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16th Australian Organic Geochemistry Conference

7-10 December, 2010, Canberra, Australia

Compiled by J. H. Chen, J. M. Hope, E. Grosjean, C. J. Boreham and J. J. Brocks

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Program and Abstracts

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J. J. Brocks

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16th Australian Organic Geochemistry Conference

7 – 10 December, 2010
Canberra, Australia

General Information

Welcome

The Organising Committee of the 16th Australian Organic Geochemistry Conference welcomes you to Canberra. We wish you an enjoyable and pleasant stay in the tranquil and beautiful Capital City of Australia and an inspiring and thought-provoking conference.

Acknowledgements

The organizers of AOGC 2010 gratefully acknowledges the generous financial assistance received from Geoscience Australia (GA), the Research School of Earth Sciences (ANU), Total, Woodside, Beach Energy, Oil Search and Intertek/GeoTech for their contributions towards the student prizes, student travel grants, hire of the conference venue as well as the conference dinner and ice breaker. We also thank GA and ANU for contributing staff and resources, and GA for printing the conference volume as an officially available GA Record.

We also acknowledge and thank Josephine Magro and Robyn Petch (ANU) for administrative support; Patrick de Deckker (RSES, ANU) for guiding us on the field trip and preparing the field notes, AOGC 2008 chair Dave McKirdy for a lot of helpful advice and engraving the AOGC Medal.

Organising Committee

Jochen Brocks (Chair, ANU), Chris Boreham (Secretariat, GA);
Junhong Chen (GA); Emmanuelle Grosjean (GA); Ziqing Hong (Treasurer, GA);
Janet Hope (ANU); Graham Logan (GA)

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Venue

The National Museum of Australia is located on a peninsula of Lake Burley Griffin with views to Parliament House and close to the lake's other attractions (National Gallery, National Portrait Gallery, High Court, National Library, New and Old Parliament House, Gallery of Australian Design, Questacon, National Botanical Gardens). The location and contact information is:

National Museum of Australia
Lawson Crescent
Acton Peninsula
CANBERRA ACT 2600
AUSTRALIA
Tel +61 2 6208 5000

The National Museum of Australia is also close to the city centre where you will find many excellent restaurants. It is also in walking distance to accommodation at University House and to budget student accommodation in colleges of the Australian National University.

Social Events

In addition to the formal scientific program (8th and 9th December). The conference includes some social activities:

Ice breaker: Tuesday evening 7 December (included in registration)

Conference dinner: Thursday evening 9 December (included in registration)

There will be an opportunity to enjoy Canberra's cultural and culinary offerings.

The guided field trip on 10 December will take us to sites of alternative energy generation with magnificent views of Lake Weereewa (aka Lake George). The ACT energy producer will give us an exclusive tour of the spectacularly located Bungendore Wind Farm. After brunch in the artist's village of Bungendore, Prof Patrick De Deckker will give us a spiel of the perplexing geology and history of ephemeral Lake Weereewa before we proceed to a local winery for lunch. The field trip is FREE. You only have to pay for your own breakfast in Bungendore and lunch at the winery.

For interstate and overseas participants with time to spare before or after the conference, we can recommend visits to Tidbinbilla Wildlife Sanctuary, the Brindabella or Snowy Mountains, or one of the numerous national museums.

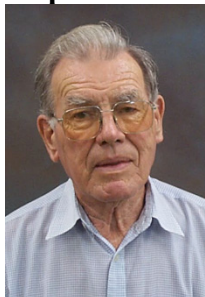
AOGC 2010 web site

The AOGC 2010 web page is located under Geoscience Australia's web site – <http://www.ga.gov.au/about-us/events/aogc-2010/index.jsp>. The conference abstracts volume is also available for downloading online.

The AOGC Medal

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

The previous winners of the AOGC medal are:



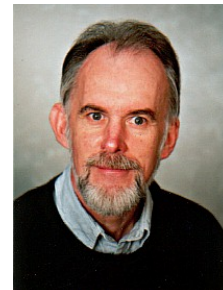
1991 John Smith
(CSIRO, North Ryde, NSW)



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)

The winner of the 2010 AOGC Medal is Dr Christopher J. Boreham



Dr Chris Boreham is an applied organic geochemist at Geoscience Australia who is well known to Australian and international research institutions and petroleum companies. For over thirty five years, Chris has been delivering ground-breaking research to Government and industry. Chris's annual production of prestigious publications and numerous presentations has resulted in his recognition as an outstanding scientist and it is fitting that he is bestowed with the AOGC 2010 Medal.

Chris received a BSc Hons in Chemistry from the University of Queensland in 1974 and a PhD in Bioinorganic Chemistry from the Australian National University in 1978. He joined the Bureau of Mineral Resources in 1980, and has continued his employment with the organisation which became the Australian Geological Survey Organisation and then Geoscience Australia.

His research interests lie in the application of biomarker and isotopes in petroleum geochemistry, the biosphere-geosphere interface as it relates to biodegradation of petroleum, burial history modelling, with specific emphasis on the chemical kinetics of source rocks to constrain timing of petroleum generation and expulsion in producing (Papuan, Bonaparte, Bowen-Surat, Browse, Carnarvon, Cooper-Eromanga, Perth, Gippsland, Otway and Bass) and frontier (Arafura, Bight, Mentelle and Georgina) basins. The impact of this research has been to reduce exploration risk, to increase the potential discovery of new resources (both petroleum and coal seam methane), and to set bench marks in environmental monitoring. The biomarker and isotopic characterisation of Australian oils and gases has been of value to the petroleum exploration industry in defining the limits of known petroleum systems, and in the identification of previously unrecognised petroleum systems. These studies are now becoming integrated into global databases. The identification of new source-specific biomarkers has been applied to the typing of oils to source rocks and in the interpretation of depositional environments. His research into the biodegradation of both oil and gas accumulations have assisted the petroleum industry to reduce risk in the production of these resources.

Recently, he has been investigating the geological controls on coal seam gas. He has also undertaken the chemical synthesis of unusual environmental markers found in oils. Now he is focussing on geochemical tracers as environmental monitors in CO₂ sequestration, as well as the bio-utilisation of CO₂ in coal seams.

Well done and best wishes for the future.

Dianne Edwards, November 2010

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AOGC 2010 – Conference Schedule

Tuesday, 7 December

- 17.00 – 18.00 Registration at the conference venue, National Museum
- 18.00 – 21.30 Welcome icebreaker party

Wednesday, 8 December

- 7.45 – 8.15 Registration and poster set-up
- 8.15 – 8.30 Opening remarks: *Jochen Brocks and Chris Boreham*

Oral Presentations

(Presenters are underlined)

Session 1:

Biomarkers

8.30 – 9.05

Keynote

Evolution and specificity of lipid biomarkers synthesized by microalgae

John K. Volkman

9.05 – 9.30

Biomarkers and stable isotopes and their role in fossil preservation

Ines M. Melendez, Kliti Grice, Kate Trinajstić, Mojgan Ladvardji, Paul F Greenwood and Katherine Thompson

9.30 – 9.55

The significance of perylenequinones and their diagenetic alteration products in Devonian reefs (Canning Basin, WA)

Svenja Tulipani, Kliti Grice, Paul F. Greenwood, Muhammad Asif and Kenneth H. Williford

9.55 – 10.20

Morning tea

Session 2:

Oil and Gas

10.20 – 10.45

Tracking hydrocarbon source and charge for the Silurian bituminous sandstone reservoirs in the Tazhong Uplift, Tarim Basin, west China

Se Gong, Keyu Liu, Herbert Volk and Feiyu Wang

- 10.45 – 11.10 Terpenoid land plant markers in Gippsland Basin oils
Herbert Volk, Manzur Ahmed, Se Gong, Chris J. Boreham, Peter Tingate, Geoffrey O'Brien and Dianne Edwards
- 11.10 – 11.35 Fluid property assessment and prediction in petroleum systems analysis
Daniel Dawson and Andrew Murray
- 11.35 – 12.00 Single carbon reactions on carbonaceous surfaces: implications for methane formation in sediments
Robert Alexander, Lyndon Berwick and Kieran Pierce
- 12.00 – 13.30 Lunch
- Session 3: Greenhouse Gas Release and Sequestration**
13.30 – 14.05 **Keynote**
The role of methane from sedimentary basins in global climate evolution
Karsten F. Kroeger, Rob H. Funell, Malcolm Geddes, Brian Horsfield, Rolando di Primio and Phil Scadden
- 14.05 – 14.30 IODP Expedition 317, Canterbury Basin, offshore NZ: on-board geochemistry results
Simon C. George, Julius S. Lipp, Toshihiro Yoshimura, George E. Claypool and Expedition 317 Shipboard Scientific Party
- 14.30 – 14.55 Application of reservoir gas geochemistry in monitoring carbon dioxide storage in the CO2CRC Otway Project, Australia
Chris Boreham, Jim Underschultz, Linda Stalker, Barry Freifeld and Dirk Kirste
- 14.55 – 15.20 Role of chemical tracers in carbon dioxide storage
Linda Stalker, Chris Boreham, Barry Freifeld, Jim Underschultz and Dirk Kirste
- 15.20 – 16.15 Afternoon tea and 3 min oral poster presentations
- Session 4: Biodegradation and Analytical Methods**
16.15 – 16.40 Australasian asphaltite strandings revisited: the effects of weathering and biodegradation on biomarker profiles
Tony Hall and David McKirdy
- 16.40 – 17.05 How does depth affect the preferential degradation process in antarctic marine sediments polluted by diesel?
Ellen Woolfenden, Ian Snape and Simon C. George

- 17.05 – 17.30 Elucidation of biodegraded Australian crude oils via catalytic
Hydropyrolysis
*Robert S. Lockhart, Minh Tam Le, Kliti Grice and
Will Meredith*
- 17.30 – 17.55 Use of MSSV pyrolysis to aid the GCMS characterisation of
immature sedimentary organic matter
*Paul Greenwood, Lyndon Berwick, Hayden McKenna, Youping
Zhou, Kliti Grice and Jean-Philippe Croue*

Thursday, 9 December

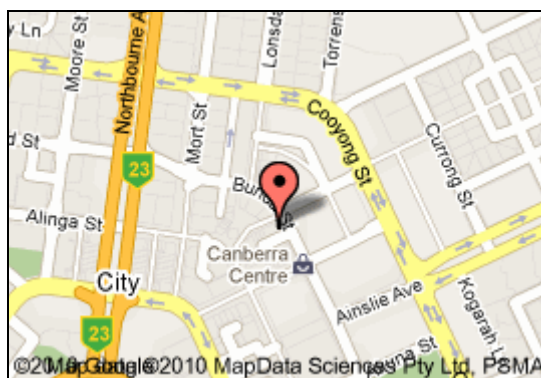
- Session 5: Stable Isotopes and Palaeoenvironments**
8.30 – 9.05 **Keynote**
Environmental influences on D/H Fractionation in Algal
Lipids
Julian P. Sachs
- 9.05 – 9.30 A unique stable C and H isotopic profile of native Australian
plant leaf *n*-alkanes
*Youping Zhou, Hayden McKenna, Kliti Grice, Paul Greenwood
and Grant Wardell-Johnson*
- 9.30 – 9.55 Stable carbon and hydrogen isotopes of components derived from
controlled burning experiments of C3 and C4 plants and their use
as environmental proxies for tracking fire history
*Caroline Jaraula, Kliti Grice, Christiane Vitzthum von
Eckstaedt, Richard Twitchett, Paul Wignall and David Kelly*
- 9.55 – 10.20 Morning tea
- Session 6: Radiocarbon**
10.20 – 10.45 Compound specific radiocarbon analysis of hypersaline microbial
biomarkers
*P. Sargent Bray, Claudia M. Jones, Stewart Fallon, Jochen J.
Brocks and Simon C. George*
- 10.45 – 11.10 The Devil's Pool – Pollen, biomarker and stable isotopes of
Holocene peat deposits reveal climate changes in south-western
Western Australia
*Tobias Ertefai, Pia Atahan, Grzegorz Skrzypek, Paul Greenwood,
Youping Zhou, Kliti Grice and John Dodson*

- 11.10 – 11.35 Factors controlling the preservation of terrestrial organic matter during transport from the Shoalhaven river catchment (NSW) to the adjacent continental shelf
Paolo A. Abballe and Allan R. Chivas
- 11.35 – 11.55 When size really does matter; measurement of ultra-small samples at the ANU Radiocarbon Dating Laboratory
Kelly M. James and Stewart J. Fallon
- 11.55 – 13.25 Lunch
- Session 7: Palaeobiogeochemistry (I)**
13.25 – 14.00 **Keynote**
New perspectives on Proterozoic inverse carbon isotope patterns of lipids and kerogen
Ann Pearson and Hilary G. Close
- 14.00 – 14.25 Compound-specific carbon isotopic signatures of biomarkers from Precambrian evaporites: pitfalls, solutions and insights into ancient biogeochemistry
Richard Schinteie, Janet M. Hope, Junhong Chen, and Jochen J. Brocks
- 14.25 – 14.50 Biomarker, isotopic and trace element signatures of an early Cambrian Lagerstätte in the Stansbury Basin, South Australia
David McKirdy, Tony Hall, Galen Halverson, Chris Nedin and Bernd Michaelson
- 14.50 – 15.45 Afternoon tea and presentation of the AOGC 2010 Medal
- Session 8: Palaeobiogeochemistry (II), Archaeology, Dust and Petroleum**
- 15.45 – 16.10 Exploring mass extinction events-using biomarkers & stable isotopes (carbon and hydrogen)
Kliti Grice, Birgit Nabbefeld, Richard Twitchett, Roger E Summons, Lindsay Hays, Kenneth Williford, Jennifer McElwain, Alexander Holman and Michael Böttcher
- 16.10 – 16.30 A reassessment of the petroleum systems in the offshore North Perth Basin
Emmanuelle Grosjean, Chris Boreham, Andrew Jones and John Kennard
- 16.30 – 16.55 Subsistence and the isotopic signature of herding in the Bronze Age Hexi Corridor, NW Gansu
Pia Atahan, John Dodson, Xiaoqiang Li, Xinying Zhou, Songmei Hu, Fiona Bertuch, Nan Sun, Kliti Grice

- 16.55 – 17.15 September 2009 Sydney dust storm – meteorological transport of a rich source of geochemicals, pollen and microbes
Chris Munday, Gwen Allison, Jochen Brocks, Patrick De Deckker, Janet Hope, Tadhg O’Loingsigh and Nigel Tapper
- 17.15 – 17.35 GC-IRMS analyses of natural gases and geochemical application
Junhong Chen and Chris Boreham
- 17.35 – 17.55 Molecular Fossils and the late rise of eukaryotes and oxygenic photosynthesis
Jochen J. Brocks and Birger Rasmussen
- 20.00 – 23.30 Conference Dinner

Location:

*Chairman & Yip Restaurant
108 Bunda St
Canberra City
(02) 6248 7109*



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Friday, 10 December

- 8.30 – 15.30 Field trip. Refer Social Events on page 4 for details.

Poster Presentations

(Poster papers are listed in alphabetical order by first authors' last names;
Presenters are underlined)

The Early Aptian Global Oceanic Event OAE1a as recorded in the Goraa-Hammam Biadha Basin (Northwestern Tunisia)

Soumaya. Abbassi, Habib. Belayouni and Moncef Saidi

Ecology of sediment nitrification and denitrification in the Fitzroy river estuary, Queensland, Australia

G. Abell, A. T. Revill, C. Smith, J. K. Volkman, S. Robert

On the geochemistry and origin of Eastern Papuan Basin oils and gases

Manzur Ahmed, Herbert Volk, David Holland, Adrian Goldberg and Tony Allan

Formation of adamantanes in sediments: carbonaceous surface reactions

Robert Alexander, Lyndon Berwick and Kieran Pierce

Sedimentary lipids and aDNA - a new biomarker approach?

Marlene Bausch, Ralph Tiedemann, Dirk Sachse

Long-term Degradation of Lubricant Oil in Antarctic Sediments

Max E. Easton, Ellen N.M. Woolfenden, Ian Snape and Simon C. George

Intact polar lipids and isotopic signatures of photosynthetic microbial mats from Shark Bay, Western Australia

Tobias Ertefai, Ricardo Jahnert, Grzegorz Skrzypek, John Dodson, Kliti Grice and Lindsay Collins

Using radiocarbon (^{14}C) to monitor atmospheric CO_2 storage

Stewart J. Fallon and Sasha. A. Wilson, Greg. M. Dipple, Shaun. L. L. Barker

Gas Stable Isotope Analysis – Sample containment and $\delta^{13}\text{C}$ stability

Jennifer van Holst, Linda Stalker, Yen Le and Stephen Sestak

Fluorescein: analysis and geochemical application in CO2CRC Otway Project

Ziqing Hong, Alex Moisis, Caroline Gibbons, Neel Jinadasa, Peter Aronetz and Chris Boreham

Biogeochemical Evolution in Neoproterozoic Oceans: The search for a 'turbid ocean'

Amber J.M. Jarrett and Jochen J. Brocks

Biomarker distributions and stable isotopes (C, H) establish the age and palaeoenvironmental conditions spanning the Permian/Triassic in the northern onshore Perth Basin

Mojgan Ladjavadi, Kliti Grice, Dianne Edwards, Chris Boreham, Ian Metcalfe, Roger Summons

Nature, origin, and precursor evolution of Indian fossil resins

Monalisa Mallick, Suryendu Dutta, Paul F. Greenwood

Genesis and Biogeochemical Evolution of Hydrocarbons in the Neo-Mesoproterozoic Sediments of the Yanshan Basin, North China

Guoyan Mu, Simon C. George, Ningning Zhong and Se Gong

Application of Biological markers to Characterize Petroleum and source rocks of Southern Indus Basin of Pakistan

Shagufta Nasir, K. Grice and Tahira Fazeelat

Laser micropyrolysis GCMS of hydrocarbon bearing fluid inclusions and petroleum source rocks

Zhang Zhi Rong and Paul Greenwood

Using organically preserved soft tissue to explore the evolution and preservation of the unique fauna from the Gogo Formation, Western Australia

Kate Trinajstić, Kliti Grice, Ines Melendez, Olaf Dellwig and Michael E. Böttcher

New molecular marker and spectroscopic tools for reconstructing wildfire history from sedimentary records

Daniel B. Wiedemeier, Simon G. Haberle, Evelyn S. Krull and Michael W.I. Schmidt

Spatial and temporal variation of vegetation in the Nature Reserve of Macquarie Marshes (NSW, Australia) reflected by organic geochemical proxies

Lili Yu, Allan R. Chivas, Adriana García and Jianfang Hu

An extraction process appropriate for studies of hydrogen isotope fractionations during plant lipid biosynthesis

Youping Zhou, Kliti Grice, Hayden McKenna, Paul Greenwood

AOGC 2010 – Abstracts

Oral Presentations

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

Evolution and specificity of lipid biomarkers synthesized by microalgae

John K. Volkman

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Microalgae are major sources of organic matter deposited in sediments and their contribution can often be inferred from the presence of specific lipids or their degradation products (collectively called biomarkers). While there are still a few biomarkers for which sources are still speculative (i.e. “orphan lipids” such as the tricyclic cheilanthanes), research over many decades has revealed plausible sources for most lipids. Indeed, with advances in molecular biology it is now feasible to assign biomarkers to specific lipid biosynthetic pathways and hence be more specific about the organisms in which these pathways occur. Although such work is still in its infancy the occurrence of specific biomarkers in dated ancient sediments provides an opportunity to understand how biosynthetic pathways have evolved over time as well as providing a window into the evolution of life and environmental change on earth.

Highly Branched Isoprenoid (HBI) Hydrocarbons: Hydrocarbons are not usually abundant in microalgae, but an exception is found in the diatoms. The genera *Haslea* and *Pleurosigma* produce C₂₅ unsaturated HBI alkenes while in *Rhizosolenia* C₂₅ and C₃₀ alkenes are found. It is now clear from detailed studies of diatoms in culture and from examination of well-dated sediment cores that the HBI-pathways evolved separately in two different diatom clusters with the oldest being about 92 million years ago (Sinninghe Damsté *et al.*, 2004) whereas diatoms as a class probably originated in the Early Jurassic. It is not yet clear what genes are involved in HBI synthesis and how they might be related to genes in other microalgae.

