Biogeochemistry from Deep Time through Petroleum Resources to Modern Environments

17th Australian Organic Geochemistry Conference

2nd – 5th December, 2012, Sydney

Program and Abstracts

Edited by Manzur Ahmed, Se Gong, Kostas Kotzakoulakis
and Simon C. George

CSIRO Earth Science and Resource Engineering and
Macquarie University

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2nd –5th December, 2012
Sydney, Australia

Acknowledgements

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Organising Committee

- Simon George – Chair (Macquarie University)
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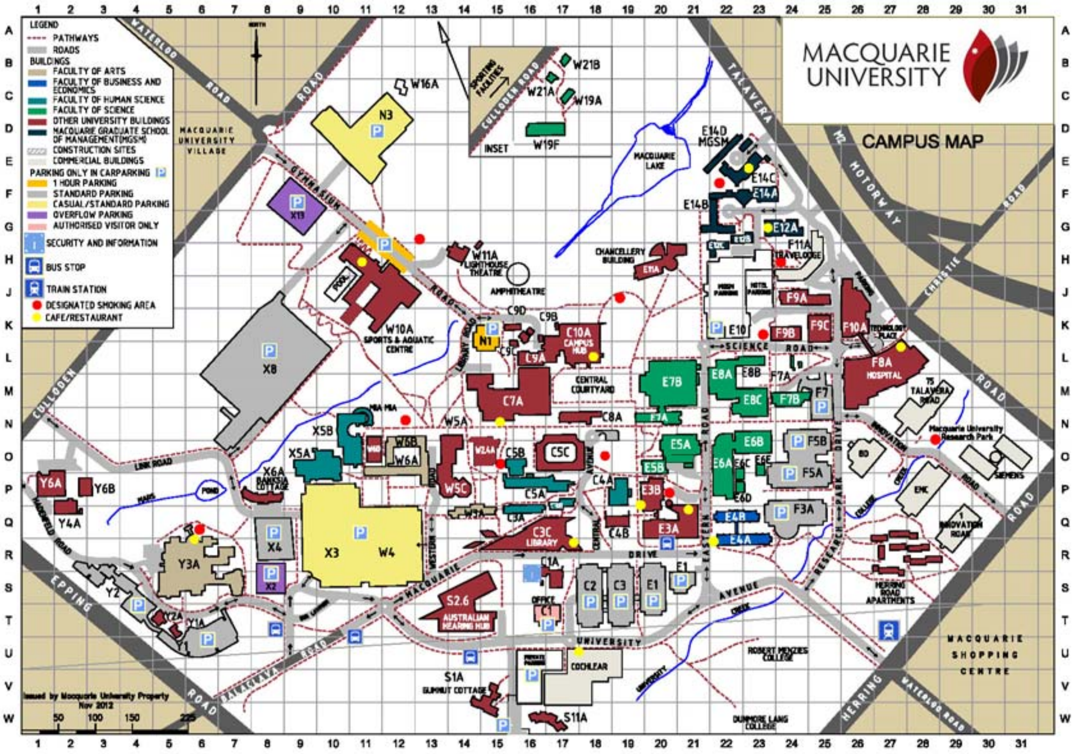
Conference venue

Oral sessions for the Australian Organic Geochemistry Conference (AOGC) will be held in Room 100, Building E7B, Macquarie University over 2 days from Monday 3rd to Tuesday 4th December. Morning and afternoon teas will be served just outside this theatrette. Lunches and the poster sessions will be held in Room 810, Building E7A (8th floor tea room, West end). There are lifts in E7A!



Social events

- Registration and Ice-breaker: 17:00-19:00, Sunday 2nd December, CSIRO Canteen, Building 53, CSIRO Earth Science and Resource Engineering, 11 Julius Avenue, North Ryde.
- The conference dinner will be on the evening of Monday the 3rd December at the Imperial Peking Harbourside, 15 Circular Quay West, The Rocks, Sydney.
- A fieldtrip to the Newcastle area has been arranged for Wednesday 5th December, which will be at no extra cost (except you buy your own lunch in Swansea RSL).
- Prizes will be offered for the best student presentations, oral and poster. The AOGC medal for a lifetime achievement in organic geochemistry will also be presented..

AOGC 2012 web site

The AOGC 2012 web page is located under Macquarie University's web site – http://eps.mq.edu.au/AOGC2012/AOGC2012.htm. The conference abstract volume is also available for downloading online.

The AOGC Medal

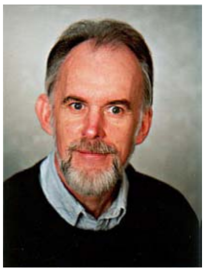
Since 1991 the AOGC has awarded a medal to distinguished members of our community for lifetime achievement in the field of Organic Geochemistry.

The previous winners of the AOGC medal are:

1991 John Smith
(CSIRO, North Ryde, NSW)

1993 Basil Johns
(University of Melbourne, VIC)

1995 Trevor Powell
(AGSO,Canberra,ACT)



1996 David McKirdy
(University of Adelaide, SA)

1998 Robert Alexander
(Curtin University, WA)

2000 Barry Batts
(Macquarie University, NSW)

2002 Roger Summons
(MIT, USA)

2004 John Volkman,
(CSIRO Marine Research, TAS)

2006 Michael Wilson
(University of Western Sydney, NSW)

2008 Robert Kagi
(Curtin University, WA)

2010 Christopher Boreham
(Geoscience Australia, ACT)

The winner of the 2012 AOGC medal is Associate Professor Simon Christopher George

Simon C. George is an Associate Professor at the Department of Earth and Planetary Sciences, Macquarie University. A product of the famed organic geochemistry research school at Newcastle upon Tyne University (UK), Simon headed down under soon after completing his formal education to take up an experimental scientist position at CSIRO (North Ryde). A distinguished 15 year career with CSIRO followed with Simon contributing various research and leadership roles to many different Project, Research and Discipline Groups, Themes, Streams and CRCs, Flagships, Clusters, Business Opportunities, Institutes and Divisional entities of the organisation. Simon has maintained a strong collaborative relationship with CSIROs Organic Geochemistry Group since departing in 2006 to take up an academic post at Macquarie University. Simon's career has continued to blossom in the academic arena. He has won close to $3M in competitive research funding; assembled a productive research team and a talented cohort of postgraduate research students; and continues to make important scientific contributions to a range of national and international groups, including recent activities with China's emerging petroleum geochemistry research industry.

Simon has been productive in his research with >83 peer reviewed papers on a range of organic geochemistry and related interests. He is one of the world's leading authorities in the analysis and interpretation of oil trapped in fluid inclusions (FIs) and has led the development of a unique suite of FI analysis techniques now widely practiced by the petroleum exploration industry to trace oil from source to reservoir. Other FI research highlights include helping develop analytical facilities to study the smallest amounts of oil possible; the detection of biological signals preserved in rocks as old as 2.4 Ga; and pre-dating previous known occurrences of oxygen producing cyanobacteria and complex life (eukaryotes) in Earth history. His interest in extremely antiquated biomarkers helped identify the 1.5 Ga source of the oldest liquid petroleum in the world (Velkerri Formation, NT).

Throughout his professional career Simon has made many significant contributions to the Australian organic geochemistry community. He has trained and mentored many early career researchers, participated in and led numerous field trips to exotic geological locations around the continent, contributed to many organic geochemical forums and convened two AOGC's (including the present). Perhaps one of Simon's most noble achievements was his successful resistance of CSIROs strong westerly migration from the 90's, saving himself and many colleagues from the feared "brain dead" affliction apparently prone to those straying more than briefly beyond the blue mountains …a seemingly paradoxical belief given his weekend penchant for rogaining/orienteering the very far reaches of the country. In closing, it should be noted that Simon is still very much in his prime, being one of the few researchers to be awarded the AOGC "mid career", and no doubt has much more to offer the organic geochemistry and broader scientific communities in the years ahead.

Congratulations Simon, a deserved winner of the 2012 AOGC medal.

Paul Greenwood (University of Western Australia)

Publications of Simon Christopher George

In review

Song, Z., Yin, Q., **George, S.C.**, Wang, L., Guo, J., Feng, Z. Submitted Nov 2011. A biomarker study of depositional paleoenvironments and source inputs for the massive formation of Upper Cretaceous lacustrine source rocks in the Songliao Basin, China. *Palaeogeography, Palaeoclimatology, Palaeoecology*.

Willson, D., Rask, J., George, S. C., deLeon P., Blank J., Bonaccorsi, R., Slocombe, J., Silburn, K., Steele, H., Gargarno, M. and McKay, C.P., submitted Mar 2012. Off-world field observations of early Life: The effectiveness of scientist astronaut field observation skills when exploring for stromatolite or microbalite fossils using the NDX-1 space suit, Pilbara Western Australia. *Planetary and Space Science*

Siljeström, S., Volk, H., **George, S.C.**, Lausmaa, J., Sjövall. P., Dutkiewicz, A., Hode, T., submitted. Analysis of single oil-bearing fluid inclusions in mid-Proterozoic sandstones (Roper Group, Australia). *GCA*

Published

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Australian Organic Geochemistry Conference 2012

Programme of Talks, Posters and Activities

Sunday 2nd December

Registration and Ice-breaker, 17:00-19:00

CSIRO North Ryde Laboratories, Building 53 canteen, CSIRO Earth Science and Resource Engineering, 11 Julius Avenue, North Ryde.

Monday 3rd December

*= student presentation

7:55-8:15 Registration, E7B 100, Macquarie University (off Eastern Road, Herring Road, North Ryde).

8:15-8:25 Welcome by Executive Dean of the Faculty Of Science, *Professor Clive Baldock*; opening announcements
Simon C. George

Session 1: **Paleoenvironmental and Palaeoclimate Reconstructions**
Chair: *Jochen Brocks*

8:25-9:00 **KEYNOTE:** GDGT-lipid paleothermometry for limnic systems in the South Island of New Zealand.
Lorenz Schwark

9:00-9:25 A subtropical east Australian record (Lake McKenzie, Fraser Island) of temperature and soil pH variations from Branched GDGT distributions in sediments during the last glacial and Holocene.
M. Woltering, P. Atahan, K. Grice., H. Heijnis, K. Taffs and J. Dodson

9:25-9:50 The origin of organic matter in surface sediments of the Shoalhaven river-estuary-continental shelf system from lipid biomarker and δ13C and Δ14C analysis of total organic carbon.
P. A. Abballe and A. R. Chivas

9:50-10:15 Biomarker records of sea-surface temperatures over the last few centuries in the Australian region.
M. J. Smith, P. De Deckker, J. J. Brocks, S. Schmidt, J. Hope, R. Lopes dos Santos and S. Schouten

10:15-10:35 Morning tea

Session 2: Petroleum Geochemistry

Chair: *Kliti Grice*

10:35-11:10	A geochemical study of the origin of oils and gases in the offshore northern Perth Basin. *E. Grosjean, C. Boreham, A. Jones and J. Kennard*
11:10-11:35	Organic geochemistry of natural oil slicks from the northeastern Gulf of Mexico. *S. Gong, M. Ahmed, D. Fuentes, C. Stalvies, S. Armand, E. Crooke, C. Trefry, A. Talukder, S. Sestak and A. Ross*
11:35-12:00	Reservoir wettability alteration during basin evolution as a key factor enabling hydrocarbon accumulation in tight reservoirs. *M. Zhao, K. Liu, S. Liu, S. Fang, X. Guo, Q. Zhuo, X. Lu and J. Fan*
12:00-12:25	Markers for secondary reactions of migrated crude oil on carbonaceous surfaces: Application to Carnarvon Basin petroleum. *R. Alexander, L. Berwick and S. Nasir*
12:25-13:25	Lunch and poster session, E7A 810.

Session 3: Biomarkers in Ancient Sediments

Chair: *Chris Boreham*

13:25-13:50	The unusual nature of the Proterozoic biomarker record and the Mat-Seal hypothesis. *Jochen J. Brocks, Maria M. Pawlowska and Nicholas J. Butterfield*
13:50-14:15	Biomarker assemblage of a pre-Ediacaran microbial mat. ** N. Gueneli, E. Legendre and J. J. Brocks*
14:15-14:40	Investigating the Syngeneity and the Palaeobiology of Hydrocarbon Biomarkers in the Fortescue Group at 2.7-2.8 Ga. ** Yosuke Hoshino, David Flannery, Malcolm R. Walter and Simon C. George*
14:40-15:05	The organic geochemistry of the Mesoproterozoic Velkerri Formation and investigations into syngenicity and indigeneity of hydrocarbons using slice experiments. ** Emma F. Flannery and Simon C. George*
15:05-15:25	Afternoon tea

Session 4: **Biomarkers in Ancient and Recent Sediments**
Chair: *Martin Kennedy*

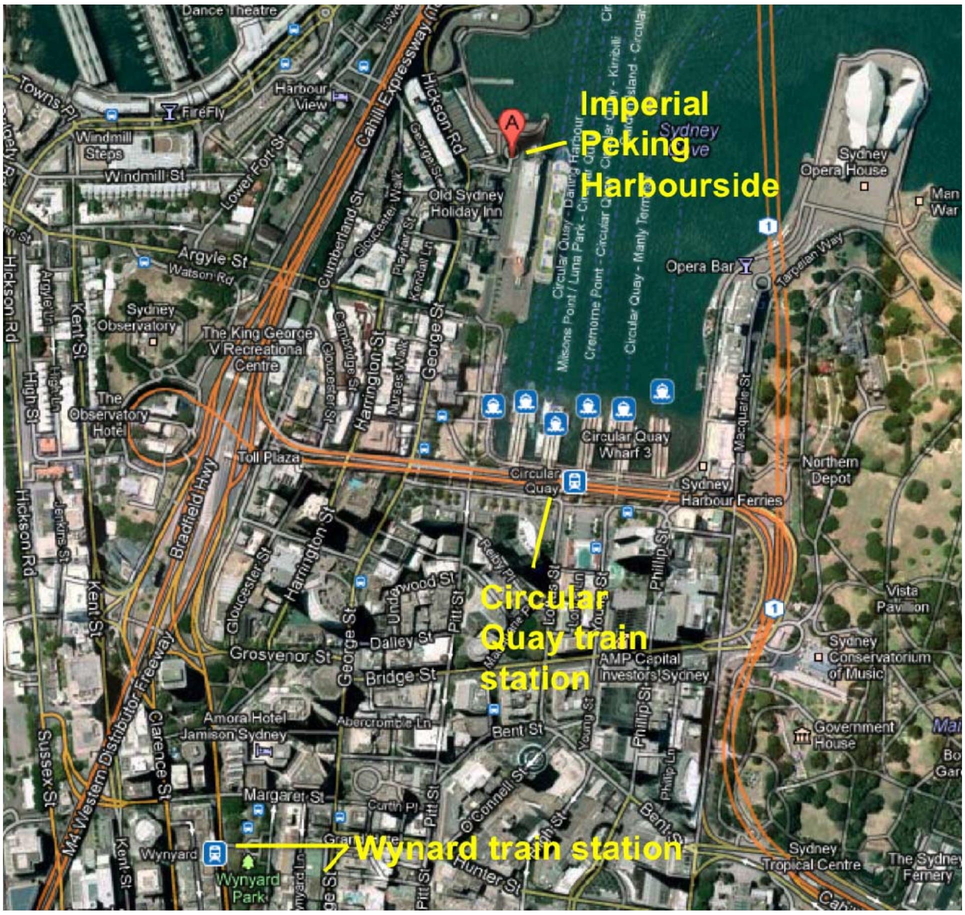
15:25-15:50 Hydrothermal destruction of hydrocarbons in Proterozoic evaporites.
** B. J. Bruisten, R. Schinteie, J. Colangelo-Lillis, L. Reuning, R. Littke and J. J. Brocks*

15:50-16:15 Analysis of hydrocarbons preserved within the kerogen-mineral matrix of the Paleoproterozoic Here's Your Chance Pb-Zn-Ag deposit.
** A. I. Holman, K. Grice, C. M. B. Jaraula, J. M. Dick, K. A. Evans, A. Schimmelmann, J. J. Brocks and P. F. Greenwood*

16:15-16:40 Evolution of biosynthetic pathways and the geological record of acyclic isoprenoid hydrocarbons such as HBI alkenes, botryococcenes and lycopadiene.
J. K. Volkman

16:40-17:05 I Dated a Salt Lake, and It Broke My Heart
P. Sargent Bray, Jochen J. Brocks, Stewart J. Fallon, Simon C. George

18:30 **Conference Dinner, Imperial Peking Harbourside,**
15 Circular Quay West, The Rocks, Sydney



Tuesday 4th December 2012

8:20-8:25	Opening announcements *Simon C. George*
Session 5:	**Recent Lipids and Environmental Organic Geochemistry**
Chair:	*Paul Greenwood*
8:25-8:50	Amino acids in deep-sea coral: what nitrogen isotopes reveal about food web dynamics in a changing climate. * *K. M. Strzepek, A. T. Revill, R. E. Thresher and S. J. Fallon*
8:50-9:15	Application of a linear transfer model for the estimation of the hydrocarbon concentration in the seawater of Antarctica following a fuel spill. * *Konstantinos Kotzakoulakis and Simon C. George*
9:15-9:40	Characterisation of organic matter in a tidally inundated tropical acid sulfate soil wetland. *L. J. Berwick, K. Grice and R. Bush*
9:40-10:05	Abiotic sulfurisation of a modern ecosystem and the preservation of early life. * *A. Pagès, K. Grice, R. Lockhart, R. Jahnert, L. Collins, M. Vacher, R. Summons, P. R. Teasdale, D. T. Welsh, J. Cleverley, M. Van Kranendonk, P. Greenwood*
Session 6:	**New Methods and Hot Topics**
Chair:	*Robert Alexander*
10:05-10:30	Flash pyrolysis GCMS analysis of fluid inclusions. *Paul Greenwood, Zhang Zhirong, Keyu Liu, Kliti Grice, Simon C. George, Louise Fisher and Robert Hough*
10:30-10:50	Morning tea
10:50-11:25	**KEYNOTE:** Organo-mineral nanocomposite control of organic carbon concentration in source rocks and unconventional (shale) reservoirs. *Martin J. Kennedy*
11:25-11:50	A volcanic clay mineral control of carbon burial during OAE II. *S. C. Loehr and M. Kennedy*

11:50-12:15 An exciting future for biomarker geochemistry in very old rocks: single oil inclusion analysis by TOF-SIMS.
Simon. C. George, Sandra Siljeström, Herbert Volk, Adriana Dutkiewicz, Jukka Lausmaa, Peter Sjövall and Tomas Hode

Session 7: Old Petroleum Systems and Coal Geochemistry
Chair: *David McKirdy*

12:15-12:40 Characteristics of a Neoproterozoic oil in the Amadeus Basin, central Australia.
** A. J. M. Jarrett and J. J. Brocks*

12:40-13:40 Lunch and poster session, E7A 810

13:40-14:05 Biomarker evidence for the origin of seep oil and solid bitumen from the Late Devonian Siljan impact structure, Sweden.
M. Ahmed, O. Lehnert, D. Fuentes, S. Sestak, G. Meinhold and S. Gong

14:05-14:30 Relationship between total organic carbon, mineral surface area and petroleum systems in the Middle Cambrian of the Southern Georgina Basin.
P. A. (Tony) Hall, T. Sturman, M. J. Kennedy, S. C. Löhr and D. M. McKirdy

14:30-14:55 Deciphering links between organic matter and uranium in lignite-hosted ores.
C. M. B. Jaraula, X. Moreau, K. Grice, L. Schwark, L. Bagas, Z.R.P. Mateo and C. McCuaig

14:55-15:20 Exceptional lipid preservation in fossils from the Gogo Formation.
** Ines M. Melendez, Kliti Grice, Lorenz Schwark, Kate Trinajstic and Roger Summons*

15:20-15:40 Afternoon tea

Session 8: Biomarker Evidence of Planetary Climate Crises & Carbon sequestration

Chair: *John Volkman*

15:40-16:05 Consistent changes in biomarkers (microbes and flora) and stable isotopes across several major extinction events of our planet.
K. Grice, C.M.B. Jaraula, K. Williford, S. Tulipani, B. Nabbefeld, R. Summons, M. Böttcher, R. Twitchett

16:05-16:30 Do Paleocene-Eocene Thermal Maximum HMW *n*-alkanes reflect plant community change or climate change?
F. A. McInerney, R. T. Bush, A. A. Baczynski, S. L. Wing, M. J. Kraus, J. I. Bloch

16:30-16:55 Otway residual CO_2 saturation test: Application of noble gas tracers

C. J Boreham, B. M. Freifeld and T. LaForce

16:55-17:20 Low molecular weight fatty acids as proxies for microbial responses to CO_2-injection into the Paaratte Formation sandstone aquifer, Otway Basin
** H. X. Leong, C. Boreham, A. Mu and J. W. Moreau*

17:20-17:30 Conference close. Presentation of prizes for the best student presentations, oral and poster. Finalisation of the plan for the next AOGC (in late 2014?). [This needs to be discussed during the meeting].
Simon C. George

Posters Presentations

Posters will be displayed at the lunch venue on both Monday and Tuesday: E7A 810, West end, Macquarie University

*= student presentation

Poster 1 Evolution of pores in organic-rich shale during thermal maturation.
** Hua Tian, Shuichang Zhang, Keyu Liu, Shaobo Liu, Jianping Chen and Hong Zhang*

Poster 2 Use of dichloromethane in GC-MS as a cause of apparent chromatographic tailing through $FeCl_2$ - plaque formation in the ion source.
Janet M. Hope and Jochen. J. Brocks

Poster 3 Geochemistry of Mesoproterozoic Hongshuizhuang Formation shales in Northern part of North China: implications for Provenance, Source Weathering and paleoclimate.
** Qingyong Luo, Simon C. George and Ningning Zhong*

Poster 4 Photic zone euxinia at the Triassic/Jurassic mass extinction evident from the presence of C_{34} metallo-porphyrins with an extended alkyl chain measured by LC-MS Orbitrap.
M. Woltering, C. M. B. Jaraula, K. Grice and C. J. Boreham

Poster 5 A non-invasive technique for characterisation of volatile and semi-volatile constituents of fulvic acid by BSTFA derivatisation coupled with gas chromatography- mass spectrometry.
** S. Farzadnia and C. R. McRae*

Poster 6 Geochemical characteristics of fluid inclusion oils from Barrauilla-1 well in Sinu offshore basin, Colombia.
S. Gong, D. Fuentes, S. Armand and J. Francisco Naranjo Vesga

Poster 7 The use of in situ derivatisation and laser pyrolysis-GC-MS for the analysis of restored paint samples.
D. Fuentes and S. Prati

Poster 8 Proterozoic rocks that retain organic compounds: insights from the McArthur Basin (Northern Territory, Australia).
T. Bover-Arnal, E. T. Baruch, B .J. Bruisten, M. J. Kennedy, J. J. Brocks, T. Hall, S. Loehr, J. Warburton and B. McLeod

Poster 9	Approaches to differentiating between different biogenic methane sources. *S. Sestak and S. Armand*
Poster 10	Multiscale Variability of the Woodford Shale, Oklahoma, USA: Organic Matter Preservation as Clay-organic Nanocomposites, and Diagenetic Links to Hydrocarbon Entrapment. ** S. A. Fraser, M. J. Kennedy and S. C. Loehr*
Poster 11	The importance of the clay mineral fraction for the selective preservation of nano-composites in black shales: An Eagle Ford Shale example. ** E. T. Baruch, M. J. Kennedy and S. Loehr*
Poster 12	Coal degradation in anaerobic sediments associated with acid mine drainage. ** Jennifer van Holst, David J. Midgley, Linda Stalker, Michael R. Gillings and Simon C. George*

Wednesday 5th December

Newcastle Field Trip, to examine the Permian coal-bearing sediments

Leader: Claus Diessel (retired, ex Newcastle University)
Organisers: Kaydy Pinetown and David Fuentes (CSIRO)

7:30 Depart Sydney (Macquarie University, Eastern Road outside E5A, 5 mins from the train station)

19:00 Expected arrival time back in Sydney (Macquarie University)

AOGC 2012 - Abstracts

Oral Presentations

(Abstracts are in order by presentation time; presenters are underlined)

GDGT-lipid paleothermometry for limnic systems

Lorenz Schwark [1,2]

[1] Institute of Geoscience, University of Kiel, Germany
[2] WA-OIGC, Curtin University, Perth, Australia

Terrestrial bacteria and archaea reflect environmental growth conditions, in particular temperatures, by adaption of their plasma membrane lipids to maintain cell fluidity and allow for trans-membrane exchange of gases and solutes. As GDGT-lipids tend to be well preserved in geological archives for up to millions of years, their composition has been applied to lake sediments and soils for paleotemperature reconstructions and widely used proxies, including the TEX86 and MBT/CBT ratio have been established. With an increasing number of terrestrial GDGT studies conducted, observations deviating from the original proposed mechanisms, proxy calibrations, and their simple applicability have been made. Amongst other the following unsolved questions require particular attention. Bacterial producers of iso-alkanoidal GDGT (br-GDGT) are still not identified and the lack of cultivable bacteria hampers laboratory calibrations under controlled conditions. Acidobacteria and non-specified denitrifiers, having been postulated as primary biosynthesizers of br-GDGT, will be discussed. In aquatic settings, allochthonous and autochthonous sources may contribute to the overall GDGT-stock in highly varying proportions, thereby reflecting soil or water temperatures, respectively. Autochthonous br-GDGT production may reflect substantial diversity due to seasonality or habitat preferences. Isoprenoidal GDGT (iso-GDGT) biosynthesized by archaea in exceptional cases have been used in limnic settings as well but generally are thought to yield meaningful paleoenvironmental information for large lakes, only.

