

EUKARYOTE-DERIVED STERANES IN PRECAMBRIAN OILS AND ROCKS: FACT OR FICTION?

Simon C. GEORGE¹, Adriana DUTKIEWICZ², Herbert VOLK³, John RIDLEY⁴, David J. MOSSMAN⁵ and Roger BUICK⁶

1. Australian Centre for Astrobiology, Macquarie University, Sydney, NSW 2109, Australia
2. School of Geosciences, University of Sydney, Sydney, NSW 2006 Australia
3. CSIRO Petroleum, PO Box 136, North Ryde, NSW 1670, Australia
4. Department of Geosciences, Colorado State University, Fort Collins, CO 80523-1482, USA
5. Department of Geography, Mount Allison University, Sackville, NB, E4L A7, Canada
6. Department of Earth and Space Science, University of Washington, Seattle, WA 98195-1310, USA

The record of steranes in Precambrian rocks has become a crucial line of evidence for the early evolution of life on Earth, as it has been argued that these are diagnostic biomarkers for eukaryotic organisms. The oldest reliable morphological evidence for eukaryotes occurs in the form of spheroidal acritarchs from the 1.8–1.9 Ga Chuanlinggou Formation in China (Knoll & Walter, 1992). In contrast, traces of side-chain alkylated steranes have been reported in hydrocarbons extracted from shales as old as 2.7 Ga from the Pilbara Craton (Brocks *et al.*, 1999). Unfortunately, controversy clouds reports of such sterane extracts based on (1) arguments for and against syngeneity of the steranes with the rocks, and (2) the interpretation that the steranes were derived from eukaryotes. It is generally accepted that the 1.4 Ga Velkerri Formation contains unequivocal steranes (Summons *et al.*, 1988), but older rocks such as the 1.64 Ga Barney Creek Formation may not (Brocks *et al.*, 2005). The geochemistry of oil-bearing fluid inclusions trapped in Precambrian rocks can help confirm the existence of ancient steranes. Textural relationships are used to constrain the relative timing of oil entrapment, and where this can be clearly demonstrated to have occurred during Precambrian diagenesis then the oil inclusions provide a unique repository of biogeochemical information on the early evolution of life on Earth. Hydrocarbons in oil inclusions may survive greenschist metamorphism (Dutkiewicz *et al.*, 1998) at temperatures of ca. 300°C, whereas free hydrocarbons in fine-grained rocks would have cracked to graphite and methane. Oil inclusions are completely encased in a mineral host which protects them from possible biodegradation and over-printing by later generations of Phanerozoic oil. Thus oil in inclusions is generally pristine, unaltered, and less susceptible to anthropogenic contamination that is difficult to eliminate from rock extracts.

Oil inclusions in ca. 2.45 Ga uraniferous fluvial metaconglomerate of the Matinenda Formation at Elliot Lake, Canada were trapped in quartz and feldspar during diagenesis and early metamorphism of the host rock, probably before ca. 2.2 Ga (Dutkiewicz *et al.*, 2006).

They contain an abundance of diverse steranes from C_{26} to C_{30} . The 2.1 Ga FA Formation sandstone of the Franceville Basin in Gabon that hosts the Oklo natural fission reactors also contains abundant oil inclusions, inside which syngenetic biomarkers including steranes are preserved (Fig. 1). Comparison with outside rinse and system blanks shows that only some C_{27} steranes are non-indigenous to the Matinenda and Oklo oil inclusions (Fig. 1). Extensive series of C_{26} , C_{28} , C_{29} and C_{30} steranes and diasteranes are absent from the blanks of both samples. This oil inclusion evidence supports the presence of steranes in other Palaeoproterozoic successions. If these diverse steranes come from eukaryotes, which is likely given the narrow range of steranes derived from prokaryotes (Summons *et al.*, 2006), this means that our strain of life not only survived the Neoproterozoic “Snowball Earth” events but also their Palaeoproterozoic equivalents.

