatures of western Australian oils through time.

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