In a study aiming at a better understanding of controlling factors on GDGT distributions in lakes, we (K. Zink, T. Bauersachs, M. Vandergoes, R. Newnham, L. Schwark) investigated 30 lakes in the South Island of New Zealand, located at different altitudes covering a range of mean annual air temperature (MAAT) ranging from 1.5-13°C. Data loggers installed within lakes and in adjacent soils provided a yearly record of local temperatures. The measured field data gave better correlations with GDGT-proxies than temperature inferred from regional climate models and thus improved present day calibration. The temperature logger data revealed exposed lakes and surrounding soils reacting to temperatures drastically, thus deviating significantly from modelled MAAT. Enhanced lake water temperature is reflected by higher MBT values, demonstrating needs for local calibration and verifying the validity of molecular paleothermometers. The distribution patterns of br-GDGTs obtained from soil, tributary sediment, lake sediment, and water filtrates at a given site differed substantially. This either indicates parallel pedogenic and aquatic production, each with a specific br-GDGT signature, or preferential soil derived GDGT influx suffering severe transport fractionation from soil to lake, or differential degradation of selected br-GDGT.

The iso-GDGT, though lower in abundance by more than two orders of magnitude, exhibit systematic variation with local temperature in lakes of minor size (diameter 0.5 to 5 km). A critical discussion of GDGT-paleothermometry in paleoenvironment reconstruction, based on the NZ and other sites, including a discussion of potential pitfalls but also specific beneficial perspectives, will be given.

A subtropical east Australian record (Lake McKenzie, Fraser Island) of temperature and soil pH variations from Branched GDGT distributions in sediments during the last glacial and Holocene.

M. Woltering[1], *P. Atahan*[2], *K. Grice*[1], *H. Heijnis*[2], *K. Taffs*[3] *and J. Dodson*[2]

[1] WA-Organic and Isotope Geochemistry Centre, Department of Chemistry, Curtin University, Perth, WA, Australia.
[2] Institute for Environmental Research, Australian Nuclear Science and Technology Organisation, Sydney, PMB 1 Menai NSW 2234, Australia
[3] Southern Cross Geoscience, Southern Cross University, PO Box 157, Lismore NSW 2480

A 47cm long sediment core was retrieved from Lake McKenzie, a perched lake on Fraser Island in Queensland. This ^{14}C and ^{210}Pb dated sediment core provides a well preserved archive for a biogeochemical derived paleotemperature reconstruction. The sediment core was analysed for Branched Glycerol Dialkyl Glycerol Tetraethers (GDGT), and the Cyclization of Branched Tetraether (CBT) and Methylation of Branched Tetraether (MBT) indices were calculated according to Peterse *et al*. (2012) and Weijers *et al*. (2007). We investigated different soil (Peterse *et al*., 2012; Weijers *et al*., 2007) and lake (Sun *et al*., 2011) calibrations to infer mean annual air temperatures (MAAT) from the observed Branched GDGT distributions in the sediment core from Lake McKenzie. Multiple lines of evidence suggest a predominantly allochthonous soil origin for the GDGTs observed in the sediment core and subsequently applying the newest soil calibration (Peterse *et al*., 2012) to the top sediment yields an estimate for MAAT that is nearly identical to the instrumentally measured temperature from a nearby weather station. The pattern and amplitude of MAAT variability, as reconstructed from the five most recent sediment samples from Lake McKenzie which covers the last 90 years, is nearly identical to the observed long term temperature variability within the instrumental temperature record from the Sandy Cape lighthouse, on the north coast of Fraser Island. This improves confidence in the accuracy of reconstructed MAAT variability using Branched GDGT distributions in the Lake McKenzie sediment core. The CBT/MBT proxy was subsequently applied to branched GDGT distributions observed in the entire sediment core to produce the first quantitative record of terrestrial temperature variability for subtropical Eastern Australia. The resulting paleorecord from Lake McKenzie provides important information on MAAT and pH variability during the end of the last glacial period (37.2-18.8 cal Ka BP) and the Holocene (12.8 cal ka BP- present day). This record does not contain information about the last glacial-interglacial transition period due to an observed hiatus in the sediment record between 18.2-13.9 cal ka BP. The temperature record from Lake McKenzie that covers the end of the last Glacial period will be discussed in terms of the commencement, extent and amplitude of the last glacial maximum for Australia. Key features of the Holocene temperature record will be discussed, including the near modern day temperatures during the early Holocene, amplitude and timing of the warmest temperature during the mid-Holocene and temperature evolution during the late Holocene. The reconstructed soil pH record from Lake McKenzie shows significantly lower soil pH values during the last glacial compared to the Holocene period. Potential causes of this observed soil pH shift will be discussed.

References:

Peterse, F., van der Meer, J., Schouten, S., Weijers, J.W.H., Fierer, N., Jackson, R.B., Kim, J.H., SinningheDamsté, J.S. (2012) Revised calibration of the MBT-CBT paleotemperature proxy based on branched tetraether membrane lipids in surface soils. *Geochim. Cosmochim. Acta*, in press.

Sun, Q., Chu, G.Q., Liu, M.M., Xie, M.M., Li, S.Q., Ling, Y.A., Wang, X.H., Shi, L.M., Jia, G.D., Lu, H.Y.(2011) Distributions and temperature dependence of branched glycerol dialkyl glycerol tetraethers in recent lacustrine sediments from China and Nepal. *J. Geophys. Res.-Biogeosci* 116.

Weijers, J.W.H., Schouten, S., van den Donker, J.C., Hopmans, E.C., Damste, J.S.S. (2007) Environmental controls on bacterial tetraether membrane lipid distribution in soils. *Geochim. Cosmochim. Acta* **71**, 703-713.

The origin of organic matter in surface sediments of the Shoalhaven river-estuary-continental shelf system from lipid biomarker and $\delta^{13}C$ and $\Delta^{14}C$ analysis of total organic carbon

P. A. Abballe and A. R. Chivas

GeoQuEST Research Centre, School of Earth and Environmental Sciences, University of Wollongong, Northfields Ave, Wollongong, NSW 2500, Australia. paa747@uow.edu.au

The fate of terrestrial organic matter (OM) during transfer towards the oceans is still a fundamental question in organic geochemistry. Blair *et al.* (2004) proposed a conceptual model that predicts the changing composition of terrestrial OM as it is transferred from catchment soils to marine sediments. The model illustrates that the composition of terrestrial OM is subject to more or less significant changes as it travels through major bioactive reservoirs such as catchment soils, river channel, floodplain, estuarine infill, and finally surface marine sediments. The extent to which such changes occur is a function essentially of the residence times of OM within each reservoir, and such residence times are linked to the combination of the geodynamic setting and climatic/environmental conditions. Within this framework it is possible to fit a number of similar studies (e.g. Burdige, 2005 and references therein, Galy *et al.*, 2007). However, since those studies have been carried out mainly on river-dominated deltas, there is still a lack of equivalent data for wave-dominated deltas in temperate climates. The Shoalhaven River is an ideal laboratory for the study of OM exported to the continental shelf where Blair *et al.* (2004)'s prediction can be possibly extended to temperate wave-dominated deltas of rivers developed on passive margins.

To achieve this aim, the organic matter (OM) content of 25 surface sediment samples collected from different locations along the Shoalhaven river channel, estuary, and adjacent continental shelf has been studied by coupling bulk OM measurements, such as total organic carbon content (TOC%), carbon/nitrogen ratio (C/N), carbon stable-isotope composition of TOC ($\delta^{13}C_{TOC}$), and radiocarbon composition of TOC ($\Delta^{14}C_{TOC}$) to lipid biomarker analysis of different classes of compounds, such as $C_{14\text{-}39}$ *n*-alkanes, polycyclic aromatic hydrocarbons (PAHs), $C_{14\text{-}30}$ *n*-alcohols, $C_{10\text{-}30}$ *n*-fatty acids, phytol, sterols (cholest-5,22E-dien-3β-ol, cholesterol, 5α-cholestan-3β-ol, 24-methylcholesta-5,22-dien-3β-ol, 24-methyl-5α-cholest-22-en-3β-ol, campesterol, stigmasterol, β-sitosterol, 24-ethyl-5α-cholestan-3β-ol, dinosterol), bishomohopanol (ββ-C_{32} hopanol), pentacyclic triterpenoid alcohols (taraxerol and β-amyrin), *iso-* and *anteiso-* $C_{15:0}$ and $C_{17:0}$ *n*-fatty acids, pentacyclic triterpenoid acids (oleanolic, betulinic and ursolic acid). Furthermore, data have been integrated with bulk sediment particle size analysis.

The main outcome of the study was that the preservation efficiency of terrestrial OM was similar to that reported for similar types of continental margins (passive margins) and in line with Blair *et al.* (2004)'s model, that is, about 70% of the terrestrial input is degraded during transfer towards marine sediments. However, whereas on river-dominated delta deposits developed on passive margins (e.g. Amazon), remineralisation of OM seems to occur mostly in the lowland plain environment and little marine OM is added to the river-dominated delta deposits (Aller, 1998), in the Shoalhaven River and adjacent continental shelf, remineralisation of terrestrial OM seems to occur mostly in the oceanic environment, and such loss is replaced by accumulation of OM from in situ marine production (Figure 1). At the same time, probably because of more limited residence times of OM in catchment areas, an amount of fossil OM escapes remineralisation in soils and is transported to the continental shelf sediments (contributing up to 25% of the marine sedimentary OM) where it is ultimately re-buried and removed from oxidation and participation in the current carbon cycle. Such amount must surely be taken into account when estimates of fossil OM re-burial are performed in order to establish its role in modulating the evolution of atmospheric CO_2 and O_2 contents throughout geological cycles (e.g. Hedges, 2002).

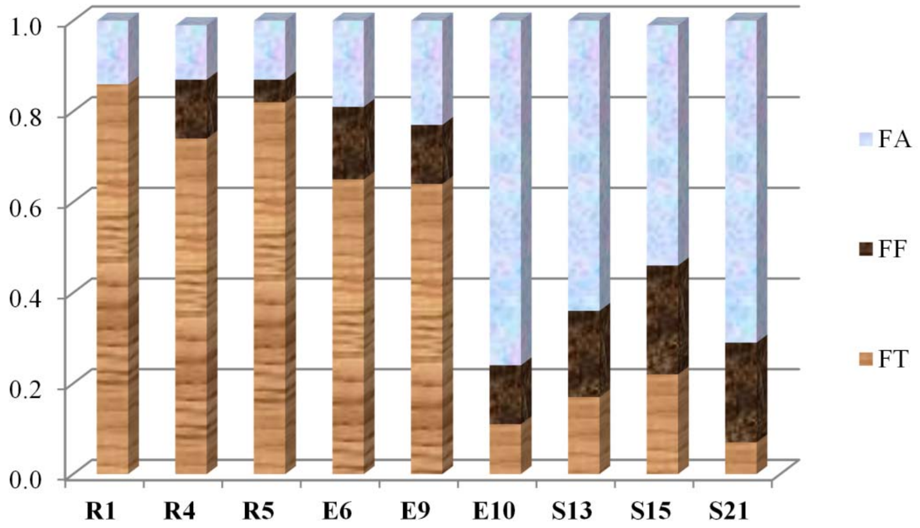


Figure 1. Plot of the fractional abundances of terrestrial (FT), fossil (FF), and aquatic/marine (FA) OM across the surface sediment samples from the Shoalhaven river-estuary-continental shelf (Sample coding: R = river, E = estuary, S = continental shelf).

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Biomarker records of sea-surface temperatures over the last few centuries in the Australian region

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The 'hockey-stick' temperature increase of the 20th century has instigated concern for a global warming trend. High-resolution temperature records that span the last several centuries are necessary in order to provide comparison to instrumental records. Available temperature records from this time interval are sourced almost exclusively from the Northern Hemisphere, predominantly from terrestrial records. There is a considerable lack of temperature records for the Southern Hemisphere, hampering the analysis of hemispheric and global temperature trends.

Specific biomarkers preserved in marine sediments may be utilised to reconstruct sea-surface temperature (SST). The lipids of some haptophyte marine algae (alkenones) and marine Thaumarchaeota (glycerol dialkyl glycerol tetraethers) in the sedimentary record are biomarkers that may be converted to SST via the $U^{K'}_{37}$ (Brassell *et al.*, 1986) and TEX_{86} (Schouten *et al.*, 2002) proxies, respectively. Recently, long chain diols presumably from eustigmatophyte algae have been proposed as an additional measure of SST via the Long chain Diol Index (LDI) (Rampen *et al.*, 2012).

In the Australian region, there are no published records using marine sediment cores that extend over the last several centuries. There are no SST records in the Australian region using this suite of organic biomarker proxies, and, furthermore, limited calibration of these proxies to modern temperatures has been undertaken in the Australian region. To address these issues, we present open-ocean SST records spanning the period 1566 – 2010 using fourteen short cores for the southern and eastern Australian region taken during two cruises in 2011. This forms both the first temperature record utilising the combined capacities of these biomarker proxies, and the first record of SST using molecular biomarkers for this time period in the entire Australian region. We compare this record to the instrumental data presented by the Australian Bureau of Meteorology and available data from long-term (~60 years) marine recording stations. Calibration of the temperature signal provided by each proxy to modern sea temperatures (WOA 09) indicates distinct seasonal differences between the three proxies. Our results indicate that the application of this ensemble of three independent biomarker proxies provides seasonal temperature information at high resolution in the Australian region.

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A geochemical study of the origin of oils and gases in the offshore northern Perth Basin

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The discovery of commercial oil in the Cliff Head-1 well in 2001 marked an important breakthrough in the exploration history of the offshore northern Perth Basin. The region had been largely underexplored before then, partly due to the perception that the main source of onshore petroleum accumulations had only marginal potential offshore. The typing of the Cliff Head oil to the Hovea Member, a < 40 m thick source rock unit straddling the Permian-Triassic boundary (PTB), provided evidence that the key onshore petroleum system extended offshore (Thomas and Barber, 2004) and revived exploration in the area. A recent reassessment of the basin's source rock potential has confirmed the widespread occurrence of good to excellent oil-prone Hovea Member source rocks in the offshore northern Perth Basin and has provided a new perspective on the basin's petroleum prospectivity (Jones *et al.*, 2011). The Late Permian Irwin River Sequence and several Jurassic Sequences were also recognized as prime potential source rocks, mostly for their gas-generative potential.

Source rock extracts, gases, oils and oil stains were analysed for their molecular and isotopic compositions to help determine how far the Early Triassic petroleum system extends offshore, and identify any evidence of effective Permian and/or Jurassic petroleum systems. The biomarker distributions of the offshore Hovea Member display distinct geochemical features including waxy n-alkanes up to *n*-C43, an anomalously high abundance of C33 *n*-alkylcyclohexane and high concentrations of isorenieratane, a diagnostic marker for photic zone euxinia (PZE). Evidence for PZE, whereby anoxic and sulphidic bottom waters extend into the photic zone, has been widely recognized in PTB sections and hydrogen sulphide poisoning was suggested as a contributing cause for the end-Permian extinction (Grice *et al.*, 2005). A negative excursion in $\delta^{13}C_{org}$ of up to 11‰ in amplitude is observed between Late Permian and Early Triassic strata as a result of extensive disruptions to the carbon cycle, resulting in generally very light $\delta^{13}C_{kerogen}$ for the offshore Hovea Member with values comprised between -33 and -29‰. This strong depletion in ^{13}C is also recorded in the carbon isotopic compositions of individual n-alkanes in the Kockatea-sourced oils and Hovea Member extracts, with most values ≤ -32‰. Biomarker patterns show little variation laterally offshore and are extremely similar to those from the onshore Hovea Member source rocks (Thomas and Barber, 2004; Thomas *et al.*, 2004), attesting to fairly uniform depositional environments across the whole basin.

The unique hydrocarbon assemblages exhibited by the Hovea Member extracts are shared by the oils recovered from Permian reservoirs in the offshore wells Cliff Head-3 and Dunsborough-1, strongly suggesting the Hovea Member is the sole source charging these accumulations. The recognition of these diagnostic attributes in oil stains from wells of the Wittecarra Terrace provides evidence for a working Early Triassic petroleum system over much of the Abrolhos Sub-basin. In this area, the Hovea Member was shown to be both of limited quality and immature for oil generation (Jones *et al*., 2011), which suggests the occurrence of effective Hovea Member kitchens in the adjacent Houtman Sub-basin. Carbon isotopic data for C_1-C_5 gases from the offshore wells Frankland-1 and Perseverance-1 indicate the gas is primarily sourced from the Hovea Member with some possible admixture from the gas-prone and ^{13}C-enriched Late Permian Irwin River Sequence.

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Organic geochemistry of natural oil slicks from the northeastern Gulf of Mexico

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It is well known that the Gulf of Mexico is subject to natural releases of hydrocarbons through natural seepage (Abrams, 1996, 2005). Marine surveys were designed in 2011 to investigate both the physical and geochemical nature of natural seepage in the area close to the 2010 Deepwater Horizon incident and release of hydrocarbons from the Macondo well.

Water, slick and sheen samples were collected over five different seafloor salt domes (Biloxi, Mobile, Dauphin, Farnella and Horn) in the northeastern Mississippi Canyon protraction area in the Gulf of Mexico. A duplicate set of the samples were subjected to extraction onboard and shipped to CSIRO laboratories in Australia. Analysis blanks, recovery spikes and trip blanks were also taken. Macondo oil from Mississippi Canyon block 252, (MC252) was also available as a reference for comparing molecular signatures.

The presence of significant humps of unresolved complex mixtures (UCM) and preferential removal of $<C_{16}$ *n*-alkanes in the samples consistently indicate that most of the slick and sheen samples have experienced a degree of weathering. Two surface sheen samples from Farnella Dome were heavily weathered with nearly all the *n*-alkanes removed resulting in extremely high Pr/nC_{17} and Ph/nC_{18} ratios. However, the weathering and degradation has not influenced the distribution of sterane, terpane and hopane biomarkers. All the samples contain abundant C_{30} 24-*n*-propylcholestanes indicating marine source rocks. Statistical analysis shows that the sheen samples from Horn Dome are more similar to MC252 oil than that from Mobile Dome. Samples from Mobile dome contain slightly higher abundances of diahopane, extended tricyclic terpanes, higher C_{29} sterane/C_{29} $\alpha\beta$ hopane ratio and lower Pr/Ph ratios compared to samples from other Domes and MC252 oil, pointing to their generation from relatively more clay rich source rock deposited in anoxic environment containing inputs from aquatic algal organic matter. Maturity based on aromatic parameters suggested the samples were generated from source rocks at peak oil window.

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Reservoir wettability alteration during basin evolution as a key enabling factor for hydrocarbon accumulation in tight reservoirs

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In a conventional petroleum system migration and accumulation are thought to primarily occur along porous and permeable conduits and in traps with good reservoir quality as oil migration and accumulation in rock formations of low porosity and permeability (e.g. tight sandstone) would require an unusually large driving force (Berg, 1975). Apart from the pore-throat size, reservoir wettability also plays an important role in controlling the capillary force. This parameter is, however, rarely considered in conventional petroleum system analysis.

Wettability refers to the preference of a solid to be in contact with one fluid rather than another. It is a key petroleum engineering parameter affecting oil recovery (Morrow *et al.*, 1990). For clastic sedimentary systems, reservoirs are generally regarded as water wet. However, reservoir wettability in subsurface can be altered under certain conditions. Organic matter in fine sedimentary rocks turns to be oil wet due to its affinity to oil (Schowalter, 1979; Hirasaki, 1991), especially when the organic matter enters into hydrocarbon generation window. Reservoir wettability can also be altered when the rock and oil in contact for sufficiently long period (Buckley *et al.*, 1989).

Recent exploration in the Kuche Depression, Tarim Basin, western China discovered giant hydrocarbon accumulations in tight sand reservoirs (Figure 1) at depth of over 6000 m and with porosity of less than 5% (e.g. Jia and Li, 1988). Detailed analysis using fluid inclusion petrography, Field Emission SEM, synchrotron micro-CT imaging revealed that these tight reservoirs contain organic residues or bitumen that form interconnected network (Figures 1 and 2). Basin modelling suggests that the area received a widespread early oil charge prior to the regional reservoir densification and a subsequent late hydrocarbon charge which resulted in these giant accumulations. It is interpreted that the early oil charge and the presence of organic matter in the reservoir formations altered the reservoir wettability and enabled the later hydrocarbons to migrate through the extremely tight reservoir formations unhindered via “imbibitions”. This finding may have wide implications for exploring tight oil accumulations elsewhere.

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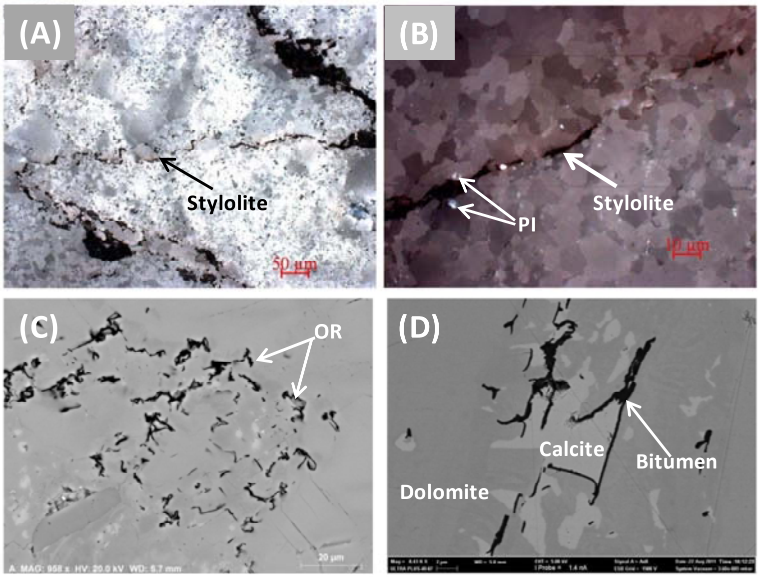

Figure 1. Photomicrographs (A and B) and Field Emission SEM images (C and D) showing the tight nature of the sandstone and organic-rich stylolite as preferential oil migration pathways, and organic residues (C) and bitumen (D) from early oil charges in tightly cemented reservoir rocks. Samples taken from tight oil reservoirs in the Kuche Depression, Tarim Basin, western China. PI, petroleum inclusions; OR, organic residues.

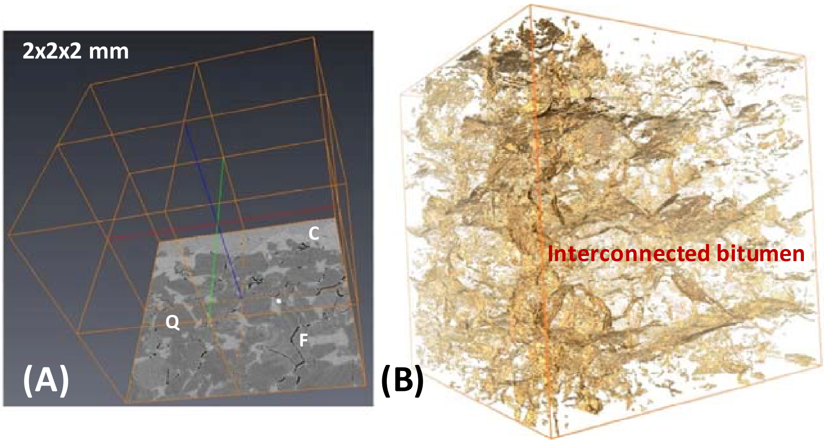

Figure 2. 3D reconstruction of bitumen and pores within a tight reservoir rock from the Tarim Basin at a depth of >6000 m with only 2% porosity showing the interconnected oil-wet network for hydrocarbon migration. The micro-CT images were obtained at the Advanced Photon Source synchrotron facility in Chicago. C, calcite; Q, quartz; F, feldspar

Markers for secondary reactions of migrated crude oil on carbonaceous surfaces: Application to Carnarvon Basin petroleum

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New geochemical techniques have been developed that enable sedimentary reprocessing of migrated crude oil to be identified. The chemical processes occur when crude oil hydrocarbons adsorb onto carbonaceous surfaces, resulting in compositional changes that can be recognised even when further thermal processes and migration occur. These reactions are one set of hydrocarbon reactions that take place on carbonaceous surfaces in sediments (Alexander *et al.,* 2012).

Identifying parameters for reprocessing of migrated crude oil on sedimentary carbonaceous surfaces (Alexander *et al*., 2012) has improved our ability to recognise multiple inputs to crude oil reservoirs. This is particularly applicable where a reprocessed hydrocarbon contribution has geochemical properties that enable it to be readily distinguished from a conventional input. This technology is now applied to crude oils from a sedimentary basin where a range of sources are available and the burial history makes reprocessing of migrated hydrocarbons feasible. The Carnarvon Basin on the western margin of the Australian continent has been a centre of petroleum exploration for over half a century, originally for crude oil but in recent times for liquid natural gas deposits (Longley *et al*., 2002). The basin consists of basin edge sediments on-shore but is mainly off-shore where sediment depths exceed 10km and major sequences cover an age range of Permian to Cretaceous. The main potential petroleum source rocks are of Jurassic, Triassic and Permian ages.