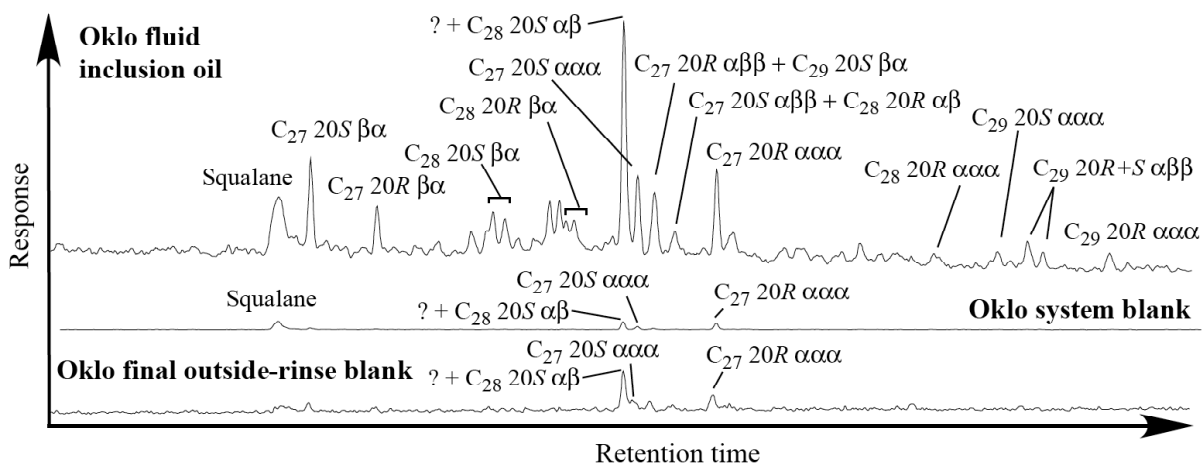


Figure 1. Partial m/z 217 mass chromatograms of the 2.1 Ga Oklo fluid inclusion oil and blanks, showing C_{27} - C_{29} steranes and diasteranes. The relative responses of the system and final outside-rinse blanks are scaled relative to the FI oil using the internal standard (squalane).

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AN EXAMPLE OF CHARGE CONTROLS ON RESERVOIR-SCALE FLUID PROPERTY VARIATIONS

Andrew BISHOP¹, Erdem IDIZ², Paul KRALERT¹, Andrew MURRAY², Mike NOSIARA¹,
Artur STANKIEWICZ² and Joe WESTRICH²

1. Shell Exploration & Production, Houston, Texas, United States.

2. Shell Exploration & Production, Rijswijk, The Netherlands.

Urdaneta Oeste is a Shell operated field situated on the southwestern edge of Lake Maracaibo, Venezuela. The field has been in operation for a long period, with in-place volumes of ~13 Bln bblsof oil and ~2.2 TCF of gas. The hydrocarbons are accumulated in four main reservoirs, namely: Icotea, Misoa, Cogollo and the Rio Negro. The shallowest reservoirs (Icotea Fm. & Misoa Fm.) have been subject to varying degrees of biodegradation, however, there is little evidence to suggest that the deeper reservoirs (Rio Negro Fm. & Cogollo Grp.) have been altered. Production is complicated by the high asphaltene concentrations in these deeper reservoirs. Stankiewicz et al. (2001) documented the asphaltene issues in the Cogollo reservoir., and a preliminary review of how the solids deposition related to geochemical processes.

The objective of this investigation has been to evaluate the controls on fluid property variation within the Rio Negro reservoir. An Integrated Charge Evaluation (ICE) project, comprising both a detailed geochemical study of available reservoir fluid samples, and a sub-regional basin model focused on the field as a whole, has been bought together to deconvolve the charge history of this reservoir. Reservoir communication / compartmentalization, and how that relates to the charge process has also been addressed. The approaches used are examples of techniques commonly applied at Shell in exploration and field appraisal.

The Rio Negro reservoir is a relatively thin (20 – 60'), distal alluvial fan sequence, comprising sands with thin shaly intercalations. The top seal for this reservoir are carbonaceous shales and clays of the Apon Fm., deposited under marine/lagoonal conditions. Porosities and permeabilities are variable but generally low (6 - 15% and 10 – 3000 mD respectively) resulting in relatively low rates of production. In terms of bulk fluid properties: oil gravities range from 27° to 32° with gas oil ratios (GOR) of the order of ~300 to 400. Asphaltene contents range from 7.8 to 13%. However, the variance of bulk properties is not systematically distributed across the reservoir. Due to the low GOR and relative undersaturation of the Rio Negro, gas lift is employed to assist with fluid recovery. This places some constraints on the geochemical evaluation, as the process impacts composition of

the light ends (e.g. C7s) and restricts gas analysis to limited data obtained from downhole MDT samples.

The source of hydrocarbons is conventionally attributed to the La Luna Fm. Typical source rock properties for the La Luna in the Maracaibo area are listed in Table 1, and these are the values used in the basin model. In addition the Aptian/Albian age Machiques Mbr. of the Apon Fm. has also been identified as an additional potential source rock in the vicinity (Perez-Infante, 1996). This source has also been included in the model, using the properties in Table 1. A 3-D basin model was run using Shell's proprietary 'Cauldron' software.

Source Rock	Average TOC (%)	Average HI	Thickness (m)
La Luna	10	553	65
Machiques	7	500	12

Table 1. Average source rock properties used in the basin model

Detailed geochemical analysis has been performed on fluid samples from 12 wells across the Rio Negro reservoir. The data acquired include complete basic oil characterization, as well as detailed molecular analysis on several different hydrocarbon fractions (i.e. gasoline fraction, adamantanes, whole oil GC, mid-range aromatics, saturate and aromatic GC-MS). CSIA has also been performed on selected species.

