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PRELIMINARY REPORTS ON THE LIPID BIOMARKER COMPOSITION OF DRILLCORE SAMPLES FROM THE AMADEUS BASIN, NORTHERN TERRITORY, AUSTRALIA

Introduction

The aim of these investigations is to analyze the lipid biomarkers composition of Neoproterozoic sedimentary successions from the Amadeus Basin in central Australia. Lipid biomarkers allow for a study of microorganisms in the context of their environments. Since the appearance of life on Earth, biospheres and geospheres have evolved together and their records are chronicled in sedimentary and metasedimentary rocks spanning billions of years (Brocks and Pearson 2005). Since life evolved to cope in different environmental niches, taxonomically diagnostic lipid biomarkers can act as indicators of palaeoenvironmental conditions as well. With regards to the reconstruction of palaeoenvironments, lipid biomarkers have, for example, been used for elucidating hypersaline conditions from Miocene/Pliocene halite-rich deposits (Grice et al. 1998), a sulfidic ocean in the Proterozoic (Brocks et al. 2005), and an apparent radiation of crenarchaeota associated with Cretaceous oceanic anoxic events (Kuypers et al. 2001). Such examples clearly demonstrate the applicability of lipid biomarker work for elucidating ancient ecosystems and environments. However, there are also important limitations, which need to be taken into account. These limitations are discussed below.

Before commencing the analyses, care was taken to circumvent any issues associated with contamination. Thus far, most lipid biomarker studies have not taken contamination problems into account. However, it has now become clear that rocks can be exposed to a variety of organic contaminants that derive, for example, from drilling fluid, diesel fumes and storage bags. Biomarker contamination would be particularly detrimental if the rock samples in question were low in total organic carbon (TOC). In addition, non-indigenous bitumen could migrate from their source rocks to the samples being analysed. Such a process may lead to non-anthropogenic contamination.

For the above reasons, the outer edges of all samples were removed by a process of cutting them off or ablating for several hours. This technique would remove the outer portions of samples where contaminants are likely to become concentrated. If a particular biomarker is exclusively present on the surface or at a greater amount than in the inside, then it is likely that the marker in question is a potential contaminant. Samples denoted “outside” and “inside” in this report refer to the outer and inner portions of a rock sample, respectively.

Note that all geochemical analyses of these samples is destructive. It requires the crushing up of rock samples, followed by solvent extraction of bitumen. The remaining rock powder is then acid digested for sulphur and iron analyses.

Currently, rock powders of samples from *Mt Charlotte 1* and *Mt Winter 1* are being analysed for sulphur isotopic analyses in the U.S.A. Rock powders of samples from *Wallara 1,* CMS 1, Illogwa Creek 6 & Elkedra 6 have been divided into two fractions, half of the samples is currently being processed for organic geochemistry in the Brocks laboratory at RSES. The other portion of samples has been sent to the UK where the iron and sulphur speciation will be analysed in the first fortnight of June, 2010.

Methods of analyses:

Processing of rock samples

Surfaces of samples to be analysed for biomarkers were either ablated for several hours or cut off to remove the outer and inner portions of the rocks. The portions were analysed separately to reveal hydrocarbon contaminants. The dried rock samples were ground to powder in an alumina ring-mill. The mill was cleaned between samples by grinding baked-out (600°C/24 h) quartz- rich sand two to three times for 60 s. Approximately 5 to 32 g rock powder were extracted with 100% dichloromethane (DCM) in a Dionex Automated Solvent Extractor. The extracts were reduced to 100-500 µL under a stream of purified nitrogen gas and separated into saturated, aromatic and polar fractions using column chromatography over 12 g annealed (450°C/24 h) and dry-packed silica gel (Silica Gel 60; 230-400mesh; EM Science). Saturated hydrocarbons were eluted with 1.5 dead volumes (DV) *n*-hexane, aromatic hydrocarbons with 2 DV *n*-hexane:DCM (1:1 v/v) and polars with 2 DV DCM:methanol (1:1 v/v). After fractionation, 2.3 µg 18-methyleicosanoic acid methyl ester (MEME) was added as an internal standard to the saturated and aromatic hydrocarbon fractions.

Gas chromatography-mass spectrometry (GC-MS)

Saturated and aromatic fractions were subsequently analysed using gas chromatography-mass spectroscopy (GC-MS) on a Micromass AutoSpec Premier equipped with a HP6890 gas chromatograph (Agilent) and a DB-5 capillary column (60 m x 0.25 mm i.d., 0.25 µm film thickness) using He as carrier gas. The MS source was operated at 260°C in EI-mode at 70 eV ionization energy and with 8000 V

acceleration voltage. Samples were injected in splitless mode into a split/splitless injector at a constant temperature of 300°C. For full-scan analyses, the GC oven was programmed at 40°C (2 min), heated to 315°C at 4°C/min, with a final hold time of 49 min. The AutoSpec full-scan duration was 0.7 s plus 0.2 s interscan delay over a mass range of 55-600 Da.

Gas chromatography-mass spectrometry-mass spectrometry (GC-MS-MS)

GC-MS-MS is a technique which allows for ions with the same base peak in GCMS experiments, such as the various isomers of C_{27}, C_{28} and C_{29} steranes to be monitored separately without interference from molecules with other molecular masses (Peters *et al.*, 2005). The Autospec MS employed in this study performs GCMSMS in Metastable Reaction Monitoring (MRM) mode. For GCMSMS (MRM), the GC oven was programmed at 60°C (2 min), heated to 100°C at 8°C/min, and further heated to 315°C at 4°C/min with a final hold time of 34 min.

The following experiments are scheduled for June to October 2010

Iron and sulfur extraction and isotope measurement.

A stepwise procedure removes different pools of iron from a sediment sample. The samples will be ground to powder (<63 mesh) in an alumina ring-mill. 0.2 g of sample is added to a plastic centrifuge tube. The sample is extracted first with sodium acetate for 24 hours (to remove carbonate Fe including sidrite), then extracted with hydroxylamine hydrochloric acid for 48 hours (to remove ferrihydrite, lepidocrocite), extracted with dithionite for 2 hours (to remove goethite, akangenite and hematite), extracted with oxalate for 6 hours (to remove magnetite) and finally extracted with boiling 12 N HCl (to remove poorly reactive sheet silicate Fe). For each extraction stage, the sample will be continuously mixed at 50°C for approximately 15 minutes or until the sample flocculates. The clear extracts of each reaction are pipetted into vials and analysed by atomic absorption spectrometry (AAS). The total iron is removed by digesting 100mg of crushed sample in a $HF:HClO_4:HNO_3$ mixture for 48 hours. The clear extract will be analysed for total iron by AAS.

The total reduced sulphur (TRS) will be extracted with the chromium reduction methodology of Canfield et al. (1986). The sulphide precipitated as Ag2S. The precipitate was weighed to determine the concentration of pyrite sulfur and the amount of Fe bound in pyrite. The sulphur was then analysed for isotopes

Biomarkers analysis of evaporitic sedimentary successions from the Amadeus Basin, Northern Territory, Australia. Cores analysed: *Mt Charlotte 1*; *Mt Winter 1*.

Research conducted by: Richard Schinteie

Rationale

The aim of this work was to investigate the microbial diversity of a Precambrian hypersaline setting using lipid biomarkers as a proxy. This work is part of a PhD thesis conducted at the Research School of Earth Sciences, Australian National University, Canberra.

In order to assess changes in microbial ecosystems over geologic time, it is important to focus on a variety of different environmental settings. Dissimilar environments offer different ecological niches which organisms can exploit. Such niches may respond differently to environmental changes over time. To reach a broader conclusion on the evolution of microbial ecosystems during the Neoproterozoic to Cambrian interval, lipid biomarkers derived from evaporites of this time frame are investigated. Evaporite deposits are particularly common in Neoproterozoic strata from the Centralian Superbasin in Australia and provide ideal sites for the investigation of ancient hypersaline settings.

Samples analysed

A total of 23 *Mt Charlotte 1* (801.3-2116.2 m depth), and five *Mt Winter 1* (1338.5-2190.1 m depth) drill core samples were analysed, to determine their lipid biomarker composition. These samples appear to have been derived from evaporitic sediments of the early Neoproterozoic (mostly Gillen Member, Bitter Springs Formation). Microscopic (see Figure 1) and X-ray powder diffraction work indicated that the majority of samples analysed for biomarkers were composed of halite, anhydrite and dolomite. Shale samples were also investigated. Unless otherwise stated, all results described pertain to those obtained from the *Mt Charlotte 1* core. Those results obtained from the *Mt Winter 1* core are described further below.