The conventional biomarker approach using trace components indicate the significant commercial accumulations have compositions that are consistent with Jurassic sources (van Aarssen *et al*., 2000, Longley *et al*., 2002). However, there is abundant evidence that multiple episodes of reservoir charging and recharging have occurred (Summons *et al*., 1998), such as 1) initial biodegradation of crude oil in shallow reservoirs followed by subsequent inputs that were less degraded (Volkman *et al*., 1983) and 2) identification of biomarker profiles in fluid inclusions (George *et al*., 1998) and 'vagrant' oils (Summons *et al*., 1998) that were inconsistent with the recognised sources of Jurassic age.

In this paper we apply a combination of the new reprocessing technology together with development in the understanding of natural product contributors to torbanite deposits to not only identify a contribution to crude oils from reprocessing of migrated oil but provide evidence of the probable age of the reprocessed hydrocarbons.

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The unusual nature of the Proterozoic biomarker record and the Mat-Seal hypothesis

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Hydrocarbon biomarkers can remain stable over hundreds of millions of years. Yet, biogenic molecules of pre-Ediacaran age (>635 Ma) are scarce in the geological record and frequently adulterated by younger contaminants (Brocks, 2011; Brocks *et al.*, 2008). In this study, we re-analysed a large proportion of known pre-Ediacaran hydrocarbon-bearing deposits and identified ten basins that contain clearly indigenous biomarkers dating back to 1,640 Ma (Brocks *et al.*, 2005; Summons *et al.*, 1988). After exclusion of contaminant hydrocarbons, the molecular fossils detected in these Precambrian sequences are distinct from their Phanerozoic counterparts. The pre-Ediacaran bitumens show significantly higher concentrations of "unresolved complex mixture" (UCM), low concentrations or absence of eukaryotic steranes, the presence of putative bacterial aromatic steroids, high relative concentrations of mono- and dimethyl alkanes, and a conspicuous carbon isotopic enrichment of straight-chain lipids relative to acyclic isoprenoids and total organic carbon. We propose that these unusual characteristics primarily derive from non-actualistic taphonomic processes based on the pervasive presence of microbial mats in the Precambrian (Pawlowska *et al.*, 2012). This "mat-seal effect" was broken with the onset of bioturbation in the Ediacaran when the primary source of fossil biomarkers switched from the benthos to the plankton.

The disturbance of soft sediments and associated microbial mat cover by infaunal burrowing was one of the most important geobiological innovations in the Neoproterozoic-Phanerozoic transition. This "Cambrian substrate revolution" (Bottjer *et al.*, 2000) had profound effects on contemporaneous ecology (Seilacher, 1999), sedimentology (Droser *et al.*, 2002) and sulphur geochemistry (Canfield and Farquhar, 2009). We argue that it also fundamentally altered the way in which organic matter was incorporated and preserved in the sedimentary record, giving rise to typical Ediacaran and Phanerozoic petroleum reserves, and potentially contributing to increasing atmospheric oxygen levels.

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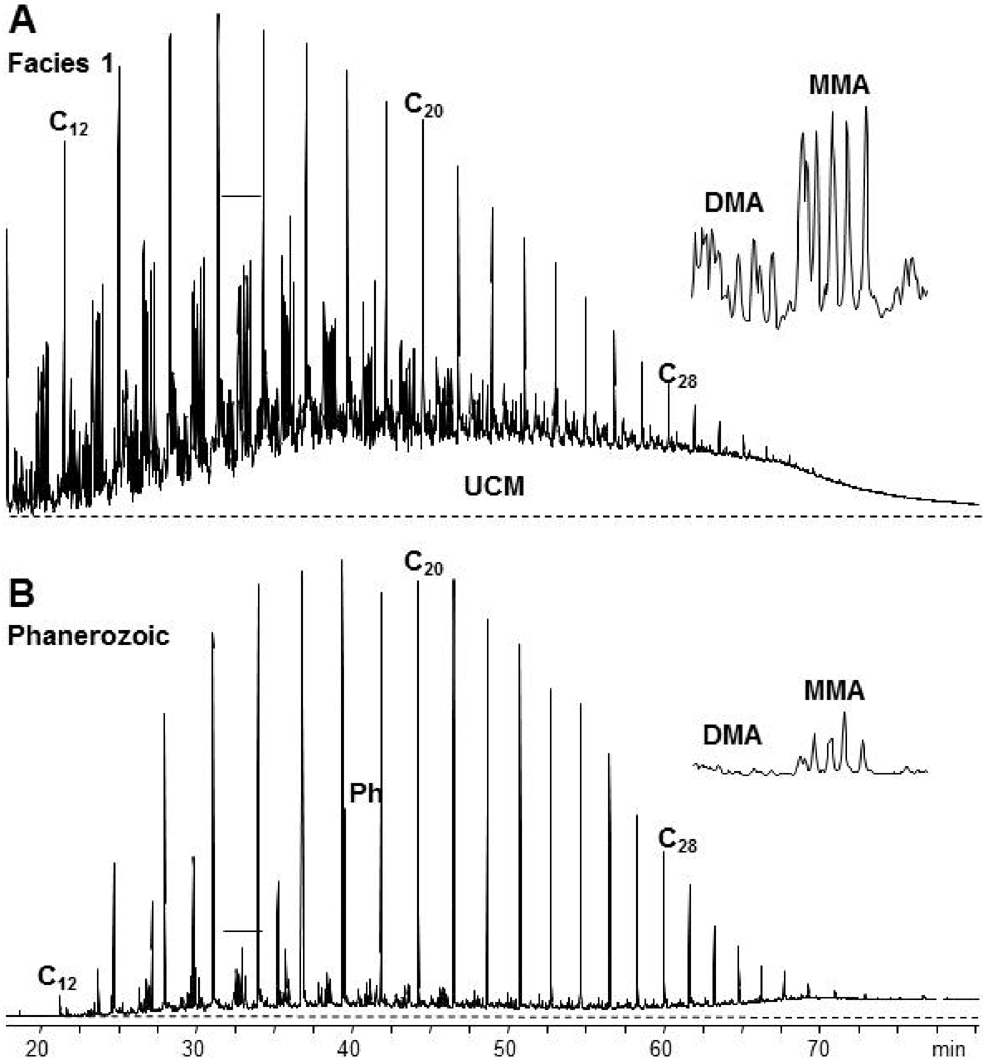

Figure 1. Figure 1. Gas chromatography–mass spectrometry (GC-MS) total ion chromatograms (TIC) of Proterozoic and Phanerozoic saturated hydrocarbon fractions from the ca. 1.1 Ga Neryuen Formation as representative of typical Proterozoic bitumen facies (A), and the AGSO-II industrial standard, representing a mixture of a variety of typical Phanerozoic oils (B). Insets show a horizontal magnification of the region eluting between *n*-C_{15} and *n*-C_{16}, highlighting the distribution of monomethyl alkanes (MMA) and dimethyl alkanes (DMA) (relative signal intensities in A to C are to scale). C_x—*n*-alkanes with carbon number x; black dots—acyclic isoprenoids (i_x) with carbon number x; Pr—pristane; Ph—phytane.

Biomarker assemblage of a pre-Ediacaran microbial mat

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Biomarkers in the pre-Ediacaran Proterozoic (>635 Ma ago)

Molecular fossils, or biomarkers, are altered biogenic compounds that not only can be preserved in the geological record for several hundreds of millions of years but also can be assigned to specific precursor molecules. Hence, biomarker analysis allows assessing groups of organisms that significantly contributed to the organic matter of ancient biological communities. This analysis may be particularly useful to elucidate the time before the last 'Snowball Earth' event >635 Ma ago where microfossils are relatively rare. However, published biomarkers only record 5 geological basins with clearly indigenous bitumens in the interval 1.1 Ga to 0.6 Ga: the 1.1 Ga Atar Group, Taoudeni Basin, NW Africa (Blumenberg *et al.*, 2012), the 1.1 Ga Oronto Group, NE USA (Pratt *et al.*, 1991), the 1.1 Ga Lakhanda and Ui Groups, Sette–Daban fold belt, Siberia (Pawlowska *et al.*, 2012), the 825 Ma Bitter Springs Fm., Amadeus Basin, Australia (McKirdy, 1977; Schinteie, 2011; Summons and Powell, 1991), and the 742 Ma Chuar Group, Grand Canyon, USA (Summons *et al.*, 1988). Here, we present a detailed study of biomarkers from microbial mats in the Taoudeni Basin.

Biomarker assemblage of a 1.1 Ga year old microbial mat (Taoudeni Basin, NW Africa)

The exquisitely well preserved Late Mesoproterozoic black shales from the Taoudeni Basin in Mauritania belong to an organic-rich mat facies (Blumenberg *et al.*, 2012) and display a very interesting composition of biomarkers. We found TOC levels as high as 16% and Rock Eval values indicating a maturity within the early oil window. *n*-Alkanes range from C_{12} to C_{37} with a maximum at C_{17} and a strong odd-over-even carbon number predominance in the range of C_{15} to C_{19}. Pristane and phytane are present but we did not detect any higher acyclic isoprenoids. Regular hopanes and 3β-methylhopanes are abundant while 2α-methylhopanes occur only in low concentrations. Furthermore, we found benzohopanes and D-ring aromatized 8,14-secohopanoids, biomarkers that are rarely reported from the Precambrian. Even though the mats contain simple fossils of eukaryotic origin (Blumenberg *et al.*, 2012), diagnostic eukaryotic steranes were not detected. Interestingly, we found triaromatic steroids methylated at C4 that are of possible methanotrophic bacterial origin (Brocks *et al.*, 2005). Most significantly, we detected aromatic carotenoid derivatives with 2,3,6- and 2,3,4-trimethyl substitution patterns as well as regularly branched oligoprenyl-curcumanes (Brocks *et al.*, 2009). This biomarker assemblage describes a shallow-water microbial mat community that was presumably inhabited by oxygenic cyanobacteria, anoxygenic phototrophic purple (*Chromatiaceae*) and green (*Chlorobiaceae*) sulphur bacteria, as well as Type-I methanotrophs. Our results not only represent the oldest direct observation of the complexity of Precambrian microbial mat ecosystems but also imply that basic modern mat structures are conserved for at least 1 billion years back in time. The role of eukaryotes, which are preserved as microfossils but not as diagnostic sterane biomarkers, remains unresolved.

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Investigating the Syngeneity and the Palaeobiology of Hydrocarbon Biomarkers in the Fortescue Group at 2.7-2.8 Ga

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It is widely accepted that the oxygenation of the previously anaerobic Earth was initiated by the oxygenic photosynthesis of cyanobacteria (Allen and Martin 2007). However, there is a great dispute over the timing of the origin of oxygenic photosynthesis. The presence of cyanobacteria at least as early as 2.7 Ga is suggested by the presence of 2α-methylhopanes, biomarkers thought diagnostic for cyanobacteria (Summons *et al*. 1999), but which are now also known from other bacterial groups (Rashby *et al*. 2007). This is well before the Great Oxidation Event at 2.4 Ga, when atmospheric free oxygen first appeared in appreciable quantities. However, some researchers have rebutted this evidence (Rasmussen *et al*. 2008), by demonstrating that some of the biomarkers are contaminants.

The syngeneity of organic compounds, including the biomarkers for cyanobacteria in Archaean rocks, is now being critically assessed, with a focus on the record preserved in the Fortescue Group of the Pilbara region in Western Australia. For this study, a number of samples from different lithologies have been investigated, including a sample of stromatolitic carbonate (Figure 1). The sample contains aliphatic compounds including n-alkanes, alkylcyclohexanes, pristane and phytane, and also aromatic compounds including naphthalenes, phenanthrenes, biphenyls, and pyrenes. Their distribution reveals the high thermal maturity of the collected rock, which is consistent with the observation that no specific biomarkers such as hopanes and steranes were detected. Another interesting result is that several high molecular weight polyaromatic hydrocarbons (PAHs) were found in one sample. There are few previous reports of similar observations (Brocks *et al*. 2003) and no consensus in regards to the interpretation. The PAHs may provide us with another source of useful information about the Archaean biota, and so their occurrence and distribution is currently being analysed.

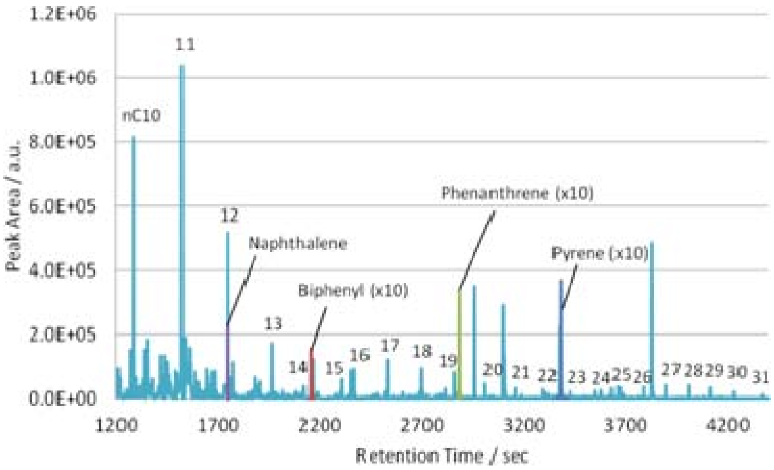

Figure 1. Selected ion chromatograms (*m/z* 57, 128, 154, 178, 202) of extracted organic matter from an Archaean stromatolitic carbonate.

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The organic geochemistry of the Mesoproterozoic Velkerri Formation and investigations into syngenicity and indigeneity of hydrocarbons using slice experiments

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The usefulness of Precambrian hydrocarbons, in particular biomarkers, relies entirely upon both their syngenicity and indigeneity, or rather whether or not they are representative of the same time period and area as the host rock (Eigenbrode, 2008). Due to both age and typically low total organic carbon content however, Precambrian basins are susceptible to hydrocarbon overprinting due to contamination.

This study investigates the presence and nature of hydrocarbon signatures in core slices (from the outside to inside of the core) from the 1.4 billion year old Velkerri Formation, McArthur Basin and assesses the likelihood of the syngenicity and indigeneity of the analysed hydrocarbons. Each slice was crushed, solvent extracted, silica column fractionated and analysed using a Leco two dimensional gas chromatograph (Agilent 7890A) operating in one dimension, coupled to a Pegasus time-of-flight-mass spectrometer (GCxGC-ToFMS).

The outside flat slice and slice A (outside curve) of McManus-1 showed contamination signatures in several compound groups, including *n*-alkanes, monomethylalkanes, bicyclic sesquiterpanes, alkylcyclohexanes, alkylnaphthalenes and alkylphenanthrenes. Although both the outside flat slice and slice A (outside curve) were subjected to secondary organic matter input, the signatures were dissimilar and had differing origins (from sawing and drilling processes respectively).

Internal slices were found to have consistent hydrocarbon signals, providing strong evidence that the organic matter in the inner slices is indigenous. This study highlights the necessity for the removal of the exposed outside of the core prior to solvent extraction, not only in lean Precambrian rocks (as determined by Brocks, 2011), but also in Precambrian rocks rich in organic matter.

Despite previous identification of sterane biomarkers in Velkerri Formation rock extracts (Summons *et al*., 1988) and oils (Jackson *et al*., 1986), no steranes were detected in any cores analysed in this study, indicating low eukaryotic input in this deep environment.

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Hydrothermal destruction of hydrocarbons in Proterozoic evaporites

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The Proterozoic era saw major global glaciations, transitions in the redox structure of the oceans and a major radiation of eukaryotes culminating in the evolution of active animals in the Ediacaran. Invaluable information about the early evolution of life, the redox state of the oceans and even mechanisms of syndepositional ore formation can be gained from indigenous Proterozoic biomarkers. One of only few successions in the world yielding clearly indigenous biomarkers predating the Cryogenian glaciations is the 825 Ma Bitter Springs Formation (BSF) in the Amadeus Basin, Central Australia. The BSF is one of the oldest known major evaporite deposits and was of great importance for the elucidation of the chemistry of Earth's early oceans (Holland, 1984). McKirdy (1977) was the first to discover biomarkers in the BSF in drill core Mount Charlotte-1 (MC-1), and Schinteie (2011) used new biomarkers from the same core for a detailed reconstruction of Proterozoic hypersaline microbial communities.

One intriguing aspect of the study by Schinteie (2011) was the observation that only ~20% of samples contained clearly indigenous biomarkers. However, it did not appear to be possible to predict biomarker presence and absence based on optical inspection and TOC content. This fact made analyses of rock samples from the basin extremely cost and labour-intensive. Therefore, to determine the mechanisms that govern biomarker preservation and destruction, we correlated hydrocarbon (HC) absence/presence data of 117 samples from MC-1 with TOC, Rock Eval, solid bitumen reflectance, HC maturity indices, mineralogy, optical inspection of thin sections, and the carbon and oxygen isotopic composition of dolomite. We found that the occurrence of indigenous HCs is restricted to certain depth-intervals only. We found clearly indigenous HCs in the core intervals 1567-1568 m, 1615-1618 m, 1650-1655 m, 1772-1780 m, and 2112-2115 m. We did not detect any indigenous HCs (except thermally mature diamondoids) above or in between these intervals. This distribution clearly indicates that biomarker preservation was not controlled by burial depth. However, upon optical inspection of thin sections and XRD analyses, there appeared to be no clear difference in sedimentary structures and mineral content between samples that did and those that did not contain HCs. HC occurrence was also clearly not controlled by organic matter content. In MC-1, HCs were found in some, but not all, light-coloured dolomites and anhydrites with very low organic carbon contents (TOC < 0.1%) but were absent from many dark-coloured layers with higher TOC contents.

A fraction of samples with low absolute HC-abundances contained relatively high concentrations of adamantanes and diamantanes. Diamondoids are thermally extremely stable, suggesting that they survived extensive thermal cracking in these particular samples. Moreover, absolute diamondoid concentrations were often particularly high in those samples where other HCs were beneath detection limits, suggesting that they were generated by thermal decomposition of other compounds. Furthermore, the maturity indicator Methyl Adamantane Index (MAI) (Chen *et al.*, 1996) correlates well with HC preservation. For 40 extracts with vitrinite reflectance equivalents Vr(MAI) ≤ 1.5%, we found that all but three contained preserved branched and *n*-alkanes. Conversely, in all extracts with Vr(MAI) >1.5% (n = 18), *n*-alkanes were beneath detection limits. This suggests that local thermal events controlled HC destruction in MC-1 with a clear preservation threshold at Vr(MAI) = 1.5%.

The carbon and oxygen isotopic composition of dolomite associated with the bitumens suggests that the major thermal influence in MC-1 was hydrothermal. MAI shows a week but significant negative correlation with $\delta^{18}O$ of dolomite ($n = 29$, $R^2 = 0.45$, $p < 0.05$), pointing to the flux of hot brines in zones of HC destruction. Moreover, in almost all samples where hydrocarbons are preserved, $\delta^{18}O$ of dolomite is relatively unaltered while $\delta^{13}C$ of dolomite is depleted by up to 8‰, indicating incorporation of OM-derived CO_2 (Fig. 1). Thus, in a $\delta^{13}C/\delta^{18}O$ cross-plot, samples with preserved biomarkers (HC+) commonly fall into a distinctive zone towards the lower right of the diagram (Fig. 1). The recognition that HC preservation in areas of the Amadeus Basin may be controlled by local hydrothermal activity will have implications for the future search for Precambrian biomarkers and on-going petroleum exploration. Ultimately, we aim to establish fast and cost-effective screening techniques for recognizing stratigraphic units that may yield indigenous Precambrian biomarkers.

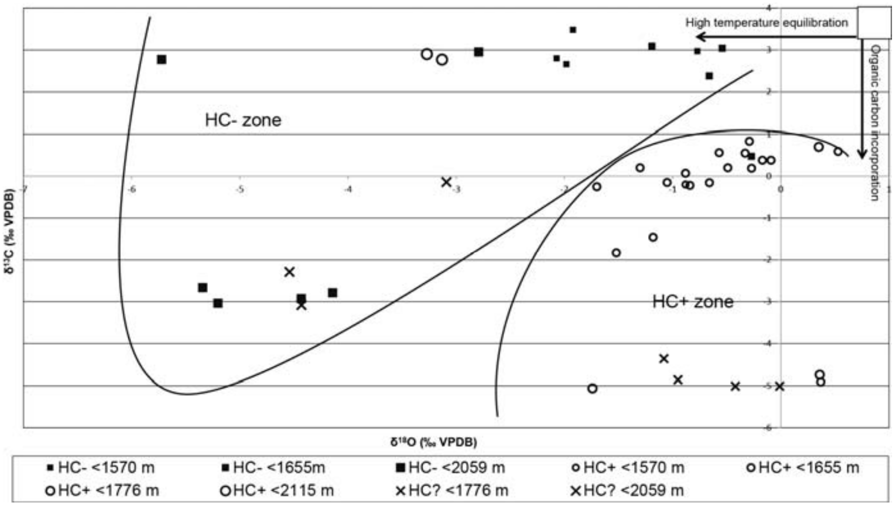

Figure 1. Crossplot of $\delta^{18}O$ and $\delta^{13}C$ of dolomite for samples that contain (open circles, 'H+') or are devoid of (filled squares, 'H-') indigenous HCs. 'x' represents samples where HC syngeneity could not be fully established ('HC?'). Sample depth is indicated by symbol size with larger symbols representing greater depth. The large open square represents the estimated initial isotopic composition of dolomite, and the arrows point in direction of high temperature equilibration and OM-derived CO_2 incorporation.

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Analysis of organic matter preserved within the kerogen-mineral matrix of the Paleoproterozoic Here's Your Chance Pb-Zn-Ag deposit

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The Barney Creek Formation (BCF) is a 1639 ± 2 Ma carbonaceous marine shale located in the McArthur Basin (Northern Territory, Australia). The BCF contains some of the best preserved known biomarkers of Proterozoic age (Brocks *et al*., 2005). It is also host to the Here's Your Chance (HYC) Pb-Zn-Ag deposit, one of the world's largest sediment-hosted Pb-Zn-Ag deposits. HYC was formed by the interaction of hot, metal-rich fluids with BCF sediments (Williford *et al*., 2011). There is great potential for organic geochemistry to provide information about ore deposition, but interpretations are complicated by significant thermal alteration and the likely transport of non-indigenous organic matter by the mineralising fluid (Williford *et al*., 2011).

Five samples were collected from HYC along the flow path of the mineralising fluid. The freely-extractable hydrocarbons (Bitumen I) from these samples have been analysed by Williford *et al*. (2011). The present study has investigated hydrocarbons that were occluded within the kerogen-mineral matrix (Bitumen II), following hydrofluoric acid digestion and extraction as per Nabbefeld *et al*. (2010). It is expected that Bitumen II is protected from the effects of migration and thermal alteration by the kerogen-mineral matrix and thus will more closely reflect the original depositional conditions. It has been shown that while certain compounds such as high molecular weight aromatics are somewhat resistant to extraction, Bitumen II has not been significantly affected by residual Bitumen I left over after extraction (Holman *et al*., 2012). We are therefore confident that Bitumen II does indeed contain organic matter closely associated with the kerogen-mineral matrix.

Bitumen II *n*-alkanes display a markedly different distribution to those of Bitumen I, characterised by an unusual even-over-odd distribution and the preservation of long-chain alkanes up to n-C_{38}, indicating a biological source such as sulfate-reducing or sulfide-oxidising bacteria (Melendez *et al*., 2012). As Bitumen II is protected from alteration and migration it is likely that these bacteria were associated with the depositional environment. Bitumen II *n*-alkanes are 5 ‰ more negative in δ^{13}C compared to Bitumen I, suggesting that Bitumen I alkanes originate from a different source. Comparison of isotopic compositions with those of isolated kerogens shows that Bitumen II alkanes are likely to be indigenous to HYC, while the Bitumen I alkanes may have migrated from an underlying formation.

The maturity of the HYC samples has been evaluated by calculating methylphenanthrene (MP) ratios for both Bitumen I and Bitumen II. The various MP ratios showed conflicting results. The ratio MPI-1 was consistently lower in Bitumen II than Bitumen I, but MPR and MPI-3 often displayed the opposite relationship. Thermodynamic calculations have revealed that the equilibrium constants of MP isomerisation reactions change with temperature (Dick *et al*., in preparation). This may explain the anomalous behaviour we have observed. Comparison of the MP ratios with other maturity indicators such as diamondoid ratios may help to constrain the thermal history of the deposit. Additionally, microscale sealed vessel (MSSV) pyrolysis has been performed on a non-mineralised organic-rich sample from the BCF to attempt to simulate the maturation of the OM associated with the mineralised zones of HYC and thus replicate the organic maturity sequence found in the BCF.

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Evolution of biosynthetic pathways and the geological record of acyclic isoprenoid hydrocarbons such as HBI alkenes, botryococcenes and lycopadiene

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The use of specific lipids (biomarkers) to assign the sources of organic matter in sediments and petroleum is well established in the organic geochemical literature. Examples from contemporary environments include long-chain alkenones as markers for haptophyte algae, highly branched isoprenoid (HBI) alkenes as markers for diatoms and long-chain alkyl diols as markers for either eustigmatophytes or diatoms depending on the location of the mid-chain hydroxy group. The concept of age-diagnostic biomarkers has also emerged (e.g. Moldowan, 2000; Brocks and Summons, 2003), which recognises that some compounds first appear in the sediment record at a defined point in time. This has proven to be a very powerful tool in assessing the age of petroleum samples (e.g. Moldowan, 2000; Sinninghe Damsté *et al.*, 2004).