Sterols: The pathways by which sterols are biosynthesized are well known and many steps are involved including cyclization of squalene epoxide (by the enzyme oxidosqualene cyclase or OSC), removal of methyl groups at C-4, alkylation in the side-chain and insertion of double bonds in both the ring system and side-chain (see Volkman, 2005 for a review). The presence/absence or expression of these genes can help explain the diversity of sterol distributions found in microalgae. A few bacteria make specific sterols, but these have distinctive structures and hence can be readily recognised in sediments (e.g. Pearson *et al.*, 2003). The enzyme OSC has been found in bacteria from the Methylococcales, Myxococcales and Planctomycetales. High contents of 4-methyl triaromatic steroids lacking C-24 alkylation in the 1.64 Gyr old Barney Creek Formation were attributed to Type I methanotrophic bacteria not algae (Brocks *et al.*, 2008), since alkylation at C-24 has not been demonstrated in bacteria. It now seems highly likely that cyanobacteria cannot synthesize sterols and that

previous reports are due either to contamination from the medium used or from yeast or fungi in the culture (e.g. Volkman, 2005).

Alkenones: Perhaps the most unusual compounds found in microalgae are the C₃₇-C₃₉ straight-chain unsaturated ketones (alkenones) and hydrocarbons found in prymnesiophyte algae such as *Emiliania* and *Gephyrocapsa*. The ratio of the di- and tri-unsaturated C₃₇ alkenones is now widely used to provide a sensitive record of sea surface temperatures when the sediments were deposited. With new techniques, such as NaBH₄ reduction, a number of additional minor alkenones have now been identified as well as the corresponding alkenols. Some haptophytes such as *Chrysotila* have been shown to contain compositionally distinctive distributions of alkenones lacking C₃₈ methyl alkenones (Rontani *et al.*, 2004). Even though it is now over 30 years since alkenones were discovered the genes responsible for their biosynthesis have not been elucidated.

Alkyl Diols: Saturated and unsaturated C₃₀ and C₃₂ alkyl diols having a mid-chain hydroxyl group at C-15 are common in marine sediments and are usually attributed to eustigmatophyte microalgae since these are still the only class of microalgae found to contain these 1,15-diols (Volkman, 2006). A structurally similar group of saturated and monounsaturated C₂₈-C₃₀ diols, but with the hydroxyl group at C-14 has now been identified in diatoms of the genus *Proboscia* (Sinninghe Damsté *et al.*, 2003). It is not known whether the structural similarity is superficial and arises from very different pathways.

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Biomarkers and stable isotopes and their role in fossil preservation

Ines M. Melendez¹, Kliti Grice¹, Kate Trinajstić¹, Mojgan Ladvardji¹, Paul F Greenwood², and Katherine Thompson¹

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The Gogo Formation of Western Australia preserves a characteristic Late Devonian (380 MYA) reef fauna. The extraordinary preservation has been as a consequence of the taphonomy of the site as well as the lack of high tectonic forces in the region (Long *et al.* 2010). Moreover, exceptional preservation of soft-tissue, including muscle bundles, nerve cells, and umbilical structures, has been identified in this macrofossils during paleontological studies (Trinajstić *et al.*, 2007; Long *et al.*, 2010). Through improved sampling and preparation techniques extensive areas of soft tissue have now been recovered from placoderms, acanthodians (spiny-finned fish) and actinopterygians (ray finned fish) from the Gogo Formation (Devonian Canning Basin, WA).

More recently Maslen *et al* (2009) have demonstrated that the Gogo Formation of the Canning Basin and the equivalent aged-Duvernay Formation of the Western Canada Sedimentary basin (and their associated oils) were deposited under highly euxinic based on the presence of biomarkers associated with green sulphur bacteria.

To investigate the presence of biomarkers in fossilised soft tissue a suite of organic geochemical methods (biomarkers and stable isotopic) have been performed. Half of a whole crustacean within a Devonian nodule was extracted and separated into different fractions. *N*-alkanes (C₁₅ to C₃₂) were identified in the saturated fraction as the main components, which have a significant depletion in ¹³C associated to the contribution of sulphate reducing bacteria. Cholestane was found to be the most dominant compound in the saturated fraction attributed to a source from algal derived sterols probably retained upon grazing (Grice *et al.*, 1998). Markers of green sulfur bacteria globally identified across Permian/Triassic mass extinction boundary have also been identified here supporting photic zone euxinic conditions (H₂S and light) (Grice *et al.*, 1996; Grice *et al.*, 2005; Nabbefeld *et al.*, 2010). A Laser-pyrolysis GC-MS of the fossilised crustacean has been attempted to establish an association of cholestane to various organs and exclude the possibility that it is derived from algae that might have contributed to the nodule matrix. Various biomarker proxies within the sample support preservation under highly euxinic conditions similar to those that occurred during the Permian/Triassic mass extinction event.

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The significance of perylenequinones and their diagenetic alteration products in Devonian reefs (Canning Basin, WA)

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Distributions of unusual compounds including low-molecular-weight A-nor-steranes - potential novel sponge biomarkers originating from stromatoporoids - and relatively high abundances of the polycyclic aromatic hydrocarbon (PAH) perylene and other structurally related aromatic compounds have been detected in Devonian samples from ancient reefs of the Canning Basin, Western Australia. Perylene has been frequently reported in a variety of Mesozoic and Cenozoic sediments, but it has only occasionally been found in Paleozoic samples (Grice *et al.*, 2009). Despite a wide occurrence, its origin in sediments remains unclear. A combustion source, which is the origin of most unsubstituted PAHs, can be excluded since abundance and occurrence of perylene in sediments usually differ from those of pyrogenic PAHs (Atahan *et al.*, 2007; Jiang *et al.*, 2000). Perylenequinone pigments present in a variety of extant organisms including wood-degrading fungi, crinoids, plants and insects have been suggested as potential precursors on the basis of structural similarities (Grice *et al.*, 2009; Jiang *et al.*, 2000). The aromatic quinone-type compounds identified in the Devonian Canning Basin samples could represent intermediate products in a formation pathway to perylene. A similar suite of compounds along with perylene was also detected in Cretaceous samples from the Lower Indus Basin, Pakistan. The distributions of these compounds and other biomarkers (including the series of A-nor-steranes) are being analysed for evidence of environmental changes preceding the Late Devonian mass extinction, which significantly affected reef-building organism such as stromatoporoids. Furthermore, catalytic hydropyrolysis (HyPy) will be performed on extant sclerosponges to investigate their sterol composition and to search for novel highly specific biomarkers potentially found in the stromatoporoid-rich Canning Basin samples. Whereas various studies have revealed a great diversity of sterol structures within the class Demospongea (Bergquist *et al.*, 1991; Silva *et al.*, 1991), the sterol compositions of sclerosponges have not been robustly investigated.

In future studies we also hope to examine the biomarker composition of additional samples from the Canning Basin to span the Givetian-Frasnian boundary.

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Tracking hydrocarbon source and charge for the Silurian bituminous sandstone reservoirs in the Tazhong Uplift, Tarim Basin, west China

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The Silurian strata in the Tazhong Uplift, Tarim Basin are characterised by the occurrence of widespread bituminous sandstones and are a major hydrocarbon exploration target. The source and charge history of oil reservoirs in the area are complicated by the presence of various types of petroleum such as bitumen, heavy oil, normal oil and light oil. In this study, we investigate the composition and fluorescence attributes of petroleum fluid inclusions (FIs) hosted in Silurian bituminous sandstones to gain insights into this petroleum system. Three quartz samples, one each from well TZ4, TZ117 and TZ11 were studied by Quantitative Grain Fluorescence (QGF, Liu *et al.*, 2005) and by Molecular Composition of Inclusions (MCI) analysis (George *et al.*, 2007), and these data were compared to two reservoir oils from well TZ117.

Both MCI and QGF data of the petroleum FIs indicate that the TZ4 FI oil is different from TZ117 and TZ11 FI oils and reservoir oils, as indicated by a higher Pr/Ph ratio, higher abundances of Ts, C₂₉ Ts and C₂₈ steranes, a lower C₃₅/(C₃₄+C₃₅) homohopanes ratio, and a higher QGF Index. Geochemical data indicate that the TZ4 FI oil is derived from a marine source rock deposited in more oxic, less reducing conditions than for the other FI oil and oils. The TZ4 FI oil may be related to the Cambrian-Lower Ordovician source rocks described by Zhang *et al* (2002). However, the TZ117 and TZ11 FI oils are geochemically similar to the reservoir oils except that the reservoir oils have slightly higher Pr/Ph ratio and lower C₃₅/C₃₄ homohopane and C₂₉ sterane/C₂₉ hopane ratios. This may be due to higher maturities for these oils, indicated by various aromatic hydrocarbon maturity parameters.

The presence of 25-norhopanes in the FI oils and wide spread bituminous sandstones suggests an early charge in shallower depths, resulting in biodegradation. The presence of *n*-alkanes and 25-norhopanes for all the FI and reservoir oils as well as the differences in biomarker information mentioned above for the TZ4, TZ117 and TZ11 FI oils indicate mixing of an early, severely biodegraded charge with a later charge that was not degraded before trapping, each from different source rocks. Biomarker data suggest that the TZ4 FI oil is derived mainly from Cambrian-Lower Ordovician source rock with a lesser contribution from Middle-Upper Ordovician

source rocks, whereas the mixing proportions in the TZ117 and TZ4 FI oils and reservoir oils appears to be reversed.

The Silurian FI oil results indicate at least two episodes of charge history in the Tazhong Uplift; the oils in the Silurian bituminous sandstone reservoirs are similar to the late oil charge, mainly derived from Middle-Upper Ordovician source rocks.

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Terpenoid land plant markers in Gippsland Basin oils

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Declining reserves in the Gippsland Basin, one of Australia's premier oil provinces, require a refined understanding of source, migration and secondary alteration of petroleum, which can be addressed with new geochemical data. The foundation of our work includes aliphatic biomarkers and stable carbon isotopes for over 60 Gippsland Basin oils. Multivariate statistical analysis was used to define two main oil families, 'GA' and 'GB' (Summons *et al.*, 2002). The larger and less variable oil family (GA) was further distinguished into sub-families: GA1 (concentrated near the basin's depocentre) and GA2 (concentrated in the northern and north eastern part of the basin). GB oils, and to a lesser degree GA2 oils, have both mature and immature biomarker features, possibly acquired during petroleum migration. Some oils remain unclassified or are classified as vagrant, but all other oils are likely to be derived from coals and carbonaceous shales of the Latrobe Group (Summons *et al.*, 2002).

Diterpanes are abundant in Gippsland Basin oils and are believed to be derived chiefly from Southern hemisphere gymnosperms, in particular of the Araucariaceae and Podocarpaceae families. A subset of 23 oils with representatives from all of the oil families defined in Summons *et al.* (2002) have been analysed quantitatively for diterpanes by magnet scan and metastable reaction monitoring (MRM) experiments. 16 β (H)-phyllocladane and sometimes 4 β (H)-19-norisopimarane are the predominant diterpanes, except for the "unassigned" Marlin 1 oil which is dominated by isopimarane. This oil also contains the highest amount of A-ring contracted lupane, indicating that angiosperm contributions are also distinct.

On the basis of studies on Cretaceous and Palaeogene sediments of the Taranaki Basin, Killops *et al.* (1995) found that higher-plant evolution can be traced by an angiosperm-derived triterpane:hopane ratio (TT/H), a gymnosperm-derived diterpane:hopane ratio (DT/H) ratio, and an angiosperm/gymnosperm index (AGI). In the Gippsland Basin oils, TT/H and DT/H values for GA1 and GA2 and most GB oils fall into a tight cluster, whereas values for two GB oils and the vagrant and unassigned oils tend to be much higher. An age-calibration of AGI values after Killops *et al.* (1995) suggests Late Cretaceous source rocks for most of the Gippsland Basin samples studied, except for the West Seahorse oil which may be derived from

Palaeogene source rocks. However, a calibration with Gippsland Basin sediment extracts would provide more solid age-constraints.

Bicadinanes are often interpreted as angiosperm markers for Dipterocarpacea, and low amounts of bicadinanes were detected for all the oils studied, using specific MRM analyses. Their abundance relative to C₃₀ αβ hopane falls within a very narrow range for GA1 oils and is more variable for other samples. The occurrence of bicadinanes in all of the studied oils is noteworthy, since Dipterocarpacea did not evolve until the Oligocene and most oils are interpreted to be derived from the Cretaceous Latrobe Group. Collectively, the study of terpenoid land plant markers in Gippsland Basin oils confirms similarities within the GA1 family and to a lesser degree of the GA2 oil family, and helps in narrowing down source facies for GB, unclassified and vagrant oils in the area.

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Fluid property assessment and prediction in petroleum systems analysis

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The distribution of hydrocarbon phases across petroleum basins and even within individual oil and gas fields can be complex. Fluid types include oils with variable gas-oil ratio (GOR), gases with variable condensate-gas ratio (CGR), gas accumulations with present-day oil rims, biodegraded oil fields with dry gas caps, and poly-phase mixtures of fresh and biodegraded oils and gas-condensates. There is a common perception that the main control on the occurrence of oil vs. gas is source rock thermal maturity. In reality, this is often only the third most important factor.

The main factor controlling the phase of petroleum is simply the pressure and temperature of the trap, which is related to the depth of the trap. Secondly, the type of source rock determines the gas to liquids ratio (GLR) of the primary charge. The extent of kerogen conversion, related to thermal maturity, is generally the third most important factor. Another important control is the migration style, i.e. whether migration is dominantly vertical or lateral and, if the latter, whether migration occurs above or below the saturation pressure of the migrating fluid. Finally, secondary alteration, e.g. biodegradation and water washing can have a major effect on the phase of the trapped fluids. Geochemical and basin modelling (a combined process known as “Integrated Charge Evaluation”) are essential tools for fluid property assessment and prediction of phase and fluid properties away from well control.

This presentation will review the factors that control fluid phase and properties and some examples of fluid property assessment and prediction will be shown. Emphasis will be placed on sample acquisition, the importance of knowing the sample “pedigree” and pitfalls associated with non-representative samples due to non-ideal sampling conditions, inappropriate storage over time and/or drilling fluid contamination.

Single carbon reactions on carbonaceous surfaces: implications for methane formation in sediments

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A feature of petroleum exploration in Australia in recent decades has been the discovery of vast reserves of natural gas but an inability to replace the diminishing reserves of crude oil (Powell, 2001; 2004). The reactions responsible for methane formation in sediments have been the subject of debate for many years. Despite the faith of petroleum geologists in the formation of methane and other light hydrocarbons via thermal decomposition of organic matter with progressive burial, laboratory heating of kerogens and oils typically yields between 10 and 60 wt% methane of the C₁-C₄ products (Mango, 2001). In contrast, natural petroleum gases typically contain between 60 and 95+ wt% methane (Mango, 1997). The predominance of methane in natural gas has led geochemists to suggest the involvement of catalysis in the sub-surface (Mango *et al.*, 1994; Shock, 1994); however the nature of the catalytic reactions has remained unclear.

In this paper we investigate novel carbon surface reactions responsible for the transformation of hydrocarbons in sediments and the formation of crude oil and natural gas. A range of common sedimentary hydrocarbons, including terminal alkenes (e.g. 1-octadecene, 1-eicosene), isoprenoid alkanes (e.g. pristane) and methyl substituted aromatics (e.g. benzenes, naphthalenes, biphenyls, phenols) were subjected to sealed tube heating experiments on activated carbon in the temperature range 170 to 340°C.

The database of reactions established through our laboratory experiments, which were broadly classified as hydrogen exchange (e.g. double bond isomerisation, hydrogenation, hydrogen exchange, dehydrogenation / aromatisation / cyclisation), carbon exchange (e.g. dealkylation, transalkylation) or heteroatom exchange, led to the proposal of a reaction mechanism to account for the observed product distributions and the formation of methane. The mechanism is based on the formation of a reactive, surface adsorbed single carbon intermediate characteristic of a surface carbene (i.e. methylene, :CH₂). This reactive single carbon species may then; a) form methane by abstracting hydrogen from the solid state surface or from surface adsorbed liquid phase hydrocarbons; b) undergo addition to a C-H bond present in the mobile liquid phase hydrocarbons or c) undergo a similar addition to a C-H bond present in the solid phase. Methane formation is thus dependent on 1) the generation and fate of the reactive single carbon units, which in turn is impacted by the type of organic substrates available in the sediment and the availability of reactive sites on the carbon surface, and 2) the availability of a hydrogen source to add to the

methylene units to form methane. Online micro-scale sealed vessel (MSSV) GC-MS analyses showed that methane was the dominant (> 50%) gaseous hydrocarbon product from all the substrates investigated, suggesting that the proposed carbon surface reactions may be a key to understanding the predominance of methane in natural petroleum gases.

A set of molecular parameters to account for the factors involved in methane formation have been developed based on the concept that methane formation in source rocks is accompanied by parallel reaction products in the liquid phase (i.e. crude oils and sediment extracts). The extent of methane formation is thus reflected by the liquid phase product: reactant ratio, enabling the gas/oil potential (GOR) of source rocks to be predicted not only from the hydrocarbon composition of reservoir oil, but also from sediment extracts recovered in exploration drilling. GOR assessment using this approach is independent of migration effects which make current approaches to reconstruct GOR unreliable due to fractionation of the gas and liquid phases. The new molecular parameters developed in this project employ product/reactant data from liquid phase hydrocarbons readily available from routine GC-MS analyses of petroleum and sediment samples and could be readily adopted into practical application in the petroleum industry.

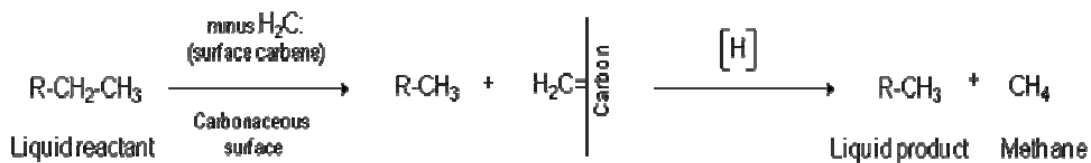


Figure 1: Reaction scheme for the formation of methane with single carbon reactions on oncarbonaceous surfaces.

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The role of methane from sedimentary basins in global climate evolution

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The current rapid increase of atmospheric CO₂, related to human activity, represents an extreme situation in Earth's history but is not unique in the past 65 Myrs of Earth's evolution (Zachos *et al.*, 2008). During the Paleocene Eocene Thermal Maximum (PETM), up to 3000 Gt of carbon were released to the surface during the initial warming event (Zeebe *et al.* 2009). This estimate is constrained by the magnitude of the $\delta^{13}\text{C}$ excursion and the rise of the Carbonate Compensation Depth (CCD) in response to increased CO₂ uptake by the oceans. While individual or a combination of several sudden methane release mechanisms, such as gas hydrate dissolution, may explain the initial $\delta^{13}\text{C}$ excursion, much higher amounts of released carbon are necessary to sustain CO₂ concentrations for tens of thousands of years (Pagani *et al.*, 2006). This is especially true for the Early Eocene, after $\delta^{13}\text{C}$ values had returned to approximately pre-PETM levels, when a renewed decrease in oceanic $\delta^{13}\text{C}$ continued for several Myrs reaching values close to PETM level (Nicolo *et al.*, 2007). Such a continuous or pulsed release of additional organic carbon to the surface over several Myrs is difficult to explain quantitatively by the mechanisms proposed to date. In this outreach, we explore how the sedimentary carbon system may have driven global climate change at a basin, regional and global scale.