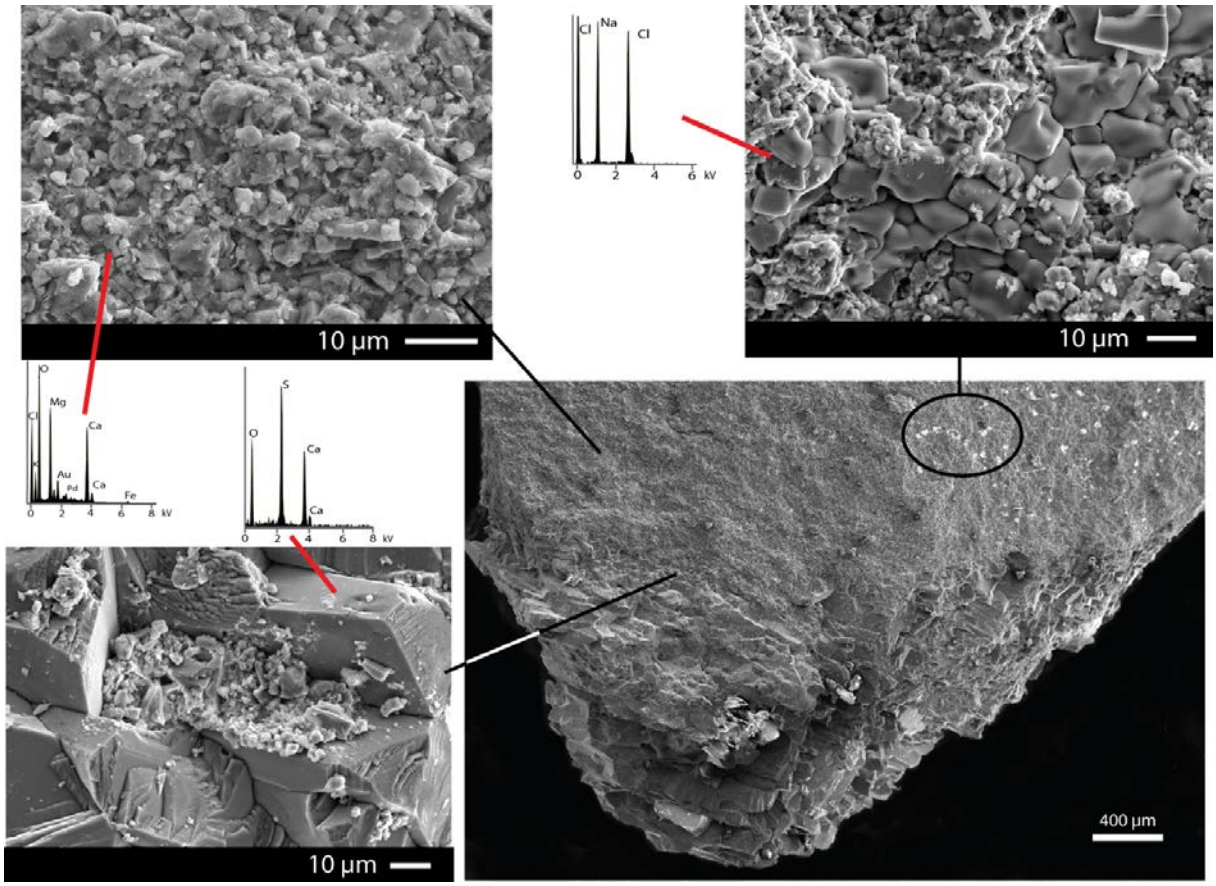

Figure 1. Scanning electron microscopy images and accompanying EDS spectra of a representative evaporitic Gillen Member sample (large image on the bottom right) containing dolomite (top left image), anhydrite (bottom left image) and halite (top right image).

Results and implications:

Whole-rock samples investigated by ablation

In several cases, the resulting patterns looked superficially typical of what is expected of Neoproterozoic samples (Fig. 2) (for comparisons with previously studied Precambrian bitumen see, for example, Summons et al. 1988a, b). The samples in this study have high ratios of monomethylalkanes and dimethylalkanes over *n*-alkanes. A reverse trend is usually observed in bitumen from the Phanerozoic.

In most samples, the concentration of docosane (nC_{22}) was particularly prominent. A predominance of this molecule has been previously observed from ancient saline environments and is proposed to serve as an indication for ancient hypersaline conditions. The biological and chemical origin(s) for the nC_{22} component is/are unknown. Some organisms (particularly algae) were found to produce the saturated hydrocarbon docosane directly (e.g. Dayananda et al. 2006). But it has also been suggested that the abundance of this compound in ancient settings is associated with the prominence of C_{22} alkenoic acids in various algae .

Acyclic isoprenoids were evident in mass/charge (*m/z)* 183 chromatograms and were tentatively identified as a series of regular (*m/z* 183, 253) and tail-to-tail (*m/z* 183, 239, 267) isoprenoids. It is possible that head-to-head isoprenoids are also present. The isoprenoids were particularly evident in samples that appeared to have been biodegraded (Fig. 3); the *n*-alkanes appeared depleted, while the isoprenoids were particularly prominent.

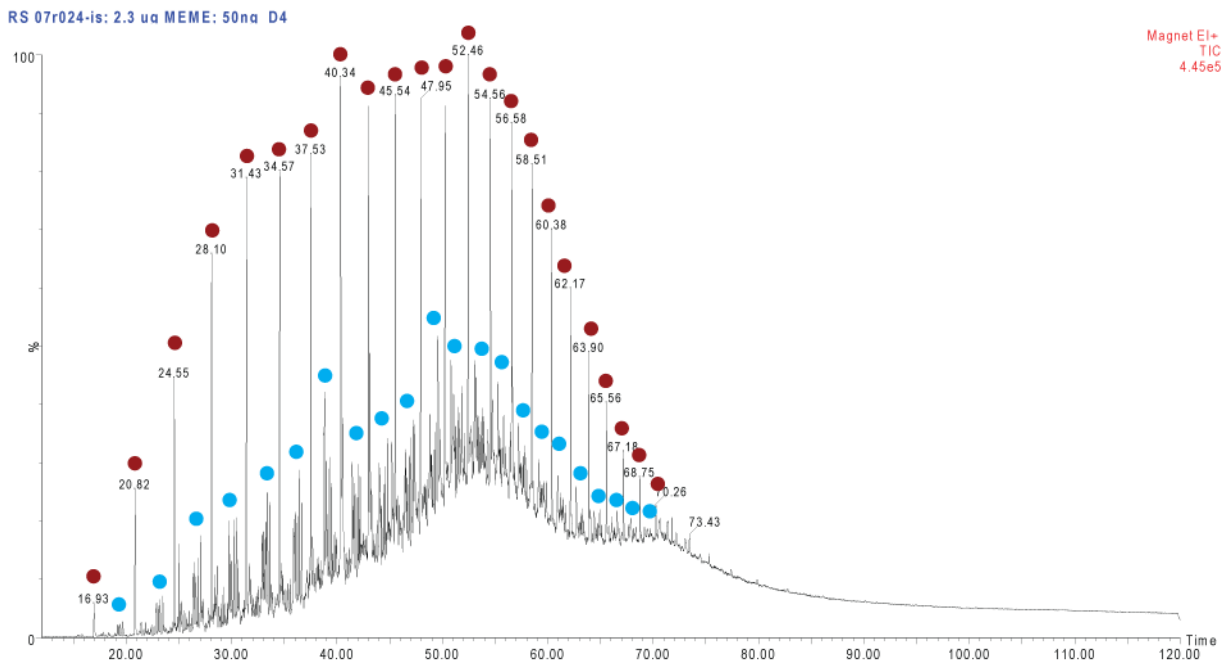

Figure 2 GC/MS full scan of Gillen Member bitumen from the Neoproterozoic Gillen Member, Mount Charlotte 1 drill core, representative for bitumens of an evaporitic lithology at depth of 5100 to 5400 m. Blue circles indicate the position of monomethylalkanes. Red circles indicate the position of *n*-alkanes.