The biosynthetic pathways for some of these biomarkers are now being elucidated, particularly those associated with acyclic isoprenoids through the recent work of Niehaus *et al.* (2011, 2012) and others. However, many pathways are still poorly understood or are seemly unrelated to those for other lipids (as for the alkenones). We are now in the enviable position of being able to use the age-dated occurrence of biomarkers in sediments combined with molecular biology studies of extant organisms to understand the evolution of biosynthetic pathways over geological time (e.g. Brocks and Summons, 2003). This time line for the first appearance of different biosynthetic pathways can then be used to calibrate the concept of age-diagnostic biomarkers and provide a basis for establishing whether the biomarker would be unique to one class of organism or not. This information can help explain why some biomarkers appear in ancient environments very different from those where organisms living today are found.

An example of this approach is the work by Sinninghe Damsté *et al.* (2004) who showed that HBI alkanes derived from the C_{25} and C_{30} HBI alkenes synthesized by diatoms (Volkman *et al.*, 1994) are not found in oils or sediments older than ca. 92 Ma. The inference is that this biosynthetic pathway first emerged about this time probably by some small changes in the genes involved in the coupling of isoprenoid units. Moreover, these authors could show by lipid and genetic analyses of many modern diatoms that the pathway must have evolved at least twice in quite distantly related genera. Since diatoms are a relatively recently evolved class of microalgae, it seems unlikely that HBI alkenes are biosynthesized by other algal classes. For the petroleum geochemist, these findings are of practical importance since any oil containing these unusual hydrocarbons must have been generated from sediments no older than 92 Ma.

The freshwater unicellular green alga *Botryococcus braunii* (Chlorophyta, Trebouxiophyceae) was first described by Kützing in 1849. Algal remains attributed to the genus *Botryococcus* have been identified in sediments ranging from Precambrian to Recent, and this species is believed to have been a major source material for petroleum generation (Glikson *et al.*, 1989). It is well known as the presumed source of organic-rich torbanite oil shales and of modern rubbery deposits in South Australia termed coorongite. Modern-day *B. braunii* exists in 3 distinct races with different biochemistry. The A race produces long-chain alkadienes and alkatrienes, the B race produces C_{30}-C_{37} botryococcenes and methylated squalenes while the L race produces lycopadiene. However the identification of the alga in older samples is only possible by transmission electron microscopy (Glikson *et al*., 1989) and isoprenoid biomarkers for this species have yet to be found in sediments older than the Eocene. Derenne *et al.* (1988) did not detect botryococcane in any of 12 torbanites from different localities that they studied. Moreover, microscopic studies of extant microalgae thought to be *B. braunii* have revealed a number of different morphologies and it is likely that many should be classified as different species (Kawachi *et al*., 2012). I suggest that it is more parsimonious to suppose that species ancestral to present-day *B. braunii,* but having a similar morphology, contributed to organic-rich deposits in the past, rather than this particular species. It is possible, as suggested by Derenne *et al.* (1988), that these species may be ancestral to the A race of *Botryococcus* □ indeed, phylogenetic trees of green algae are consistent with this view – but species having a more conventional green algal biochemistry is also possible.

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I Dated a Salt Lake, and It Broke My Heart

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Radiocarbon analyses of source-specific fractions of organic matter are now useful to characterise millennia scale soil carbon flux and to assign dates to young sedimentary features. Here, radiocarbon dates of bulk organic carbon are compared with dates of aliphatic hydrocarbons (primarily long chain *n*-alkanes) from a hypersaline lake in south eastern Australia. The age-depth profiles of the bulk and aliphatic hydrocarbons form three groups dependent on the presence or absence of microbial communities and sediment disconformities. However, the ages of the aliphatic hydrocarbons are significantly older than the bulk organic extracts, suggesting the presence of an active reservoir of ancient organic carbon, likely through aeolian reworking of sediments. Reworking of sediments exposes carbon to oxidative effects and removal, and accordingly total organic carbon content in these sediments is low with recalcitrant hydrocarbons predominating. Additionally, the compound class specific radiocarbon analysis improved signal-to-noise in the data, and also identified a change in biomarker source in time unidentifiable by conventional biomarker or isotope analysis. While the radiocarbon data is ultimately unsuitable for dating, the data greatly enhances the interpretation of the distribution of organic carbon in the sediments and provides clues to the behaviour of long term carbon storage in arid terrestrial organic carbon reservoirs.

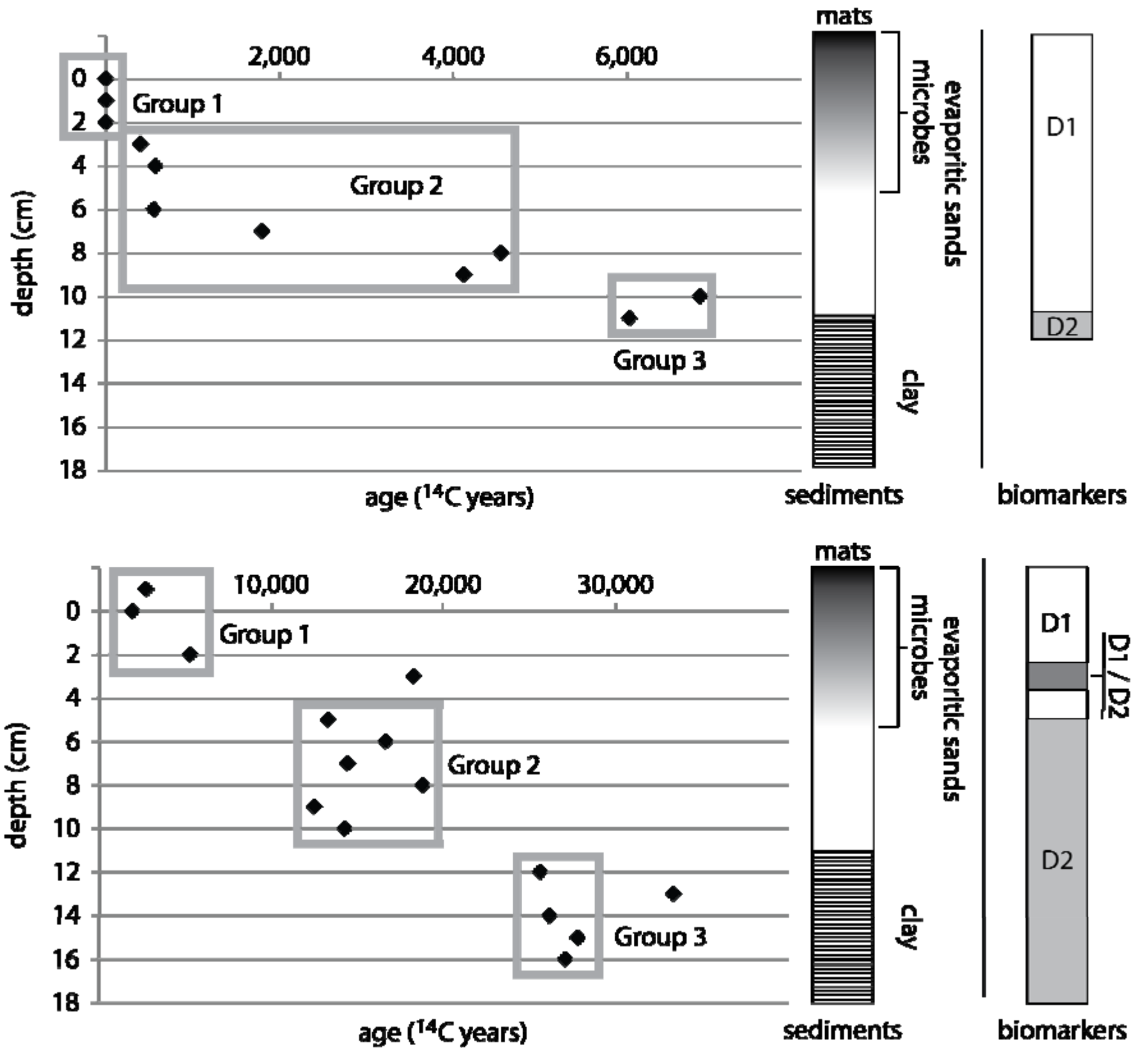

Figure 1. Comparison of radiocarbon ages for the bulk organic matter (top) and aliphatic hydrocarbons (bottom) from a hypersaline lake. D1 refers to a biomarker content dominated by complex polar biomarkers sourced from the active organismal consortia in and around the lake. D2 refers to a biomarker content of nearly exclusively long chain *n*-alkanes. D1/D2 refers to a section of the core containing elements of both D1 and D2; specifically this section is dominated by long chain *n*-alkanes y*et al*so contains significant amounts of archaeol and other complex polar biomarkers.

Amino acids in deep-sea coral: what nitrogen isotopes reveal about food web dynamics in a changing climate

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The East Australian Current (EAC) has strengthened over the past 50 years, caused by the overall spin-up of the South Pacific Gyre. While increasing sea surface temperatures are well constrained along the East Australian coastline, the flow on effects occurring in open ocean marine ecosystems are more difficult to document. In this study, the nitrogen isotope composition of individual amino acids in the deep-sea Bamboo Coral *Lepidisis* spp. (Isididae) are used to reconstruct a century of nutrient distribution and food web dynamics from two sites on the Lord Howe Rise.

There is enormous potential for deep-sea corals to act as archives of surface and deepwater processes, due to their longevity, distribution and feeding strategies. Bamboo Corals continuously integrate surface-derived particulates into discrete protein bands within their skeleton; analogous to sedimentary organic matter records down core. However, the interpretation of isotopic signatures from bulk samples extracted from these skeletons can be confounded due to the *a priori* information needed to differentiate between trophic enrichment and the original isotopic composition at the base of the food web. By comparing amino acids that remain relatively unchanged from the ‘source’, to those that fractionate significantly with ‘trophic’ transfer, an internally consistent record of regional food web dynamics emerges (McClelland and Montoya, 2002; Popp *et al*., 2007). In addition, investigating the spread of ‘trophic’ amino acids provides insight in to the reprocessing, or reworking, of the particulate food source through the water column (McCarthy *et al.*, 2007).

The compound specific approach provides strong evidence that while the isotopic values at the base of the food chain are consistent between the two sites, the corals at these sites occupy different trophic niches. Furthermore, coherent patterns emerging from the base values indicate that multi-decadal climate forcing may be influencing regional ecosystems. We discuss these results in the context of the physical mechanisms that dictate the regional distribution of phytoplankton and nitrogen-fixing organisms.

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Application of a linear transfer model for the estimation of the hydrocarbon concentration in the seawater of Antarctica following a fuel spill

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Despite the widespread use and transport of fuels in Antarctica, there is very limited data available on the behaviour and weathering of these fuels in the Antarctic marine environment, and the potential impacts of a fuel spill on marine biota are largely unknown. Dissolution of compounds from the nonaqueous phase of the fuel into the aqueous phase is one of the main processes responsible for the toxicity of spilled fuel to marine organisms. Understanding the kinetics of this process is crucial in modeling and predicting the effects of a spill. This exchange process occurring in the marine environment was simulated in the lab by a slow stirring batch system, commonly used to measure solubility and partition coefficients.

Detailed gas chromatography-mass spectrometry analyses were performed on the fuel and seawater in order to identify and quantify all the hydrocarbons present in the organic and the aqueous phase and thus determine their partition coefficients. This experimental data was found to agree with the predictions of Schluep *et al*. (2001), who devised a linear transfer model, which was modified in this work for the unique Antarctic conditions. These modifications included the addition of salinity and its effect on the dissolution of hydrocarbons into the aqueous phase, as well as the addition of a correction for the low temperature of the marine environment of Antarctica.

Generally the application of this model is found to be valid for the low solubilities of hydrocarbons in marine fuels. Therefore the model can be used to estimate the concentration of hydrocarbons in the seawater of Antarctica as a function of the exposure time to the fuel spill.

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Characterisation of organic matter in a tidally inundated tropical acid sulfate soil wetland

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The acidification of large areas of Australian coastal landscapes has significant environmental, economic and social impacts. Acid sulfate soils (ASS) are soils and sediments containing significant quantities of iron sulfides (e.g. pyrite). Widespread around coastal Australia, ASS are benign under saturated or highly reducing conditions. However, oxidation of iron sulfides by exposure to air, either naturally (e.g. prolonged drought) or through human intervention (e.g. drainage, excavation) can cause severe soil acidification (Dent and Pons, 1995). Highly acidic drainage waters (pH < 4) from ASS pose a direct environmental threat and also contribute to the release and transport of aluminium and other heavy metal contaminants toxic to vegetation and aquatic biota (Fitzpatrick *et al.*, 1998).

Rehabilitation of ASS landscapes is a complex and costly problem. An innovative remediation method based on tidal exchange was implemented in 2002 at East Trinity Inlet, a Holocene sedimentary coastal plain located approximately 1km from the Cairns CBD in Far North Queensland. In the early 1970s a tide-excluding sea wall was constructed at this site and >700 ha of estuarine floodplains supporting diverse mangrove and samphire communities were drained and cleared for agriculture. Oxidation of the underlying sulfide-rich sediments resulted in severely acidic soils and waters (Hicks *et al.*, 1999), reflected in drastically diminished populations of aquatic biota, mangroves and major fish kills. Re-establishing regular marine tidal inundation to various parts of the East Trinity site has proved relatively successful at neutralising acidity and improving soil and water quality (Powell and Martens, 2005). Reductive transformation and redistribution of reactive iron and sulfur species has resulted in an iron hyper-enriched redox gradient across the seawater inundation interface (Keene *et al.*, 2010). The long term implications of these processes will influence the effectiveness and continued application of this remediation approach to contemporary coastal ASS (Johnston *et al.*, 2009, Burton *et al.*, 2011).

While significant research has been conducted on the inorganic geochemistry of tidally re-flooded ASS (Burton *et al.*, 2011 and references therein), the role of organic carbon on Fe/S mineralisation remains poorly understood. Cross-disciplinary integration of organic geochemical data with microbial community and inorganic geochemical data should provide fundamental knowledge regarding the primary sources and mechanistic role of sedimentary organic carbon in the biogeochemical cycling of iron and sulfur in such environments. Therefore, a range of analytical techniques are currently being employed to comprehensively characterise the molecular and stable isotopic composition of organic matter (OM) from several core sections recovered from key sites within the East Trinity wetland. Biomarker information from the analysis of extractable lipid hydrocarbons, combined with the chemical derivitisation products of polar components and analytical pyrolysis data from refractory macromolecular fractions will be used to provide a holistic interpretation of the nature, abundance, distribution and sources of the OM in this environment. The East Trinity sediments are rich in biomarker information reflecting a variety of terrestrial, marine and microbial inputs. Dominant lipid classes include *n*-alkanes, methyl alkanes, sesqui-, di- and triterpenoids, highly branched isoprenoids, sterols and steranes, hopanes, fatty acids and *n*-alcohols (Figure 1). This paper will provide an overview of some of the results obtained to date, with particular emphasis on the impact of tidal inundation on the nature and quantity of the OM present in the surface sedimentary layers.

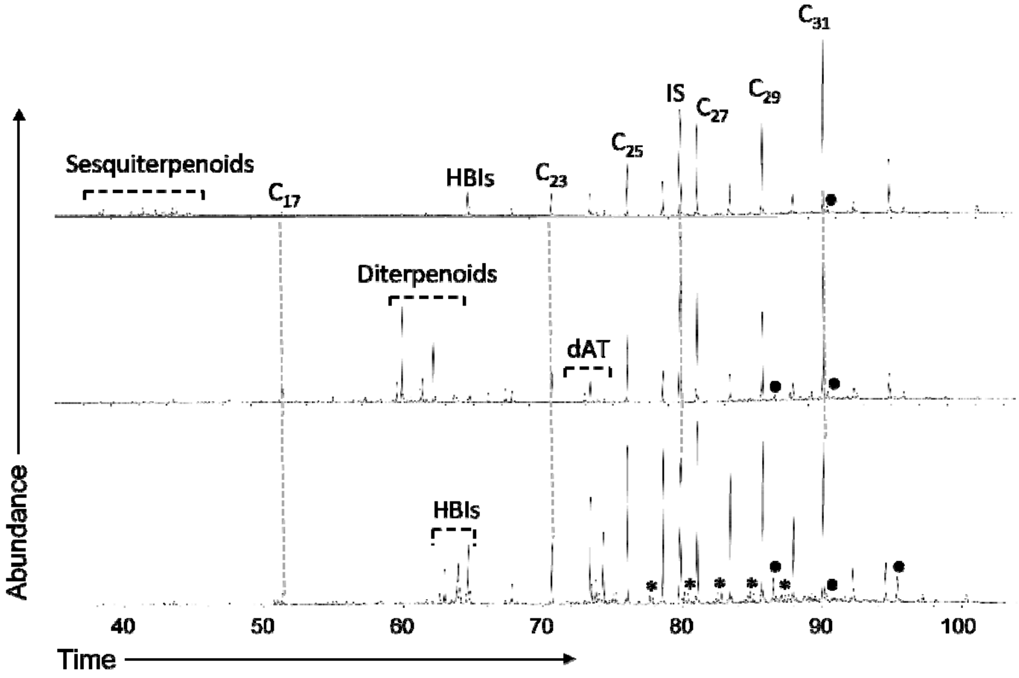

Figure 1. GC-MS chromatograms of saturate hydrocarbon fractions from East Trinity surface sediments (0-6 cm) across a transect spanning a) supratidal, b) intertidal and c) subtidal zones. C_x – *n*-alkanes, dAT – des-A-triterpenes, HBIs – C_{25} highly branched isoprenoids, * - methyl alkanes, • - hopenes, IS – internal standard.

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Abiotic sulfurisation of a modern ecosystem and the preservation of early life

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Living microbial mats from Shark Bay, Western Australia, are thought to provide excellent analogy with past environments and fossil stromatolites. Sulfurisation is known as a key process for the preservation of biolipids during the earliest stage of diagenesis and sulfurised organic matter has been previously reported in stromatolites (Lepot *et al.*, 2009). The formation of organic sulfur compounds (OSCs) requires the production of H_2S by sulfate-reducing bacteria (SRB) and specific environmental conditions (Damste and de Leeuw, 1990). *In-situ* measurements were made of sulfide and iron (II) distributions (mm-resolution) across a modern layered smooth mat from Shark Bay. The two-dimensional distributions showed suitable conditions for the formation of OSCs, with an iron (II) concentration below 50 μM and a sulfide concentration up to 500 μM. For the first time in a living system, aliphatic and aromatic sulfur-bound biomarkers were found in the four different layers of the mat and showed a very different distribution than the ones from the free extracts, suggesting a contemporary sulfurisation of the modern ecosystem had occurred. Fully reduced carotenoids were identified in the sulfur-bound fractions implying that H_2S produced by SRB was the hydrogen donor (Hebting *et al.*, 2006). Through an increase of alkalinity, SRB also promote the precipitation of carbonates which favours mat lithification and formation of microbialites (Reid *et al.*, 2000). The carbonate-bound biomarkers from each layer of the mat showed a predominance of long-chain *n*-alkanes. This biomarker signature was recently found in a chert old of 2.3 billion years old and was associated to the presence of SRB (van Kranendonk *et al.*, 2012). The enriched isotopic signature of the carbonate-bound biomarkers suggests that the SRB, living in this hypersaline environment, were strongly involved in carbonate recycling. The study of sulfur-bound and carbonate-bound biomarkers in this mat allows a correlation of biomarkers between a modern mat and a chert old of 2.3 billion years old (van Kranendonk *et al.*, 2012).

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Flash pyrolysis GCMS analysis of fluid inclusions

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Fluid inclusions (FIs) are ubiquitous throughout sedimentary environments and studies of their molecular or stable isotopic composition can assist both mineral and petroleum exploration (Gizė, 1999; George *et al.*, 1997, 2007). The data from such analyses, for example, may provide information about the fluids responsible for mineral precipitation (Gizė, 1999b, Polito, 1999), palaeo-oil charges or migrating oil. Most FIs contain simple gases such as CO_2, H_2O (± salts) and sometimes CH_4 and higher MW hydrocarbons. The FIs in petroliferous sediments often also include liquid hydrocarbons.

The molecular composition of FIs is commonly studied by GCMS after they are opened by methods including mechanical crushing, thermal decrepitation, laser drilling or carbonate dissolution with ethyl diamine tetra-acetic acid (Horsfield and McLimans, 1984; Greenwood *et al.*, 1998; Polito, 1999; George *et al.*, 2007). Microscale Sealed Vessel Pyrolysis (MSSVpy), where FIs are crushed in a purpose built injector port, has long been marketed as a specialised method for FI analysis. In a different approach, we recently used a pyroprobe to successfully open gas and oil-bearing inclusions through the flash pyrolysis application of heat only. High thermal energies can be used to decrepitate inclusions close to the surface of the host crystal (Horsfield and McLimans, 1984). Our initial pyroprobe pyrolysis GCMS results on a small suite of natural and synthetically prepared oil-bearing fluid inclusions have been achieved with similar analytical sensitivity to MSSVpy. The hydrocarbon profiles measured following flash pyrolysis were also shown to be similar to data (e.g., Jabiru inclusions, George *et al.*, 1997) from MSSVpy as well as the reliable molecular composition of inclusions (MCI) which involves off-line crushing under solvent followed by liquid chromatography and GCMS. The Pyroprobe GCMS analysis of synthetically prepared oil FIs also showed a close correlation to the parent oil (Figure 1). This positive correlation suggests that relatively universal flash pyrolysers are a convenient alternative to the specialised MSSVpy device for on-line GCMS analysis of FIs.

Flash pyrolysis can also be used to measure the $\delta^{13}C$ values of the gaseous constituents of FIs and this approach would seem far simpler to the sophisticated analytical systems developed to support previous on-line $\delta^{13}C$ measurement of FI gases – e.g., vacuum lines with crushing devices directly interfaced with isotope ratio mass spectrometers (Potter and Longstaffe, 2007). Whereas the molecular complexity of oils represents a significant challenge to GCirMS, the different constituents of gas FIs can be sufficiently resolved with specialised gas columns for discrete $\delta^{13}C$ measurement. The integrity of pyrolysis generated isotopic data measured still needs to be established. There has been some concern that thermal (and crushing) methods may distort the molecular or isotopic composition of gas FIs (Polito, 1999; Potter and Longstaffe, 2007), although our present data and previous studies on oil-bearing FIs have shown that the molecular profile of C_7-C_{35} liquid hydrocarbons in FIs do not appear to be affected by thermal decrepitation (e.g., Horsfield and McLimans, 1984; Greenwood *et al.*, 1998).

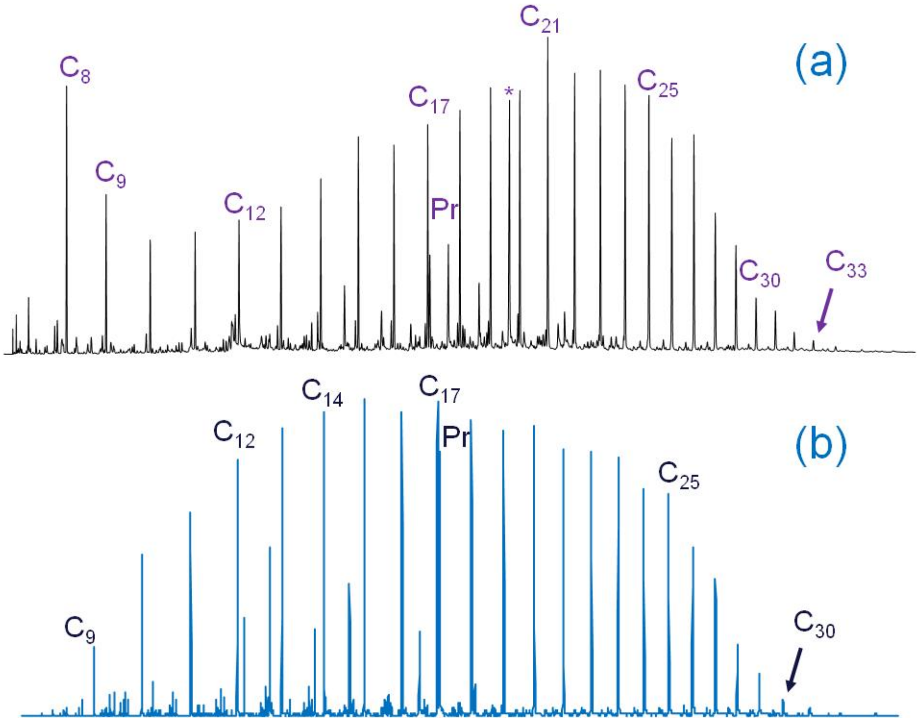

Figure 1. GCMS chromatograms from (a) pyroprobe opened synthetically prepared Halibut A-1 oil (Bass Strait) containing FIs opened by pyroprobe pyrolysis; and (b) the aliphatic fraction of Halibut A-1 oil.