The mass of organic carbon in sedimentary basins amounts to a staggering 10¹⁶ tons (Berner *et al.* 1989), dwarfing the mass contained in coal, oil, gas and all living systems by ten thousand-fold. The changing fate of this giant mass during subsidence and uplift, via chemical, physical and biological processes, not only controls fossil energy resource occurrence worldwide, but also has an enormous capacity for driving global climate: only a tiny proportion of leakage, particularly when focused through the clathrate cycle, could result in globally significant greenhouse gas emissions. Geochemists are able to model the mobilization of carbon through thermal and biogenic cracking of kerogen and migration into oil and gas traps. From petroleum systems models it is evident, that most oil and gas is not trapped but either lost during migration or through leakage to the surface. Leakage to the surface is documented by countless seep structures such as pockmarks, mud volcanoes and chimneys. The mobilization of organic carbon in sedimentary basins and leakage to the surface has not necessarily been constant through time. Tectono-climatic factors have the potential to control the rate of carbon mobilization:

- 1) The presence of source rocks in the sedimentary column is controlled by carbon sedimentation rate. For example the Upper Jurassic and Aptian-Turonian intervals were characterized by numerous black shale events and have sourced more than half of all known petroleum occurrences (Klemme and Ulmishek, 1991).
- 2) First and second order tectono-sedimentary cycles controlled rates of burial and organic matter maturation
- 3) Organic matter maturation may have responded to heat transfer in the basin during warm climatic periods such as the late Paleocene – Early Eocene.

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IODP Expedition 317, Canterbury Basin, offshore NZ: on-board geochemistry results

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Integrated Ocean Drilling Program Expedition 317 (4 November 2009 to 4 January 2010) drilled a transect of four shelf-upper slope sites off the eastern South Island, New Zealand (Canterbury Basin), in water depths of 85–344 m. The expedition was aimed at understanding the relative importance of eustasy and tectonic and sedimentary processes in controlling the development of continental margin sedimentary cycles (sequences). Drilling concentrated on late Miocene to Recent stratigraphy, during which period the high rate of sediment supply from the nearby, uplifting Southern Alps resulted in a high-resolution record of depositional cyclicity that was influenced by north-flowing ocean currents. Sedimentary sequences were cored in a transect of three sites on the continental shelf (landward to basinward, Sites U1351, U1353, U1354) and one site on the continental slope (U1352). The drilling transect provides a record of depositional cycles across shallow water shelf environments that were directly affected by local relative sea level change. Site U1352 represents a complete section from modern slope terrigenous sediment to hard Eocene limestone, with all associated lithological, biostratigraphical, physical, geochemical, and microbiological transitions.

Comprehensive on-board geochemistry was carried out on all four holes, and comprised headspace and porespace gas analysis, analysis of major and some minor element constituents of interstitial water squeezed from the sediments (liquid analysis), and sediment bulk geochemistry (solids analysis). These data have been presented in summary form in the preliminary report (Expedition 317 Scientists, 2010). This talk will focus on the shallow biogeochemical processes that have been shown to be driven by the microbially-mediated remineralization of organic matter buried with the sediments.

A combination of routine residual dissolved gas analysis and high resolution water sampling (every section of recovered cores) in the shallow sections from each site allowed profiles covering the biogeochemical zones of sulfate reduction, anaerobic

oxidation of methane (AOM), and methanogenesis to be examined in great detail. Sites U1353 and U1354 are located on the shelf in water depths of 85 and 120 m, respectively. Both sites are characterized by the absence or low levels of methanogenic activity in the top 150 m leading to low methane concentrations. At Site U1353 no hydrocarbons above background levels were detected, and sulfate remains close to seawater concentration with the exception of slightly decreased sulfate in a lower salinity interval at 20-70 m. No sulfate-methane transition is apparent, suggesting that either (1) methanogenesis did not occur in the sediments, (2) previously generated methane was lost when the shelf was emergent, or (3) methane was oxidized when sulfate was replenished by diffusion after a subsequent sea level rise. Hydrocarbon monitoring at Site U1354 showed two peaks in methane content, a small one (23 ppmv) at 33-75 m, and below about 200 m where methane increased above 20,000 ppmv. In both cases, methane begins to increase where sulfate has dropped to zero, and the shallow methane peak disappears where sulfate reappears in the cores. These alternations of methanogenesis appear to be related to changes in sedimentation rate. The upper and lower methane zones correspond to periods of rapid sedimentation (200-400 m/Ma) in which sulfate was depleted and methane was generated. The intermediate depths (60-200 m) were periods of slower sedimentation (<50 m/Ma) when pore waters could be replenished with sulfate by diffusion from overlying seawater.

Sites U1351 and U1352 are located further offshore and show similar geochemical profiles that are distinct from Sites U1353 and U1354. At both sites a classical sulfate-methane transition (SMT) zone is located around 15-16 m CSF. In sediments below the SMT sulfate is virtually absent and methane concentrations increase dramatically from background levels in the low ppmv range to >10,000 ppmv. The alkalinity at the SMT maximizes at 10 mM and 24 mM for Site U1351 and U1352, respectively. The apparent levels of carbon oxidized and the low levels of ammonium and phosphate generated at Site U1351 suggest that sulfate reduction is primarily fueled by anaerobic oxidation of methane, whereas at Site U1352 both anaerobic oxidation of methane and organic matter oxidation are coupled with the removal of sulfate.

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Application of reservoir gas geochemistry in monitoring carbon dioxide storage in the CO2CRC Otway Project, Australia

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The CO2CRC Otway Project in south-western Victoria, Australia has injected over 17 months 65,445 tonnes of a mixed CO₂-rich fluid (75.4 % CO₂, 20.5 % CH₄, remainder wet gas and N₂) into the water leg of a depleted natural gas reservoir at a depth of ~2 km. The Otway Project is the first to be specifically designed to monitor the movement and demonstrate the containment of supercritical CO₂ in a depleted natural gas field (Sharma *et al.*, 2009). Pressurised sub-surface fluids were collected from the Naylor-1 observation well using a tri-level U-tube sampling system (Freifeld *et al.*, 2005; involving continuous ¼ SS tubing from reservoir level to surface) located near the crest of the fault-bounded anticlinal trap, 300 m up-dip of the CRC-1 gas injection well. Relative to the pre-injection gas-water contact (GWC), only the shallowest U-tube initially accessed the residual methane-rich gas cap. The pre-injection gas cap at Naylor-1 contains CO₂ at 1.5 mol%, which is 15 times less than the CO₂ content in the injected gas from the Buttress-1 supply well and its CO₂ is depleted in 13C by 4.5‰ VPDB compared to the injected supercritical CO₂. Additional assurance of the arrival of injected gas at the observation well is provided by the use of the added tracer compounds, CD₄, Kr and SF₆ in the injected gas stream (Stalker *et al.* this volume). The U-tube assembly's performance was continually monitored for the blockage caused by precipitation of dissolved hydrocarbon wax as gas is brought to surface and accompanied by a temperature drop to ~30°C at the wellhead from ~85°C at reservoir level. A novel solvent injection system was deployed to mitigate this wax build-up.

The initial breakthrough of the migrating dissolved CO₂ front occurs between 100 and 121 days after CO₂ injection began, as evidenced by slight increase in mol% CO₂ above background levels at the middle U-tube (U2 in Fig. 1), located an average 2.3 m below the pre-injection GWC, and further supported by positive responses of both the carbon isotopic composition of CO₂ and the artificial tracers. The major CO₂ increase to ~60 mol% at the middle U-tube, together with the transition from sampling formation water with dissolved gas to sampling free gas, occurred several weeks after the initial breakthrough (Fig. 1). After another ~3 months the CO₂ content in the lowest U-tube (U3), a further average 4.5 m deeper than the middle U-tube, increased to ~60 mol%, similarly accompanied by a transition to sampling predominantly gases. Around this time, the CO₂ content of the upper U-tube (U1), located in the gas cap and an average 10.4 m above the pre-injection GWC, increased to ~20 mol% on day 247 (Fig. 1). Subsequently, the CO₂ content in the upper U-tube approaches 30 mol% while the lower two U-tubes show a gradual decrease in CO₂ to ~48 mol% (Fig. 1), resulting from mixing of injected and indigenous fluids and partitioning between dissolved and free gas phases.

Within the range of plausible static geological models (Dance *et al.*, 2009), there is good agreement between the observed composition changes in the collected fluids from U2 and U3 and those predicted by dynamic reservoir models. However, the degree of CO₂ increase at U1 level in the reservoir was not predicted by these pre-injection models (Underschultz *et al.*, in press). The reason for this discordance is still under investigation. Nevertheless, the results obtained from the CO2CRC Otway Project give us confidence that we are able to better anticipate the challenges for rapid deployment of CO₂ storage in a commercial environment at much larger scales.

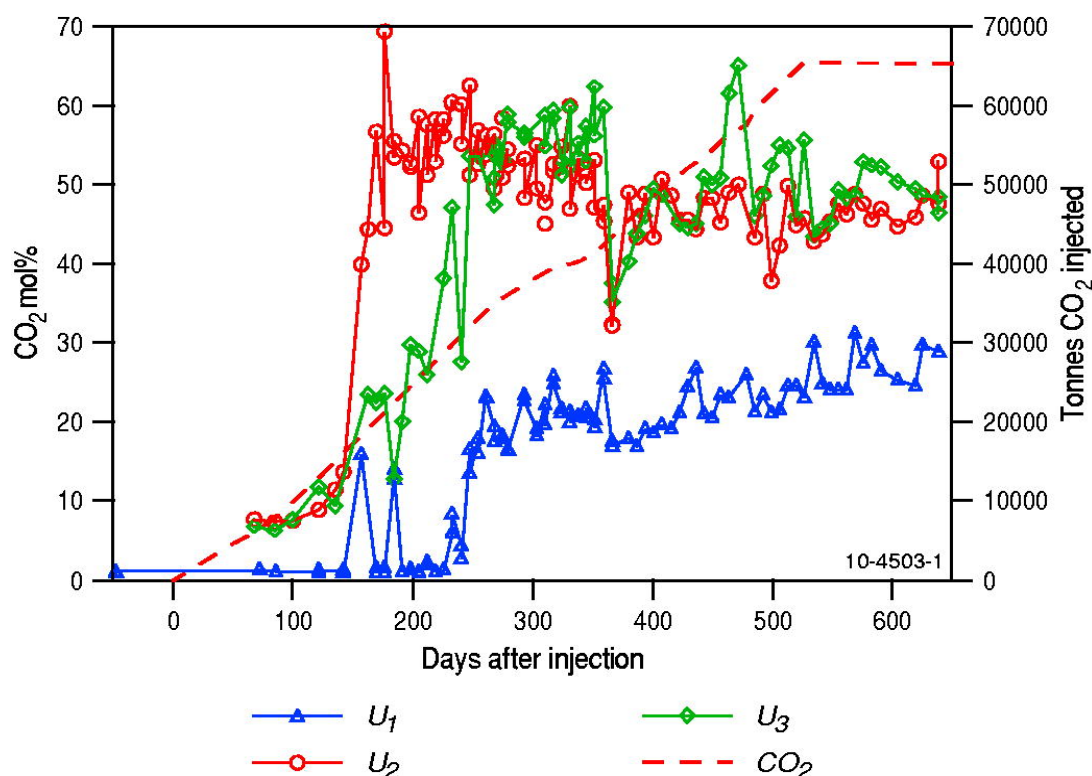


Figure 1: Time series of U-tubes 1, 2 and 3 showing CO₂ content (mol% as N₂-free basis) of samples collected at Naylor-1 observation well, and cumulative tonnes of CO₂-rich fluid injected into the CRC-1 well.

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Role of chemical tracers in carbon dioxide storage

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Chemical tracers are being used to measure, monitor and verify the presence of sequestered carbon dioxide at a number of test sites. The types used may be regarded as “native” or “in situ” i.e., pre-existing or indigenous to a site, while others might be “external” or added as an exotic species to the test site.

At the CO2CRC Otway Project in Victoria, Australia, quantities of SF₆, Kr and CD₄ were added to the gas mix being sequestered at the depleted Naylor gas field. The sequestered gas consists of 75% CO₂ and 20% CH₄ (in a balance of wet gases and nitrogen) and is produced from the nearby Buttress field. The monitoring well Naylor-1 has been sampling the reservoir fluids over a period prior to injection (i.e., baseline) and has continued through the onset of injection on the 18th March, 2008, past injection ceasing on the 30th August, 2009 to the present.

Three different points were sampled in the Naylor-1 monitoring well via the U-tube system (Freifeld *et al*, 2005). This system allows the collection of reservoir fluids and their return to surface while retaining in-situ pressure without degassing. U1 is the U-tube located in the free gas cap, U2 is located just below the gas-water-contact prior to gas injection and U3 collects fluids 5m below U2.

Analyses of tracers, hydrocarbons and formation fluid samples show evidence of changing processes as the reservoir chemistry evolves (Figure 1): from pre-injection (1) to the first arrival of dissolved CO₂ (2), to the supercritical gas reaching U2 at the gas-water-contact (3) and filling down past the deepest sampling point at U3 (4) in the monitoring well. When injection stopped, a total of 65,445 tonnes of gas had been injected (5), and continues to migrate away from the injector well and mix with the existing fluids (6).

Partitioning of the different tracers between the gas and water phase suggests minimal water contact and discrete flow paths akin to oil migration and “wetting of pathways”. Sampling and analysis continues presently in order to evaluate rates of mixing in the structure. Modelling of the results is underway to better understand the processes and rates involved.

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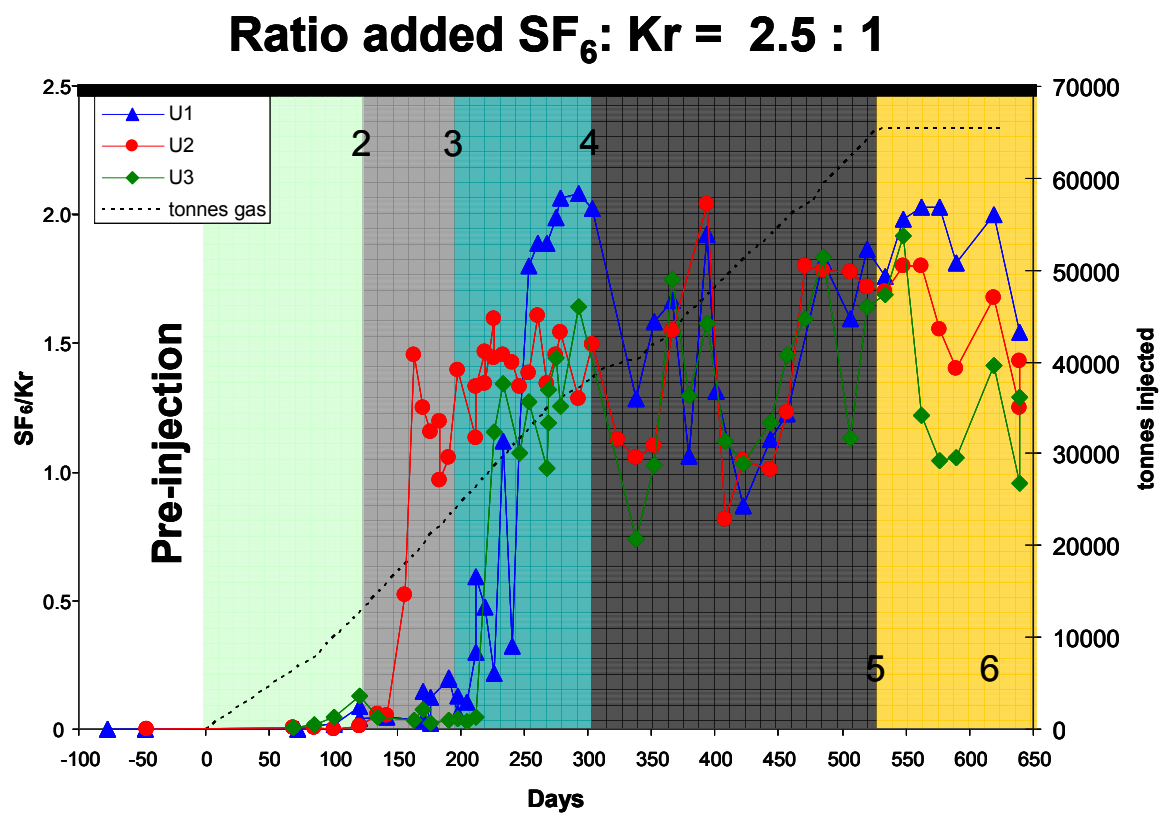


Figure 1: Ratio of SF₆/Kr for each U-tube at baseline, during injection, and beyond.

Australasian asphaltite strandings revisited: the effects of weathering and biodegradation on biomarker profiles

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Asphaltic bitumens, long known to strand along the coastline of southern Australia and as far afield as New Zealand and Macquarie Island (Padley, 1995), are now widely regarded as artefacts of submarine oil seepage. Their biomarker and isotopic compositions are remarkably uniform (Currie *et al.*, 1992; Volkman *et al.*, 1992; McKirdy *et al.*, 1994; Edwards *et al.*, 1998) suggesting that they represent a single oil family expelled from a marine shale containing S-rich Type II kerogen, probably deposited during a Cretaceous oceanic anoxic event (Boreham *et al.*, 2001). While no such anoxic/sulphidic lithofacies of appropriate thermal maturity has yet been intersected by drilling, suitable hydrocarbon kitchens may exist in the offshore Otway Basin (Boult *et al.*, 2005) and Bight Basin (Boreham, 2008). With low API gravities (4–18°) many of the stranded asphaltites are heavier than seawater, implying that for much of their time in the ocean they were bottom drifters. Their degree of weathering (including biodegradation) will reflect, at least in part, the duration of their exposure to the marine environment. For any individual asphaltite specimen, this in turn will depend on the proximity of the seafloor seep to the stranding site, an important consideration when attempting to locate the oil kitchen in which it was generated.

In this study we determined the alkane biomarker profiles of asphaltite specimens from four localities: Eyre Peninsula (n = 2), Kangaroo Island (n = 4), and the Limestone Coast (n = 3) in South Australia and Invercargill, New Zealand (n = 2). Saturates fractions prepared from sub-samples of the interior and the outer, weathered surface of each specimen were analysed by GC-MS operating in full scan and SIM modes. Some 43 biomarker ratios were calculated. The interior portions exhibit similar distributions of isoprenoid alkanes, terpanes and steranes (standard deviation for individual ratios commonly <10%). No distinction could be made between the Australian and New Zealand strandings implying a common source, despite their widely separated localities.

All the asphaltites lack 25-norhopanes and may be characterised as only moderately biodegraded. Comparison of the interior and weathered surface of each specimen likewise revealed only minor differences. Depletion of n-alkanes was apparent only in the <C₁₄ range; and all specimens displayed a minor decrease (~5%) in the contribution of hopanoids to the relative abundances of tricyclic terpanes, pentacyclic triterpanes and steranes. There is a preferential degradation of C₃₅ over C₃₁–C₃₄ hopanes, with the homohopane index decreasing (as expected: Peters *et al.*, 2005) by an average of 28%.

The general trend evident in the sterane distributions is for depletion of 20R relative to 20S $\alpha\alpha\alpha$ isomers (avg. 7%), again as expected (McKirdy *et al.*, 1983). Moreover, the C₂₇ $\alpha\alpha\alpha$ 20R sterane increases relative to the C₂₈ and C₂₉ homologues, with C₂₈ showing the greatest depletion (avg. 5%). Collectively, these results suggest that the stranded asphaltites have had a relatively short exposure to the processes of aerobic biodegradation, possibly in the order of 10 years by comparison with the outcomes of laboratory culture experiments undertaken by Goodwin *et al.* (1983). Finally, given their degree of degradation, these Australasian asphaltites seem likely to be products of low intensity seeps (Wenger and Isaksen, 2002), with those from the Limestone Coast and Kangaroo Island being less weathered than those from Eyre Peninsula and New Zealand.

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How Does Depth Affect the Preferential Degradation Process in Antarctic Marine Sediments Polluted by Diesel?

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Degradation of oil occurs by numerous processes such as weathering, dissolution, dispersal, migration and biodegradation. Biodegradation of oils are known to take longer in cold climates, increasing potential environmental and ecotoxicological hazards.