IS

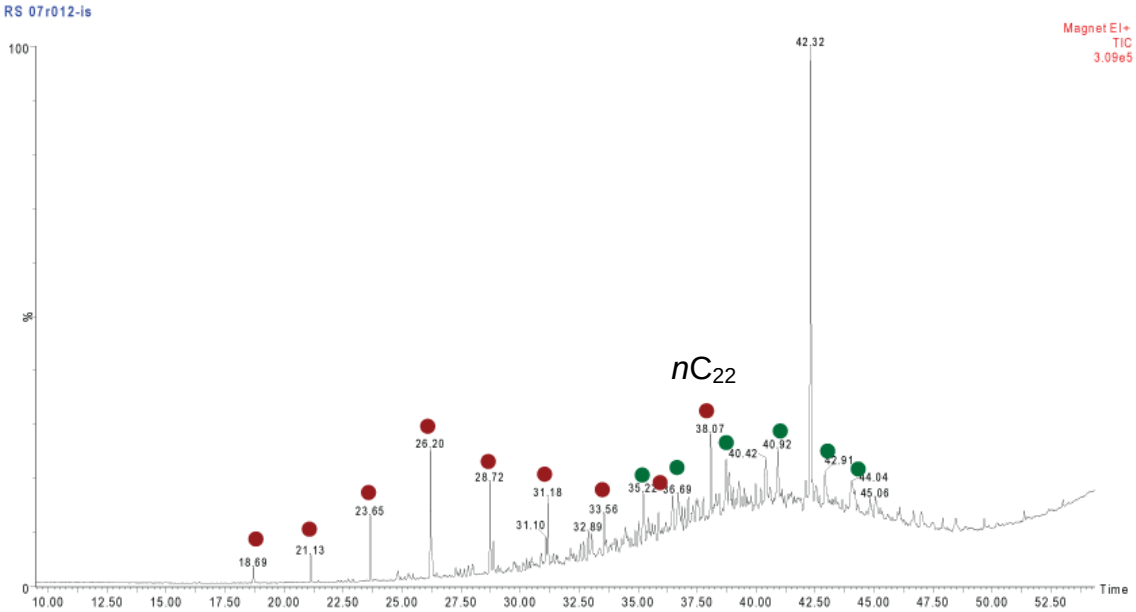

Figure 3 Example of biodegraded bitumen from a mud rock that was associated with halite, *Mt Charlotte 1*. Red circles indicate the position of *n*-alkanes. Green circles indicate isoprenoids. IS = internal standard. Note the relatively high concentration of nC_{22}.

As mentioned above, interior/exterior experiments (by ablating the surfaces) were conducted on *all Mt. Charlotte 1* samples analysed. Such analyses were particularly successful in highlighting significant differences in biomarker compositions between the inner and outer portions of the rock samples. For example, numerous hopanes and steranes were observed only in the outer portions, but were absent in the inside. While the inside-outside experiments were straight forward for some molecules, finding explanations for the differential distributions of numerous *n*-alkanes, monomethylalkanes, isoprenoids and aromatic compounds was not. In most samples, these molecules were predominantly present in the outer portion (Fig. 4). While the same molecules were also present in the inner portions of most samples, they were usually present at lower concentration. In some instances, the ratio of outside to inside concentrations for certain molecules were at a value of > 5. In other samples, it was closer to one. In the most extreme cases, hardly any molecules (including aromatics) were to be found in the inside (Fig. 3). Finding precise explanations for such differential distributions is difficult. It may be that a large number of these molecules were derived from contaminants such as drilling fluids, diesel fumes, and storage material. Alternatively, the molecules came from indigenous sources of Neoproterozoic and/or Cambrian rock and migrated (possibly as oil) through nearby rocks that were devoid of bitumen. Such “oils” could settle on exposed surfaces or within cracks and pores of rocks.

Halite crystals investigated by ablation

Large, subangular halite crystals (1-3.8 cm in width; 4.1-2.7 cm in length) from the Cambrian Chandler Formation were also investigated for their potential biomarker content. Only crystals were selected that did not appear oxidized (i.e. were red in colour). The results of this study (not shown in graphical form here), indicated that virtually all hydrocarbons were concentrated on the exteriors, while the interiors were largely devoid of biomarkers. The hydrocarbon patterns also displayed a predominance of nC_{22}, as well as a higher concentration of high molecular weight *n*-alkanes. A higher relative concentration of these heavier molecules is likely a result of evaporation of the lighter counterparts. It is postulated that the smooth surface of halite enhances the evaporation processes in comparison to clay.

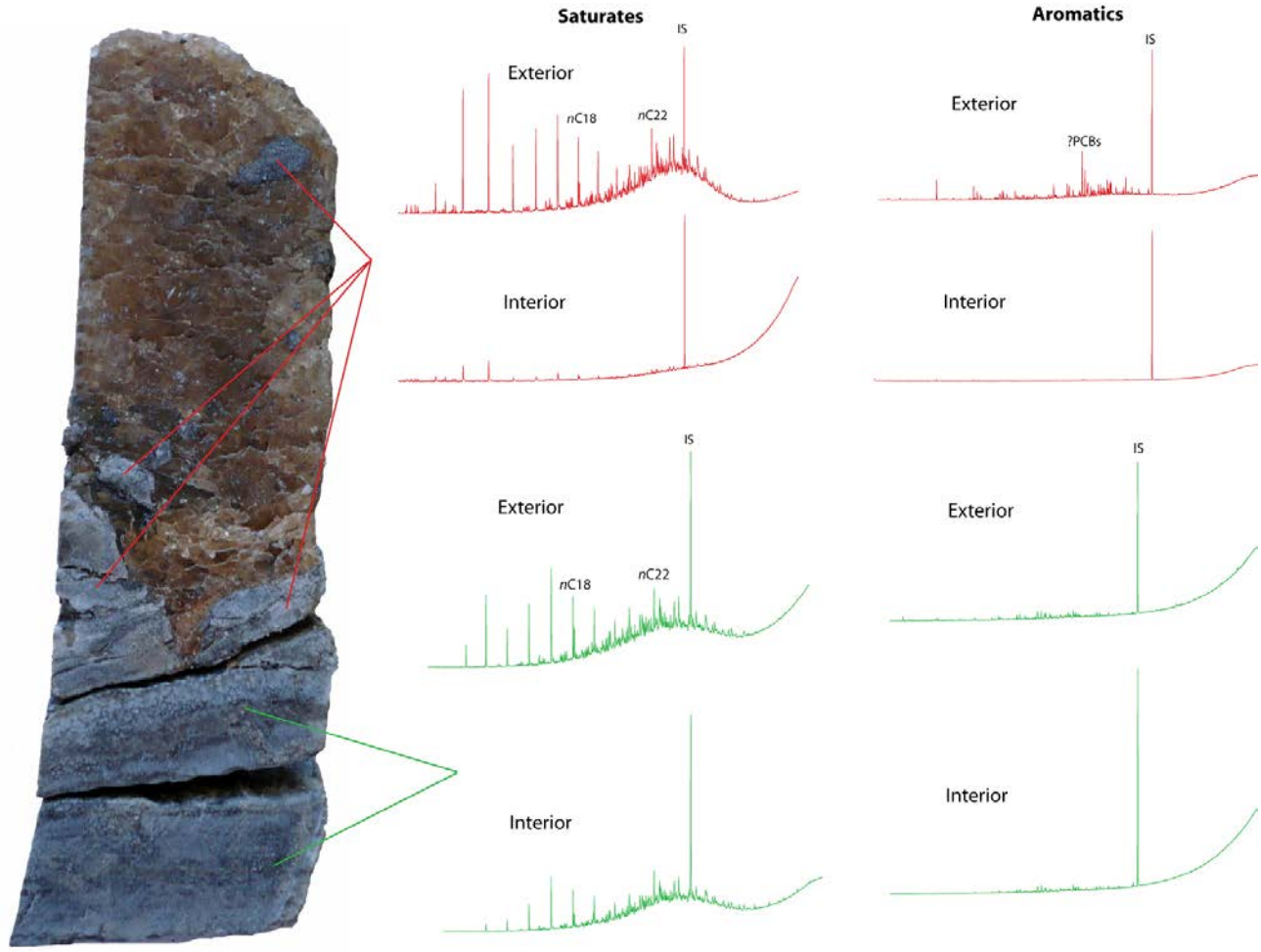

Figure 4 Biomarker patterns obtained from mud rocks and overlying halite. This sample (see text) is from the Neoproterozoic Gillen Member and was collected from the Mount Charlotte 1 drill core. Position of nC_{22} is indicated. Position of nC_{18} is indicated for reference. IS=internal standard. ?PCBs=peaks indicating the possible presence of polychlorinated biphenyls in the aromatic fraction.

Whole-rock samples investigated by sawing

In an attempt to distinguish between indigenous biomarkers and contaminants, a total of 18 additional samples were selected from the Mt Charlotte 1 drill core stored in Canberra. These samples were also derived from evaporitic facies of the Neoproterozoic Gillen Member and the Cambrian Chandler Formation. The aim was to conduct alternative interior/exterior experiments by removing the exterior of the samples with a precision saw. Since the rounded surfaces of drill core rocks would come into direct contact with drilling fluids, it is most probable that they contain the highest concentration of contaminants. Therefore, by separating these exterior surfaces and comparing their hydrocarbon contents with the interior portions, it should be possible to detect possible contaminants.