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Organo-mineral nanocomposite control of organic carbon concentration in source rocks and unconventional (shale) reservoirs

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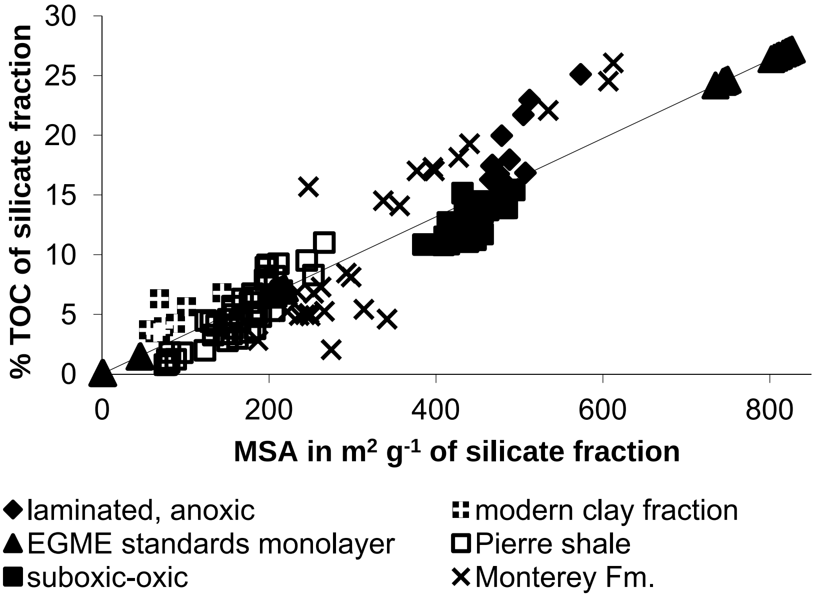
Production surveys from unconventional (shale) reservoirs show significant variability between wells and even between frac stages in single wells. This variability is inconsistent with the homogenous source/reservoir concept of a resource play and implies geological variability as an influence in gas and oil production. One little considered, though potentially significant geological consideration specific to unconventional reservoirs, is the intimate (nano-scale) relation between organic carbon and reactive mineral surfaces typical of modern sediments. Shale is characterized by a significant percentage of clay minerals with reactive surfaces known to preserve, catalyse, or polymerize organic molecules. These organo-clay composites have different thermal stability than discrete organic particles and may influence the timing of hydrocarbon generation and over pressure through mineralogical transformations such as illitization. Data presented here from classic source intervals including the Monterey Fm., Pierre Shale, Woodford Fm. and Green River Fm, show a strong first order relationship between mineral surface area (MSA) and TOC that indicates the majority of organic carbon occurs as sub-micron scale organo-mineral composites and not as particulate organic compounds. This relationship was initially established in the depositional environment where mineral surfaces acted to preserve and stabilize organic matter. Examples from thermally immature late Cretaceous aged deep ocean sediments from the West African Deep Ivorian Basin and Eastern Atlantic Demara Rise including ocean anoxic events 2 and 3 show a strong relation between MSA and TOC ($r^2 > 0.9$). These findings link cyclical variation in TOC from 3% - < 20% to variations in detrital clay mineralogy resulting from precessional timed changes in continental climate conditions on the African and South American continents rather than ocean scale anoxia. A positive relationship between MSA and TOC can also be maintained through burial. Illitization of the Woodford Shale maintained proportionality between TOC and MSA however the loss of MSA with the collapse of interlayers increased the TOC:MSA and expelled



organic matter from interlayer sites. These data show that the initial controls of clay mineral delivery to marine environments (provenance, continental climate, shelf sedimentology) determine TOC in sediment and will continue to influence hydrocarbon production through burial and diagenesis to well-completion. These findings raise the question how gas/oil are distributed in self-sourced shales if most organic matter is mineral associated at molecular scale. Micro-porosity or local migration to interbedded permeable silt intervals provides two alternatives.

A volcanic clay mineral control of carbon burial during OAE II

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The geological record is punctuated by intervals of widespread organic carbon (OC) enrichment commonly referred to as Ocean Anoxic Events (OAEs). OAE2, at the Cenomanian-Turonian boundary, is considered the most consistent and widespread of the various OC enriched intervals identified as resulting from an OAE and shows evidence of intermittent and persistent deep-water anoxia and a general continuity of black shale deposition across Atlantic and Tethyan basins (Arthur *et al.*, 1987). A broadly coincident positive $\delta^{13}C$ excursion indicates enhanced global OC burial during this period (Erbacher *et al.*, 2005). OC enrichment in OAE2 sediments is most commonly attributed to a reduced rate of OC degradation associated with anoxia. Oxygen-depletion is thought to have been caused by increased primary productivity, sluggish circulation, warm bottom-waters containing less dissolved oxygen or release of hydrothermal fluids associate with magmatic activity.

However, recent work on OAE sediments has shown that dm-scale TOC variability reflects local or regional scale controls such as the impact of orbital forcing on continental climate and runoff (Beckmann *et al.*, 2005). A direct continental influence on OC enrichment through the preservative effect of detrital minerals has also been demonstrated. This work identifies a quantitative association between mineral surface area (MSA) and TOC in both modern and ancient continental margin sediments (Mayer, 1994; Kennedy and Wagner, 2011). These findings imply that OC enrichment is strongly influenced by MSA availability, which is in turn a function of the type and local abundance of detrital clay minerals. This raises the question of the relative importance for OM preservation in an OAE of oceanographic controls on oxygen *versus* mineral surface preservational effects. In addition, if a clay mineral preservative effect is identified it is unclear how local continental mechanisms that control detrital clay mineral composition and flux can account for the widespread black shale formation typical of OAE2.

Here we show a first order relation (r^2 0.93) between OC concentration and sediment MSA (Figure 1) in OAE2 black shales from the western North Atlantic margin (ODP Leg 207, Demerara Rise), suggestive of a clay mineral preservative effect provided by abundant smectite clays. Trace metal data and benthic foraminifera assemblages show that minor variations in oxygen availability are out of phase with OC enrichment in these sediments. OM in the Demerara Rise black shales is highly degraded and mostly amorphous, macerals with recognizable particulate precursors are rare (Summerhayes, 1981). High-resolution X-ray (STXM) and electron (TEM) transmission microscopy confirms that preserved OM is mainly nano-scale and associated with smectite clays, rather than primary particles. Based on these findings we argue that smectites with high MSA provided the dominant OC preservation effect during OAE2, whereas oxygen availability played a second order role.

If smectite accounts for organic carbon preservation, then how does one explain widespread intervals of smectite concentration such as OAE2? Sr, Os, Nd and S isotope anomalies measured across the C isotope excursion used to define OAE2 show an increase in mantel derived metals at geographically distant locations (e.g. Turgeon and Creaser, 2008; Adams *et al.*, 2010), most likely linked to volcanic activity associated with the Caribbean and Madagascar large igneous province. Smectitic clays are a major weathering product of volcanic materials (Chamley, 1989) and periods of enhanced volcanism are known to contribute to increased formation of smectite rich marine shales. It is likely that the widespread concentration of smectite in the OAE 2 interval can be traced to continental weathering of volcanic material coupled to high sea level stand at the Cenomanian/Turonian boundary.

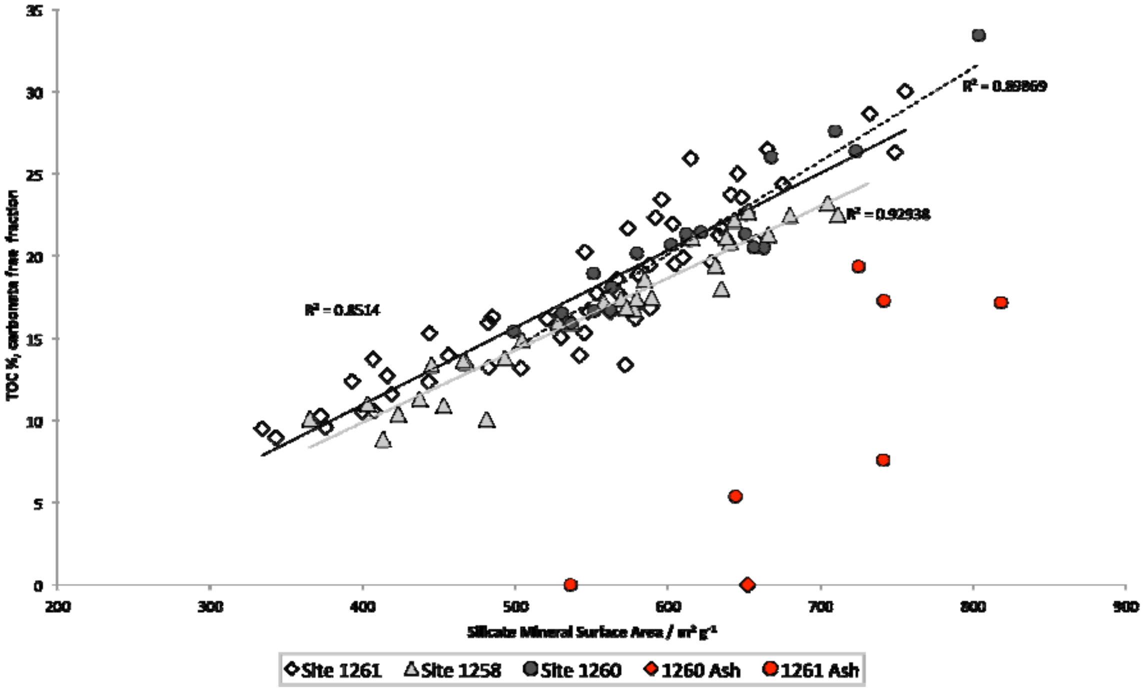

Figure 1: MSA of the silicate fraction (corrected for carbonate and OC dilution) vs TOC of carbonate free fraction, all sites. MSA accounts for up to 92.9% of all TOC variation, excluding altered ash samples (red).

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An exciting future for biomarker geochemistry in very old rocks: single oil inclusion analysis by TOF-SIMS

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Organic biomarkers extracted from black shales and other carbonaceous sedimentary rocks are valuable sources of information on the biodiversity and environment of early Earth. However, many Precambrian biomarkers are suspected of being younger contamination. An alternative approach is to study biomarkers trapped in oil-bearing fluid inclusions by bulk crushing samples and subsequently analysing the extracted hydrocarbons with gas chromatography-mass spectrometry. However, this method does not constrain the biomarkers to one particular oil inclusion, which means that if several different generations of oil inclusions are present in the sample, a mix of the content from these oil inclusions will be analysed. In addition, samples with few and/or small inclusions are often below the detection limit.

Previous work using time-of-flight secondary ion mass spectrometry (ToF-SIMS) has shown that it is possible to detect hopanes and steranes in single oil-bearing fluid inclusions (Siljeström *et al*., 2010). In this work, single fluid inclusion analysis has been performed on Proterozoic samples for the first time. Four individual oil-bearing fluid inclusions, found in 1430 Ma sandstone from the Roper Superbasin in Northern Australia, were analysed (Figure 1). ToF-SIMS spectra were reconstructed from selected regions (voxels) of the profiled volumes. The ToF-SIMS spectra of the oil in the different inclusions are very similar to each other and differed considerably from spectra collected from the surface before sputtering and analysis, indicating minimal input from any surface contaminants to these spectra. The spectra are consistent with the presence of *n*-alkanes/branched alkanes, monocyclic alkanes, bicyclic alkanes, aromatic hydrocarbons, steranes, aromatic steroids and hopanes (Figure 2). These results are in agreement with those obtained from bulk crushing of inclusions trapped in the same samples, except for the detection of steranes and aromatic steroids. Steranes mostly originate from lipids found in the cell membranes of eukaryotes, so the data are consistent with eukaryotes existing at least by 1430 Ma.

The ability to study minute amounts of organic compounds with high spatial control is of great value, since the input from different organic phases can be better constrained, including different generations of inclusions and contaminants. The ToF-SIMS analysis technique is applied to individual oil inclusions, thus opening up the possibility of extending the hydrocarbon and biomarker composition of fluid inclusions further back into deep time, allowing us to trace the early evolution of life on Earth, and search for life on other planets or moons.

Acknowledgements: Funding from the Swedish Research Council (Contract No. 60573901), the Swedish National Space Board (Contract No. 140/06) and the Australian Research Council (ARC DP0556493) is gratefully acknowledged.

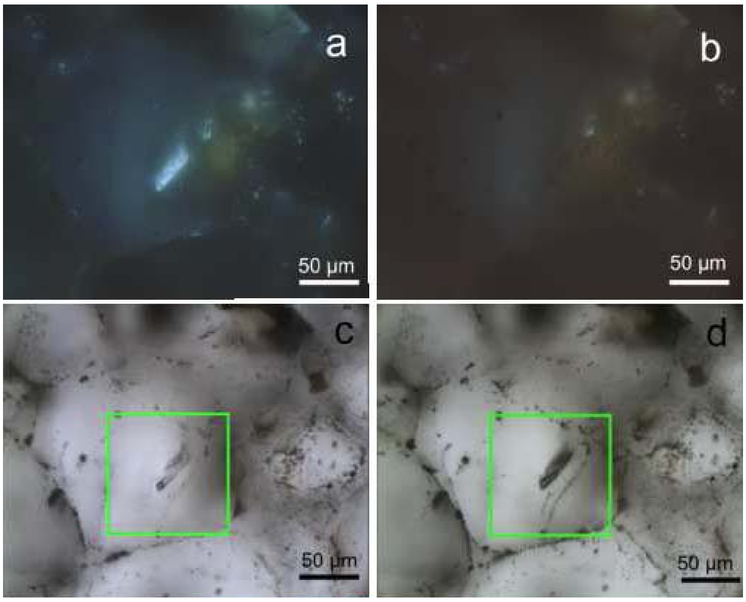

Figure 1. Fluorescence micrographs of an oil-bearing fluid inclusion (a) before and (b) after opening and analysis. Transmission micrographs of the same oil-bearing fluid inclusion (c) before and (d) after opening and analysis.

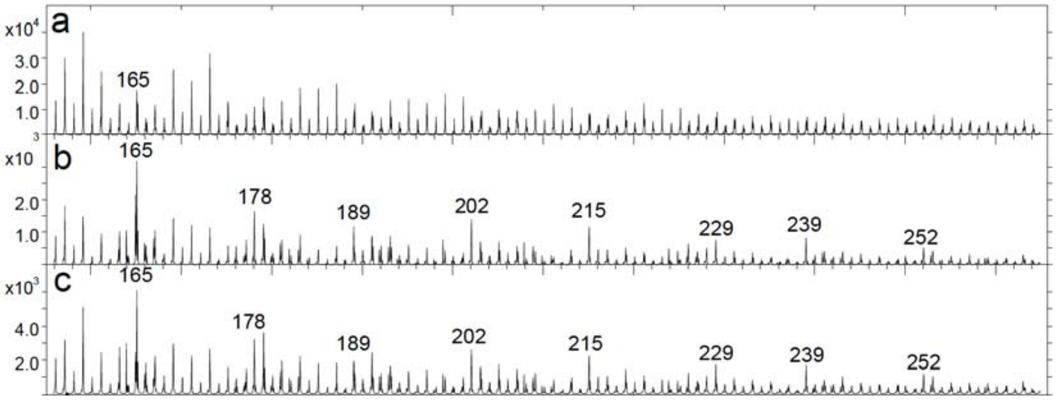

Figure 2. Positive ToF-SIMS spectra (*m/z* 155.0-265.0) of (a) the Jamison oil at -20°C, (b) the oil from the fluid inclusion in Figure 1c, and (c) the oil from another fluid inclusion. Labelled peaks indicate aromatic moieties.

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Characteristics of a Neoproterozoic oil from the Amadeus Basin, central Australia

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Neoproterozoic sediments from the central Australian Amadeus Basin might hold commercial hydrocarbon deposits. They contain sub-economic gas such as the Dingo and Ooramina fields (Marshall *et al.,* 2006), and a live oil bleed was observed in the ~825 Ma Bitter Springs Formation in the Finke-1 drillcore. Moreover, a live oil bleed has recently been discovered in comparatively younger Neoproterozoic shales of the ~550 Ma Pertatataka Formation. This oil contains a unique assemblage of hydrocarbons. Ratios of monomethyl alkanes to *n*-alkanes are high relative to typical Phanerozoic oils. Also abundant are acyclic isoprenoids up to C_{24} and intact C_{40} carotenoids. Moreover, we detected three new series of regularly branched aryl isoprenoids in the oil. Hopanes are abundant including 2α- and 3β-methylated homologues as well as an unusual series of so-called 'farrihopanes'. However, saturated steranes and aromatic steroids could not be detected in the oil, which is unusual for thermally well preserved hydrocarbons of Ediacaran age. By comparison with different stratigraphic units in the basin, we deduce that the highly characteristic oil is self-sourced from the Pertatataka Formation.

New stratigraphic correlations in the Centralian Superbasin show Neoproterozoic sediments with elevated TOC spanning an area > 90,000 km^2. Therefore, by characterising the unique hydrocarbon assemblage in seep oils and inferring potential source rock horizons, there is potential to uncover Neoproterozoic petroleum systems in the Amadeus Basin.

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Biomarker evidence for the origin of seep oil and solid bitumen from the Late Devonian Siljan impact structure, Sweden

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The Late Devonian Siljan meteorite crater in Dalarna, central Sweden, is the largest impact structure in Europe and among the largest in the world (Earth Impact Database of the "Planetary and Space Science Centre", New Brunswick, Canada; www.passc.net). The preservation of Ordovician and Silurian strata in this ring-like depression (Figure 1) provides an excellent opportunity to study Palaeozoic organic matter and palaeoenvironments in a region where only Precambrian basement rocks are generally exposed. An earlier study of Palaeozoic shale, limestone and seep oils suggested that the meteor impact locally thermally altered the rocks, allowing for geologically instantaneous hydrocarbon generation and expulsion, resulting in the formation of seep oils in the Siljan structure (Vlierboom *et al*., 1986). The current study assesses aliphatic and aromatic hydrocarbon biomarker distributions in a seep oil from the Solberga Quarry and three solid bitumen samples recovered from Darriwilian (Middle Ordovician) limestones between the depth interval 224.3 - 236.9 m from the Solberga 1 borehole, in the south-east corner of the Siljan structure (Figure 1). The core was drilled in 2011 by AB IGRENE, a Swedish company, exploring for natural gas and is under investigation as part of pilot studies related to CISP (Concentric Impact Structures in the Palaeozoic), an integral part of the "Swedish Deep Drilling Program" (SDDP).

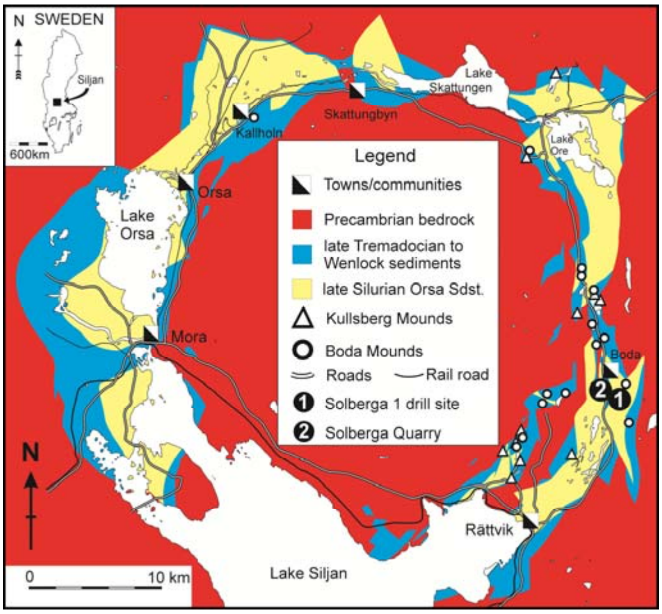

Figure 1. Geological map of the Siljan impact structure (modified from Ebbestad and Högström 2007) showing the location of Solberga 1 borehole and Solberga Qarry.

The seep oil and the solvent extracts of solid bitumen from the Siljan structure have molecular distributions indicating their alteration by moderate to severe levels of biodegradation, which caused partial to complete loss of the susceptible normal alkanes and low molecular weight aromatic hydrocarbons, although the majority of the less susceptible aliphatic and aromatic hydrocarbon biomarkers remain largely unaffected. The presence of nearly equal abundances of pristane and phytane (Pr/Ph = 0.91-1.3) and significant amounts of gammacerane, C_{35} homohopanes ($C_{35}/(C_{35}+C_{34})$ homohopanes = 0.39-0.50), dibenzothiophene (dibenzothiophene/ phenanthrene = 0.31-0.50), tetracyclic polyprenoids (Ta+Tb/ C_{27} $\beta\alpha$ diasteranes = 0.33-10.78), 28,30-bisnorhopane and 25,28,30-trisnorhopane are collectively suggestive of generation of the oil and solid bitumen from source rock(s) deposited in anoxic marine and/or lacustrine environments (Peters *et al.*, 2005). High amounts of C_{23} tricyclic terpane (C_{23}/C_{21} tricyclic terpanes = 1.3-1.9) together with the presence of significant amounts of C_{28} to C_{36} extended tricyclic terpanes (extended tricyclic ratio = 0.42-2.35) is suggestive of a contribution of aquatic algal organic matter to the source rocks. This is corroborated by very low abundances of C_{19} and C_{20} tricyclic terpanes and C_{24} tetracyclic terpane, providing evidence against terrestrial higher plant derived organic matter inputs. High diasterane contents (diasteranes/steranes = 1.2-2.8) consistently indicate generation of the Siljan oil and solid bitumens from clay-rich marine shale. However, the source rock of these samples may have received minor contributions from carbonate source rocks containing prokaryotic organic matter as indicated by the presence of variable amounts of C_{29} $\alpha\beta$ hopane (C_{29} $\alpha\beta$ hopane/C_{30} $\alpha\beta$ hopane = 0.60-1.4), C_{30} 30-norhopane and 2α-methylhopanes (after Peters *et al.*, 2005). Sterane and diasterane distributions are highly dominated by C_{29} homologues, similar to many other Palaeozoic oils (Grantham, 1986). The majority of the aliphatic and aromatic hydrocarbon maturity parameters are suggestive of a peak oil window maturity (0.8-1.0 % vitrinite reflectance equivalent) for the source rock(s) of the oil and bitumen. The seep oil, with biomarker characteristics pointing to generation from predominantly marine source rocks, is more similar to the solid bitumen from 224.3 m than to that from 236.9 m, whereas the bitumen from the 224.7 m has pronounced fingerprints of contributions from mixed marine and lacustrine source rocks. Therefore, oils with different source characteristics have been generated and expelled from the Early Palaeozoic rock sections in the Siljan impact structure.

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Relationship between total organic carbon, mineral surface area and petroleum systems in the Middle Cambrian of the Southern Georgina Basin.

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The past decade has seen a major energy boom in North America, driven by gas and oil production from shale. These organic rich facies are recognised as self sourcing and sealing ‘unconventional’ reservoirs which currently account for 24% of North America’s natural gas production, a figure anticipated to rise to 45-49% by 2035 (EIA 2011). Similar ‘tight reservoirs’ are envisaged in a number of Australian basins (e.g., Cooper, Georgina and Amadeus) and a new exploration drive to tap these resources is underway.

In the southern Georgina Basin the focus of this search for unconventional resources is the Lower Arthur Creek ‘hot’ shale. With thicknesses ranging from 10 to 40m and TOCs from 0.5 to >10%, the rich Cambrian age source rocks are comparable to North American unconventional shale plays such as the Eagle Ford and Horn River. Oil stains identified in the facies are sourced from oil prone Type II kerogen, with a range of maturities exhibited across the basin grade from immature in the north to overmature in the south (Boreham and Ambrose, 2007). We will be reporting data from 3 cores across this maturity range investigating the association between organic matter (OM) and mineral surface area (MSA) within the Lower Arthur Creek formation and underlying ‘conventional’ Thorntonia Limestone, as well as their relationship to the previously identified petroleum systems of the region.

A relationship between the concentration of organic matter and the available mineral surface area of clay minerals within the host matrix (Keil *et al.*, 1994; Kennedy *et al.,* 2002; Kennedy & Wagner, 2011) has previously been observed in both recent and ancient sediments. This suggests OM may be preserved via physical sheltering within clay mineral aggregates or through interlayer adsorption in expanding clays (smectite and mixed layer illite/smectite). Our data for the Arthur Creek Formation shows a correlation between MSA and TOC (Figure 1), however, smectite was not identified within any samples from the more mature cores, suggesting that the relationship observed persists despite diagenetic illitization.

Thermal extraction GCMS of the samples also revealed significant differences in the organic components characterised across the sedimentary successions. In the more easterly, less mature core, profiles range from immature (R^o_{calc} 0.5) in-situ hydrocarbons, extracted from organic rich laminated sections, with *n*-alkane, arylisoprenoid and alkyl cyclohexane distributions typical of the Arthur Creek(!) Petroleum System (ACPS), found within metres of more mature (R^o_{calc} 0.8), migrated and biodegraded (~PM4 of Peters and Moldowan, 1993) oils stains which correlate to the Thorntonia(!) Petroleum System (TPS) (McKirdy, 1991; Boreham and Ambrose, 2007). The core from within the oil-mature section of the basin provided hydrocarbon profiles typical of the ACPS in the upper section with a biodegraded TPS profile on the boundary between the stratigraphic units. Below this, evolved hydrocarbons were significantly different and characterised by low molecular weight aromatic hydrocarbons (e.g., toluene, m- and p-xylene, trimethyl benzene and tetramethyl benzene isomers). The core from within the gas-mature south-westerly section of the basin shows a biodegraded (~PM4) oil in the upper section, with alkylcyclohexanes typical of the ACPS. At the base of the Arthur Creek formation an undegraded ACPS hydrocarbon profile was observed. In the underlying Thorntonia Limestone a mildly biodegraded (~PM1) paraffinic oil was observed with the *n*-alkane profile exhibiting a marked odd-even preference, identifying it as part of the TPS.

Comparing the TOC/MSA distributions with the hydrocarbon types identified by GCMS there appears to be a correspondence between the non-degraded oils and closest correlations of TOC/MSA.