Antarctic aerobic microbial communities in marine sediments from bays surrounding Casey Station have shown potential to degrade hydrocarbons within various oils used at Australian Antarctic bases. After analysis of 0-10 mm surface sections of Special Antarctic Blend (SAB) diesel spiked marine sediment cores, taken from a water depth of 13-19m over a 5 year period at O'Brien Bay, Casey Station, it was apparent that biodegradation was not the most abundant degradation process occurring (Figure 1). If biodegradation was taking place, the *n*-alkanes would degrade prior to the low molecular weight aromatics hydrocarbons. However, in these samples methylnaphthalenes degrade more rapidly than the *n*-alkanes and the C₃ alkylbenzenes (Figure 1). This could be a result of preferential dissolution; methylnaphthalenes are more water soluble than the *n*-alkanes present in SAB diesel. In addition, ratios of specific isomers within compound groups (e.g. 2-MN/1-MN) can be used to establish whether biodegradation is occurring. These ratios did not change in the analysed samples, providing supporting evidence that biodegradation is not the prominent degradation process in the surface marine sediments in O'Brien Bay (Woolfenden *et al.*, submitted).

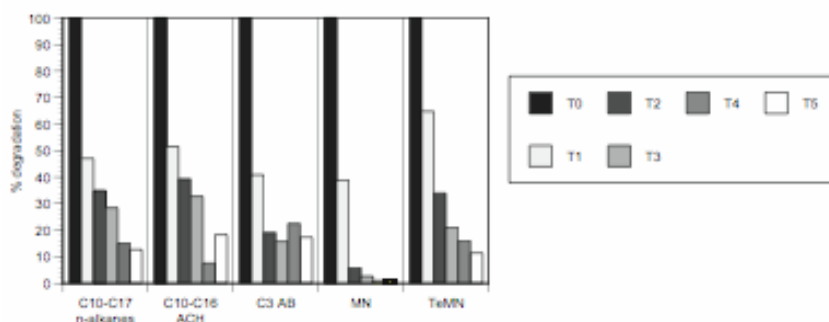


Figure 1: The rate of degradation of groups of components within SAB diesel at normalised concentrations. ACH = alkylcyclohexanes; AB = alkylbenzenes; MN = methylnaphthalenes; TeMN = tetramethylnaphthalenes. %RSD = 34 - 123%.

To address this issue, samples have been taken at 10 mm intervals from deeper (10-80 mm) in these marine sediment cores. Analytical results are expected to show more prominent biodegradation close to the surface (20-50 mm), as the physical processes should not have affected more than 20 mm deep into the sediments, but there should have been a significant population of aerobic microbial communities that would have consumed hydrocarbons. At 80 mm the results are expected to show very little biodegradation of SAB diesel, as the microbial communities become anaerobic and consume hydrocarbons at a much slower rate.

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The Rate of Degradation and the Compositional Changes of Diesel in Antarctic Marine Sediment. *Organic Geochemistry*

Elucidation of biodegraded Australian crude oils via catalytic Hydropyrolysis

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Asphaltene fractions isolated from a series of biodegraded crude oils, reservoired in Australian sedimentary basins (Gippsland and Carnarvon Basins), have been subjected to catalytic Hydropyrolysis in order to investigate the characterisation potential of the “bound” hydrocarbon product. Fixed bed Hydropyrolysis (Hypy) is pyrolysis assisted by high hydrogen pressure (~15 MPa) and a dispersed sulfidic Mo catalyst. Developed as a rapid characterisation technique, Hypy possesses proven ability to release high yields (>65%) of covalently-bound biomarkers from petroleum source rocks and high volatile coals, with overall conversions of organic matter >85% (Love *et al.*, 1995; Love *et al.*, 1996). Owing to a unique hydrogen gas sweep mechanism, Hydropyrolysate’s benefit from superior carbon skeletal preservation where compared with more conventional pyrolysis methods (Lockhart *et al.*, 2008; Love *et al.*, 1996; Murray *et al.*, 1998), thus providing a more accurate representation of the parent organic matter.

Results support the findings of previous workers, who have consistently demonstrated the ability of Hypy to maximise yield of the significant pool of highly informative biomarkers covalently-bound within the complex macromolecular structures of a range of solvent insoluble organic fractions (Bowden *et al.*, 2006; Russell *et al.*, 2004; Sonibare *et al.*, 2009). The crude oils examined range in severity of biodegradation, from non-biodegraded oils to those lacking straight-chain, branched and cyclic alkanes, while the most strongly altered samples display depletion of polycyclic aromatic compounds and large unresolved complex mixtures (Grice *et al.*, 2000). As demonstrated by [Figure 1](#), Hypy generates a “bound” oil from the isolated asphaltene, which is believed to represent “an occluded remnant of the original oil,” prior to the onset of biodegradation (Liao *et al.*, 2006; Sonibare *et al.*, 2009). These findings provide further evidence of the potential application of Hypy as a powerful geochemical correlative and characterisation technique.

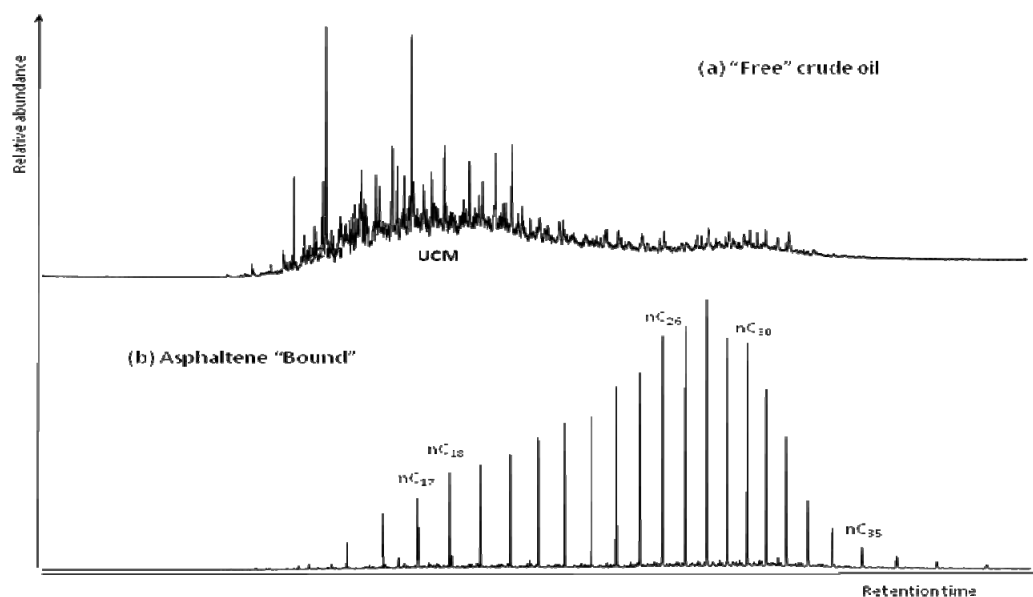


Figure 1: Total Ion Chromatograms (TIC) showing (a) the saturate fraction of a biodegraded Australian crude oil (Gippsland Basin) and (b) corresponding results obtained following catalytic hydropyrolysis of the asphaltene fraction. UCM = unresolved complex mixture.

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Use of MSSV pyrolysis to aid the GCMS characterisation of immature sedimentary organic matter

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Analytical pyrolysis is one of the more commonly applied methods of geo- and bio-macromolecular characterisation, yet is limited to the GC–MS detection of thermally labile, apolar products which usually represent only a small proportion of the gross sample (Saiz-Jimenez, 1994). The hydrocarbon products of mature samples such as kerogen appear to provide compositional information about gross structure and not about atypical, readily volatilised apolar moieties (Larter and Horsfield, 1993). However, the high structural polarity of the biochemicals which persist in thermally immature OM can be particularly problematic for pyrolysis characterisation.

Controlled thermal treatment strategies such as microscale sealed vessel pyrolysis (MSSVpy) have recently been shown to promote the reduction of polar organic structural moieties and significantly increase the yields of GC amenable products from immature organic sediments and dissolved organic carbon (Berwick *et al.*, 2010a, 2010b). MSSVpy consistently produced higher product concentrations from a selection of natural organic matter (NOM) and humic materials than more traditionally applied flash pyrolysis. Many structures, including those with bulky and structurally diagnostic substituents, do not survive excessive thermal energies. MSSVpy was primarily developed to characterize petroleum source rocks and study the kinetics of hydrocarbon generation (e.g., Horsfield *et al.*, 1989), but has been used in a number of other analytical applications. One of these was the release of hydrocarbon biomarkers trapped and preserved within the asphaltene fraction of heavily biodegraded oils (Ruble *et al.*, 2000).

This paper will provide examples of how MSSVpy of immature organic materials (e.g. biomass, aquatic natural organic matter and native plants) has aided several different industry and research applications.

Biomarkers of Native Australian flora - The presence of higher plant-derived biomarkers in the sedimentary record allows for the tracking of palaeo-flora distributions over geological time, which in turn can contribute to the reconstruction of palaeo-environments and climates. However, knowledge of biomarkers specific to certain families or groups of flora is first required. To this end, a suite of WA natives were thermally treated by MSSVpy and several terpenoid-derived compounds showing varying levels of taxonomic specificity were identified.

Structure and origin of aquatic NOM - The analytical value of MSSVpy to NOM characterisation was assessed with the holistic characterisation of NOM isolated from the North Pine Reservoir (SE Queensland; Berwick *et al.*, 2010) using a range of organic analytical methods (e.g., MSSVpy, HP-SEC, ¹³C NMR, FTIR). The major alkyl-aromatics (e.g., benzenes, naphthalenes, phenol) from MSSVpy of the HPO fraction were largely attributed to aliphatic

terpenoids, which are highly resistant to conventional treatment practices and can be problematic to potable systems. These and the protein source of the N-organics detected in the TPI fraction were both attributed to algae, which periodically impacted the reservoir in bloom proportions. Such biochemical sources of aquatic NOM have often proved elusive to chemical analysis.

Waste water contaminants - MSSVpy of organic fractions from the effluents of two waste water treatment plants included organic species indicative of industrial chemicals (e.g., dioxanes, *n*-alkyl substituted benzenes and high molecular weight alkyl phenols), pharmaceuticals (e.g. N-, S- and O-heterocycles) and domestic sewage (e.g., steranes/sterenes; high relative yields of S- and N-organics) of concern to public health, indicating they were not entirely removed by the standard waste treatment procedures used. Flash pyrolysis was only able to detect trace amounts of some of these anthropogenics. MSSVpy of the effluent fractions also showed high molecular weight N-products (e.g., alkyl indoles, carbazoles, β -carbolines) of naturally occurring or treatment biota, all implicated as potential precursors for toxic N-DBPs.

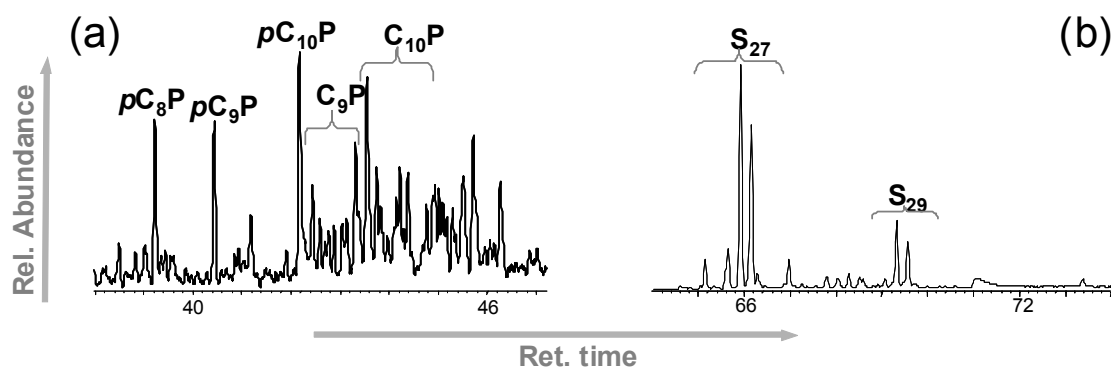


Figure 1: Summed ion chromatograms from the MSSVpy-GCMS analysis of organic fractions of a waste water effluent showing a) m/z 135+149+163+206+220+234 highlighting *p*-alkyl phenols (pC_nP) of the HPO fraction; and b) m/z 215+217 highlighting sterane/sterenes (S_n) of the COL fraction.

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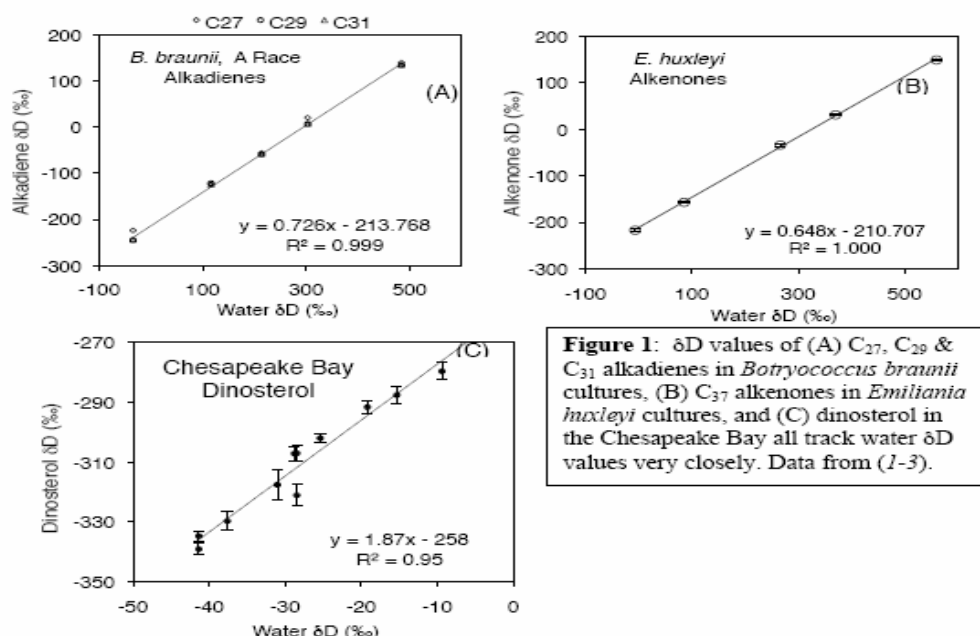
Environmental influences on D/H Fractionation in Algal Lipids

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The use of compound-specific D/H ratios to decipher biochemical, geochemical, oceanographic, and climatic processes is expanding rapidly. The relative success of these efforts depends on an understanding of the environmental conditions that influence the deuterium depletion relative to environmental water observed in algal and plant lipids, and the sensitivity of D/H fractionation responses to changes in those environmental conditions. Here we present results isotope techniques in paleoceanography, geochemistry and ecology are the environmental influences on the magnitude of that fractionation. Here again, the influence on D/H ratios in algal lipids of the most basic environmental parameters such as from field studies and culture studies that indicate that salinity, nutrient-limited growth rate and temperature each influence D/H fractionation in algal lipids to varying degrees, depending on the algae and the lipid.

Well established at this point is the fact that all lipids in algae are depleted in deuterium by approximately 100-400‰ relative to the water in which they grew (Sessions *et al.*, 1999). Beyond that several studies have shown that D/H ratios in algal lipids track water D/H ratios with near-perfection (Zhang and Sachs, 2007; Englebrecht and Sachs, 2005; Sachs and Schwab, in press; Sauer *et al.*, 2001; Schouten *et al.*, 2006) (Figure 1). The biosynthetic steps in which the D/H fractionation occurs are just starting to be worked out (Zhang and Sachs, 2007; Sessions, 2006; Sessions *et al.*, 2002; Zhang *et al.*, 2009; Schwab and Sachs, 2009) but remain largely unknown. Of equal or greater importance for the application of hydrogen temperature, salinity, light levels and nutrient concentrations remains largely unknown. Most of our knowledge of these effects comes from a single paper by Schouten *et al.* (2006) in which two species of coccolithophorids were grown in batch cultures at three temperatures between 10°-21°C and at five salinities between 25-35 PSU, and a single lipid class, the C₃₇ and C₃₈ alkenones, was analyzed. In that culture study and in the field study of Huang *et al.* (2002) little or no influence of temperature on D/H fractionation in lipids was observed. Yet our data from two species of cultured green algae suggests that D/H fractionation increases as temperature increases (Zhang *et al.*, 2009). Schouten *et al.* (2006) additionally observed a decrease in D/H fractionation with increasing salinity, a result corroborated by our data from saline ponds on Christmas Island (Sachse and Sachs, 2008) and the Chesapeake Bay estuary (Sachs and Schwab, in press) over the salinity range 8-149 PSU. But the sensitivity of D/H fractionation to salinity varied 4-fold among different lipids in these studies.



To our knowledge no published studies on D/H fractionation in phytoplankton exist in which the growth rate was controlled. We conducted nine continuous culture experiments, or chemostats, four with the coccolithophorid *Emiliania huxleyi* and five with the marine diatom *Thalassiosira pseudonana*, at constant growth rates controlled by N limitation. Our results indicate that there is a substantial increase in D/H fractionation with increasing growth rate in sterols from both species, isoprenoid lipids synthesized via the mevalonic acid (MVA) pathway, and a smaller or negligible increase in D/H fractionation in acetogenic lipids.

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A unique stable C and H isotopic profile of native Australian plant leaf n-alkanes

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The distribution and stable carbon and hydrogen compositions of *n*-alkanes in higher plant leaf waxes are a valuable source of information for past growth environment (hence climate) reconstruction (Nabbefeld *et al.*, 2010), photosynthetic mode discrimination (Chikaraishi *et al.*, 2004) and ascertaining metabolic pathways (Zhou *et al.*, 2010; Kroumova *et al.*, 1994; Kroumova and Wagner, 1999).

Odd-carbon-numbered (OCN) *n*-alkanes are typically much more abundant than even-carbon-numbered (ECN) *n*-alkanes in higher plant leaves. Up to now, all plant species investigated showed that OCN-*n*-alkanes are relatively enriched in ¹³C but depleted in ²H than their neighbouring ECN-*n*-alkanes regardless of environmental conditions (Zhou *et al.*, 2010; Kuhn *et al.*, 2010). This led to Zhou *et al.* (2010) hypothesising that a common pyruvate precursor is involved in the biosynthesis of both OCN- and ECN-*n*-alkanes in higher plant leaves. Furthermore, a kinetic isotope effect (KIE) associated with competition for the common pyruvate precursor pool was suggested to account for the observed odd-over-even enrichment of ¹³C and depletion of ²H.

However, in a recent attempt to characterise isotopic profile of biomarkers of native Australian plant species for potential (paleo)climatic reconstruction (Mackenna, 2009), only one species (*Melaleuca sp.*, Figure 1) exhibited an isotopic profile consistent with the aforementioned profile. Several species showed the opposite pattern (odd-over-even depletion of ¹³C) whilst the others showed no obvious isotopic pattern. The unique *n*-alkane C isotopic profile of Australia native plant species raises an interesting issue regarding the roles of the enzymes involved in leaf *n*-alkane synthesis and calls for a re-evaluation of the hypothesis of Zhou *et al.* (2010). Work is currently underway to expand our investigation of the C (and H) isotopic characteristics of native species.