For this type of experiment, quarter cores of samples were collected which possessed the rounded exterior surfaces. It was also ensured that these samples possessed no visible cracks. Prior to sawing, all samples were wetted with distilled water and dried in a fume hood. Samples with cracks would hold moisture slightly longer than other areas. By observing this drying process, cracks could be more easily identified.

Numerous samples displayed distinct differences between the interior and exterior. The differences were especially evident in the differential distributions of hopanes (Fig. 5) and steranes (Fig. 6). *Mt Charlotte 1* samples yielded numerous hydrocarbon patterns that had a strong Precambrian appearance (e.g. high dimethyl- and monomethylalkane concentrations relative to their *n*-alkane equivalents). In addition, samples deemed evaporitic contained a strong predominance of iC_{25} and iC_{30} (Fig. 7). These molecules are commonly observed in hypersaline environments. Membrane lipids of halophilic Archaea, contain glycerol ethers with C_{20} and C_{25} regularly branched acyclic isoprenoid side chains. Degradation products of these glycerol ethers are often preserved in sedimentary rocks associated with evaporitic deposits. For example, Grice et al. (1998) discovered hydrocarbons in Miocene/Pliocene sediments from the Dead Sea Basin, Israel, with regular isoprenoids of 19 to 25 carbon atoms.

The exterior surfaces possessed greater concentrations of higher molecular weight *n*-alkanes, particularly $\geq nC_{19}$. A higher concentration of heavy hydrocarbons in the exterior may be a result of the type of contaminants that came into contact with these samples, or a result of higher evaporation rates of light hydrocarbons encountered on the exterior surfaces. While higher evaporation rates would lower the concentrations of hydrocarbons of low molecular weight, it would not be able to do so to heavier ones. A clearer picture on the differential distribution of nC_{22} has also emerged in these samples (Fig. 8). This molecule has been observed to be at significantly higher concentrations in the exterior than in the interior. Indeed, full scan profiles show that this molecule is only prominent on the exterior. Therefore, the predominance of nC_{22} in *Mt Charlotte 1* samples is the result of contamination. However, whether this molecule was present in drilling fluid contaminants is unclear. It may also be possible that this molecule is present in horizons not yet identified. As mentioned above, a predominance of this molecule in hydrocarbon profiles is rare and usually associated with hypersaline settings. However, other sources for docosane (e.g. artificial contaminants) should not be excluded. Regardless, the above results clearly demonstrate the value of interior/exterior experiments in assessing actual patterns that would otherwise be overprinted by contamination.

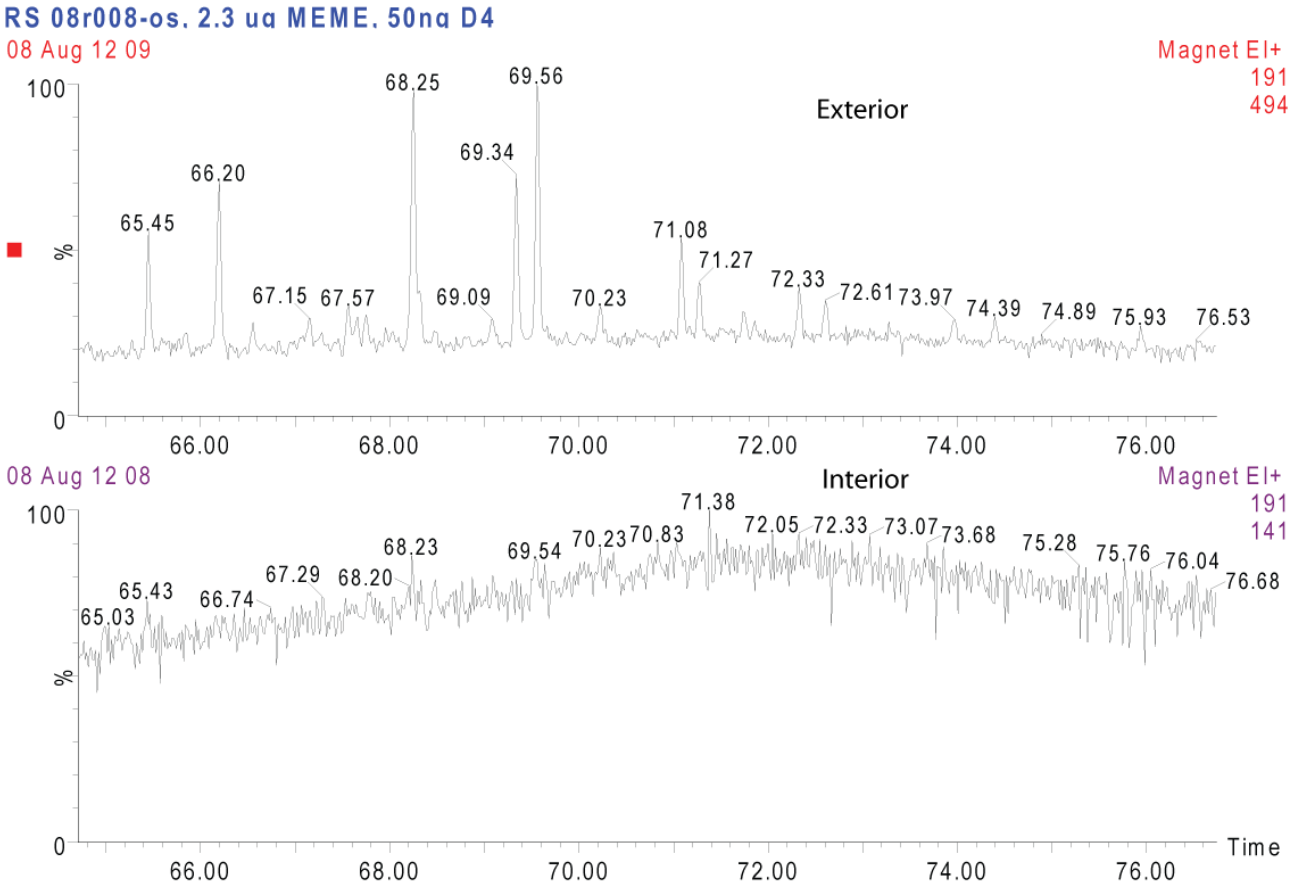

Figure 5 Gas chromatograms of hopanes. The upper chromatogram is from the exterior of a Gillen Member sample and is generally representative for MtCharlotte-1 core evaporites (see Table), while the bottom one is from the interior of the same sample. Chromatograms are visualized at m/z 191.

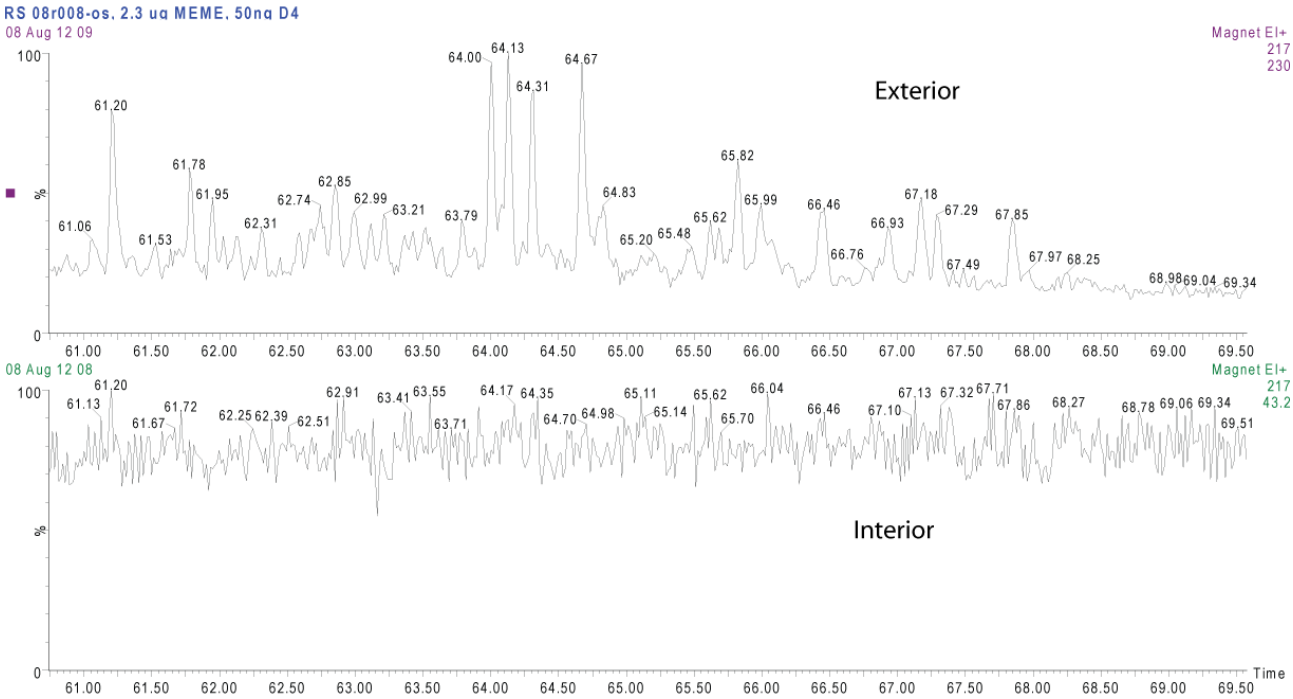

Figure 6 Gas chromatograms of steranes. The upper chromatogram is from the exterior of a Gillen Member sample and is generally representative for MtCharlotte-1 core evaporites (see Table), while the bottom one is from the interior of the same sample. Chromatograms are visualized at m/z 217.