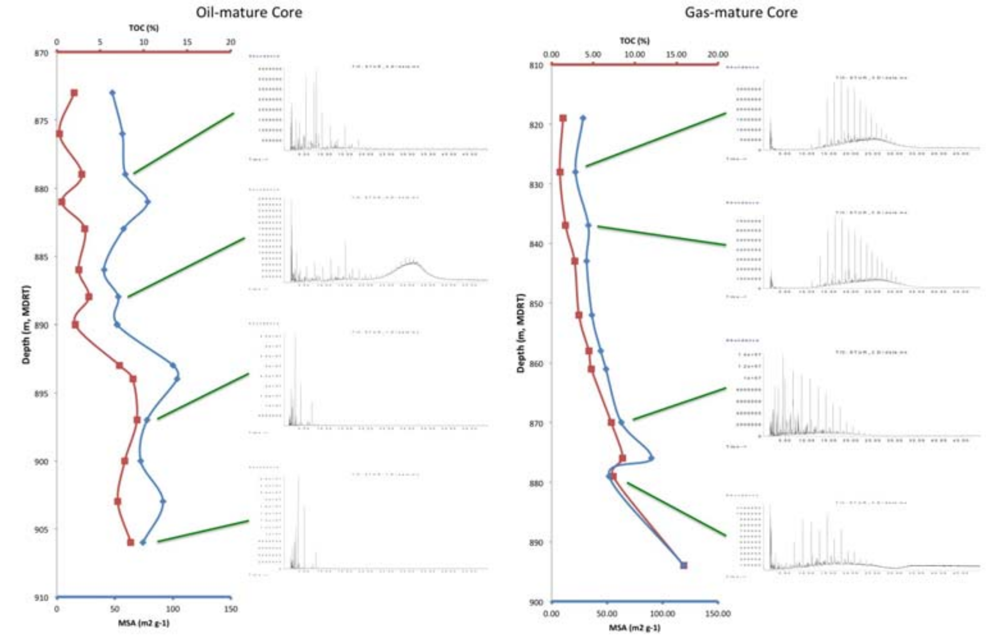

Figure 1. TOC (red) and MSA (blue) from oil-mature core (left) and gas-mature core (right) with associated thermal extraction GCMS hydrocarbon profiles.

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Deciphering links between organic matter and uranium in lignite-hosted ores

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Australia has the world's largest resources of uranium ore, with a diversity of high grade deposit types. However, low-cost uranium ores at existing deposits are becoming scarce, so alternative deposits and exploration techniques are now being evaluated (IAEA, 2009). Genesis of uranium ores, particularly those hosted in peat (Halbach *et al.*, 1980) and lignite (Ilger *et al.*, 1987) can be closely linked to organic matter (Alexandre and Kyser, 2006). The Mulga Rock uranium in Western Australia is a multi-element deposit hosted primarily in lignites. Although relatively low in uranium concentration (0.03%), the deposit is shallow (40-60 m), extends 7 km^2 and is concentrated in the top 2 m of a reduction-oxidation (redox) front in a paleochannel network incised into Permian and Precambrian rocks (Douglas *et al*, 2011). The Permian rocks are part of the Paleozoic Gunbarrel Basin, a major catchment hosting paleochannel deposits (Figure 1). Drill cores freshly collected from the identified prospects Emperor, Shogun, Ambassador, and Princess deposits at Mulga Rock, including an area devoid of mineralisation, were chosen to represent laterally mineralised versus barren areas. Within the drill cores, samples were collected from the redox front (>1000 ppm) down to low (<100 ppm) uranium concentrations. The samples have been analysed for their saturated, aromatic, free fatty acids, ketone, and alcohol contents across these gradients. Distribution of *n*-alkanes is compared using the carbon preference index and average chain lengths. Maturity parameters are calculated using hopane, sterane and aromatic moieties. The maturity parameters are evaluated against thermal and or radiative effects. Initial results of the thermal maturity test of a "barren" sample are compared to the maturity trends in the mineralized samples and to the famous Cambro-Ordovician Alum Shale in the Balkans (Dahl *et al.*, 1988). Significant differences at Mulga Rock are evident between the 'barren' and 'mineralised' samples showing higher proportions of plant-derived components in the 'barren' and an unusual *n*-alkane trend in the 'mineralised' samples, showing consistent changes with increasing uranium concentrations with depth (Figure 2). These results will contribute to understanding the role of the organic matter in uranium-ore genesis and accumulation.

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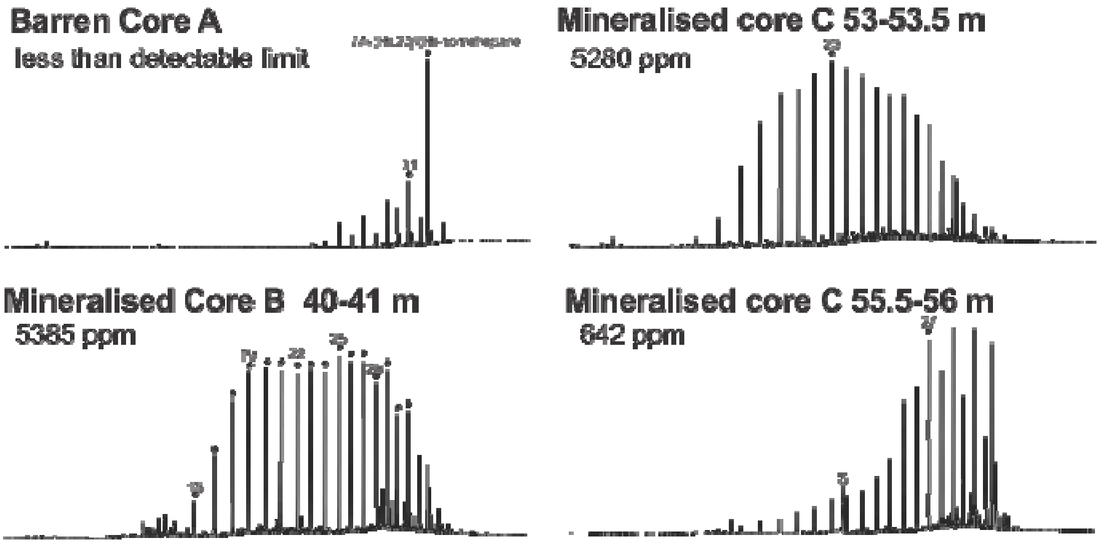

Figure 1. Mulga Rock in the Gunbarrel Basin (yellow line) of Western Australia is host to lignite-hosted uranium ores that accumulated from paleo-channel deposits (dashed white lines) and at the reduction-oxidation front of paleo-groundwater levels c.a. 40 to 60 m below present sea level. Emperor (E), Shogun (S), Princess, and Ambassador (A) are the key areas of exploration (inset).

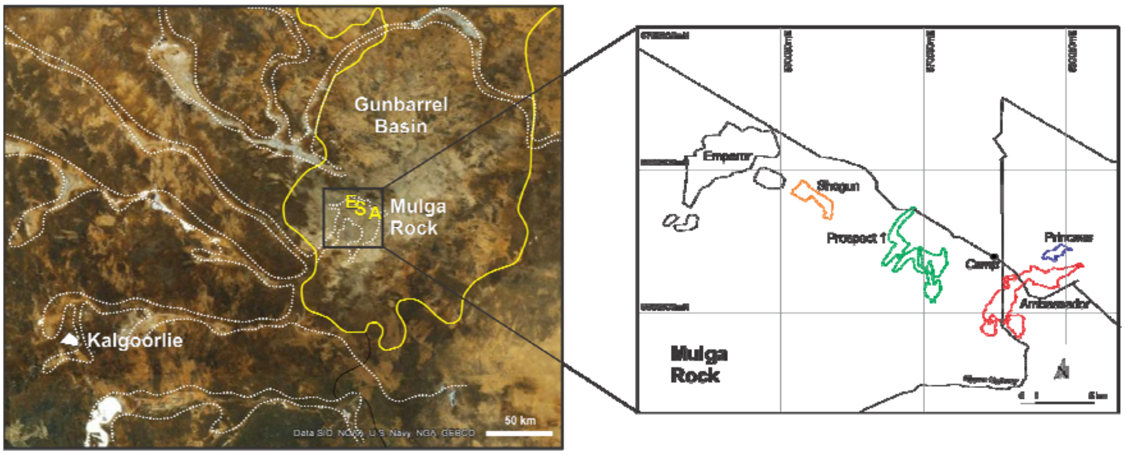

Figure 2. Total ion chromatograms of barren and mineralised cores with uranium concentrations indicated. Cores A and B are in Princess deposit only 100 m apart and samples are from similar core depths. Core C is from Ambassador deposit with the highest U concentration at the redox boundary (53-53.5 m).

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Exceptional fossil and biomarker preservation in the Gogo Formation

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The Gogo Formation, located in the Canning Basin, north-western Western Australia, shows remarkable preservation of a Late Devonian (380 MYA) reef fauna. The exceptional preservation, including original bone and mineralized soft tissues, is believed to result from a combination of rapid burial and cementation within a relatively tectonically stable environment (Long and Trinajstic, 2010). However, recently was recognise the presence of an active sulfur cycle in this Devonian system, including sulfate reduction and the resulting photic zone euxinia (PZE) playing a pivotal role in the preservation of a soft tissue body invertebrate fossil and a series of exceptional low-maturity biomarker and lipids (Melendez *et al.*, 2012).

Further investigation is needed to establish palaeoenvironmental conditions that control the formation of carbonate concretion preserving fossil tissue and/or fossil remains in the Gogo formation. Here we show from the occurrence and distribution of biomarkers within carbonate concretions and surrounding black shales from the Gogo Formation, the role of the PZE during the preservation.

The concretions have been separated and extracted into different fractions (saturated, aromatic and polar fraction). Different *n*-alkanes distributions are observed ranging from C_{15} to C_{35}. Biomarkers as steranes, hopanes, isoprenoids and branched alkanes show distribution that varies from the inner part of the concretions to the external black shales, suggesting different sources. Biomarkers are derived from phytoplankton in the upper water column but also others, exclusive to the concretions, are remains of bacterial communities living in an enclosed system during the carbonate precipitation. Abundant Chlorobi biomarkers were present in both, concretions and shales, supporting photic zone euxinic conditions (H_2S and light) in the water column (c.f Grice *et al.*, 2005), but showing difference strengths of euxinia. The exceptional preservation of lipids biomarkers (phytoplanktonic, Chlorobi derived, and complex steroids) within the concretions points to rapid encasement of the Gogo fauna preventing the tissue and sinking OM from further decomposition.

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Consistent changes in biomarkers (microbes and flora) and stable isotopes across several major extinction events of our planet

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The interaction of biological and geological processes has created the Earth and driven the evolution of its biodiversity from early life. Organisms have continually adapted to changing environments, the evolution of individual species has consequently impacted the chemical and physical properties of Earth. Life's signatures that reveal the evolution of biological forms and their geological consequences are not only restricted to visible remnants (e.g. fossils), but also can encompass biomarkers, isotopic signals and mineral associated fabrics. The changes in isotopic signals appear to be consistently similar for several major geological events of our planet. The 'mother' of all mass extinction events at the close of the Permian near to the Permian/Triassic Boundary (Grice *et al*., 2005) shows remarkably similar conditions to the series of events leading to the fourth largest extinction near to the Triassic/Jurassic boundary of the Phanerozoic (Jaraula *et al*., 2012). There is a consistent association with massive volcanism, synchronous isotopic perturbations in marine and atmosphere carbon reservoirs based on $\delta^{13}C$ of plant waxes and marine sourced biomarkers. Chlorobi derived biomarkers and excursions in $\delta^{34}S$ of pyrite confirm photic zone euxinia occurring at the onset of the marine collapse in both the end Permian and end the Triassic events. Further the isotopic changes are also strongly related to the collapse/ recycling of organic matter from the marine and terrestrial ecosystems (Nabbefeld *et al*., 2010).

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Do Palaeocene-Eocene Thermal Maximum HMW *n*-alkanes record plant community change or climate change?

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The Palaeocene-Eocene Thermal Maximum (PETM) represents a period of rapid (~5-20 kyr) and extreme (5-9˚C) global warming driven by a massive release of carbon to the ocean-atmosphere system that caused deep-ocean acidification and a large (2.5-5‰) negative carbon isotope excursion (CIE). Both marine and terrestrial organisms shifted their ranges causing significant ecological reorganization (See McInerney and Wing, 2011, for review). The Bighorn Basin of Wyoming, USA, contains records of fossil plants, fossil vertebrates, paleosols and biomarkers from the PETM. We have measured sections and collected fossils and sediments from ~35 km transect in the southeastern Bighorn Basin. Prominent beds have been traced on-foot and mapped using differential GPS to correlate sections. Within this sedimentological, biostratigraphic and paleoecological framework, we have analysed the high molecular weight (HMW) *n*-alkanes as biomarkers of terrestrial plant leaf waxes.

The HMW *n*-alkanes at the PETM record a negative CIE of 4-5‰ and the CIE increases from C_{25} to C_{31}. In addition, the average chain length (ACL) increases during the PETM. Both the increase in the CIE with chain length and the increase in ACL were initially hypothesized to be the result of the large-scale plant community change (Smith *et al*., 2007). Plant communities shifted from being mixed conifer-angiosperm to purely angiosperm communities during the PETM (Wing *et al*., 2005).

To examine whether plant type is a primary control on CIE and ACL changes seen during the PETM, we conducted a meta-analysis of *n*-alkane chain length abundances from published and unpublished data on more than 2000 modern plants from 89 sources. We find that angiosperms produce 1-2 orders of magnitude more *n*-alkanes than do gymnosperms. Thus, changes in the gymnosperm contribution to a mixed soil *n*-alkane pool would likely have a negligible effect on either the CIE or ACL. Our results also indicate that turnover among angiosperm species is similarly unlikely to have caused the observed ACL excursion. Firstly, we measured abundances of *n*-alkanes from "representative" groups of living relatives of PETM and pre/post-PETM communities collected from the Chicago Botanic Garden and found no significant difference in chain length distributions. Secondly, the meta-analysis shows that *n*-alkane chain length distributions vary tremendously within large vascular plant groups. Functional group distinctions such as woody plants or graminoids as well as phylogenetic groups at the family level or higher cannot not readily be distinguished based on *n*-alkane abundances. Together, these results suggest the CIE and ACL patterns observed during the PETM are not due to plant community change.

Nonetheless, *n*-alkane abundances change in coherent ways both spatially and temporally with climate-driven changes in plant community. Therefore, shifts in ACL most likely are driven directly by climate rather than by plant community. Longer chain lengths are more hydrophobic and therefore would be more beneficial when plants are trying to minimize water loss under warmer and drier conditions. The climate during the PETM in the Bighorn Basin was both warmer, and initially drier (Wing *et al.*, 2005; Kraus and Riggins, 2007; Secord *et al.*, 2012) and thus could well have driven the shift in ACL. Future research will characterize variation in *n*-alkane abundances within individual species across modern-day climatic gradients.

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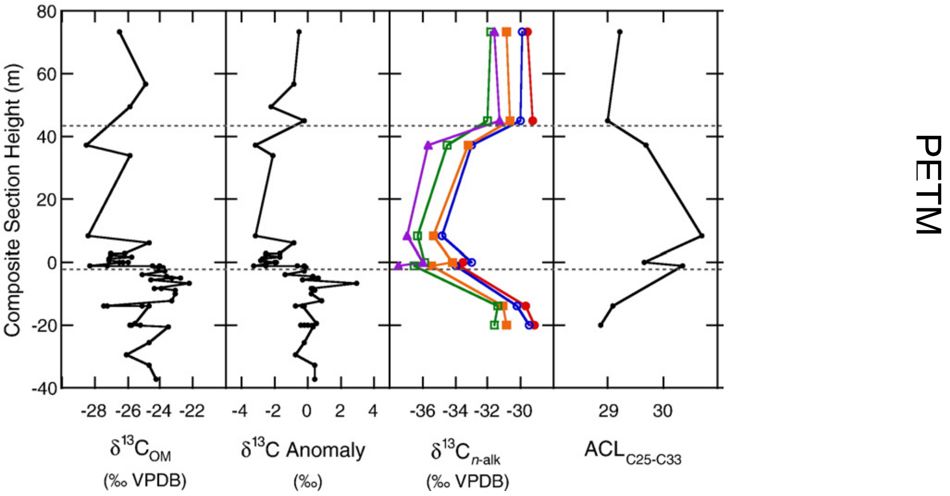

Figure 1. A) Bulk δ^{13}C of organic matter. B) Difference between measured (A) and on the weight % organic carbon (Wing *et al.*, 2005). C) δ^{13}C for C_{25} to C_{33} *n*-alkanes. C_{25}: red circles, C_{27}: open blue circles, C_{29}: orange squares, C_{31}: open green squares, C_{33}: purple triangles. D) ACL for C_{25} through C_{33}. Modified from Smith *et al.*, 2007.

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Otway residual CO_2 saturation test: Application of noble gas tracers

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The noble gases krypton (Kr) and xenon (Xe) were a critical component in the design of a single-well injection-withdrawal test in the Paaratte Formation sandstone reservoir, onshore Otway Basin to measure the residual gas (CO_2) saturation (S_{gr}). Their ability to partition between the mobile water phase and immobile gas phase was used in a desktop study to evaluate the extent of residual CO_2 phase trapping (Zhang *et al.*, 2011). The partitioning of tracer in combination with the hydraulic and thermal tests should reduce the estimation uncertainty in S_{gr} (Zhang *et al.*, 2011). Furthermore, performing a reference test provides information on formation dispersivity, resulting in reduced parametric and geological uncertainty and helps constrain synthetic models (Zhang *et al.*, 2011). The use of two tracers with different partitioning coefficients further constrains S_{gr} estimation.

The Otway Phase 2B field test was conducted from June to September 2011 (Paterson *et al.*, submitted). To collect suitable fluid samples from the test well for analysis, a U-tube assembly was deployed enabling a pressurised water sample to be taken directly from the reservoir level and transferred to the surface into a high pressure stainless steel cylinder under reservoir pressure conditions (2030 psi). Subsequently, a 150 mL pressurised water sample was taken for wet chemical analysis (alkalinity, electrical conductivity, pH and salinity) in a purpose-built field laboratory. To collect a gas phase sample for analysis a valve at the top of the high pressure storage cylinder was opened across a pressure regulator and the exsolved gas was collected in both an isotube and aluminized gas bag once the initial pressure had reduced to 900 psi. The gases were analysed in a field laboratory for Kr, Xe, CO_2, O_2, N_2 and CH_4 by gas chromatography-thermal conductivity and pulsed discharge helium ionisation detection and by mass spectrometry. Gas analysis was a major component of: 1) **Background sampling** - periodic collection of U-tube-derived gases showed baseline concentration of gases for Kr and Xe were below GC detection limits (< 1ppm) while CO_2 and CH_4 concentrations averaged 202 and 56 ppm, respectively. The balance of the gas was N_2 resulting from the initial 4.7 L N_2 in the SS storage cylinder at atmospheric pressure before filling with Paaratte water and its associated dissolved gases; 2) **Reference Test -** intended to characterise the formation, in particular estimate the heterogeneity and effective dispersivity of the formation. In this test the two tracers should both act as conservative tracers as there is only water present in the aquifer. At the start of the water injection phase 2.46 kg of Kr and 3.62 kg of Xe were added at a constant flow rate over 120 minutes to the Paaratte formation water, which was being re-injected from the surface storage tanks at a rate of ~150 tonnes/day. Water injection continued for another 14 hours (push) with the injection of 100 tonnes of water. Following the injection phase, a 24 hours soak period ensued before water production commenced and continued (pull) uninterrupted for another 3.4 days producing 170 tonnes of water. Round-the-clock U-tube sampling produced splits of derived water and gas at 90 minute intervals for near real-time aqueous and gas analysis. The tracer breakthrough curve (BTC) with the concentration of Kr and Xe (maxima at 434 and 424 ppm, respectively) was plotted against the cumulative water production for the reference test. The balance of the gas was N_2; 3) **Characterisation Test -** intended to characterise the residual CO_2 saturation and measure any changes in effective reservoir properties as a result of the trapped residual phase. During this test the two tracers should both act as partitioning tracers, since both Kr and Xe will preferentially enter the residual CO_2 phase. At the start of the water injection phase 2.96 kg of Kr (791 L @STP) and 4.30 kg of Xe (734 L @STP) were co-inject at a constant flow rate over 100 minutes to the Paaratte formation with water being re-injected from the surface storage tanks at a flow rate of ~180 tonnes/day together. CO_2 was injected through a 3/8" capillary line and mixed downhole within the injection tubing at a position high above the Paaratte Formation to maintain near CO_2-saturated water (~1 mol CO_2/kg water) under reservoir conditions. A total of 104 tonnes of water at saturation with CO_2 was injection injected over a span of 12 hours. After a further 24 hours, continuous water production (pull) proceeded for close to 4 days, producing a total of 180 tonnes of water. During this time, U-tube-derived water and gas samples were continuously sampled with a U-tube sampling period of ~90 minutes. BTC curves the concentration of Kr and Xe (maxima at 264 and 180 ppm, respectively) plotted against the cumulative water production for the characterisation test. The balance of the gas was CO_2 and N_2 with an average CO_2/N_2 ratio of 5.65 ±1.17 σ and, 4) **Dissolution Test -** CO_2-free formation water was injected into the Paaratte Formation resulting in dissolution of the residual CO_2 phase and remobilisation of the noble gas tracers back into the water phase. Subsequent water production and gas sampling produced the BTCs for Kr and Xe (maxima at 181 and 169 ppm, respectively) with the flattening of the tracer tail used to guide the end of the Otway Phase 2 test sequence.

The noble gas data provided real-time analytical results enabling sound operational decisions to be made (e.g. when to stop water production and sampling). Tracer BTCs were observed in both the reference and characterisation tests with the latter showing a much broader elution profile, in accord with noble gas tracer partitioning between the water and residual CO_2 phases. Upon destruction of the residual CO_2, the released noble gases showed a different though characteristic BTC. There were several limitations in the data collected that have made interpretation of test results challenging. In particular, we found that the exsolution of the tracer gases and the CO_2 is very nonlinear resulting in strong sensitivity of the tracer concentration on the time when the gas sample was acquired. With hindsight we realize the importance of collecting dissolved gases from formation pressure down to ambient conditions.

The low tracer recovery yields in both the reference and characterisation tests, brought about by a combination of incomplete tracer dissolution during injection, and losses in reservoir 'thief' zones of preferential water flow without significant CO_2 saturation, and inadequacies in sampling protocol, resulted in a numerical modelling approach focused on the change in the shape of the BTC. TOUGH modelling using a one-dimensional, radial approach and applying a dimensionless numerical dispersion as a proxy for the effective dispersivity enabled good matching of BTC between field and modelled data, resulting in an estimation of S_{gr}, which is in agreement with S_{gr} values estimated from other independent test measurements.

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Low molecular weight fatty acids as proxies for microbial responses to CO_2-injection into the Paaratte Formation sandstone aquifer, Otway Basin

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CO_2 geosequestration programs are gaining in international interest, as the need to reduce atmospheric carbon dioxide levels becomes more immediate. The CO2CRC Otway project involves a pilot CO_2 geosequestration study in the sandstone Paaratte Formation of the Otway Basin (south-western Victoria, Australia). Stage 2B of the Otway project was undertaken from June to September 2011 and was designed as a single well experiment to determine residual CO_2 saturation within the low salinity aquifer of the Paaratte Formation (Paterson *et al*., submitted). The test allowed formation waters to be collected from the CRC-2 borehole before and after CO_2 injection using a specially designed "U-tube" sampling array consisting to two continuous lengths of ¼" SS tubing joined in the subsurface by a tee attached to a check valve and filter (Boreham *et al*., 2011). This arrangement is a closed system allowing samples to be obtained at formation pressures and temperatures, and free from contamination. In order to sample the formation water, high pressure N_2 was applied to one of the tubing lines and the water 'lifted' to the surface and collected in 150ml stainless steel cylinders at reservoir pressure. Samples were subjected to a range of inorganic and organic geochemical analyses to determine the pre-injection conditions of the Paaratte aquifer, as well as its response to CO_2 injection. Among these analyses was a study of the microbial community response to CO_2 injection (Mu *et al.,* in prep.). Here we report the fate of groundwater organic carbon during a CO_2 geosequestration experiment, with a focus on low-molecular weight fatty acids in order to understand the potential metabolic energy available for microbial respiration.

Four formation waters were available for this study: U-tube lifts 12 and 16 were collected in June 2011 and represent the initial 190 and 330 tonnes, respectively, of the total of 510 tonnes of water produced (not via the U-tube) and stored in surface tanks in preparation for the Stage 2B test sequence; Lift 167 was water collected in August 2011 during the characterisation test following the establishment of the residual CO_2 saturation then subsequent production of 167.6 tonnes of formation water and; lift 221 in January 2012 represents water collected post dissolution test and approximately 4 months after the completion of the Otway Stage 2B (Paterson *et al*., submitted). A sample of drilling mud collected during the drilling of the CRC-2 borehole was also analysed in order to resolve contaminant organic compounds from *in situ* compounds in the formation waters. Furthermore, the 3 chemicals (propylene glycol diacetate, triacetin and tripropionin) employed in the organic tracer test (Myers *et al*., 2012), which was conducted between the end of the characterisation test and dissolution tests (Paterson *et al*., 2011), were also analysed for low molecular weight hydrolysis products. The experimental procedure involved liquid-liquid extraction of the formation waters (adjusted to pH 2 with HCl) with dichloromethane, concentration of the solvent and GCMS analysis on a BP21 narrow bore fused silica column (30 m x 0.25 mm od).