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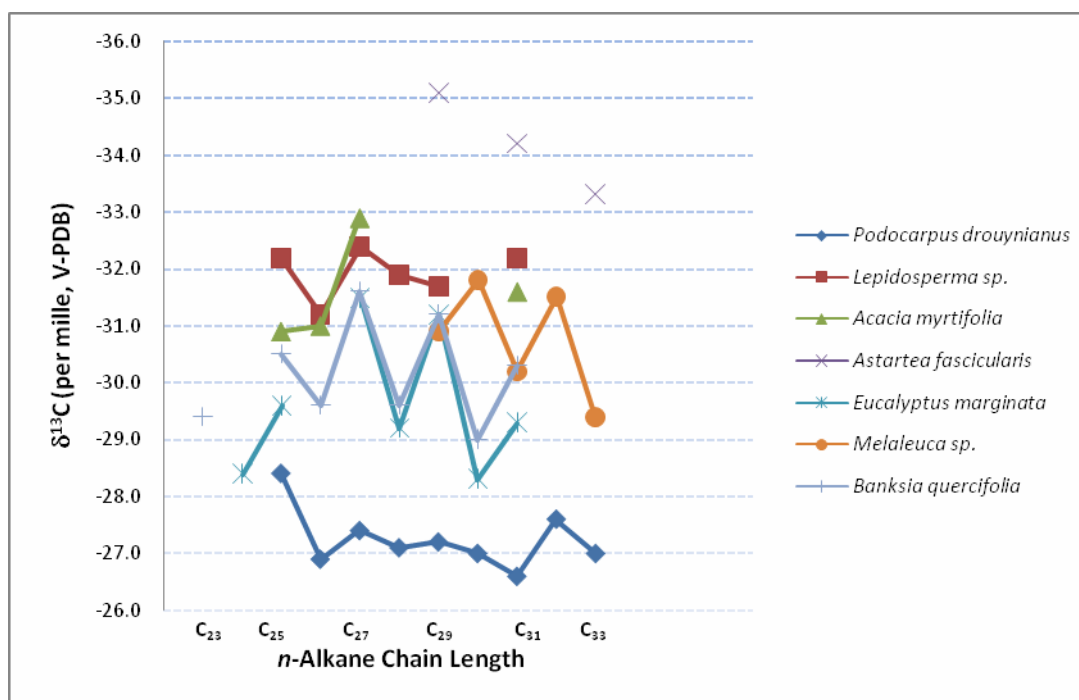


Figure 1: $\delta^{13}\text{C}$ of leaf *n*-alkanes from 7 Australia native plant species at Lake Surprise, Western Australia (data from the Honours thesis of Hayden Mackenna (Mackenna, 2009)).

Stable carbon and hydrogen isotopes of components derived from controlled burning experiments of C3 and C4 plants and their use as environmental proxies for tracking fire history

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A controlled burning experiment was conducted separately on native Australian C3 eucalyptus trees (Marri, Karri, Jarrah), conifer, and wild oats and C4 *Themeda triandra*. The resulting ashes and volatile organic compounds emitted, along with the unburnt leaves were analysed for changes in biomarker distributions and their stable carbon and hydrogen isotopic compositions. As expected, the leaves primarily contain odd/over/even predominance of long chain *n*-alkanes and their $\delta^{13}\text{C}_{n\text{-alkanes}}$ are consistent to those reported for C3 (-22 to -42 ‰) and C4 (-9 to -29) plants (e.g. Rieley *et al.*, 1991; Krull *et al.*, 2006). Aromatic compounds in all samples were minimal. In the ashes, *n*-alkanes are still predominant, but are shorter with $\delta^{13}\text{C}_{n\text{-alkanes}}$ more enriched compared to the unburnt leaves. Volatile organic compounds (VOCs) were trapped on a Tenax resin and analysed by Thermal Desorption-GC-ir-MS to yield compound-specific $\delta^{13}\text{C}$ (Table 1; Vitzthum von Eckstaedt *et al.*, 2010 submitted).

Table 1: Results of compound-specific carbon isotope analysis ($\delta^{13}\text{C}$ in per mil) of volatile aromatic compounds emitted during controlled burning experiments.

compound	$\delta^{13}\text{C}$ (‰) C3 plants		$\delta^{13}\text{C}$ (‰) C4 plants	
	Max	Min	Max	Min
benzene	-26.3	-30.4	-14.7	-17.8
toluene	-26.3	-29.4	-14.0	-18.1
ethylbenzene	-26.3	-26.3		
<i>m</i> -xylene	-25.2	-26.8		
styrene	-25.4	-29.0	-13.2	-16.4
naphthalene	-24.6	-26.5	-17.4	-18.3
bulk (‰):	-24.6	-30.4	-13.2	-18.3

Rock samples across the Triassic/Jurassic (Tr/J) extinction boundary from St. Audries bay, Lyme Regis and Westburyon-Severn in England and Larne, Ireland, are currently being processed and analysed focusing on terrestrial plant (i.e. waxes), marine derived biomarkers and high molecular weight polyaromatic hydrocarbons. The molecular and compound-specific carbon and hydrogen isotopic compositions for these markers are tracked before, during and after the Tr/J extinction event (also see Grice *et al.*, 2010 in this volume; Williford *et al.*, 2010). The $\delta^{13}\text{C}$ are compared with marine carbonates to investigate environmental changes and δD excursions are hypothesized to be influenced by massive burn events associated with the Tr/J extinction.

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Compound Specific Radiocarbon Analysis of Hypersaline Microbial Biomarkers

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Compound specific radiocarbon analysis (CSRA) is a powerful method for understanding the flow and timing of carbon in modern and Quaternary ecologies and can unlock terrestrial ecological records in Australia. Here we present bulk- (total extractable) and compound specific- radiocarbon data from a hypersaline playa, Lake Tyrrell, in northwest Victoria. A shallow core has been characterized using mineralogy, biomarkers, and radiocarbon to reconstruct the timing of changes in hydrologic regimes and to assess the provenance and recalcitrant behaviour of important biomarker classes. Coincident and coherent changes in biomarker distribution, mineralogy, and radiocarbon content in preliminary data have demonstrated the feasibility of characterizing Australian playas by radiocarbon analysis of biomarkers. CSRA has also been used to date the shallow core, with sediment ages reaching 7,500 years (*Figure 1*). These analyses have been used to constrain the timing of sedimentary changes, reflecting local and regional ecological changes. Furthermore, radiocarbon data has been used to exclude potential sources of contamination, providing a novel strategy for anthropogenic contamination detection in biomarker studies. Analyses of this type can contribute significantly towards reconstructing Quaternary history in the Southern Hemisphere, and provides the geoscientist with powerful and critical tools to investigate diverse environments.

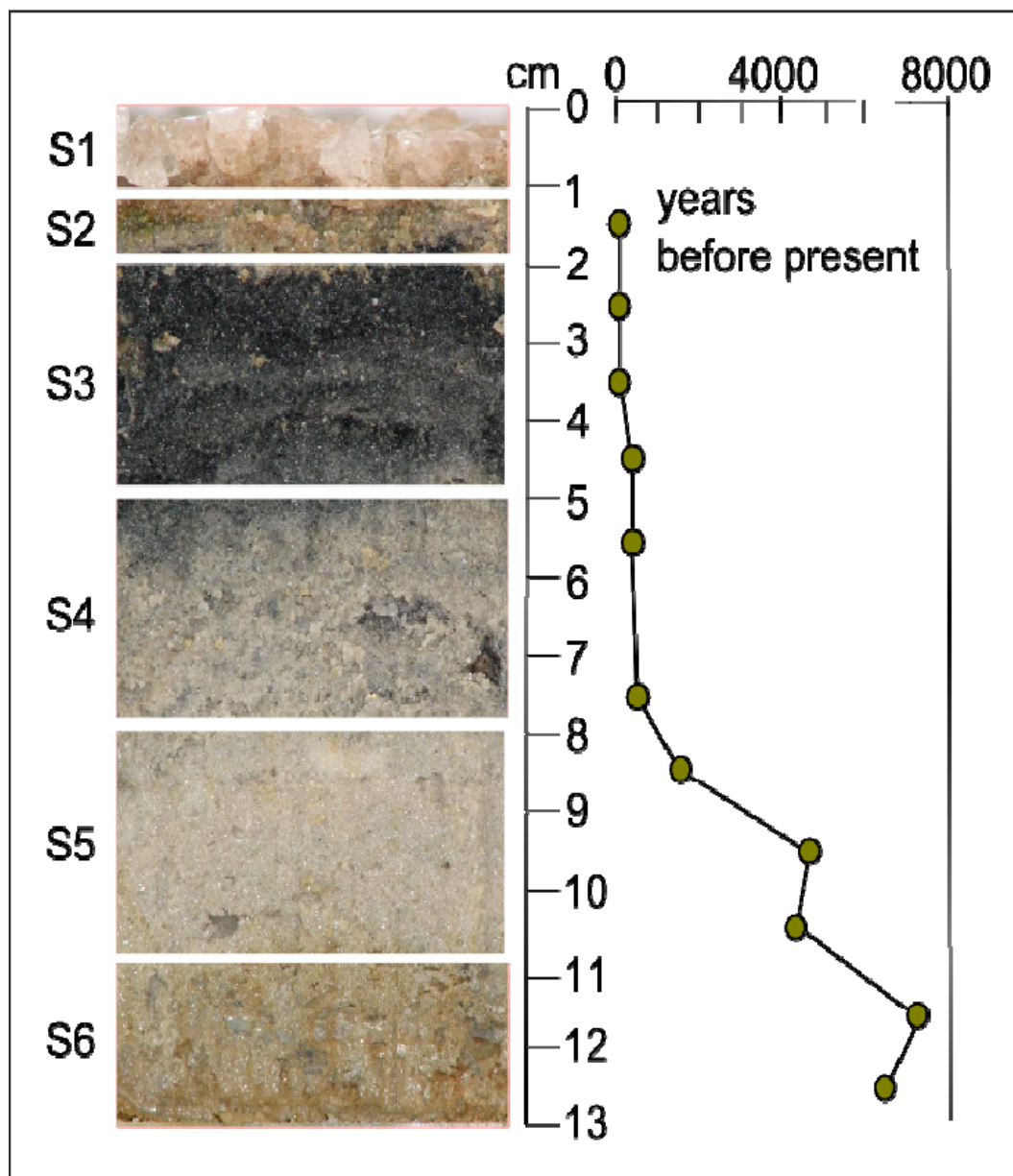


Figure 1: A shallow core collected from Lake Tyrrell, in northwest Victoria

The Devil's Pool – Pollen, biomarker and stable isotopes of Holocene peat deposits reveal climate changes in south-western Western Australia

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The Devil's Pool is a small lake located within the Leeuwin–Naturaliste Park ~1 km from the shore of the Indian Ocean (SW/Western Australia), where ~9 m thick peat deposit represents ~9,000 yrs of continuous sedimentation. Significant changes in vegetation over time likely resulted from a combined influence of several environmental factors, such as changes in climate, hydrology, plant succession and fire regime (e.g. Dortch, 2004). In order to date and determine the reason for the vegetation changes, we utilize several complementary, biogeochemical methods including biomarker (and microbial membrane lipids), radiocarbon dating and stable HCN isotope analysis of bulk and specific compounds.

The range of $\delta^{13}\text{C}_{\text{bulk}}$ variations ($-29.6 \pm 1.6\text{‰}$) suggests C3 plants as a major source of the organic matter (OM). The parallel trends in $\delta^{15}\text{N}_{\text{bulk}}$ and C:N ratios (lower C:N ratio associated with positive $\delta^{15}\text{N}_{\text{bulk}}$) suggest high decomposition of organic matter (cf. Engel *et al.*, 2010) in the upper part of the core, while lower zones reflect decreasing and varying degrees of OM turnover. Oscillating redox conditions due to water table changes may have facilitated degradation on top. The evaluation of microbial biomass supports a higher carbon turnover by increased abundance and diversity of phospholipid fatty acids in the upper section. Pollen analyses are in accordance with sedimentary fluctuations and indicate more open vegetation in recent times as opposed to dense Eucalyptus forests in early to mid Holocene periods. The system likely fluctuated between swampy marshlands and open water bodies due to changes in moisture availability. The distribution of plant-specific biomarkers, such as plant waxes and di- and sesterterpenoids (e.g. rosane) are in good accordance with the zonation based on pollen diversity. Mid- and long-chain *n*-alkanes (C_{21} - C_{27}) show different deuterium isotope values from each other (-122 and -160‰ vs. VSMOW) and point towards distinct source organisms (chlorophytes and metaphytes), a feature similar to other Australian settings, such as the Coorong lagoon complex (McKirdy *et al.*, 2010). Further ^{14}C -AMS dating will improve our understanding of the

evolutionary history of this pre-and postcolonial inhabited area and its certain anthropogenic influence on the environment.

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Factors controlling the preservation of terrestrial organic matter during transport from the Shoalhaven river catchment (NSW) to the adjacent continental shelf

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Understanding the fate of terrestrial organic matter (TOM) in marine sediments is a fundamental question in organic geochemistry. Environmental conditions affect the preservation of potentially different fractions of TOM (e.g. land plant debris, soil-derived OM, fossil kerogen) during transport to oceanic sediments. The relative amounts of these fractions that are preserved in surface marine sediments play an important role in the overall organic matter (OM) burial and significantly feedback with atmospheric chemistry (CO_2 and O_2 contents) throughout geological cycles. The overall composition of TOM also provides useful information on the biological/climatic settings of the adjacent continents at the time of deposition.

The main challenges associated with these studies are:

1. The identification and quantification of TOM (and its fractions) in marine sediments.
2. Providing methods for a mechanistic and quantitative understanding of the processes undergone by TOM during transport from continental areas to marine sediments in different environmental conditions.

The present research addresses these points by studying the sediment mineralogy and the composition of organic matter (OM) currently accumulating on the surface beds of the Shoalhaven river-estuary-continental shelf system (NSW).

More specifically, surface sediments samples were collected from the Shoalhaven River at the confluence of the two major streams draining the catchment area (Tallowa Dam), from the Shoalhaven estuary, and from the adjacent continental shelf mud belt supported by the fluvial inputs. The siliciclastic portion of sediment is characterized by grain size analysis, and XRD and XRF analysis of the less than 63 μm sediment fraction. The OM content is studied by coupling bulk OM analyses [i.e. the total organic carbon percentage (TOC%), the carbon stable-isotope composition ($\delta^{13}\text{C}$) of TOC, the OC/TN (organic carbon/total nitrogen) ratio, and the radiocarbon content ($\Delta^{14}\text{C}$) of TOC] to compound-specific $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ analysis of lipid biomarkers.

Preliminary results (*Figures 1 and 2*) suggest that the OM accumulating in continental shelf sediments is not only of marine origin, but a large fraction of it seems to be of terrestrial origin, probably from OM previously stored in soils.

In order to quantify the compositional changes of OM during its transfer from catchment areas to surface marine sediments, compound-specific (whose measurements are in progress) and bulk $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$ data are used to solve sets of simultaneous equations (one for each sedimentary environment: i.e. river bed, estuary bed, continental shelf bed) to budget the fractional amounts of OM (i.e. OM derived from land plant litter, soils, fossil sources, autochthonous contributions) accumulating in each setting. Furthermore, from the differences in some of the $\Delta^{14}\text{C}$ values originated from the systems outputs, an estimate is provided for the average residence times of OM within each major bioactive reservoir (soil, estuarine sediments, and surface layer of the continental shelf) during OM transport.

The present study provides a method to firstly quantify in more detail the compositional changes of OM during transfer from catchments to marine sediments, and secondly to quantify the average residence times of OM within each major bioactive sedimentary environment. These data, in combination with the XRD and XRF measurements, provide quantitative insights into the role of both mineralogy and residence times on the preservation of the different fractions of TOM until burial in marine sediments.

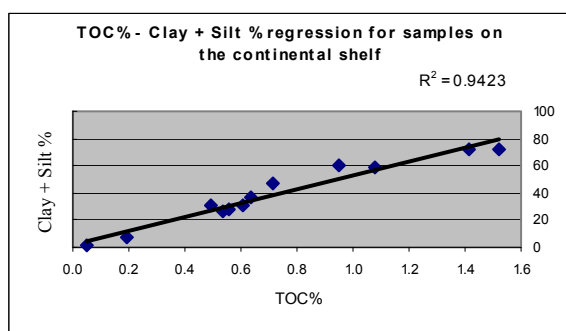


Figure 1 suggests either that the strong fine sediment-OM association is completely destroyed when OM enters the ocean, so that mineral surfaces get “loaded” again with *in situ* production; or that during transport the more labile fraction of TOM (i.e. recent plant debris) is mostly degraded, while only the OM in association with minerals (i.e. aged soil-derived OM and/or fossil kerogen) survives and accumulates in marine sediments.

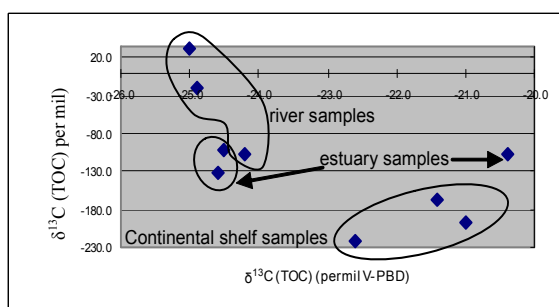


Figure 2 shows that the ^{14}C content of the bulk OC gradually decreases from fluvial to continental shelf samples, displaying contemporary OC accumulating on the riverbed and few hundred years old OC accumulating on the seafloor. This suggests that the OC in marine sediments may be partially composed of the more refractory (likely older, as hypothesized in Figure 1 caption) fractions of terrestrial OM.

When size really does matter; measurement of ultra-small samples at the ANU Radiocarbon Dating Laboratory

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There is increasing demand for, and scientific potential in, gleaned radiocarbon ages from materials and compounds containing less than a few hundred micrograms of carbon. This motivated the development of procedures for handling “ultra-small” samples (10-100 µg C) at the ANU’s Radiocarbon Dating Laboratory. This report outlines the protocol for the dedicated graphite line that minimizes contamination and fractionation during the production of graphite targets. Multiple aliquots of CO₂ derived from the primary standard Oxalic Acid 1 (OX1) were processed over a range of temperatures, pressures, and catalysts (zinc and iron) to ensure enhanced reaction rates and optimal yields. A suite of ultra-small standards (modern, dead, 4,500 and 18,000 yrs) was processed to identify the source of, and quantify, the background contribution of exogenous carbon. In total, more than 180 targets were produced. Performance by our NEC Single Stage Accelerator Mass Spectrometer was monitored and tuning parameters adjusted to maximize beam intensity; with online measurement of ¹²C and ¹³C enabling the correction of machine induced isotopic fractionation. We present the equations for data correction and appropriate error propagation that were derived from the matrix of experiments, and apply them to a set of our own raw data. By maximizing the precision and accuracy of our measurements we intend to facilitate the application of compound specific radiocarbon in marine biogeochemical research, and provide a commercial service for use by Australia’s greater scientific community.

New perspectives on Proterozoic inverse carbon isotope patterns of lipids and kerogen

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In marine sedimentary deposits dating to the Proterozoic, $\delta^{13}\text{C}$ values for *n*-alkyl lipids are more positive than for syngenetic kerogen. This pattern is the inverse of biosynthetic expectations, and it has been suggested that it results from selective preservation of lipids from ^{13}C -enriched heterotrophic populations (Logan *et al.*, 1995). Although this pattern disappears from the sedimentary record across the Cambrian boundary, we recently found evidence for ^{13}C -enriched *n*-alkyl lipids in the modern, oligotrophic Pacific Ocean (Close *et al.*, 2010). In these biomass-poor waters, the lipids of 0.2-0.5 μm particulate matter, representing the prokaryotic size class, contain excess ^{13}C ($\sim -19\text{‰}$) relative to the same lipids in larger size classes ($>0.5 \mu\text{m}$; $\sim -23\text{‰}$). They also are enriched relative to the sterols of eukaryotes ($\sim -26\text{‰}$) and the total particulate matter ($\sim -21\text{‰}$). Our radiocarbon (^{14}C) measurements show that prokaryotic lipids are exported to depth, consistent with claims that the contribution of picoplankton to export is proportional to their total net primary production (Richardson *et al.*, 2007).