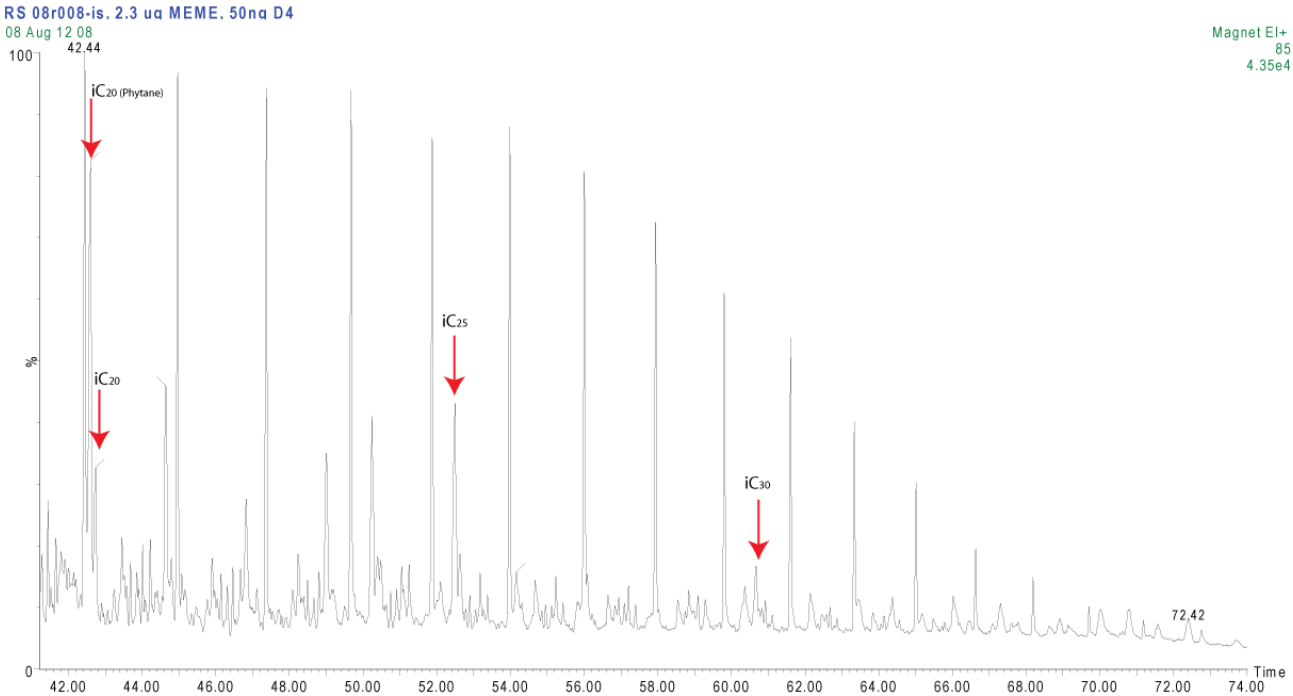

Figure 7 Gas chromatogram of an evaporite sample highlighting acyclic isoprenoids. The sample was collected from the Neoproterozoic Gillen Member and is generally representative for analyzed evaporite samples of *Mt Charlotte 1* drill core (see Table). Red arrows indicate acyclic isoprenoids of particular interest. Not the elevated concentrations of iC_{25} and iC_{30}. Also note the presence of an additional iC_{20} isoprenoid next to phytane. Chromatogram is visualized at m/z 85.

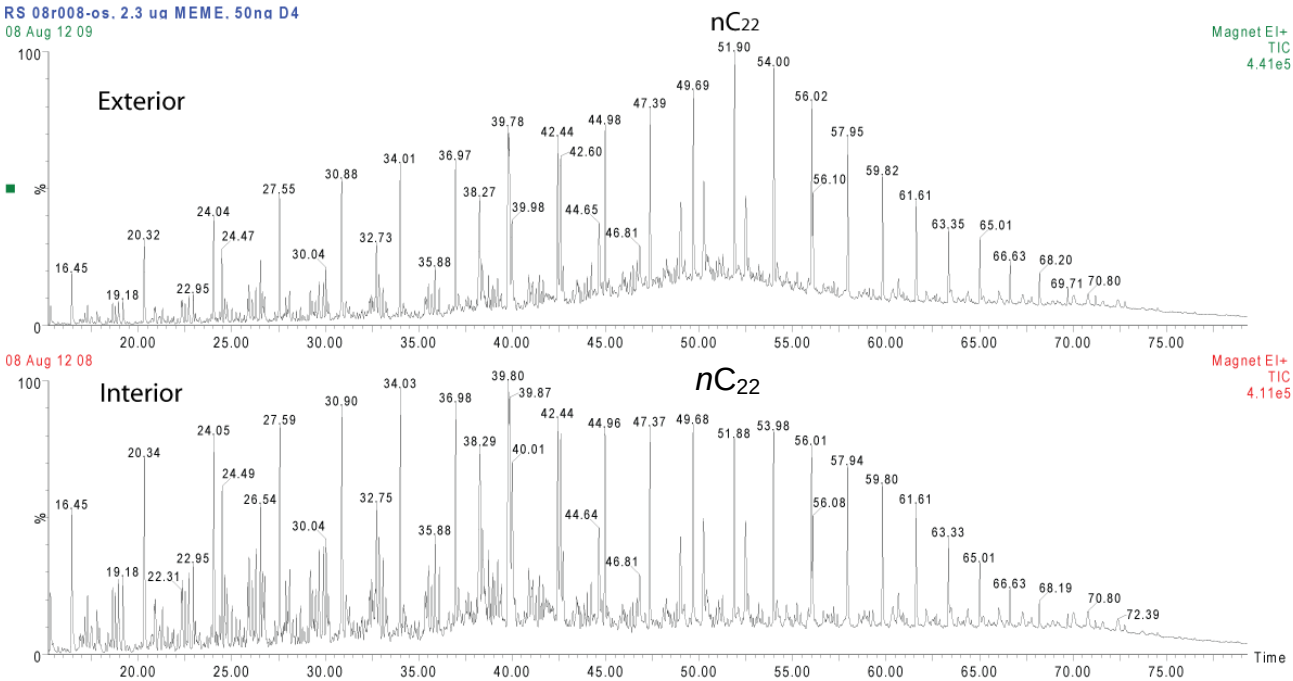

Figure 8 Gas chromatogram of evaporite sample at full scan. Sample was collected from the Neoproterozoic Gillen Member and is generally representative for analyzed evaporite samples of *Mt Charlotte 1* drill core (see Table). Note that nC_{22} is present at a higher concentration of the exterior than in the interior.

Broad classification of indigenous Precambrian biomarkers

Three major indigenous patterns from extracts of the Gillen Member were able to be discerned (Figure 9). These patterns are broadly described below. The aim here is to provide a simple overview of each type of GC pattern.

One type of GC pattern was characterized by high concentrations of mono- and dimethylalkanes relative to *n*-alkanes, and a low abundance of isoprenoids. The latter would be present in the form of low concentrations of regular as well as head-to-head isoprenoids relative to *n*-alkanes (Figure 9A). This type of pattern would be derived from rocks with relatively low concentrations of anhydrite and a greater concentration of dolomite and siliciclastics. Rocks of this type tend to be quite dark in color.

Another type of GC pattern would yield a hydrocarbon signature that also exhibits high concentrations of mono- and dimethylalkanes relative to *n*-alkanes (Figure 9B). However, this pattern is characterized by significantly high concentrations of regular and irregular (tail-to-tail and head-to-head) isoprenoids. This type of pattern is derived from samples that have a much larger concentration of anhydrite relative to the first patterns. Nevertheless, significant concentrations of dolomite are still present in the form of flat as well as twisted and deformed laminae. Siliciclastics may also be present in the form of quartz.