Polyglycols from the drilling mud were identified in lifts 12, 167 and 221 but not in lift16, indicating that pristine formation water was only sampled using the U-tube in the latter lift. Although precautionary chemical analysis (pH, electrical conductivity, alkalinity and fluorescein dye) were undertaken to ensure only pristine formation water was produced initially into the surface storage tanks, the occurrence of drilling mud additives indicates that low level contaminated formation water was indeed re-injected and re-produced during the Otway Stage 2B test sequence. Up to 100 times more low-molecular weight C_2–C_{10} *n*-alkyl fatty acids were detected in Lift 221 (post the dissolution test where the residual CO_2 saturation was partially destroyed), when compared to the other 3 lifts. Lifts 16 (pre-reference test, pre-CO_2 injection) and 167 (reference test, post CO_2 injection) had comparable levels of fatty acids with levels slightly higher than in lift 12 (pre-reference test, pre-CO_2 injection). The dominance of acetic acid (C_2) and proponic acid (C_3) in Lift 221 can be partially attributed to the hydrolysis products of the organic tracers. However, the absence of C_{4+} fatty acids in the neat organic tracers or as reaction products thereof supports enhancement of these acids via another mechanism, most likely as metabolites of a microbial assemblage changed in response to CO_2 injection. DNA analysis showed that the microbial community shifted from thermophilic Firmicutes to Proteobacteria before and after CO_2 injection, respectively. An overall decrease in microbial population may also have occurred during the Stage 2B experiment.

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AOGC 2012 - Abstracts

Poster Presentations

(Abstracts are in order by Poster Number; presenters are underlined)

Evolution of pores in organic-rich shale during thermal maturation

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Shale gas has increasingly become an important natural gas inventory in the United States over the past decade (Sondergeld *et al.*, 2010). A higher abundance of organic matter can provide excellent original organic richness and high generation potential, resulting in higher gas-in-place (GIP) volumes (Bowker, 2007). In the Barnett mudstones, Loucks *et al.* (2009) reported that the internal porosities can be up to 20.2% for organic grains. Some gas is believed to be partly stored in shale source rocks as adsorbed gas within the organic matrix (Jarvie *et al.*, 2007). Therefore, it is important to understand the evolution of pores in organic matter during the process of thermal maturation in order to quantitatively predict shale gas storage capacity and reserves. This study aims to document the changes of dimension, morphology, and abundance of pores in organic matter during thermal maturation by pyrolysing immature organic-rich shale, so as to evaluate the storage capacity of shale at different maturities.

An immature shale outcrop sample from the Fushun Basin, northeastern China was used for the pyrolysis experiment. During the experiment, the solid residues recovered at different temperatures were used to represent shales of different maturities. The initial sample used is immature shale with a vitrinite reflectance value of 0.55%, TOC of 14.1%, and Hydrogen Index of 1009. A set of mature outcrop and core samples was also selected to compare with the pyrolysis residues. The pore of the pyrolysis solid residues and mature shale samples were analyzed using Small Angle X-ray Scattering (SAXS), SEM and N2 gas adsorption (BET theory). The solvent extracts from the residues were analyzed using the Total Scanning Fluorescence (TSF) method (Barwise and Hay, 1996) to estimate the yield and maturity at different pyrolysis stages.

As shown in Fig. 1, the pore width peak values increase with pyrolysis temperature. When the pyrolysis temperatures increase from 300 °C (Sample FS-300) to 600 °C (Sample FS-600), the pore width peak values increase from 0.5 (FS-300) to 4.2 (FS-600), and the pore width modal values increase from 24 nm (FS-300）to 30 nm (FS-600). The average pore width increases from 12.3 nm (FS-300）to 16.7 nm (Sample FS-600), an increase of approximately 35%.

With an increasing pyrolysis temperature, the surface areas increase from 354 m2/kg (FS-300) to 3,102 m2/kg (FS-600), while pore volumes increase from 0.6448 cc/kg (FS-300) to 10.89 cc/kg (FS-600) (Fig. 2), indicating that additional pores had developed in the solid products during the progressive pyrolysis.

Scanning Electron Microscopic (SEM) observation of the pyrolysis residues indicates that with increasing pyrolysis temperatures, the pores in the shale become more abundant. The residues at low-pyrolysis temperatures contain fewer and relatively small pores compared with that at high- pyrolysis temperature.

TSF intensity and R1 parameter indicate that oil generation reaches a maximum around 400-450 °C with R1 values of 2.7-2.8, suggesting a light mature oil (Barwise and Hay, 1996). The decrease of the TSF intensity and the abrupt drop of the R1 value to 0.8 at 500 °C indicate the occurrence of thermal cracking of the oil generated.

The study has found that pore volumes in the organic matter can increase significantly during shale maturation. As the pyrolysis temperature increases from 300 °C to 600°C the average pore dimensions increase by 35%, surface areas increase by more than 770% and pore volumes increase by over 1500%. The measured (SAXS and N2 adsorption) and observed (SEM) porosity enhancement during the pyrolysis experiment is interpreted to be directly caused by hydrocarbon generation. The discovery of the intimate relationship between thermal maturation and porosity enhancement in shale may provide some important insight on shale gas exploration and reserve prediction.

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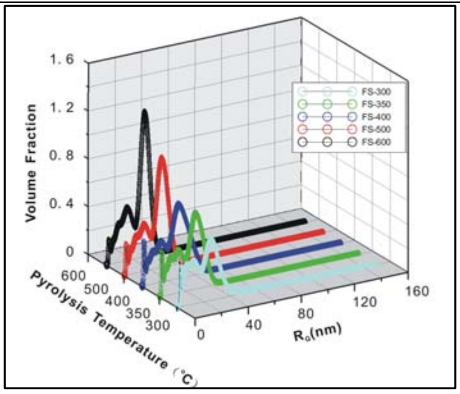

Figure 1. Volume fractions of pyrolysis residues at different temperatures derived from SAXS showing continuous volume fractions of pyrolysis residues at different temperatures with the peak values representing the mode of the pore widths.

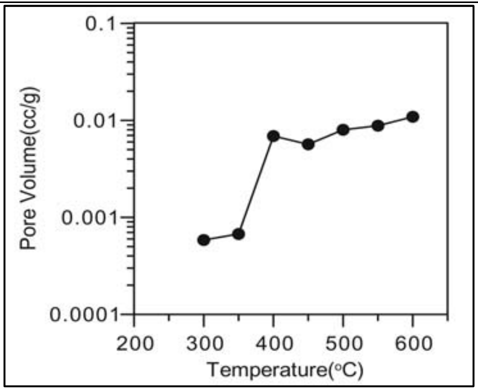

Figure 2. Plot of the N_2 gas adsorption data of the pyrolysis residues showing that the pore volume increases with the pyrolysis temperature. Note the abrupt increase of pore volume at 350-400 °C.

Use of dichloromethane in GC-MS as a cause of apparent chromatographic tailing by $FeCl_2$ - plaque formation in the ion source

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Observation of an unusual chromatographic tailing phenomenon

Problems with chromatographic tailing in GC-MS experiments are usually a problem associated with a deteriorating or contaminated GC-column, a dirty GC-injector, leaks, and cold spots in the transfer line. Much less common are problems associated with the ion source of the mass spectrometer. Here we investigate persistent problems with apparent chromatographic tailing and loss of sensitivity of C_{19+} hydrocarbons on our Agilent 6789 – Autospec Premier GC-MS system caused by the injection of samples in halogenated solvent.

We encountered rapid deterioration of chromatographic peak shape shortly after delivery of the new GC-MS instrument. However, cleaning and exchange of the GC injector, and cutting and exchange of the GC-column did not improve the tailing problem. Moreover, a thorough investigation of the transfer line with a thermocouple excluded cold spots as a cause. Peak shape deterioration was also not linked to a leak. However, perfect chromatographic peak shape was instantly restored whenever a new, cleaned inner source was inserted into the MS. However, the problem commonly returned after injection of a single hydrocarbon sample in DCM and became progressively worse with number of injections (Figure 1). Re-insertion of dirty ion sources also immediately caused return of the same deteriorated peak shape, making it unlikely that the tailing phenomenon was caused by the build-up of electric charge within the ion source. It is more likely that the problem is associated with surface corrosion or accumulation of a film of an unknown contaminant. However, visual inspection of the metal surfaces did not show any sign of contamination and corrosion even under a stereomicroscope. Moreover, we swabbed the inner source surfaces with DCM-wetted cotton but did not detect any GC-amenable residues.

To investigate the nature of any surficial build-up, we ran the MS under full scan mode and attempted to desorb contaminants by heating of the ion source from the standard operating temperature of 260°C to 320°C. We observed a strong thermal desorption signal that increased linearly with temperature and contained predominant ions at *m/z* 56, 57, 91, 93, 126 (base ion) and 128, consistent with Fe^+, $FeCl^+$ and $FeCl_2^+$. To confirm these assignments, we recorded the putative iron chloride signal at 5,000 mass resolution, and this yielded four detectable mass to charge ratios *m/z* 125.873 (computed value *m/z* 125.8727), 127. 870 (127.8697), 129. 866 (129.8668) and 90.904 (90.9038). These masses are diagnostic for the major isotopic species of $FeCl_2^+$ and $FeCl^+$ and are likely derived from $FeCl_2$, which is known to be desorbed from iron surfaces into the gas phase at temperatures around 280°C (Smentkowski *et al.*, 1989).

A suggested mechanism for tailing and $FeCl_2$ formation in the ion source

From metallurgical studies it is well established that halogenated solvents decompose on iron surfaces at relatively low temperatures. For example, Smentkowski *et al.* (1989) describe that iron surfaces 'aggressively attack' haloalkanes and break C-Cl bonds to produce products such as $:CCl_2$ and $FeCl_2$ close to room temperature. For instance, irreversible dissociative adsorption of C_2Cl_2 occurs at 52°C. C_2Cl_4 is already completely

decomposed on iron at only -93°C, and at 177°C the dissociated carbon atoms diffuse into the metal lattice while $FeCl_2$ desorbs into the gas phase (Smentkowski *et al.*, 1989). At temperatures as low as -73°C, CCl_4 suffers quantitative decomposition into adsorbed chlorine and carbon via $Fe(s) + CCl_4 \rightarrow FeCl_2(s) + :CCl_2(g)$. CCl_4 even readily reacts with freshly cleaved stainless steel (Smentkowski *et al.*, 1990). At 200°C and above, DCM thermally decomposes on the surface of iron to form a sub-µm layer of $FeCl_2$ and carbon (Kotvis *et al.*, 1993). We suggest that similar mechanisms caused build-up of $FeCl_2$ on metal surfaces in the ion source of our mass spectrometer, and that these activated surfaces caused the tailing phenomenon.
This conjecture is supported by Figure 1 that demonstrates that the concentration of $FeCl_2$ in the gas phase of the ion source increases linearly with the number of DCM injections, indicating a cumulative build-up of $FeCl_2$ in the ion source. Moreover, the figure shows that the magnitude of chromatographic tailing correlates with $FeCl_2$ concentrations. As tailing became worse with increasing molecular mass of the analysed hydrocarbons, we hypothesize that $FeCl_2$ coated surfaces in the MS source adsorb hydrocarbons and release them over several seconds back into the gas phase where they are ionized and recorded as an apparent chromatographic tail.

We were able to remedy the tailing problem on our instrument by exclusive use of non-halogenated solvents.

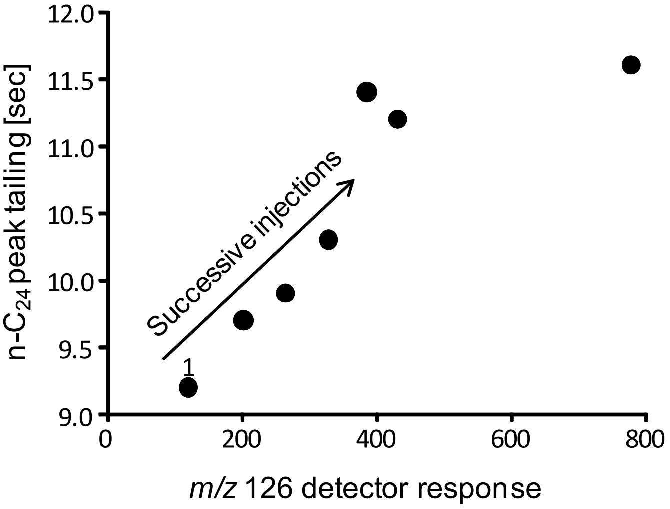

Figure 1. Correlation between ion source contamination with $FeCl_2$ and chromatographic tailing of *n*-C_{24}. '1' is the response of a freshly cleaned ion source and the progression of data points to the right corresponds to successive injections of the hydrocarbon mixture in DCM. Tailing intensity of the *n*-C_{24} chromatographic signal is given as peak width in seconds at 10% peak height. The x-axis shows the *m/z* 126 ($FeCl_2^+$) detector response (arbitrary units) as determined 17.0 min after injection.

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Geochemistry of Mesoproterozoic Hongshuizhuang Formation shales in northern part of North China: implications for provenance, source weathering and paleoclimate

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The Hongshuizhuang Formation shales (~1.4 Ga) from the northern part of North China are Mesoproterozoic organic-rich sediments which may record important environmental and biological information at that time. Major and trace elements contents of the Hongshuizhuang Formation shales were analysed in order to determine their provenance, source weathering and paleoclimate.

The high ratios of Th/Sc, Al_2O_3/TiO_2, La/Sc, La/Co, Th/Cr and Th/Co, the low values of Cr/Zr and TiO_2/Zr, and Eu_{an}, the Co/Y-Ti/Zr diagram and the La–Th–Sc ternary diagram indicate that the provenance of the Hongshuizhuang Formation shales was mainly granodiorites. A ternary plot of (Al_2O_3–(CaO^*+Na_2O)–K_2O) for the studied samples indicate they have a moderate Chemical Index of Alteration (CIA which is the terminology that demonstrates the degree of chemical weathering (Nesbitt and Young, 1982) ranging from 60.93 to 77.25 (Figure 1). The chemical weathering trend of the elements suggests that the composition of the Hongshuizhuang Formation shales was affected by K-metasomatism which can lead to underestimation of the value of CIA (Figure 1). The original CIA was likely higher than 90. The high original CIA, the high Chemical Index of Weathering (CIW) and the high Plagioclase Index of Alteration (PIA) illustrate that the provenance of the Hongshuizhuang Formation shales had experienced intense chemical weathering.

Intense chemical weathering and the SiO_2 vs. (Al_2O_3 +K_2O+Na_2O) relationship (Figure 2) indicate the paleoclimate was warm and wet during the deposition of the Hongshuizhuang Formation, consistent with the high CO_2 concentration in the atmosphere during the Mesoproterozoic.

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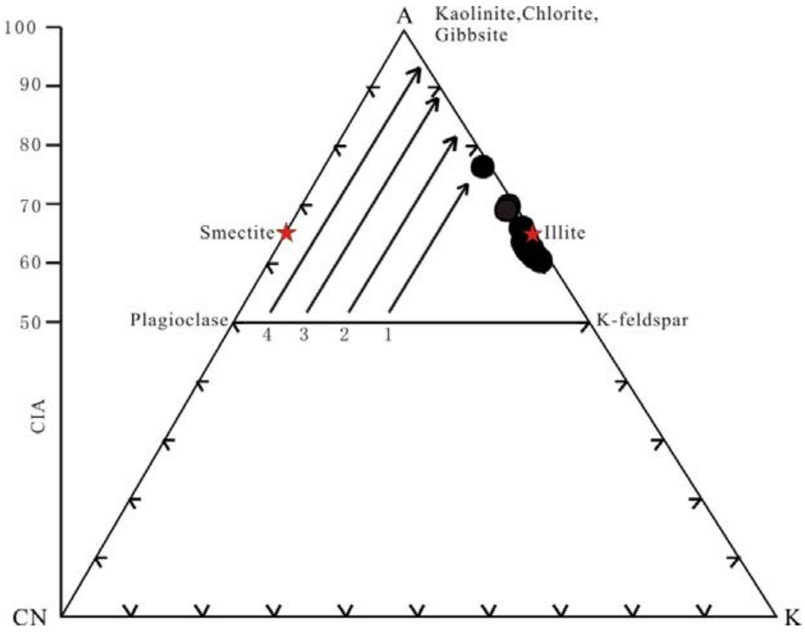

Figure 1. Ternary plot of (Al_2O_3–(CaO^*+Na_2O)–K_2O) (A–CN–K) for the Hongshuizhuang Formation shales. Numbers 1–4 denote compositional trends of initial weathering profiles of different rocks. 1–granite ; 2–adamellite ; 3–granodiorite ; 4–tonalite. The red stars represent smectite and illite, respectively (after Nesbitt and Young, 1982).

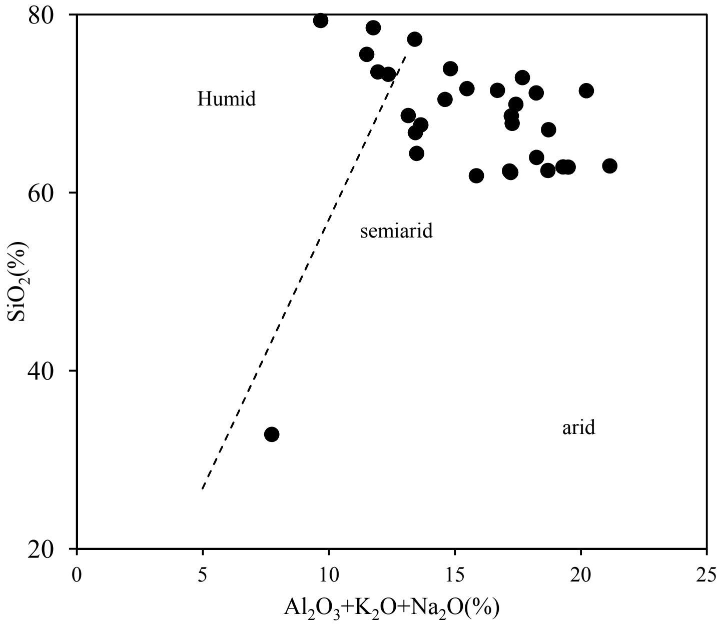

Figure 2. Bivariate SiO_2–(Al_2O_3+K_2O+Na_2O) paleoclimate discrimination diagram for the Hongshuizhuang Formation shales. Fields after Suttner and Dutta (1986).

Photic zone euxinia at the Triassic/Jurassic mass extinction evident from the presence of C_{34} metallo-porphyrins with an extended alkyl chain measured by LC-MS Orbitrap

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The late-Triassic mass extinction, ~201.4 million years ago (Schoene *et al*., 2010), is one of the five major extinction events of the Phanerozoic (Raup and Sepkoski, 1982). The ecological impact on the Earth's biosphere (McGhee Jr *et al*., 2004) is ranked third, whereas diversity loss is ranked fourth. This translates up to 50% of marine biodiversity loss and major terrestrial ecosystem changes. Corals and other important extant marine groups were affected. The end Triassic extinction event can potentially serve as an ancient analogue for an extreme global warming-related crisis and studying this event is therefore important for extending the understanding of both climatic and biogeochemical dynamics for the predicted and ongoing rapid warming as a result of fossil fuel emissions. Recently Jaraula *et al.* (2012) and Grice *et al.* (these proceedings) have presented substantial evidence from Chlorobi-derived biomarkers (isorenieratane and aryl isoprenoids) indicative of photic zone euxinia (PZE), during and after the extinction event from analyses of mudstones from a Triassic-Jurassic Boundary (TJB) section at St. Audrie's Bay, UK. Distinctive water chemistry and organic matter inputs at this site are further supported from stable carbon isotopes of biomarkers, kerogen and carbonates, and $\delta^{34}S$ of pyrite.

Here we present results of metallo-porphyrin (nickel and vanadyl) analyses performed on the same mudstones with new methods developed on a LC-MS Oribtrap. The detection of C_{34} alkyl porphyrin bearing an *iso*butyl substituent at C-8 attests to an origin from the precursor bacteriochlorophylls *c, d (e)* from Chlorobi (Grice *et al.,* 1996) presenting additional evidence of persistent PZE across the TJB. Furthermore vanadyl/nickel porphyrin are in agreement with pristane/phytane showing a similar evolution of redox conditions in the TJB section. Porphyrin maturity indices based on relative proportions of ETIO define and DPEP define structures in both metallo-porphyrins are subsequently compared to other organic matter maturity indices derived from the saturated and aromatic hydrocarbons. Additionally changes in the entire suite of porphyrin abundances and distributions throughout the TJB mudstone section from St. Audrie's Bay will be compared to other biomarker and isotopic data from the same section to investigate potential indications of what may have controlled porphyrin distributions observed at this location. Further work is currently underway to measure metalloporphyrin complexes in some major Australian mineral deposits and also from controlled laboratory experiments using porphyrins and metals.

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A non-invasive technique for characterisation of volatile and semi-volatile constituents of fulvic acid by gas chromatography- mass spectrometry

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Humic substances are complex heterogeneous organic material and major components of marine and terrestrial natural organic matter (NOM). Fulvic acid is the smaller molecular weight fraction of humic substances found in water and sediment. It plays an important role in soil fertility and bioavailability because of its ability to attach metal ions and organic pollutants and transfer them through organic and aqueous phase.

Molecular -level characterisation of fulvic acid is difficult due to heterogeneity and complexity of the molecule. Traditionally, GC analysis of fulvic materials was based on hydrolysis followed by derivatisation to obtain volatile components prior to GC/MS analysis (Allard, 2006). Thermochemolysis followed by methylation has been recently considered as an alternative because of its ease and low cost (Lehtonen *et al.* 2004). However, application of aforementioned methods inevitably leads to a major alteration of the original structure which can negatively affect characterisation studies. Moreover, the pathways that starting material spends to form the products remains ambiguous and not fully understandable.

In the present study, we employed a non-invasive, one-step derivatisation techniques using only BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) as a robust trimethylsilylation reagent to reach the reasonable level of volatility without interruption of original structure. Trimethylsilylation has been applied before on warkish peat fulvic acid with the similar methodology but with limited success in terms of component level analysis, the compounds identified were mostly of volatile organic acids and fully characterisation of all of the detected compounds was not considered.

Here, we conducted the TMS- derivatisation without using a solvent but with higher amount of BSTFA in a single and shorter step. A comprehensive component level characterisation was also performed which covers all of the volatile constituents to even larger molecules like disaccharides. Moreover because of non-invasive nature of the reaction, constituents detected are supposed to be related to the original structure of fulvic acid.

In order to investigate the applicability of the method on different fulvic acids, Five fulvic acid standards including Warkish Peat, Elliot Soil, Suwannee River, Nordic Aquatic and Pony Lake were derivatised by BSTFA containing 1 % TMCS as a catalyst in a sealed glass vial with teflon-cap .The reaction mixture was exposed to 45 min sonication in 60˚C and subsequent 15 -hours heating at 80˚C in a conventional oven. Figure1 shows a typical total ion chromatogram of TMS-derivatised Antarctic fulvic acid obtained by current method.

As expected, compounds identified in five soil and aqueous fulvic acid standard belongs to different families of organic compounds but mainly consisted of fatty acids and carbohydrates. All of the monosaccharides which has already been reported in fulvic acids by other methods were also detected by our technique. Generally, the nature of monosaccharides seemed to be independent of the origin of fulvic acid, however, the difference between soil, peat and aqueous fulvic acids appeared to be quantitative rather than qualitative which is in agreement with quantitative ^{13}C NMR reported data of fulvic acid standards (Thorn *et al.*, 1989). A broad range of long and short-chain fatty acids were also identified in all five fulvic acid standards mostly of straight-chain and branched mono and di- carboxylic acid. Additionally, aromatic acids like hydroxyl benzoic acid, di hydroxyl benzene, di hydroxyl benzoic acid and hydroxyl methoxy benzoic acid (vanillic acid) were observed in five fulvic acids, the last compound has been used previously as a model molecule in fulvic acid structural analysis and proved to be a part of Suwannee river fulvic acid (Saleh *et al.,*1989).

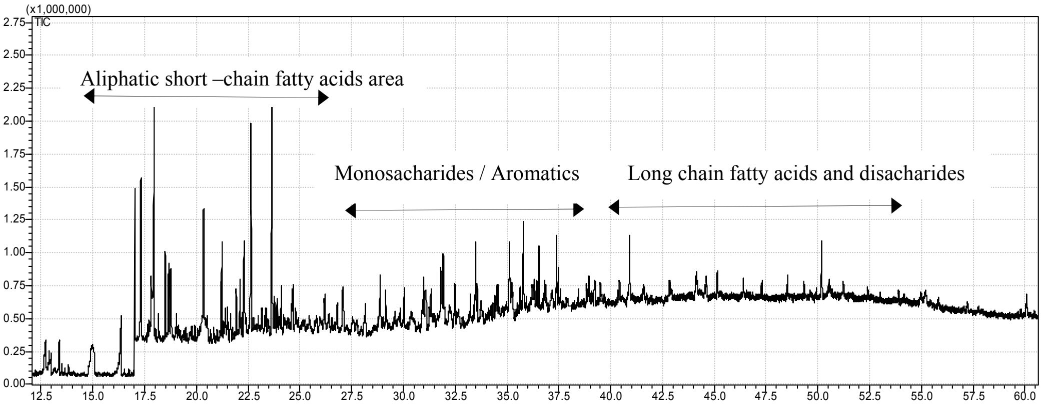

Figure 1. Total ion chromatogram of TMS-derivatised Antarctic fulvic ac

Together these results suggest that current methodology not only enables detection of a wide range of fulvic acid constituents in a single step but can be potentially beneficial to molecular-level structural studies consistent with other approaches based on model molecular analysis.