The modern evidence indicates a need for a quantitative model of the relative contribution of primary and heterotrophic lipid to buried organic matter, in order to apply this model to the Proterozoic. We have formulated a degradation model to calculate the ^{13}C content of sedimentary kerogen and lipid (Close *et al.*, 2010). The model addresses two scenarios. The first scenario (Figure 1a) explores preferential preservation of heterotrophic lipid, thereby quantifying the existing hypothesis (Logan *et al.*, 1995). In the second (Figure 1b, c), we model inverse signatures that could result from a numerical dominance of prokaryotic phytoplankton. Photosynthetic prokaryotes bearing a relative ^{13}C enrichment would then contribute the majority of preserved lipids, while eukaryotic biomass would dominate the total organic carbon (TOC). The mixed primary producer model generates inverse ^{13}C patterns over a wider range of processing and degradation conditions. This model also successfully can explain why there are large variations in the ^{13}C content of the isoprenoid lipids pristane and phytane relative to *n*-alkyl lipid in the Proterozoic, while the observed difference between *n*-alkyl lipid and kerogen generally is more constant. Our results suggest that the disappearance of the inverse ^{13}C signature across the Cambrian boundary is a natural consequence of the fundamental shift to oceans dominated by eukaryotic phytoplankton.

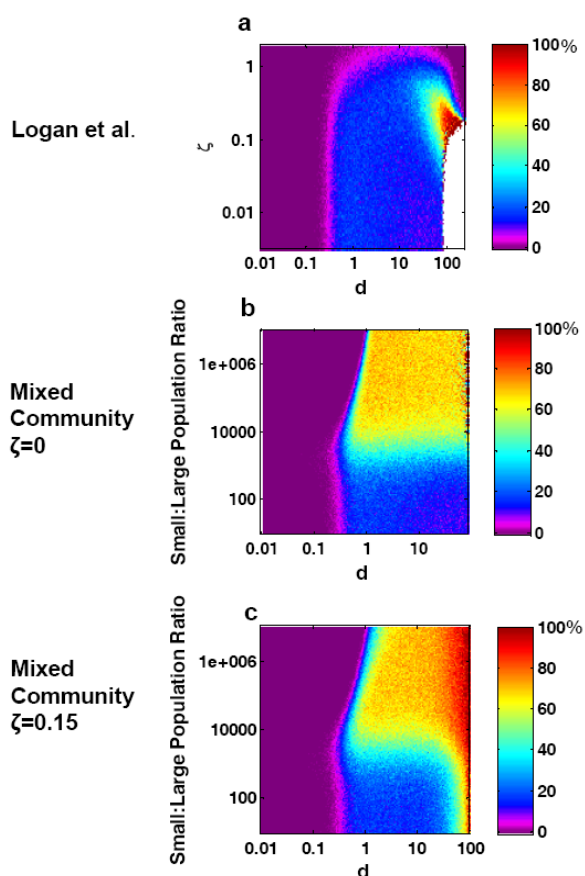


Figure 1: Results of $> 6 \times 10^6$ Monte Carlo simulations of a heterotrophic enrichment model (a) and two runs of a mixed phytoplanktonic community model (b, c). Color map indicates the percentage of simulations resulting in an inverse ($> 0\text{‰}$) value for $\Delta\delta_{n\text{-alkyl-TOC}}$, *i.e.*, lipids enriched in ^{13}C relative to kerogen. The x-axes show degradation extent, d , a unitless proxy for time-integrated total organic matter processing; d of 40 is equivalent to $> 99\%$ of total organic matter respired. The y-axis in (a) represents a trophic-level processing variable, ζ , which allows organic matter to build up in higher trophic levels as ζ increases. The y-axes in (b) and (c) show Prokaryote to Eukaryote community ratios, and versions are shown both for when $\zeta=0$ (b) and $\zeta=0.15$ (c). The greater areas of warm colors in (b) and (c) reflect a larger range of conditions over which a positive signal in $\Delta\delta$ would be preserved in marine sediments. All models assume ^{13}C enrichment of $1.5 \pm 0.5\text{‰}$ per trophic level, and heterotrophic efficiency (carbon transferred to next level) between 0.05-0.6.

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Compound-specific carbon isotopic signatures of biomarkers from Precambrian evaporites: pitfalls, solutions and insights into ancient biogeochemistry

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Single-compound carbon isotopes of Precambrian biomarkers (*n*-alkanes and isoprenoids) were analysed from evaporites of the Amadeus Basin in central Australia. These evaporites are derived from the Gillen Member of the Neoproterozoic (~800 Ma) Bitter Springs Formation and represent one of the oldest known hypersaline settings in the world (Lindsay, 1987). Evaporites from this formation have played a central role in understanding the evolution of sea water chemistry (Holland, 1984), and are currently a target in the search for biomarkers of some of the oldest halophilic microorganisms in the geological record (Schinteie and Brocks, 2009, 2010).

Evaporite samples from this study revealed biomarker signatures characteristic of both a Precambrian age and a hypersaline setting. However, to better understand the carbon isotopic signatures recorded in these biomarkers and to assess the impact of hydrocarbon contamination on these results, we combined for the first time exterior-interior rock experiments with single-compound carbon isotopic measurements. In these studies, exterior rock surfaces were cut off and their hydrocarbon and single-compound isotopic signature were analysed separately from the remaining interior portions. Through the application of this technique, we were able to quantitatively evaluate if indigenous biomarkers are present and assess whether their carbon isotopic values represent actual Precambrian signatures or a recent overprint of contaminants.

From this experiment, we observed that the *n*-alkanes from the interior rock portions recorded relatively heavy $\delta^{13}\text{C}$ values of up to -20‰. Results from these interior samples can be regarded as autochthonous signatures that are free of contamination. These results tend to contrast with those from the exterior, where the $\delta^{13}\text{C}$ values are significantly lighter. Differences in $\delta^{13}\text{C}$ values of up to 10‰ have been measured between these two rock portions. These results are in agreement with concentration measurements of *n*-alkanes between the exterior and interior. They show that hydrocarbon contaminants are predominantly present on the outer rock surfaces, overprint on indigenous hydrocarbons and exert a significant influence on the indigenous carbon isotopic signatures.

We also observed that the regular isoprenoids pristane and phytane became severely overprinted by contaminant versions of these molecules. The contaminant isoprenoids were depleted in $\delta^{13}\text{C}$ relative to the *n*-alkanes. As with the *n*-alkanes, this process also exerted a significant influence on the $\delta^{13}\text{C}$ values by masking the indigenous signals by up to 6‰. Such discrepancies are significant, since carbon isotopic values of pristane and phytane have been used to assess their provenances and understand ^{13}C contents in primary products over time.

Through the application of exterior/interior rock experiments, we will show that more accurate insights into $\delta^{13}\text{C}$ values of ancient biomarkers can be established. Such a study has direct implications in evaluating ancient biogeochemical signatures of organic carbon as well as oil-source rock correlation studies of evaporites.

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Biomarker, isotopic and trace element signatures of an early Cambrian Lagerstätte in the Stansbury Basin, South Australia

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While fossil assemblages of soft-bodied organisms (Lagerstätten) are rare, they are unusually common in marine sedimentary sequences of early and mid-Cambrian age (Allison and Briggs, 1993). Not surprisingly, their mode of preservation has been the subject of much debate. The Emu Bay Shale biota, found at Big Gully on the north coast of Kangaroo Island, is by far the best Burgess Shale-type (BST) fauna in the southern hemisphere (Nedin, 1995). Such fauna are characteristically preserved as two-dimensional compression fossils, comprising carbonaceous films on bedding surfaces of the host marine mudstones. The Big Gully assemblage comprises at least 45 taxa, suggesting a habitat very favourable for life. Its preservation is exceptional, with gut remains and other soft parts quite common. Predation and scavenging were minimal and the finely laminated texture of the host mudstone attests to a lack of burrowing and bioturbation. Notwithstanding earlier studies suggesting otherwise, Gaines *et al.* (2008) concluded that conservation of organic tissues, rather than authigenic mineralisation of their more labile components, is the principal taphonomic pathway responsible for BST deposits. Insofar as such preservation requires suppression of the early diagenetic processes that normally result in the rapid decay of organic matter at or near the sea floor, the oxicity of the bottom waters, below which the Emu Bay Shale accumulated, becomes critically important. Here we determine the palaeo-redox status of the fossiliferous basal portion of the formation using total organic carbon (TOC) concentrations, isotopic signatures ($\delta^{13}\text{C}_{\text{org}}$) and biomarker alkanes, in combination with selected trace element proxies. We also establish its degree of thermal alteration as a datum for use in taphonomic comparisons with other Cambrian Lagerstätten.

Oxygen-depleted bottom waters favour the preservation of sedimentary organic matter. The greater the depletion, the higher the TOC content of the underlying sediment, although enhanced productivity in the photic zone can also lead to the same outcome. Assuming a normal level of primary planktonic productivity across its inner-shelf depocentre, the Emu Bay Shale appears to contain insufficient organic

matter (TOC = 0.25–0.55%) to have accumulated under stable anoxic conditions. Even allowing for the inevitable loss of organic carbon during the oil- and gas-generation phases of thermal maturation, to a present rank equivalent to ~1.5% vitrinite reflectance (kerogen H/C = 0.48; Weaver index of illite crystallinity = 3.8), its *original* TOC content is likely to have been <1%. Like organic matter, certain trace metals also are commonly enriched in modern muds and ancient black shales that were deposited in anoxic marine settings (Calvert and Pedersen, 1993). A series of elemental ratios have been devised in which one metal (the numerator) is redox sensitive, while the other (denominator) is essentially independent of Eh. Of these U/Th, V/Cr and Ni/Co (Jones and Manning, 1994) and V/Sc (Kimura and Watanabe, 2001) have proved to be the most reliable and, when measured in the Emu Bay Shale, confirm that it was deposited beneath an *oxic* water column. In this respect it is similar to the archetypical Burgess Shale Formation (Powell *et al.*, 2003).

Micro-scale sealed vessel (MSSV) pyrolysis of kerogen isolated from a solvent-extracted sample of the Emu Bay Shale provided independent confirmation of its redox status. The thermal extract (300°C for 1 h; equivalent to bitumen II) and kerogen pyrolysis (325°C for 24 h) both yielded alkanes displaying a low ratio of pristane to phytane (pr/ph = 1.2, sub-oxic) and *n*-alkanes with a marked OEP in the <C₂₀ range. The latter feature is diagnostic of *Gloecapsomorpha prisca* (Foster *et al.*, 1989) and is the first indication that mats of this colonial cyanobacterium were involved in the taphonomy of a BST deposit. Its $\delta^{13}\text{C}_{\text{org}}$ values (-28 to -32‰) are consistent with the contribution of cyanobacterial biomass to the kerogen.

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Exploring mass extinction events -using biomarkers & stable isotopes (carbon and hydrogen)

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The Late Permian mass extinction event was the most profound extinctions of the entire Phanerozoic. Biomarker evidence for photic zone euxinic (PZE) conditions within Permian/Triassic (P/Tr) sections, where concentrations of sulfide, are sufficient to support anoxygenic photosynthesis, come from components derived from pigments of green sulfur bacteria (Grice *et al.*, 2005; Hays *et al.*, 2007; Nabbefeld *et al.*, 2010a). We present evidence for such conditions at 6 localities globally. It has been proposed by researchers that a chemocline upward excursion probably provided a trigger for the extinction, releasing toxic H₂S to the ocean's surface and into the atmosphere. Perturbations in the marine sulfur cycle and thus the redox-state of the ancient seas are also reflected in $\delta^{34}\text{S}$ of pyrite (e.g. from China, Italy, Iran, Western Australia, East Greenland, Western Canada and Spitsbergen) supporting widespread euxinic conditions in both Palaeotethys and Panthalassa oceans (e.g. Grice *et al.*, 2005; Hays *et al.*, 2007).

The aromatic biomarkers, dibenzothiophene, dibenzofuran and biphenyl have been detected in high abundances in samples prior to the marine ecosystem collapse in East Greenland, Spitsbergen, South China and Western Canada (Fenton *et al.*, 2007; Nabbefeld *et al.*, 2010b and 2010c). We have proposed that lignin derived from land plants, present during the Late Permian is their likely source. We provide sedimentological data, biomarker abundances and compound specific isotopic data ($\delta^{13}\text{C}$ and δD) along with bulk isotopes ($\delta^{34}\text{S}_{\text{pyrite}}$, $\delta^{13}\text{C}_{\text{carbonate}}$, $\delta^{13}\text{C}_{\text{org}}$) for several Late Permian sections. At two localities sedimentological and geochemical data supports a marine transgression and collapse of the marine ecosystem occurring in the Late Permian (Fenton *et al.*, 2007; Nabbefeld *et al.*, 2010b). $\delta^{13}\text{C}$ data of algal and land-plant derived biomarkers, $\delta^{13}\text{C}$ carbonate & organic matter support synchronous changes in $\delta^{13}\text{C}$ of marine and atmospheric CO₂, attributed to a ¹³C-depleted source (¹³C depleted methane and/or CO₂ derived from degradation of organic matter due to the marine ecosystem collapse- Nabbefeld *et al.*, 2010a). Evidence for waxing and waning of PZE throughout the Late Permian is provided by *Chlorobiaceae*-derived biomarkers and $\delta^{34}\text{S}_{\text{pyrite}}$, implying multiple phases of H₂S outgassing and potentially several prolonged pulses of extinction at several global localities. A rapid decrease in abundance of various land plant biomarkers prior to the marine ecosystem collapse indicates a demise of land plants during the Late Permian and/or increasing distance from the palaeoshoreline as a consequence of marine transgression. We suggest that high levels of CO₂ and H₂S were drivers of the extinction associated with the P/Tr boundary.

The Triassic/Jurassic (T/J) extinction is regarded as being the fourth most acute extinction event of the Phanerozoic in terms of ecological impact. A number of mechanisms have been proposed to

account for the mass extinction, including the release of CO₂ associated with emplacement of the Central Atlantic Magmatic Province (CAMP). A negative carbon isotope excursion has been detected in many sections, also supporting a perturbation in the global carbon cycle. The onset of the negative anomaly coincides with palynological biozone boundaries in Australia, an ecological collapse of terrestrial flora and ecological upheaval and extinction in the marine benthos. It is clear that major and abrupt ecological change including 80% extinction among terrestrial plant species coincides with increased atmospheric CO₂ concentration (CO_{2atm}, based on stomatal analysis of fossil Ginkgoales leaves) and a negative excursion in $\delta^{13}\text{C}$ of fossil wood from a Tr/J section at Astartekløft, East Greenland. $\delta^{13}\text{C}$ of the C₂₉ land plant *n*-alkane shows a 5‰ negative shift that corresponds with similar shifts in fossil wood, increasing CO_{2atm} and peak plant extinction. During the interval containing the rise in CO_{2atm} leading up to peak plant extinctions, δD of the *n*-C₂₉ shifts positively (~35‰), which we attribute in part to an increasing degree of evaporative fractionation in leaf water due to increasingly elevated leaf temperatures. After peak plant extinctions, δD of *n*-C₂₉ shifts negatively to -160‰. This is likely due to a decrease in evaporative fractionation due to lower leaf temperatures in surviving plants that probably had smaller leaves and were less prone to heat stress, a declining influence of biomass burning and finally, a return to lower temperatures as CO_{2atm} dropped. Resin-derived biomarkers are abundant in the bed containing peak plant extinctions attributed to resins of gymnosperms produced under extreme environmental stress (Williford *et al.*, 2010). The effect of combustion on δD and $\delta^{13}\text{C}$ of land plant compounds is being determined and a global T/J extinction study is underway (see Jaraula *et al.*, 2010, these proceedings).

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A reassessment of the petroleum systems in the offshore North Perth Basin

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The onshore North Perth Basin has been extensively explored for more than forty years leading to the discovery of several oil and gas fields and its petroleum systems are fairly well established. Onshore oils are known to originate primarily from a constrained section at the base of the Lower Triassic Kockatea Shale, the so-called Hovea Member (Thomas and Barber, 2004), whose sapropelic interval contains excellent oil-prone source rocks. Kockatea Shale-sourced oils display very distinct geochemical signatures, the most typical of which are the presence of C₃₃ *n*-alkylcyclohexane and ¹³C depleted *n*-alkane carbon isotopic values (< -32‰).

The offshore hydrocarbon potential of the North Perth Basin on the other hand has long been regarded as poor mainly due to the perception that the Kockatea Shale and in particular the Hovea Member, is either non-existent or lean with limited source quality (Crostella, 2001; Thomas and Barber, 2004). This view was challenged in 2001 by the discovery of Kockatea Shale-sourced oil in the offshore Cliff Head-1 well. The Cliff Head oil field has since become commercial and has revived exploration in this area with more than 20 wells drilled since 2003. However, limited geochemical studies have been carried out on these new wells and the paucity of data has precluded a clear understanding of the petroleum prospectivity in the offshore North Perth Basin.

This study aims at reassessing the petroleum systems in the offshore North Perth Basin with a particular focus on determining the extent of the Lower Triassic petroleum system offshore. Sixteen wells including six recently drilled wells with no previous geochemical data were sampled for source rock and oil stain analyses. Based on revised stratigraphic interpretation of these wells, the Hovea Member is now firmly recognized in 17 offshore wells and preliminary results indicate that it shows good to excellent source rock potential for generating black oil. More than half of these samples have TOC greater than 1% associated with S₂ exceeding 5 mg hydrocarbons/g rock (Figure 1). In the Abrolhos Sub-basin, the best source quality for the Hovea Member is shown in the Dunsborough-1, Perseverance-1 and Hadda-1 wells, demonstrating that good oil-prone Lower Triassic source rocks are spatially widely distributed offshore. Standard vitrinite reflectance measurements (R_o) indicate that the Hovea Member source rocks are immature to marginally mature in the Abrolhos sub-basin. However, fluorescence alteration of multiple macerals (FAMM) analyses shows that the thermal maturity of the Hovea Member is actually underestimated by 0.1 to 0.3% R_o due to vitrinite suppression. This interpretation is supported by vitrinite reflectance-fluorescence analyses once normal vitrinites are selected. Analysis of oil stains from offshore wells Hadda-1 and as far north as

Morangie-1 and Livet-1 suggests they are sourced from the Kockatea Shale and confirms that the Lower Triassic petroleum system is indeed effective over a more extensive geographic area offshore than what was previously thought. The widespread effective source potential of the Kockatea Shale is also corroborated by the recognition of palaeo-oil columns beneath the regional Kockatea Shale seal on the basis of fluid inclusion data (Grains with Oil Inclusions; GOI) in six offshore wells (Kempton *et al.*, in prep.). These new data greatly enhance the petroleum prospectivity of the region. Evidence for effective Permian and Jurassic petroleum systems will also be presented.

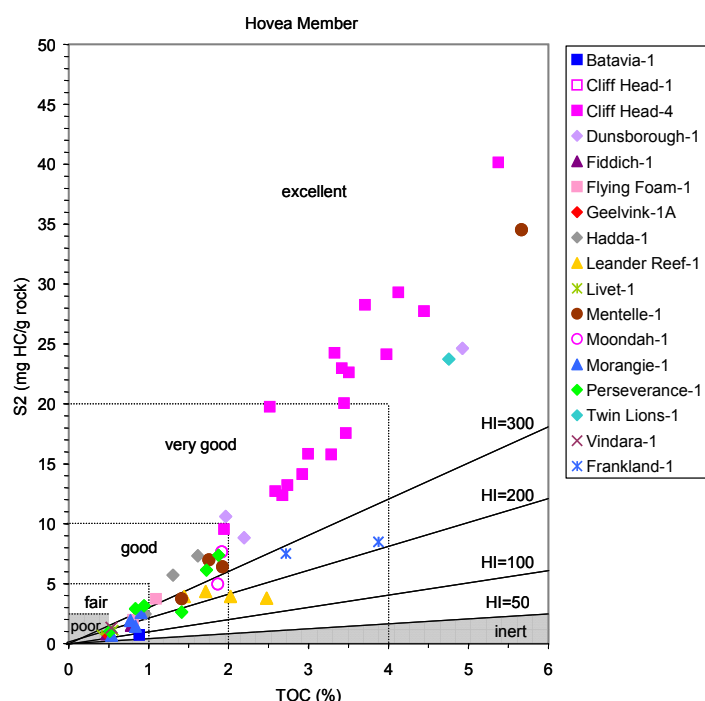


Figure 1: Plot of total organic carbon (TOC%) versus Rock-Eval pyrolysis S2 for the Hovea Member source rocks of all offshore North Perth wells.