The third and final pattern is characterized by relatively low concentrations of mono- and dimethylalkanes relative to n-alkanes (Figure 9C). Furthermore, the relative concentration of *n*-alkanes relative to the regular isoprenoids is also particularly low. The concentration of extracted bitumen is also quite relatively low, as is witnessed by the higher concentration of internal standard relative to the n-alkanes and isoprenoids. This observation is in contrast to the previous two patterns, which exhibited much higher yields of bitumen. The third GC- pattern is derived from samples composed of high concentrations of anhydrite with very little input of dolomite or siliciclastics.

Further work is currently being conducted to fully characterize these samples. Forthcoming results will be published soon.

As mentioned above, five *Mt Winter 1* drill core samples were also analysed for lipid biomarkers. These were also derived from Neoproterozoic evaporite sequences. Unfortunately no indigeneous biomarkers were obtained from these samples.

<u>Biomarkers analysis of glacial sedimentary successions from the Amadeus Basin, Northern Territory, Australia. Cores analysed: Erldunda 1.</u>

A total of two samples from the Neoproterozoic section of the *Erldunda 1* core were analysed for lipid biomarkers. The depths of these samples are uncertain, but were collected from the top and middle of core 5. The sediments of these rock samples have been deposited during a glaciation event. Unfortunately no indigeneous biomarkers were obtained from these samples.

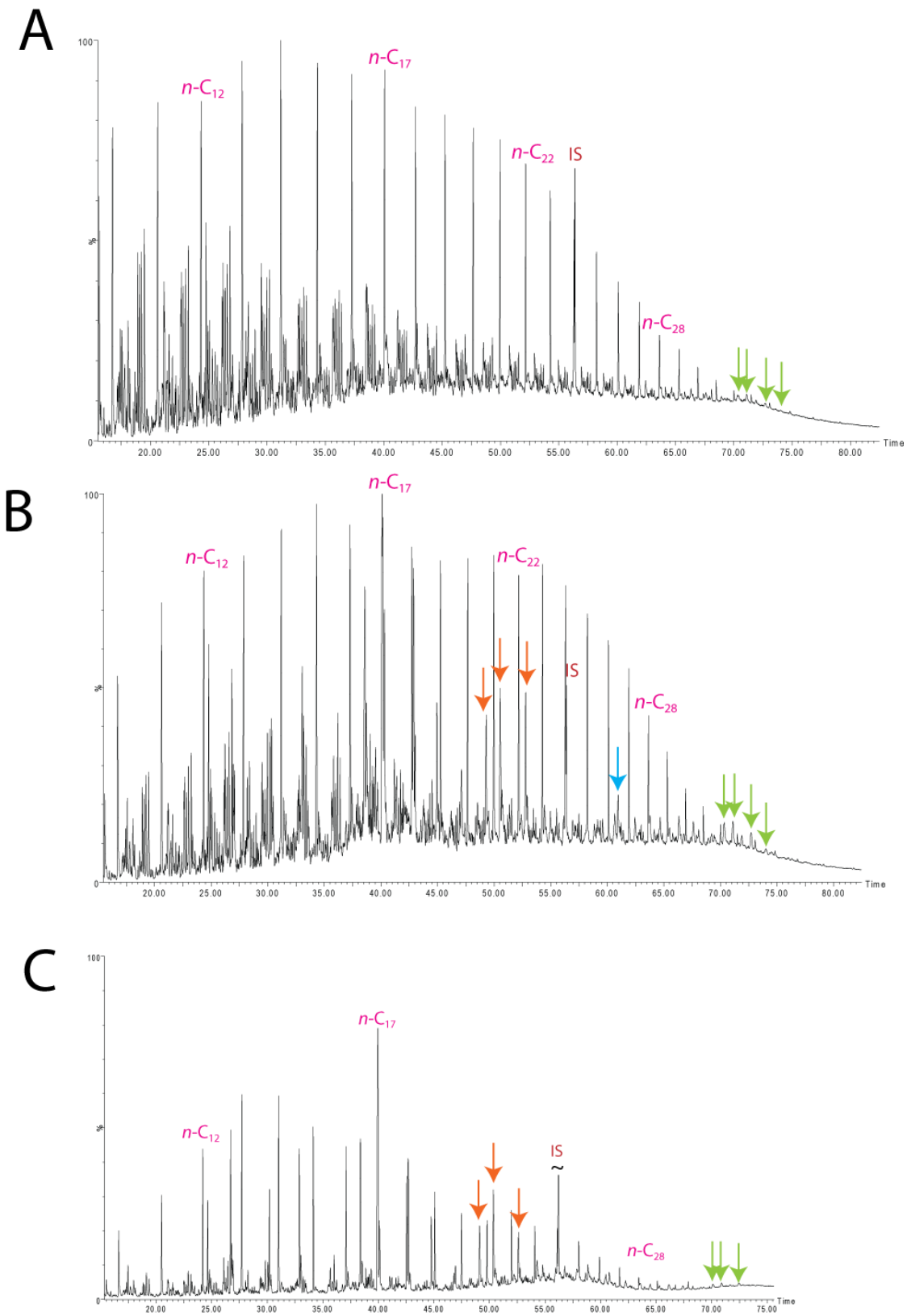

Figure 9. Gas chromatograms of three representative bitumen extracts from the *Mt Charlotte 1* drillcore. See text for discussion. Green arrows = head-to-head isoprenoids, orange arrows = regular isoprenoids, blue arrow = tail-to-tail isoprenoids.

Biomarkers analysis of Proterozoic sedimentary successions from the Amadeus Basin, Northern Territory, Australia. Cores analysed: Wallara 1, CMS 1, Illogwa Creek 6 & Elkedra 6.

Research conducted by Amber Jarrett

This work is part of a PhD thesis at the Research School of Earth Sciences (RSES), Australian National University, Canberra. The commencement date of the PhD project was delayed six months (starting date January 2010). Therefore, a large fraction of samples still need to be processed in the coming months. It is expected that the more complicated analyses, and analyses that can only be performed in overseas laboratories, will be completed by the end of 2011.

Introduction:

The aim of this study is to investigate the biogeochemistry of late Neoproterozoic (~800 to 542 Ma) oceans. The late Neoproterozoic is of interest as it was the most tumultuous period in Earth's history. It saw the greatest perturbations of the carbon cycle, the most extensive ice ages ('Snowball Earth' events), the rise of atmospheric oxygen and the advent of animal life followed by an exponential diversification of animals in the 'Cambrian Explosion'. This study hopes to resolve some of the relationships between microbial diversity and ocean chemistry in the Neoproterozoic by using drill cores obtained from the NTGS drill core store.

The Wallara 1 drill core spans from the Gillen Member of the Bitter Springs Formation (~853Ma) to the late Cambrian Goyder formation (> 542 Ma). It includes a major 'Snowball Earth' event, which has been globally correlated to the Sturtian glaciation (Kendall et al., 2006). Isotopic, elemental and fossiliferous data has been published on the Wallara 1 drill core (Burges et al., 2000; Calver, 2000; Kendall et al., 2006; Preiss, 2000; Schaefer & Burgess, 2003; Walter et al., 2000). Biomarker data from this study will complement the existing publications and give a broader overview on the microbial assemblages in the Neoproterozoic and their relationships with ocean chemistry. Small biomarker studies on *Wallara 1* have been published. For example, McKirdy et al. (2006) analysed sterane concentrations in the lower Pertatataka Formation as a proxy for eukaryote diversity pre-Acraman impact. Furthermore, Logan et al. (1999) analysed biomarkers in the microbial mats of the Pertatataka formation and found two distinct microbial sources- a planktonic (<nC20) and benthic (>nC20) microbial mat communities.

Samples analysed:

To date, a large fraction of samples from *Wallara 1, CMS 1, Illogwa Creek 6 & Elkedra 6* have been ground to powder (37 samples in total) and extracted for biomarkers. The extracted powder has been sent to the United Kingdom where they will be digested for total iron, iron speciation and iron and sulphur isotopic analysis. These samples will be analysed in the first fortnight of June (Monday 31st May – Friday 11th June, 2010). Work is currently underway extracting the samples for GC-MS, preliminary results for Wallara-1 are completed and will be discussed below.

Preliminary Results and implications:

General overview of the Wallara 1 drill core

The Wallara 1 drill core appears recrystallised in many places which may indicate high temperatures and possibly high thermal maturity. Bitumen may have been cracked into oil and gas and migrated out of its original place of deposition. For a biomarker study, samples with low to medium thermal maturities are desired as they still contain most of the indigenous molecules (Peters et al., 2005). Initial screening of samples began with an examination and selection of very black (organic rich) samples which did not appear to have been recrystallised. Figure 10 depicts the samples selected and the gas chromatograms.