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Geochemical characteristics of fluid inclusion oils from Ecopetrol-B well in Sinu offshore basin, Colombia

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The geological evolution of the Sinu offshore basin is very complex. Multiple types of liquid and gaseous hydrocarbons have been found (Sanchez and Permanyer, 2006) but there is no firm oil-source correlation. Analysis of fluid inclusion oils aims to help understanding correlations with possible source rocks.

Five samples from different depths of the Ecopetrol-B well drilled offshore Colombia were analysed. Petrographic investigation of the samples indicates that inclusions are mainly hosted in fracture trails of detrital quartz with GOI values ranging from 1.4% to 2.3%. The combination of the on- and off-line molecular composition of inclusions (MCI) was used to obtain detailed aliphatic and aromatic biomarker and low molecular weight hydrocarbon distributions.

Geochemical data based on off-line analysis indicate that the FI oils are derived from a marine source rock with eukaryotic contribution from algae, as indicated by the presence of C_{30} steranes, high sterane/hopane ratios, low DBT/P ratios, the dominance of C_{27} steranes and abundant extended tricyclics terpanes (up to C_{36}). The depositional environment of the source rock was probably oxic to sub-oxic, as indicated by the relatively high pristine/phytane ratio and the low abundance of 28,30-bisnorhopane. The FI oils contain some contribution from higher plant, indicated by a small quantity of oleanane and the presence of A-ring contracted oleanoids. This indicates that the oils were generated from Upper Cretaceous or younger source rocks deposited after the radiation of angiosperms. Terrestrial plant contributions are also indicated by relatively high abundances of 1,2,5-TMN and 1,2,5,6-TeMN and moderately abundant cadalene. Benzene and toluene are dominated in all the samples based on the on-line analysis which indicate these water soluble compounds most likely originated from co-eval aqueous inclusions (Ruble *et al.*, 1998). Thermal maturity based on aromatic hydrocarbon parameters suggests that the FI oils from Ecopetrol-B well have been derived from source rocks within the peak oil generation window, at a vitrinite reflectance equivalent (VRE) of 0.9%-1.3%. This is confirmed by parameters based on low molecular weight hydrocarbons, while biomarker maturity parameters tend to indicate a somewhat lower maturity level (ca. 0.6-0.7 VRE), possibly due to mixing or a different kinetic behaviour of these parameters.

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The use of in situ derivatisation and laser pyrolysis-GC-MS for the analysis of restored paint samples.

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The use of laser pyrolysis to obtain spatially resolved information from geological samples such as torbanites and fluid inclusions has been well established (Greenwood *et al*., 1996, Greenwood *et al*., 1998, Volk *et al*., 2010).

Similar to a geological sample, restored paint samples consist of various individual and unique layers containing different mixtures of compounds (i.e., pigments and binders). The study of these compounds can reveal what production techniques have been used, can detect causes and mechanisms of degradation as well as develop and evaluate methods of restoration (Ciliberto *et al*., 2000). The challenges in analysing different paint layers are as difficult as for analysing geological samples, due to lack of spatial resolution and uneven distribution of sample layers. Glycerides in these materials are responsible for the desired properties in particular layers. Laser pyrolysis of glycerides produce fatty acids and require further treatment for analysis by GC-MS. The in situ

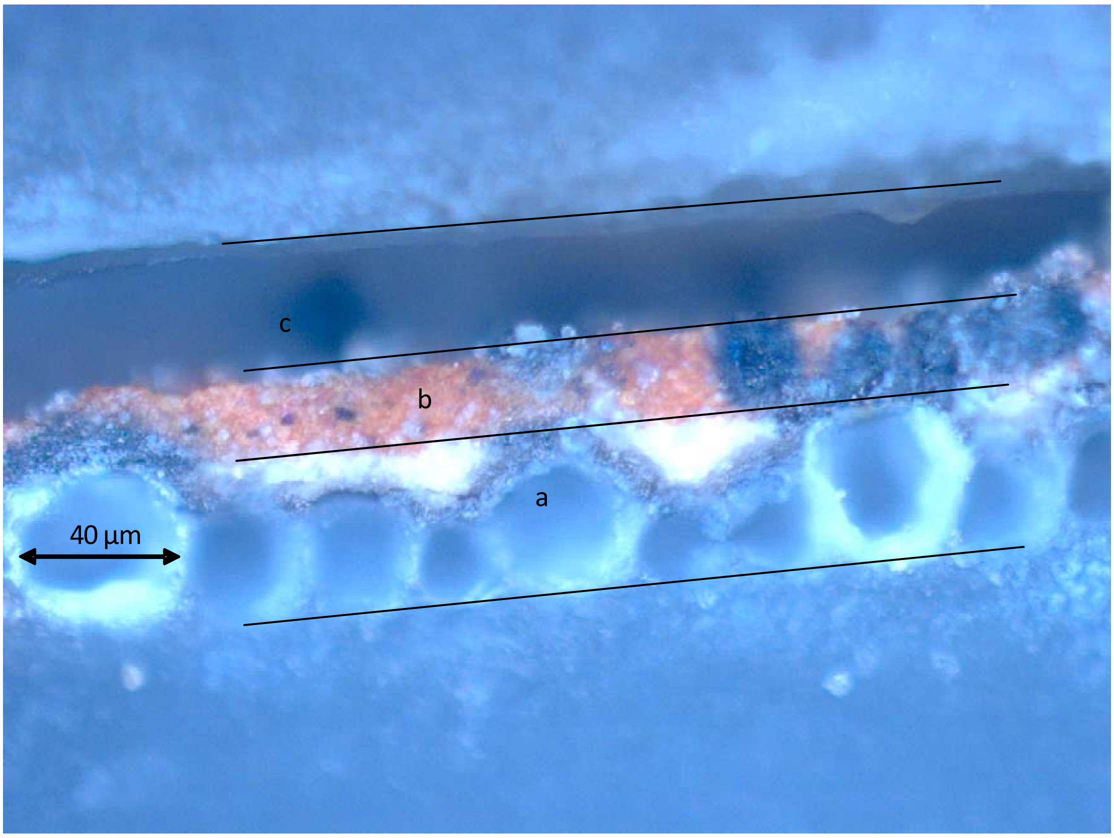

Figure 1. Laser micro pyrolysis spots on sample OR2 consisting of a) preparation layer b) painting layer and c) varnish layer.

derivatisation of such compounds has already been shown to overcome this problem by converting to volatile esters and ester derivatives (Chiavari *et al*., 2001)

In this study we aim to combine the spatial resolution of laser micropyrolysis-GC-MS technique with the in situ derivatising ability of trimethylammonium hydroxide (TMAH) to reconstruct the composition of individual layers of restored paint samples.

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Proterozoic rocks that retain organic compounds: insights from the McArthur Basin (Northern Territory, Australia)

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Attention has been drawn over the past 2 years to Proterozoic rocks in the Northern Territory of Australia for conventional and unconventional oil and gas exploration. Proven source rocks, the presence of potential reservoirs, and significant and widespread shows of hydrocarbons make of these Precambrian successions priority targets for the petroleum industry.

In the McArthur Basin, part of this exploration is focused on the Barney Creek and Velkerri lithostratigraphic units, which are respectively Paleoproterozoic and Mesoproterozoic in age. These stratigraphic intervals are hundreds of metres thick and mainly comprise dolomitized mudstones, siltstones and very fine sandstones, which contain elevated concentrations of organic matter (TOC values up to >8%; e.g., Crick *et al.*, 1988). Their inferred depositional settings range between lacustrine and deep marine (Jackson and Raiswell, 1991; Bull, 1998).

Proterozoic rocks have commonly been subjected to a long and complex history of deformation and metamorphism over geological time. Therefore, the preservation in the McArthur Basin of carbon-based chemical compounds derived from biota in such ancient sedimentary successions is highly unusual, and the mechanisms that enabled this scenario are yet to be identified.

In this contribution, based on the examination of mineral drill hole cores, we investigate the sedimentological conditions under which these organic compounds were trapped and preserved.

Acknowledgements: This is a contribution to the project "Geological controls of Palaeo-Proterozoic black shale deposition in the McArthur Basin, Northern Territory of Australia" funded by Imperial Oil & Gas Pty Ltd.

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Approaches to differentiating between different biogenic methane sources

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Biogenic methane from multiple sources can complicate interpretations of origin for gas emitting at the Earth's surface. In the case of areas proximal to coal seam gas (CSG) occurrences, the three main possible inputs are,

1) coal seams where the CSG displays a biogenic methane signature as evident by its carbon isotopic values ($\delta^{13}C$ -65 to -50‰),
2) aquifers used for agricultural borewater which exsolve biogenic methane during water production,
3) recently buried organic debris undergoing methanogenesis to produce biogenic methane in river and pond sediments.

Differentiating the biogenic methane inputs can be complicated and difficult to de-convolute; definitive origins may be complicated by mixing, migration and oxidative alteration processes (see Whiticar, 1999).

Analysis of surface gas samples from areas near CSG occurrences tend to be "dry" in that they mainly consist of methane (CH_4) with small amounts of carbon dioxide (CO_2), nitrogen (N_2), water vapour and in places, trace amounts of hydrogen sulphide (H_2S).

Current analytical methodologies for gas geochemistry focus on,

i) molecular gas composition

ii) carbon isotopes, $\delta^{13}C$ of CH_4 and CO_2 and

iii) hydrogen isotopes, δD of CH_4

δD will shows a greater range of isotopic fractionation than for $\delta^{13}C$, hence is expected to give the best chance of distinguishing between the two primary biogenic metabolic pathways recognised for methanogenesis: fermentation of acetate and reduction of CO_2. δD of methane typically ranges from -400 to -200‰ in freshwater sediments (Hoefs, 2009).

Other approaches available to potentially help differentiate biogenic methane sources are,

A) ^{14}C age dating of methane to give an age guide as to whether the carbon source for the methane is ancient (i.e. coal/rock-derived CO_2/bicarbonate ions (HCO_3^-) in pore water) or recent fresh water sediments and nutrients (i.e. meteoric water inputs to ground water aquifers and flood borne sediments trapping modern day terrestrial plant matter),

B) $\delta^{13}C$ analysis of dissolved inorganic carbon (DIC); DIC of borewater, CSG production water and the porewater from river sediments/mud may allow correlations of possible carbon sources,
C) nitrogen (N_2) isotopic analysis, but this may not be very diagnostic since the fractionation in nature is small and samples are prone to air contamination which contains ~78% N_2 with a defined isotopic value of 0 ‰,
D) sulphur isotope analysis of gaseous sulphur species, but since H_2S is normally only detected in trace amounts (~1ppm or less), it would be below detection limits for most analyses. (however, if large quantities of methane were bubbled through silver nitrate solution, sufficient silver sulphide could be precipitated for subsequent sulphur isotope analysis by EA-IRMS analysis),
E) stable isotope analyses of noble gases and radioactive tritium (^3H, characteristic of atmospheric inputs) which are present in trace levels is possible but questions remain as to whether sufficient differentiation between atmospheric/meteoric water inputs versus deeper basement/mantle inputs would shed any further light on source contributions.
F) analysis of clumped isotopologues of CH_4 and CO_2 which offers the possibility of gaining a new generation of stable isotope techniques that don't destroy the complexity and fine structure embedded in molecules of interest; current techniques destroy that information by combusting or reducing methane to form CO_2 or H_2 respectively. With new high resolution gas source stable isotope instruments currently being developed (e.g. Jones, 2012), all of the richness of natural variations in clumped istopologues will be available for interpretation.

In most cases, access to limited volumes of gas limit the analyses that can be routinely performed. The use of molecular composition, and carbon and hydrogen isotopes are at present the proven methods for helping to elucidate complex sources of gas.

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Multiscale Variability of the Woodford Shale, Oklahoma, USA: Organic Matter Preservation as Clay-organic Nanocomposites, and Diagenetic Links to Hydrocarbon Entrapment

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Regional and within well variability in hydrocarbon production from organic carbon-rich shales has demonstrated unconventional reservoirs are highly complex and require in-depth understanding of geological factors to make successful predictions (Jenkins *et al*., 2008). Variability is apparent in porosity and permeability, mechanical properties which control fracture susceptibility crucial for enhanced hydrocarbon release, as well as in concentrations of organic carbon (OC) (Harris *et al*., 2011; Romero and Philp, 2012). The economically successful, though variable, Woodford Shale (Oklahoma, USA) shows a strong correlation between mineral surface area (MSA) and total organic carbon (TOC), $R^2 = 0.85$. Consistent with a mineral surface preservative effect on OC, the relationship extends across samples with TOCs ranging from <0.5% to 18% studied from multiple cores. When plotted against sample depth, the TOC and MSA data illustrate the heterogeneity of the MSA and TOC in the core, highlighting the systematic stratigraphic co-variant relationship between TOC and MSA (Figure 1). Alterations of up to 10% TOC are matched by similar shifts in MSA showing no apparent lead or lag.

Transmission electron microscopy (TEM) performed on ~80 nanometre thick ultramicrotomed thin sections confirms quantitative geochemical clay-OC associations at the nanoscopic scale of interaction (Figure 2). These TEM micrographs show nanoscale organic carbon-rich clay laminae separated by biogenic quartz with inclusions of pyrite, dolomite and quartz grains throughout the clay laminae. Energy Dispersive Spectrometry (EDS) spot analyses, identifying elemental chemistry at 80 - 100 nm resolution, reveal that organic carbon is entirely constrained to clay the laminae. Grey zones encapsulated by clay aggregates (Figure 2, Image A2) appear homogeneous at low magnifications and are similar to the organic matter 'blebs' described by Salmon *et al*. (2000). However, closer inspection (up to 120,000 x magnifications) resolves these zones into laminated clay particles occurring at nanoscales (Figure 2, Images A3, A2). Whilst some OM may have originally adsorbed onto detrital illite, it is highly probable that OM previously associated with smectite interlayers could have been expelled through layer collapse during illitization, yet remaining in proximal association with clays. This common process is inevitable with progressive sediment burial and commonly coincides with the depth and temperature of hydrocarbon generation in the oil window (Abid and Hesse, 2007). TEM micrographs of later stage, sub-micron quartz diagenetic cements show these are fabric displacive, which may explain how the opposing mechanisms of hydrocarbon leaching and entrapment can co-exist for over 300 million years. The association of clay and organic rich carbon reduces fracability in intervals of high TOC, however, quartz cements increase brittleness and fracture susceptibility (Harris *et al*., 2011). Determining key modes of how and where organic carbon is preserved during deposition and early diagenesis in proven gas shales, such as the Woodford Shale, encompassing a more holistic approach may enhance the prediction of prospective hydrocarbon resources in frontier basins.

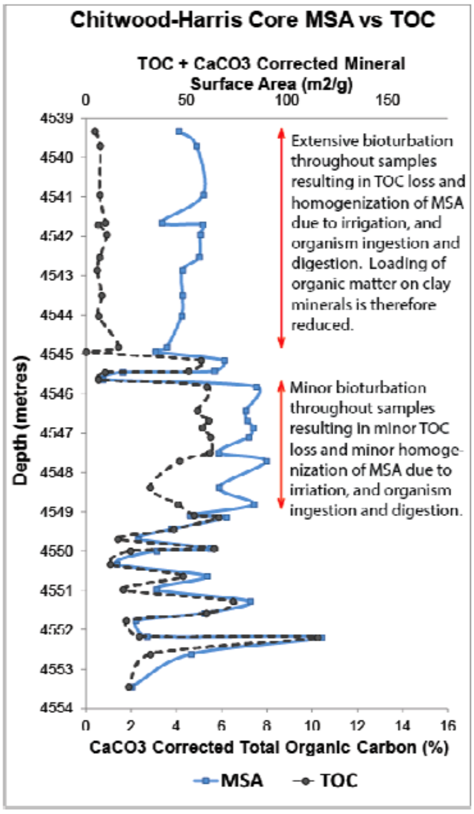
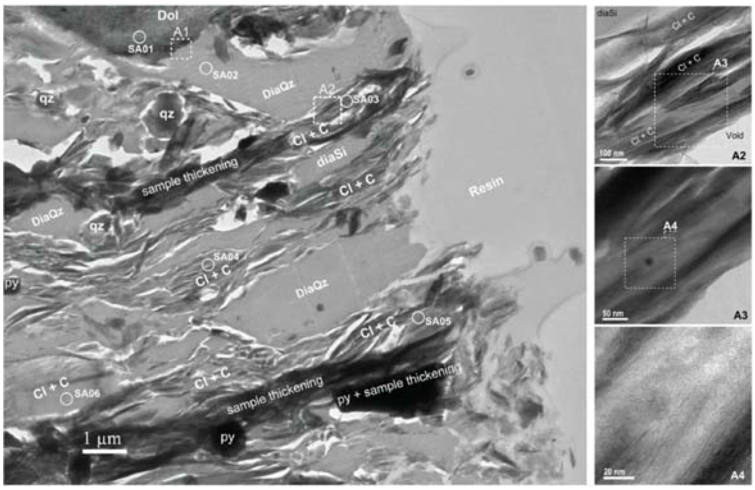


Figure 1 (left) TOC and $CaCO_3$ corrected MSA plotted against $CaCO_3$ corrected TOC% for the Chitwood-Harris core according to depth (metres). This illustrates the co-variant SP relationship of TOC% with MSA on a sample to sample basis that remains in phase. Exceptions particularly in the upper zone (4539.3 - 4544.8 m) are resulting from bioturbation wherein both irrigation of sediment, and OM digestion significantly reduced TOC, leading to significantly reduced OM loading onto minerals and homogenisation of MSA variability prior to burial.

Figure 2 (below) TEM photomicrograph of an ultra-thin section from the East Fitts core (Sample EF-3422.4). Organic carbon (OC) is hosted exclusively within clay layers where it forms an organo-clay nanocomposite (Cl+C). Clay layers are planar to shale laminae 300 – 900 nm thick) separated by biogenic diagenetic quartz labelled 'DiaQz'. Note, dolomite (dol) grain at top left, and pyrite labelled 'py'. SA marks locations of elemental spot analysis by Energy Dispersive Spectroscopy Spectrometry (EDS). Dark zones are zones of sample thickening. This contrast is a result of the lack of electron penetration of the TEM.



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The importance of the clay mineral fraction for the selective preservation of nano-composites in black shales: An Eagle Ford Shale example

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Unconventional shale plays are revolutionizing the petroleum industry worldwide. Their ability to store large volumes of hydrocarbons and typically widespread geographical occurrence make them attractive resource targets. However, these systems pose exploitation challenges due to the poor understanding of the primary controls on hydrocarbon distribution throughout the reservoir.

Shale is commonly composed of a mixture of clay minerals, quartz, feldspars, carbonate, organic material and small amounts of other minerals (Singh, 2008). However, in organic carbon enriched black shales, the clay component plays a fundamental role in the preservation of organic matter (OM) thanks to their strong adsorption and catalytic properties (Michot and Villieras, 2006) as well as high effective mineral surface area (MSA) (Bishop and Philp, 1994). There is evidence that supports a quantitative relationship between organic carbon and MSA. Several studies suggest a mechanistic relationship, due to preservative effects of MSA on OM (Mayer, 1994; Kennedy *et al.*, 2002; Kennedy and Wagner, 2011; Loehr *et al.*, 2012). Preservation processes could be explained via adsorption/encapsulation with clay fraction facilitating a selective preservation of OM during deposition and burial (Keil and Hedges, 1993; Bishop and Philp, 1994; Mayer, 1994; Kennedy *et al.*, 2002; Kennedy and Wagner, 2011). Other hypothesis suggests that the formation of clay/OM nanocomposites could also favor preservation, however, direct evidence for nanocomposite development is currently lacking.

Our study will test the role of clay MSA as a control on OM preservation and occurrence in the worldwide class unconventional Eagle Ford Shale reservoir (Texas). Objectives include improving 1) the current understanding of distributions of organic matter and 2) predictions on the likelihood for organic porosity development after maturation as a function of OM preservation. Technique approach includes the application of particle separation and the ethylene glycol monoethyl ether (EGME) methods for characterization of the MSA to total organic carbon (TOC) relationship and scanning and transmission electron microscopy (SEM and TEM) for capturing OM/clay distributions at the micro and nano-scales.

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Coal degradation in anaerobic sediments associated with acid mine drainage

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Acid mine drainage (AMD) is the formation and run off of acidic water, most commonly associated with the mining of coal and metals. It is a significant environmental hazard because acidified water causes accumulation of heavy metals, loss of biodiversity and, particularly in sites with coal-mining history, emissions of greenhouse gases. AMD occurs when sulfur-rich mine tailings, in particular pyrite (FeS_2), are left at derelict mines. These tailings are stable in the anoxic subsurface, but reactive when they come into contact with water and oxygen (Eq. 1) (Johnson and Hallberg 2005).

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \tag{1}$$

Microbial activity at AMD sites associated with coal mining results in the production of methane and carbon dioxide. To date, much of the work on AMD has focused on the microbiology and biogeochemistry of the surface water, and relatively little is known about the microbiological processes occurring in the anaerobic sediments associated with these environments. To better understand these processes, we used Illumina-based metagenomics to examine microbial diversity in the anaerobic sediment zones of a coal-fueled AMD system from Neath in the Hunter Valley, NSW, Australia.

Small subunit ribosomal RNA sequences identified from the metagenomic sequence data were predominantly prokaryotic. Most were bacteria (94.5%)(Fig. 1), while 5.4% were archaeal. Further analysis of the microbial communities within the Neath AMD sediment will investigate genes for key enzymes used to degrade coal. Subsequently, we will assign these metabolic functions to particular organisms.

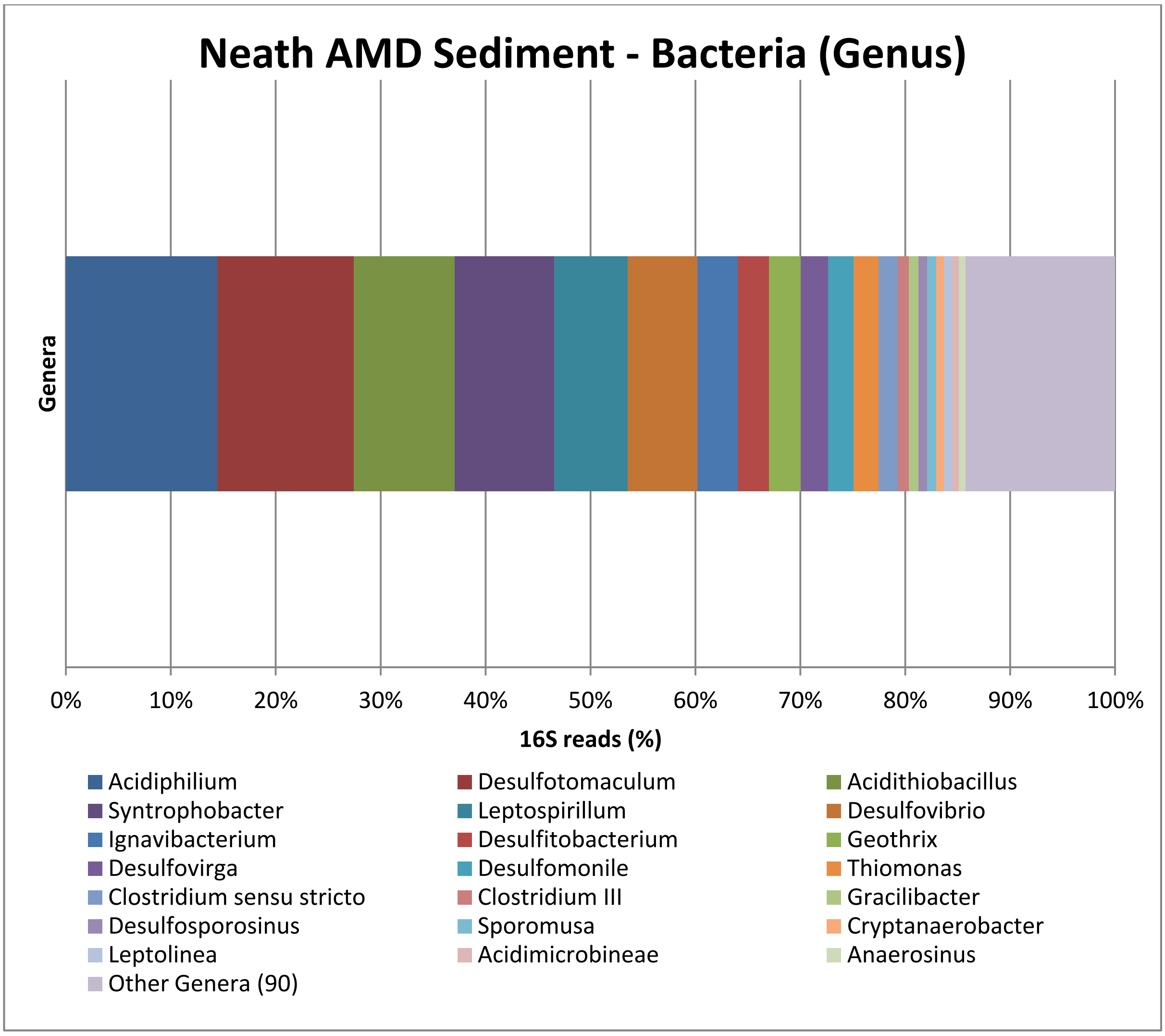

Figure 1. Bacterial genera within the Neath acid mine drainage sediment sample (genus identification >90% confidence interval; >5 counts of ribosomal DNA).

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