The results of the ICE study show that fluid properties in the Rio Negro are controlled by a complex charge history, with oils of varying maturity accumulating in the reservoir via separate charge entry points. The main phase of charge has been from the Miocene and continues to the present day. Faulting within the reservoir has helped preserve the observed variability resulting from the charge history by impairing fluid homogenization, and presenting clear evidence for compartmentalization.

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GLOBAL AND LOCAL CHANGES IN ABUNDANCES AND δD AND $\delta^{13}C$ OF BIOMARKERS ACROSS THE PERMIAN-TRIASSIC BOUNDARY

Birgit NABBefeld¹, Kliti GRICE¹, Richard TWITCHETT², Roger SUMMONS³, Steven TURGEON⁴, Arndt SCHIMMELMANN⁵, Stephen FENTON¹, Michael E. BÖTTCHER⁶ and Lindsay HAYS³

1. *Department of Applied Chemistry, Curtin University of Technology, Perth, Australia*
2. *Plymouth University, Plymouth, United Kingdom*
3. *Massachusetts Institute of Technology, Cambridge MA, USA*
4. *Department of Earth and Atmospheric Science, University of Alberta, Edmonton, Alberta, Canada*
5. *Department of Geological Sciences, Indiana University, Bloomington, Indiana, USA*
6. *Institut für Ostseeforschung Warnemünde, Rostock, Germany*

The most pronounced mass extinction in the Phanerozoic occurred near the Permian-Triassic (P/Tr) boundary (ca. 252 My ago) (Berner, 2002; Benton & Twitchett, 2003) resulting in loss of up to 95% of marine- and 75% of terrestrial species (Erwin, 1994). Volcanism, methane release from the melting of gas hydrates, bolide impact, global anoxia, oceanic overturn of stagnant deep ocean waters, and outcropping of hydrogen sulphide (Becker et al., 2004; Wignall, 2001; Krull & Retallack 2000; Wignall and Twitchett, 1996; Knoll et al., 1996; Grice et al. 2005a) are mechanisms frequently invoked and strongly debated. It has been suggested that the extinction is a “tangled web of causality” with several mechanisms contributing to the biotic crisis (Erwin, 1994; Racki and Wignall, 2005).

In the present study we focus not only on the extinction horizon but also on the prolonged recovery of the event. A multidisciplinary approach has been undertaken and includes a molecular (biomarker), stable carbon and hydrogen isotopic approach along with palynology, sedimentology, trace elements abundances and sulphur isotope studies of pyrite across the Permian-Triassic boundary and extending into the Early Triassic. Several sediment cores and samples spanning the boundary from a variety of palaeogeographical locations (Western Australia, East Greenland, Spitsbergen and Western Canada) are under investigation to establish a global data set. For the first time, biomarker abundances paired with carbon and hydrogen isotopes and sulphur isotopes of sulphides are being used to correlate events (including changes in the redox conditions) surrounding the collapse of both the marine and terrestrial ecosystems through this major crisis interval in an expanded section (40 m) from East Greenland.

Previous palynological studies on the Schuchert Dal Section have highlighted key changes in the terrestrial plant taxa through the latest Permian and earliest Triassic, displayed in the distribution of spores and pollen (e.g. Looy et al. 2001). Throughout the same period of time, significant changes are observed in the type and abundance of selected biomarkers.

Aromatic compounds (e.g. dibenzothiophene, dibenzofuran and biphenyl) and biomarkers derived from photosynthetic green sulphur bacteria are of particular interest. Recent data of the Schuchert Dal Section from samples just before the extinction horizon are characterised by high abundances of dibenzothiophene (DBT), dibenzofuran (DBF) and biphenyl (BP). We suggest that lignin derived from the woody plants present during this period could be the major source of these compounds. Just above the extinction interval, there is a dramatic decrease in the abundance of these aromatic compounds which coincides with a sudden change in $\delta^{34}\text{S}$ of sulphide minerals from -50‰ to -25‰ due to variations in the redox state of the ocean (Grice et al., 2005a). This trend is not unique to the Schuchert Dal Section as similar trends have also been observed in the Hovea-3 P/Tr section from Western Australia (Grice et al., 2005a). It is suggested that two processes are probably operating here, namely a change in redox conditions and the extinction and/or sea level transgression which could account for the absence of woody material. Further data from other sections (Spitsbergen, Western Canada) will help establish whether these processes are represented globally.

At the same time we are carrying out stable carbon and hydrogen isotopes (D/H and $^{13}\text{C}/^{12}\text{C}$) studies of selected biomarkers by compound specific isotope analyses in order to investigate appreciable changes in the biogeochemical cycling of carbon and hydrogen across the P/Tr boundary. By comparing $^{13}\text{C}/^{12}\text{C}$ and D/H of plants and algae from the land and marine realm, respectively, it is anticipated that the synchronous disturbance in oceanic and atmospheric chemistry during the end-Permian mass extinction event and its protracted recovery will be established. To support this data, D/H of kerogen (Schimmelmann et al., 2006) of selected P/Tr samples of various locations will be determined.

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