Unfortunately, the Aralka, Areyonga and Bitter Springs Formations did not yield the desired biomarkers (Figure 10). The saturate fractions are almost completely empty and the aromatic fractions are dominated by molecules such as adamantanes which can withstand high temperatures. Therefore the samples appear to have been exposed to very high temperatures. This is consistent with a study by Gibson et al. (2005) who used Apatite Fission Track Analysis (AFTA) on Wallara 1 samples to determine dual hydrocarbon generation events for this well which exposed the Neoproterozoic source rocks within the gas generation window.

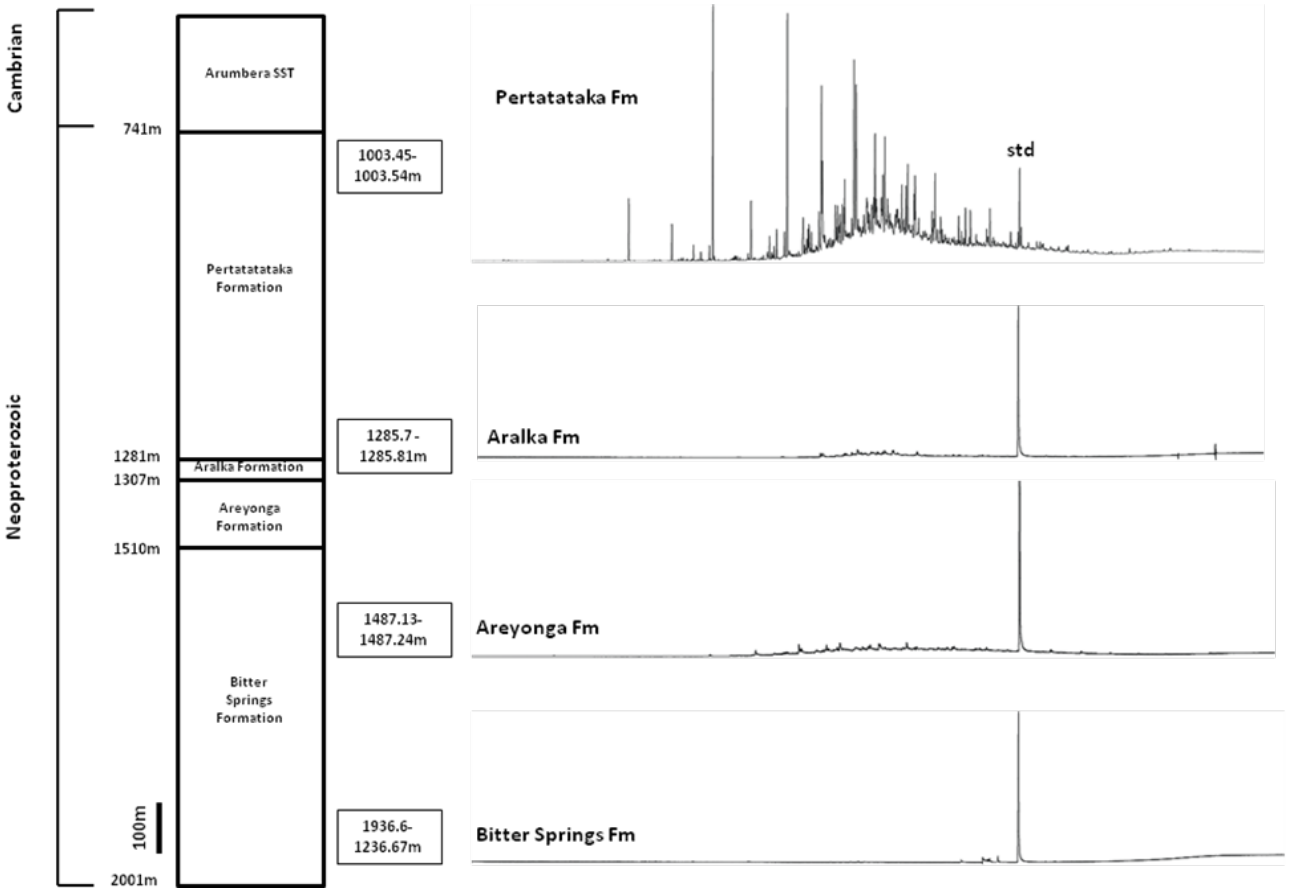

Figure 10. Gas chromatograms of major formations in the Wallara 1 drill core (whole rock extracts). The Wallara 1 drill core appears to have been exposed to high temperatures which must have generated oil and gas that was expelled from the rock.

Detailed analysis of the Pertatataka Formation, Wallara 1 drill core

The Pertatataka Formation contains a more thermally immature abundance of biomarkers compared with the underlying Aralka, Areyonga and Bitter Springs formations (Figure 10). The biomarker assemblages in the Pertatataka formation have been e.g. by Arouri et al., 2000; Logan et al. 1997; Logan et al. 1999; McKirdy et al., 2006. To test whether the samples contain indigenous hydrocarbons or merely artefacts of anthropogenic contamination, the exterior surfaces of rock samples were removed. Approximately 3 mm was trimmed from each surface or if the samples were too small to cut, they were exposed to micro-ablation until the angular rock fragments were well rounded and significant amounts of the exterior had been removed. The results of the interior/exterior experiments can be seen in Figure 11.

The results indicate that the Pertatataka formation in Wallara-1 is surficially contaminated; the interior fractions contain only low bitumen concentrations that were thermal and biologically degraded (Figure 12). The interior fractions appear to be consistent with the thermal maturity of the rest of the Wallara 1 drill core which has been reported to have been exposed to multiple heating events (Gibson et al., 2005).

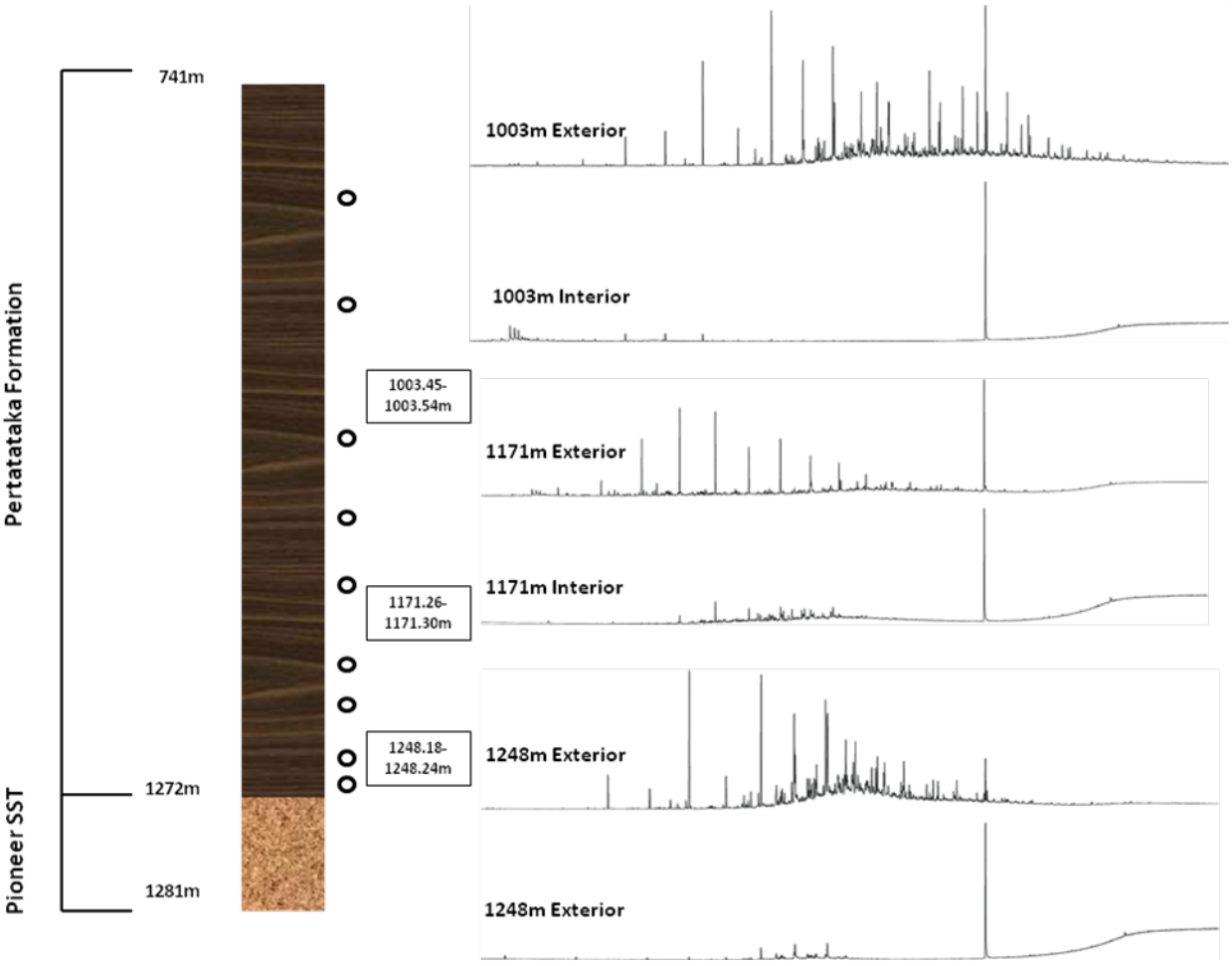

Figure 11. Biomarker analysis of the Pertatataka Formation, Wallara 1 drill core. Circles indicate sample locations through the formation. The interior/exterior experiments for representative samples at 1003 m, 1171 m and 1248 m are shown on the right. The exterior fractions contain biomarker assemblages similar to those previously recorded in the literature, while the interiors contain few biomarkers.