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Subsistence and the isotopic signature of herding in the Bronze Age Hexi Corridor, NW Gansu

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The Asian millets (*Panicum miliaceum* and *Setaria italica*) have short growing seasons, are tolerant of cold and arid conditions, and are commonly cultivated in marginally arable areas of north China. Previous work finds these plants to have dominated the diets of agriculturalists and livestock there at various times since the Yangshao Period (ca. 7000-5000 BP). Intensive millet cultivation may have helped societies persist when climatic conditions were less agriculturally favourable, however, heavy reliance on the cereal may have led to poorer population health, as people adopted less varied diets.

Carbon and nitrogen stable isotope values for bone collagen from sites in the Hexi Corridor, dating to approximately 2292-1692 BC, are presented. The isotope results show human and most domestic omnivore fauna shared diets dominated by millet (a C4 plant), and consumed only minimal amounts of animal protein (flesh, milk or blood products). These findings contrast with the archaeological assemblages which include abundant faunal bones and hunting tools. The narrow dietary focus towards a single cereal, in the marginally arable Hexi Corridor region, suggests that societies there would have been highly vulnerable to any shift in the region's hydrology.

The minimal proportions of C4 plants detected in the diets of the *Bos* and *Caprinae* sampled suggests that herded animals were mostly taken beyond the agricultural zone to graze. This dietary separation of herded animals from cultivated millet would have allowed them to function as an emergency food source in times of crop failure. The wide range in herbivore $\delta^{15}\text{N}$ values (4.1‰ to 11.8‰) indicate individual grazing ranges were varied and were probably in distinctly different ecological zones.

September 2009 Sydney dust storm – meteorological transport of a rich source of geochemicals, pollen and microbes

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Australia is the main source of dust in the Southern hemisphere yet little is known about the composition of this dust. The aim of this study was to characterise the meteorology, microbiology, geochemistry, and pollen content of the Sydney dust storm in September 2009. On September 23rd, a large cold front caused a major dust event that spanned ~2,500 km from north to south along the Australian east coast (Figure 1A). The previous day, pre-frontal north-westerly winds carried dust from the Lake Eyre Basin of central Australia to the city of Canberra where dust, aerosol and rain samples were collected for analysis.

Trace elements were measured using ICP-MS while organic solvents were examined using GC-MS on samples collected from rain fallout. Aerosol samples for microbiological analysis were collected on cellulose nitrate filters using vacuum pumps and rain was collected in a glass bottle using a sterilised funnel. Culture-dependent analysis was conducted on the aerosol and rain samples using 3 different media. Sequencing of the 16S rDNA was used to identify bacterial isolates. For culture-independent analysis, DNA was extracted directly from the filter and used to create a 16S rDNA library in *Escherichia coli*. The DNA was then sequenced in the same way as for the culture based analysis.

Trace elements measured from dust samples taken along the trajectory of the dust plume showed substantial differences during the dust fallout, indicating that additional material was entrained along the trajectory of the dust plume, a result supported by the analysis of pollen diversity. Similar to a previous event (September 2002), the dust was extremely rich in pollen, analysis of which confirmed the origin to central Australia.

Analysis of solvent extracts revealed high concentrations of the pharmacologically active plant lipids oleanolic acid (160 grams per tonne of dust), betulinic acid (27 g/tonne) and ursolic acid (570 g/tonne). Further investigation is needed into the source of the plants and the mechanism(s) of concentration. A high level of alkanes was also detected.

Analysis of colony forming units per cubic metre (CFU/m³) showed that there were similar bacterial loads in the air during the day and overnight (8×10^2 and 5×10^2 CFU/m³ respectively) with up to 10^4 CFU/mL present in the rainwater. Representatives from seven different bacterial families were cultured, with Bacillaceae, in the Firmicutes phylum, the most numerous (Figure 1B). The diversity of taxa was greatest in the rain samples and lowest in the day time air sample, suggesting that the rain precipitated material and associated microorganisms out of the atmosphere. Culture-independent analysis of the same samples showed a much more diverse microflora, dominated by the Actinobacteria phylum. This data indicates that only a very small proportion of bacteria can be cultivated, consistent with the literature.

This storm mobilised 5-10 million tons of dust which caused airport closures and other major costly disruptions. Our investigation of the dust composition indicates that it is also a rich source of geochemicals, pollen and microorganisms.

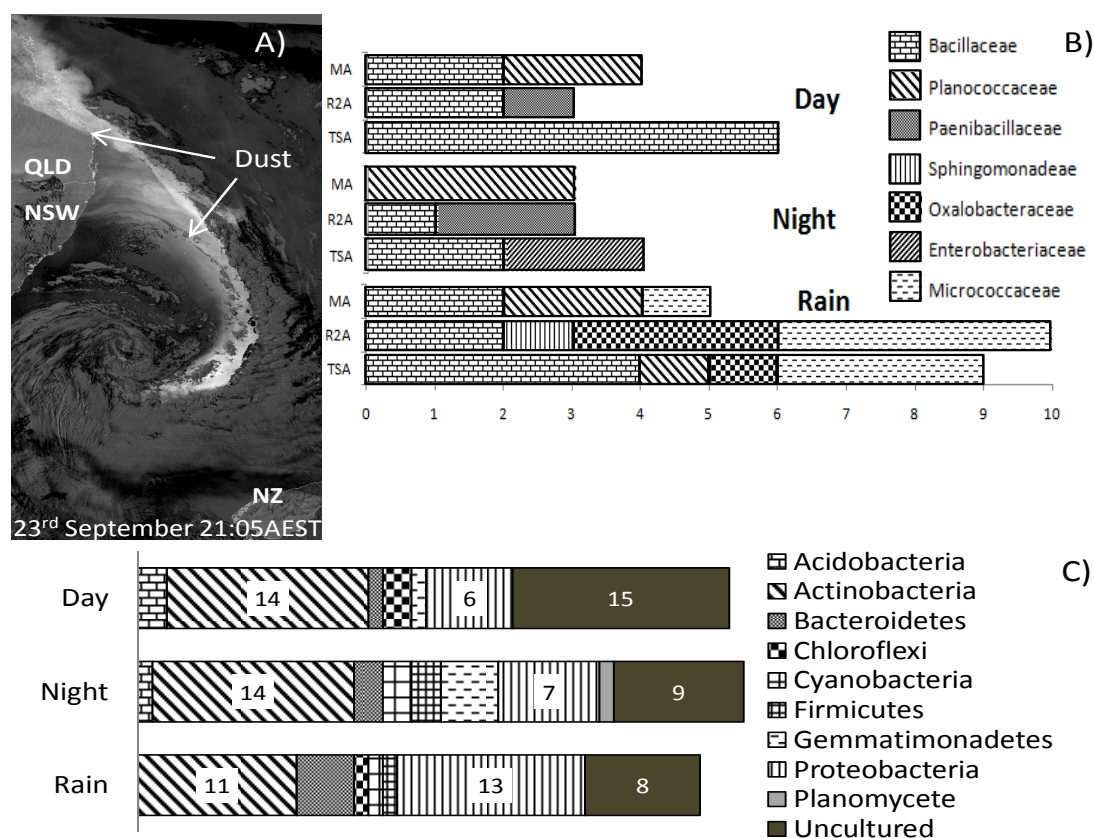


Figure 1: A) Satellite image taken of the Australian East Coast at 9.05pm AEST time on 23/9/09. B) Diversity of families in culture-dependent samples. MA, R2A and TSA represent media used for cultivation. C) Diversity of phyla in culture-independent samples.

GC-IRMS analyses of natural gases and geochemical application

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Natural gases are composed of a limited number of individual compounds, mainly of C₁-C₅ hydrocarbons and non-hydrocarbon compounds (CO₂, N₂, noble gases etc.). Their compositions and isotopes of single compounds provide critical information to decipher the origin and evolution of natural gases. Efficient analysis of these compounds is paramount for timely application of this important dataset.

The following discussion is based on the carbon isotopes and the methods developed for their efficient analysis. Similar principles are also applicable to the analysis of hydrogen isotopic composition of natural gases.

C₁-C₅ and CO₂: Methane, ethane and CO₂ can be analysed under the same GC conditions. Complications arise when difference in concentrations of these compounds are large. Variable injections are required with increased volumes and adjusted split ratios needed to produce strong peaks for reliable results (0.3V to 7V; equivalent to 0.0064µg to 0.1484µg carbon). Another issue is the use of cryo-trapping when methane is very dominant over CO₂. It is recommended here that a cold trap be avoided if back-flushing methane is enough to obtain CO₂ signal over 300mV. This will save precious analytical time.

Ethane, propane, C₄ and C₅ can also be analysed with programmed timed events which will automatically start GC programs and switch between back-flush and straight flow modes. Compared to a conventional program, the 'automatic' program frees up operator attention to processing previous results and preparing for the next sample injection. It also allows for more consistency in analytical conditions between different runs. Cold trapping can be applied to enrich C₂₊ compounds when they are in very low abundance.

Neo-pentane: Until recently *neo*-pentane (*neo*-C₅) was not routinely analysed in natural gases due to its extremely low concentration. Nevertheless, elevated *neo*-pentane contents can be found in biodegraded natural gases due to its relative inertness compared to the other gaseous hydrocarbons. In such altered natural gases, *neo*-pentane has been very effective in gas correlation studies and it also retains a strong isotopic source signal even at relative high gas maturities (Boreham *et al.*, 2008a, 2008b). *Neo*-pentane analysis can be readily achieved at ambient temperature with appropriate up-scaling. Typically, a large volume of gas sample of up to 20mL (with multiple injections of 2ml) and a split ratio of 25:1 (4000 times that of a typical methane analysis of 40µl and with a 200:1 split ratio) results in *neo*-C₅ effectively focussing at the front to a Poraplot Q stationary phase capillary column. The GC-IRMS analysis is completed by temperature programming and careful attention to back-flushing C₄ and C₅ between the periods when *neo*-C₅ is eluted (Figure 1).

Table 1 displays $\delta^{13}\text{C}$ of *neo*-pentane for selected Perth Basin gases. The data shows a wide range in $\delta^{13}\text{C}$ attributed to source rocks varying in age from Permian to Jurassic. Importantly, it is also able to differentiate between the effect of source and maturity.

N_2 : The isotopes of N_2 have just recently been analysed from various Australian basins. Geoscience Australia's extensive database on natural gas composition was used to choose a subset of gases with elevated N_2 concentrations (5-79 mol%). This preliminary study was undertaken to see if N_2 isotopes can provide useful geochemistry information on natural gas distribution and evolution. Our results provide evidence for variations in N_2 isotopes among the gases from several Australian basins. During the analysis of N_2 isotopes, the oxidation furnace temperature was set at 600°C (900°C for carbon isotope analysis) to prevent the loss of N_2 by transferring into nitrogen oxides. The N_2 of air was used as a standard.

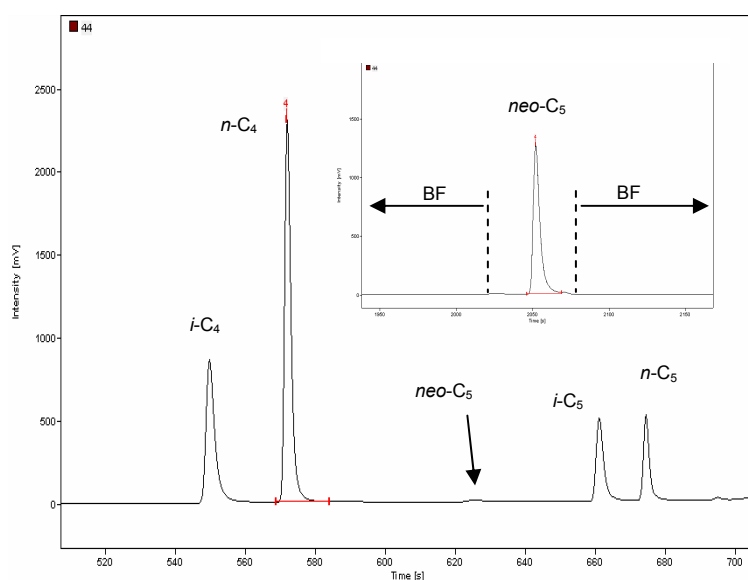


Figure 1: The GC-IRMS traces display the neo-pentane analyses. The neo-pentane produced a very weak signal in the analysis to obtain isotopic data for $i-C_4$, $n-C_4$, $i-C_5$ and $n-C_5$. In another run targeting neo-pentane, it produced a good peak with about 1.3V intensity with 8 mL injection (insert picture; $i-C_4$, $n-C_4$, $i-C_5$ and $n-C_5$ were back-flushed (BF)).

Table 1: Carbon isotopes of C_4 – C_5 hydrocarbons in Perth Basin natural gases.

Samples	Source	$\delta^{13}C$ (‰)				
		neo- C_5	$i-C_4$	$n-C_4$	$i-C_5$	$n-C_5$
1	Jurassic	-26.86	-25.01	-26.13	-25.00	-24.68
2	E. Triassic	-34.42	-31.07	-33.24	-31.39	-31.73
3	E. Triassic	-35.49	-31.74	-33.58	-31.80	-32.11
4	E. Triassic	-36.19	-32.37	-32.66	-31.77	-31.29
5	E. Triassic*	-36.75	-32.43	-31.48	-32.34	-31.44
6	Permian	-30.68	-25.91	-26.95	-24.83	-24.39

* High maturity

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Molecular Fossils and the late rise of eukaryotes and oxygenic photosynthesis

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Hydrocarbon biomarkers are the molecular fossils of natural products such as lipids and pigments. They can yield a wealth of information about early microbial ecosystems and are particularly valuable when preserved in >1 billion-year-old (Ga) sedimentary rocks where conventional fossils are often lacking. In particular, the detection of traces of biomarkers in 2.7 Ga shales from Western Australia was celebrated as a breakthrough (Brocks *et al.*, 1999). The 1999 discovery, which was later confirmed by several independent studies (Sherman *et al.*, 2007; Ventura *et al.*, 2007; Eigenbrode, 2008; Eigenbrode *et al.*, 2008; Waldbauer *et al.*, 2009), led to far-reaching conclusions about the early evolution of oxygenic photosynthesis and ancestral eukaryotes (Brocks *et al.*, 2003). However, here we present new data based on the carbon isotopic composition of solidified hydrocarbons (Rasmussen *et al.*, 2008) and the spatial distribution of liquid hydrocarbons within the original 2.7 Ga shales (Brocks, 2010). The data demonstrates that the molecules must have entered the rock much later in Earth's history and therefore provide no information about the Archean biosphere or environment.

The absence of reliable biomarkers of Archean age (>2.5 Ga) has immense implications for our understanding of Earth's early biosphere. 2 α -methylhopanes were interpreted as evidence for the existence of cyanobacteria at 2.7 Ga, about ~300 million years before the atmosphere became mildly oxygenated in the Great Oxidation Event (GOE) between 2.45 and 2.32 Ga. The oldest direct fossil evidence for cyanobacteria now reverts back to 2.15 Ga, and the most ancient robust sign for oxygenic photosynthesis becomes the GOE itself. Moreover, the presence of steranes was interpreted as evidence for the existence of ancestral eukaryotes at 2.7 Ga. However, without the steranes, the oldest fossil evidence for the domain now falls into the range 1.78-1.68 Ga. Recognition that the biomarkers from Archean rocks were not, in fact, of Archean age renders permissive hypotheses about a late evolution of oxygenic photosynthesis, and an anoxygenic phototrophic origin of the vast deposits of Archean banded iron formation.

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AOGC 2010 – Abstracts

Poster Presentations

(Abstracts are in alphabetical order by first authors' last names; Presenters are underlined)

The Early Aptian Global Oceanic Event OAE1a as recorded in the Goraa-Hammam Biadha Basin (Northwestern Tunisia)

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The Early Aptian OAE1a represents the first globally-distributed black shale event of the Cretaceous and therefore is regarded as a major turning point of Mid-Cretaceous paleogeography. Furthermore, this OAE1a has a widespread distribution in the Tethyan and Peritethyan realms, and is known under many names according to its location: Fischschiefer in the lower Saxony basin in Germany, Niveau Goguel in the Vocontian basin in France and Livello Selli in the Umbria-Marche basin in Central Italy.

This organic geochemical study, based on both Rock-Eval and total lipidic extracts data, of two outcropping sections across the Goraa-Hammam Biadha Basin has led to the following results and conclusions: **(1)** the Barremian-Aptian series are made up of pelagic succession which is characterized by cyclically arranged marls and argillaceous/massive limestones with the occurrence of some thin black shale horizons; **(2)** the most organically-rich materials appear to be associated with massive limestones and with black shales; **(3)** The Barremian-Aptian series exhibits significant thickness variations along a NW-SE axis. The greatest thickness (up to 90 meters) is reached towards the Triassic massif of Arkou-Fedj El Hdoum, while to the NW, close to the Triassic Massif of Thibar, the series is only 30 meters thick; **(4)** along a NW-SE axis addressed across the investigated basin, the Total Organic Carbon (TOC) average amounts decrease from 2.5% to 1.7%, the highest TOC 5.8% was in the north western part of the study basin; **(5)** the total pyrolytic yields (S1+S2) are also found to decrease from 8.3 mg HC/ g rock in the NW to 1.7 mg HC/g rock in the SE, thus confirming that the Barremian-Aptian series contains good potential oil and gas prone source rocks (Hydrogen Index values for immature rocks are up to 435 mg HC/g TOC), with a singular and uncommon petroleum potential differentiation ([Figure 1](#)) along a NW-SE axis; **(6)** in terms of thermal maturity evolution (deduced from the Tmax measured values), the late Barremian-Aptian organic matter displays a variable and increasing thermal maturity in the same direction as the thickening trend (immature to early mature source rocks ($T_{max} = 438^{\circ}\text{C}$) to the NW, and over mature source rocks ($T_{max} = 495^{\circ}\text{C}$) to the SE).

The occurrence of these sediments reflects restricted conditions leading to the accumulation of nutrients and mainly to the development of anoxia. An anoxic environment within the basin can be explained by the existence of a physical barrier which prohibited the interaction and the mixing of waters with the open sea. In addition, differences in the sedimentary column-thickness and the variability of the geochemical attributes between the two studied sections (along a NW-SE axis) suggest that the investigated area formed a subsiding zone dipping eastward and southeastward ([Figure 2](#)).

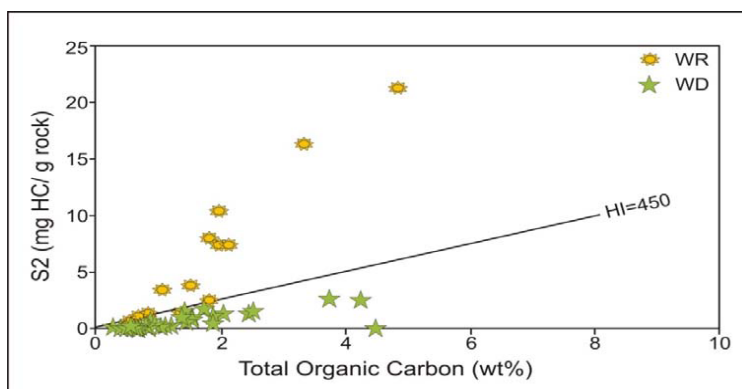


Figure 1: S2 versus TOC diagrams of the WR section (NW) and WD section (SE). (Langford and Blanc-Valleron, 1990). These values plot along a line that has a slope derived HI of 450 mgHC/gTOC, which indicates an oil and gas-prone type II kerogen

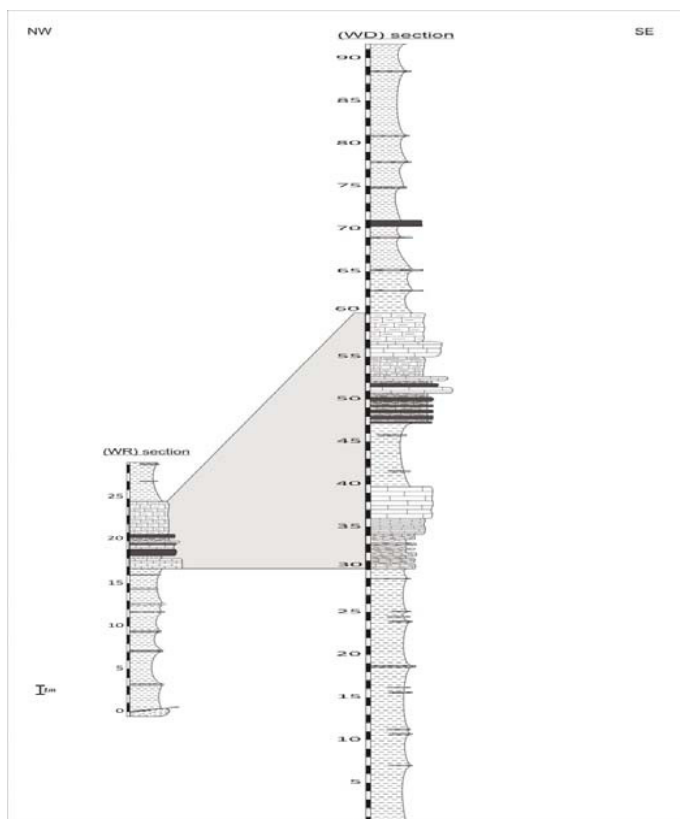


Figure 2 : Lateral correlation between the two studied sections along a NW-SE axis.