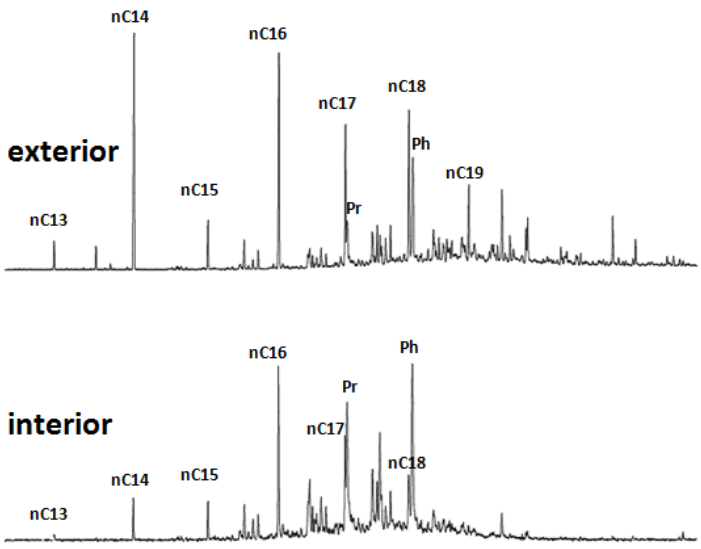

Figure 12. Magnification of the *n*-alkanes (m/z 85) in sample 09B087 (1112.18- 1112.24 m) from the Pertatataka Formation. The exterior fraction contains *n*-alkanes with an even-over-odd predominance which may indicate plastic contaminants. The interior fraction contains a predominance of Pristane (Pr) and Phytane (Ph) compared with the *n*-alkanes which may indicate biodegradation.

A metastable reaction monitoring (MRM) experiment of the C_{27}, C_{28} and C_{29} sterane concentrations indicate that steranes in the Pertatataka samples are contaminants (Figure 13). This is a significant result as steranes have been previously published from the Wallara 1 drill core in the past (Logan et al., 1999; McKirdy et al., 2006).

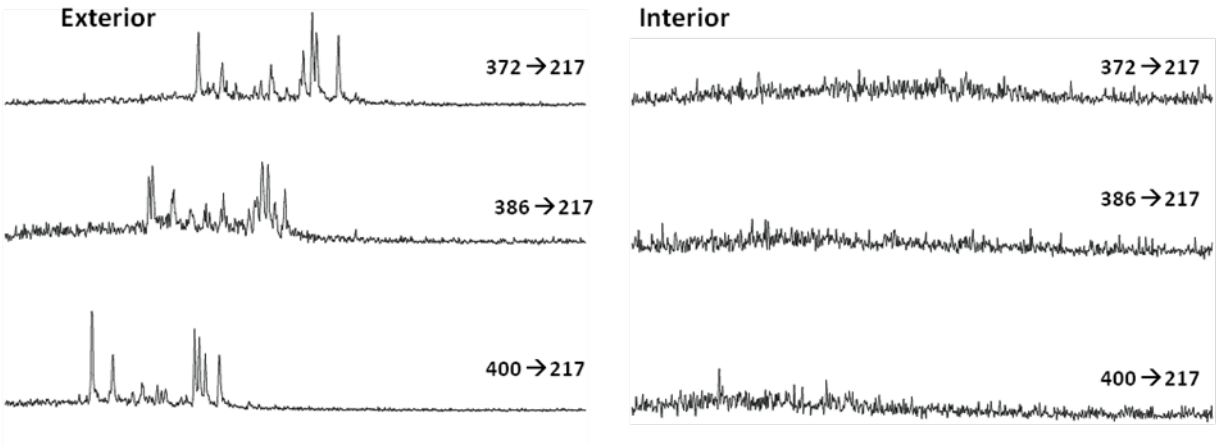

Figure 13. MRM results from sample 098B087 (1112.18- 1112.24 m) from the Pertatataka Formation. The exterior contains significant quantities of C_{27}(372 → 217 trace), C_{28} (386 → 217 trace) and C_{29} (400 → 217 trace) steranes. The interior fraction is empty and does not contain indigenous steranes.

The preliminary results from the Wallara 1 drill core have yielded exciting information. It has been proven that biomarker results published in the literature are artifacts of contamination and that Wallara 1 has been altered to temperatures too high to yield information on the biomarker assemblages of the time.

Work will continue extracting and quantifying biomarkers in the Wallara 1 drill core to assess hydrocarbon infiltration, as well as iron speciation which may provide information on the redox state of the oceans in the Neoproterozoic.

References:

Arouri, K. R., Greenwood, P. F., Walter, M. R. (2000). Biological affinities of Neoproterozoic acritarchs from Australia: microscopic and chemical characterisation. Organic Geochemistry, 31(1), 75-89

Canfield, D. E., R. Raiswell, et al. (1986). The Use of Chromium Reduction in the Analysis of Reduced Inorganic Sulfur in Sediments and Shales. Chemical Geology **54**(1-2): 149-155.

Brocks J.J., and Pearson A. 2005. Building the biomarker tree of life. Reviews in Mineralogy and Geochemistry, v. 59, p. 233-258.

Dyananda C., Sarada R., Srinivas P., Shamala T.R., Ravishankar G.A. 2006. Presence of methyl branched fatty acids and saturated hydrocarbons in botryococcene producing strain of Botryococcus braunii. Acta Physiologiae Plantarum, v. 28, p. 251-256.

Grice K., Schouten S., Nissenbaum A., Charrach J., and Sinninghe Damstè J.S. 1998. Isotopically heavy carbon in the C21 to C25 regular isoprenoids in halite-rich deposits from the Sdom Formation, Dead Sea Basin, Israel. Organic Geochemistry, v. 28, p. 349-359.

Kendall, B., R. A. Creaser, et al. (2006). "Re-Os geochronology of postglacial black shales in Australia: Constraints on the timing of â€œSturtianâ€ glaciation." Geology **34**(9): 729-732.

Kuypers M.M.M., Blokker P., Erbacher J., Kinkel H., Pancost R.D., Schouten S., Sinninghe Damsté J.S. 2001. Massive expansion of marine Archaea during a mid-Creataceous oceanic anoxic event. Science, 293, 92-94.

Logan, G. A., Summons, R. E., Hayes, J. M. (1997). An isotopic biogeochemical study of Neoproterozoic and early Cambrian sediments from the Centralian Superbasin. Geochemica Et Cosmochimica Acta, 61(24), 5391-5409.

Logan, G. A., C. R. Calver, et al. (1999). "Terminal Proterozoic mid-shelf benthic microbial mats in the Centralian Superbasin and their environmental significance." Geochimica Et Cosmochimica Acta **63**(9): 1345-1358.

McKirdy, D. M., L. J. Webster, et al. (2006). "Contrasting sterane signatures in Neoproterozoic marine rocks of Australia before and after the Acraman asteroid impact." Organic Geochemistry **37**(2): 189-207.

Peters, K. E., Walters, C. C., Moldowan, J. M. (2005). The Biomarker Guide 2nd Edition. Cambridge University Press, United Kingdom

Summons R.E., Powell T.G., and Boreham C.J. 1988a. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. Geochimica et Cosmochimica Acta, v. 52, p. 1747-1763.

Summons R.E., Brassell, S.C., Eglinton G., Evans E, Horodyski R.J., Robinson N., and Ward D.M. 1988b. Distinctive hydrocarbon biomarkers from fossiliferous sediments of the Late Proterozoic Walcott Member, Chuar Group, Grand Canyon, Arizona. Geochimica et Cosmochimica Acta, v. 52, p. 2625-2637.

Wang R.L., Brassell S.C., Fu J.M., Sheng G.Y. 1998. Molecular indicators of microbial contributions to recent and Tertiary hypersaline lacustrine sediments in China. Hydrobiologia, v. 381, p. 77-103.