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Ecology of sediment nitrification and denitrification in the Fitzroy river estuary, Queensland, Australia

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Nitrogen is an essential nutrient for primary productivity in marine environments. Denitrification in marine sediments contributes significantly to the removal of dissolved inorganic nitrogen as dinitrogen gas, thus becoming unavailable for phytoplankton uptake. Using marker genes for nitrite reductase (*nirS/K*) and ammonia mono-oxygenase (*amoA*) the abundance and composition of denitrifying and nitrifying bacteria has been studied in the mid to high tidal zone down a transect of the Fitzroy river in Queensland

Samples were taken during March, July, September and December at 21 sites (Figure 1). Physical parameters (salinity, DO, temperature etc) were measured. Samples for the analysis of nitrogen and carbon isotope ratios, lipid biomarkers of primary productivity and heterotrophic bacteria as well as molecular analyses were also taken. The abundance and diversity of key nitrogen cycling genes were determined using a combination of Q-PCR, T-RFLP and sequencing from 12 of the sites. Variation in the diversity and abundance of N-cycling assemblages was assessed across the sites and seasons using multivariate analysis.

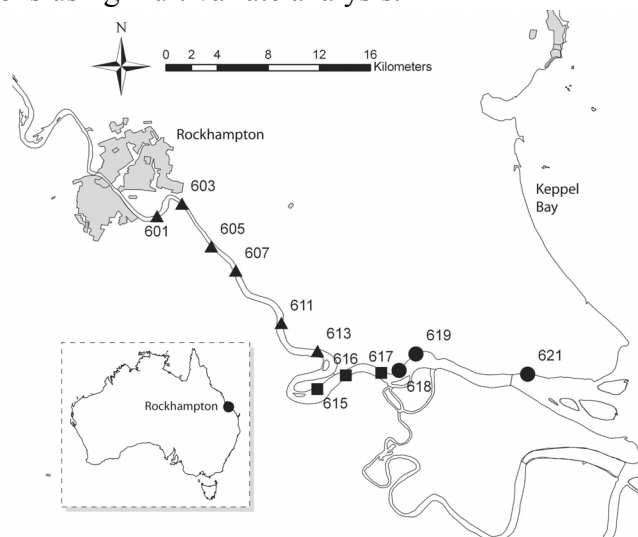


Figure 1: Sampling sites.

Seasonal changes in the estuary were characterized by a change in salinity from relatively low salinity during the wet season (March) to much higher salinity during the dry season (December). Primary productivity in the estuary was 2.5 to 3 times higher in the cooler months of July and September than during March and December, whilst markers of heterotrophic bacteria showed a similar but more muted trend. The

nitrifying communities were dominated across all sites and seasons by ammonia-oxidizing archaea (AOA), whilst the denitrifying community was dominated by the *cd1* nitrite reductase (*nirS*) gene. There was no significant change in the seasonal abundance of nitrifiers or denitrifiers across sites. Denitrifying communities were significantly more diverse than nitrifiers with the *nirS* gene also showing the highest variability in abundance of all the groups assayed.

Two-way crossed ANOSIM analysis demonstrated a significant difference between sites across all seasons for AOA ($P=0.001$), but no significant difference between seasons, whilst *nirS* communities were significantly different between seasons ($P=0.002$), but not between sites (Figure 2). Analysis of the composition of *nirS* communities demonstrated a number of dominant TRFs found in all samples analysed that changed in dominance during the year. *amoA* communities did not change significantly with season, but were site-specific with samples in the upper estuary being dominated by TRF 10 whilst samples in the upper and mid estuary were dominated by TRFs 25 and 32 respectively.

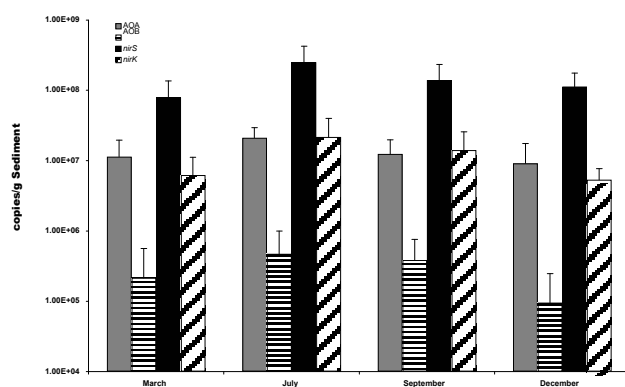


Figure 2: Temporal variation in gene abundance (error bars show standard deviation).

In conclusion, a robust community is involved in nitrogen cycling in the Fitzroy river with a number of dominant groups of nitrifiers and denitrifiers detected across all samples and seasons. Nitrifying communities were less diverse and showed a more site-specific composition, possibly related to lower proliferation rates. Denitrifying communities demonstrated a higher diversity and changed significantly between seasons, suggesting successional adaptation to environmental changes. The study revealed significant diversity in the nitrogen cycling genes including a number of groups that have not been detected previously.

On the geochemistry and origin of Eastern Papuan Basin oils and gases

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This study presents a detailed organic geochemical assessment of oils, condensates and natural gases in the Eastern Papuan Basin and makes inferences on palaeo-depositional environment, lithology, maturity, age and identity of potential source rocks in this emerging petroleum province.

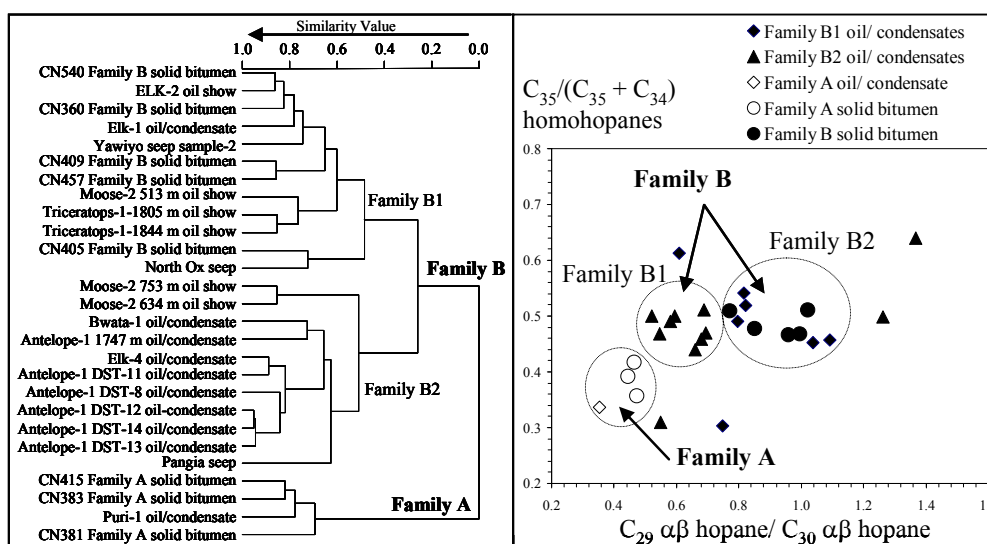


Figure 1: (Left) Dendrogram of hierarchical cluster analysis (HCA) of 15 source variables. Data from solid bitumens; Puri-1 oil/condensate and Bwata-1 oil/condensate are from George *et al.* (2007). (Right) Cross plot of $C_{29} \alpha\beta \text{ hopane} / C_{30} \alpha\beta \text{ hopane}$ versus $C_{35} / (C_{35} + C_{34}) \text{ homohopanes}$ showing the genetic groups of oil/condensates in the Eastern Papuan Basin. Parameters used for cluster analysis: Pr/Ph, C_{30}^*/C_{29} Ts, C_{29}^*/C_{29} ab hopane, C_{30}^*/C_{30} ab hopane, $C_{35}/(C_{35} + C_{34})$ homohopanes, Homohopanes/ $C_{30} \alpha\beta \text{ hopane}$, Oleanane/ $C_{30} \alpha\beta \text{ hopane}$, $C_{29} \text{ ab hopane} / C_{30} \alpha\beta \text{ hopane}$, $C_{31} \alpha\beta \text{ hopanes} / C_{30} \alpha\beta \text{ hopane}$, C_{23}/C_{21} tricyclic terpanes, C_{24} tetracyclic/ C_{23} tricyclic terpanes, $C_{19}/(C_{19} + C_{23})$ tricyclic terpanes, C_{29} steranes/ $C_{29} \alpha\beta \text{ hopanes}$, $C_{32} 2\alpha \text{ Me} / (C_{32} 2\alpha \text{ Me} + C_{31} \text{ab hopanes})$ and $C_{30}/(C_{27} + C_{28} + C_{29}) \alpha\alpha\alpha 20R \text{ steranes} (\%)$.

A hierarchical cluster analysis of fifteen source specific parameters derived from a variety of aliphatic hydrocarbon biomarkers divides the Eastern Papuan Basin oils/condensates into two major groups (Figure 1 left). “Family A” samples have been generated at peak to late oil-window maturities from a clay-rich marine source rock containing predominantly terrestrial higher plant derived organic matter deposited in suboxic to anoxic environments. Biomarker signatures are related to those of the oils from the Papuan Fold Belt (western Papuan Basin), and similar to those oils, this family was probably also generated from the Late Jurassic Imburu Formation. The

second group “Family B” consists of samples spread over approximately 160 km strike extent in the eastern part of the basin from Pangia in the west to the Aure Scarp in the east. These “Family B” samples appear to have a more marine signature and were also generated at peak to late oil-window maturities. The influence of prokaryotic organic matter seems to be greater in these samples, as suggested by higher abundances of C₂₉ $\alpha\beta$ hopane and C₃₅ homohopanes (Figure 1 right) and a range of other parameters. This indicates that these oils/condensates have been generated from marine source rocks deposited in sub-oxic to anoxic environments, possibly comprising calcareous lithologies (after Peters *et al.*, 2005). Land plant input is also present but is less than for “Family A” samples. The “Family B” oils/condensates can be subdivided into two subgroups (“Family B1” and “Family B2”) depending on the extent of mixing of hydrocarbons generated from different organic matter types. The presence of oleanane \pm lupane and the isomeric distributions of nordiacholestanes and norcholestanes suggest that “Family B” oils/condensates are derived from Cretaceous or younger source rock(s), possibly from the Ieru or Chim Formation. This is supported by recent InterOil studies indicating that > 1000 m of Cretaceous marine sediments may be present in the area. The presence of two major groups of oils/condensates in the Eastern Papuan Basin is consistent with the previously identified two main groups of solid bitumens in the Subu area (George *et al.*, 2007). Most of the 13 fine-grained sediments from the Miocene Aure Bed and Late Cretaceous Pale and Subu Sandstone Formations have TOC values < 0.5%; 4 samples with TOC values between 0.5 and 0.9 % show little hydrocarbon generation potential based on Rock Eval and extract analyses (George *et al.*, 2007). The molecular and carbon isotopic composition of Antelope-1 gases show very little variation and can be interpreted as thermogenic gases generated from marine source rocks, consistent with the source characterisation of “Family B” oils/condensates.

This study suggests that the majority of Eastern Papuan Basin oils/condensates (“Family B”) are derived from marine source rock(s), containing predominantly prokaryotic organic matter mixed with variable amounts of terrestrial higher plant inputs. Age-specific biomarkers suggest Cretaceous source rocks. Whereas the exact origin of “Family B” hydrocarbons is unclear, source rock intervals may be present in the Cretaceous Ieru/Chim Formations deposited in marine environments. Other possible source rocks could be Eocene carbonates and Palaeocene clastics and carbonate correlatives of the Moogli Mudstone and Pima Sandstone.

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Formation of adamantanes in sediments: carbonaceous surface reactions

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Diamondoids are hydrocarbons that have a carbon skeleton that is superimposable on the diamond lattice. Adamantane is the cage-shaped primary unit of diamondoids that occurs widely in sediments and petroleum. The first report of adamantane isolated from petroleum extends back seven decades (Landa and Machacek, 1933), but unlike many petroleum hydrocarbons, the molecular structures of the diamondoids bear no obvious relationship to naturally occurring precursor biochemicals. They are therefore geosynthetic compounds. However, both the precursors and the reaction conditions for their geosynthesis remain unclear, although the involvement of catalytic processes has been suggested (Petrov, 1987; Wei *et al.*, 2006a, 2006b).

We report here the formation of adamantane and alkyl adamantanes from laboratory heating experiments of β -ionone and isohexyl-2,3,6-trimethylcyclohexane with activated carbon in the temperature range 170 to 320°C. Both compounds possess molecular skeletons representative of ubiquitous sedimentary hydrocarbons (i.e. alkyl cyclohexanes). The reaction scheme for the formation of alkyl adamantanes from β -ionone is shown in [Figure 1](#). The initially formed adamantanes from these sedimentary reactants undergo methyl transfer and dealkylation reactions on carbon surfaces to yield adamantanes commonly found in crude oils. This is the first report of a novel hydrocarbon reaction on a carbonaceous surface that accounts for the occurrence and distribution of adamantanes in sediments and crude oils and complements several other sedimentary reactions recently reported to occur on carbonaceous surfaces (Alexander *et al.*, 2009, Asif *et al.*, 2009, 2010).

Evidence to support the proposed carbon surface reaction mechanism for rearrangement, demethylation and hydrogen exchange of adamantanes was obtained by way of separate heating experiments of model diamondoid compounds with activated carbon. Laboratory heating of adamantane yielded protoadamantane (tricyclo [4.3.1.0.^{3,8}] decane), a tricyclic ring isomer with a combination of ring sizes that differs from the all six-carbon ring system of most diamondoids. Isomers of tricyclic C₁₁ and C₁₂ compounds with multiple combinations of carbon ring sizes occur in crude oils and have been classified as protoadamantanes (Petrov, 1987), despite the use of this name for the specific 10 carbon diamondoid referred to above. The ring isomerisation reported here for conversion of adamantane to protoadamantane on the activated carbon surface suggests a new mechanism for rearrangement reactions of alkyl adamantanes and may also account for the distribution of alkyl protoadamantanes reported in petroleum (Petrov, 1987).

Evidence that the adamantane reactions occurring on activated carbon are also likely to take place on other carbonaceous surfaces available in sediments was obtained by using a coal sample as the carbon surface. The reaction employed was the exchange of hydrogen on adamantane with deuterium from surface adsorbed D₂O. A marked change in the mass spectrum of adamantane was evident in experiments with both activated carbon and Collie coal and provides compelling evidence that the reactions of diamondoids proceed via a carbon surface reaction mechanism. These findings have the potential to further develop our understanding of the chemical reactions that cause geochemical changes during petroleum formation.

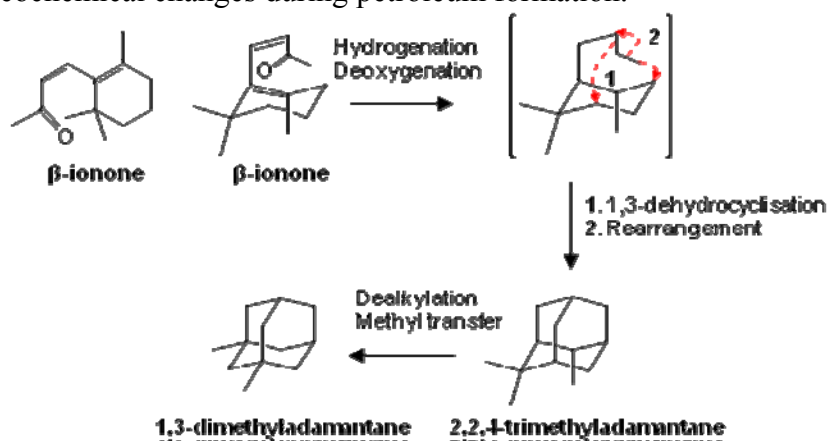


Figure 1: Reaction scheme for the formation of alkyl adamantanes from β -ionone.

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Sedimentary lipids and aDNA - a new biomarker approach?

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Lipid biomarkers in lake sediments - remains of plants and organisms - are widely used to reconstruct past changes in lake ecosystems. However, the source-specificity of these lipid biomarkers is often limited due to their widespread distribution within biota. To resolve this we test a new approach which employs ancient DNA (aDNA) as a biomarker. Under certain conditions aDNA can be preserved in sediments and has been isolated from up to 400,000-year-old sediments (Hofreiter *et al.* 2000, Willerslev *et al.* 2003). aDNA can provide more detailed information on plant species and is therefore a potentially promising tool that is expected to increase knowledge of changes in past ecosystems and its causes.

aDNA is degraded rapidly within sediments. Therefore only limited amounts and fragments of aDNA are preserved which makes extraction challenging. Over the last few years, protocols have been developed which ensure efficient purification and identification of aDNA. In the study presented here, three different lake surface sediments from distinct climate zones (tropical, temperate, boreal) are investigated to evaluate a) the preservation state of aDNA in these sediments and b) if plant-derived aDNA represent current ecosystem composition. A comparison of aDNA with the lipid content of lake sediments will be conducted to test if aDNA can provide better constraints on the specific sources of ubiquitous lipid biomarkers, such as leaf wax lipids. Together with other geochemical proxies (e.g. isotopes) this information will improve our understanding of organic matter preservation in different sediment settings and will lead to new insights into the causes of changes in lake ecosystems in the past.

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Long-term Degradation of Lubricant Oil in Antarctic Sediments

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The idealised view of Antarctica as one of Earth's last remaining pristine environments is being tested as a result of a significant legacy of petroleum pollution on the continent. Lubricant oils used in machinery for Antarctic research and exploration are inevitably released to the environment via general usage or direct spills, causing some concern as to its impact.

A simulated marine spill has been carried out by the Australian Antarctic Division (AAD) over a five year period, in which sieved (500 µm) Antarctic sea-bed sediments were doped with various petroleum products and left in a shallow marine environment to examine the extent and rate of natural degradation. Of these pollutants, an unused Mobil lubricant oil (OW/40; Exxon Mobil) is being analysed qualitatively and quantitatively by gas chromatography-mass spectroscopy (GC-MS) to determine the extent of degradation of the oil and its components.

Replicate samples were collected over the time frame of the experiment (at 0, 5, 52, 64, 104 and 260 weeks after deployment), with the top 0–1 cm of sediment sampled at all time periods, in addition to depth profiles with samples from every 1 cm to ~10 cm depth at 5, 63 and 260 weeks. Sediment cores were frozen and sliced into 1 cm sections for solvent extraction (DCM:H₂O, 9:10), and each sample was spiked with a mixture of internal standards. The sample set was then analysed by GC-MS and the components of the lubricant oil were identified by retention time behaviour and mass spectral library searching and interpretation. Selected components were quantified relative to an internal standard.

The aim of this honours project is to achieve a full picture of the extent of degradation of each compound contained within the lubricant oil by both physical processes (such as water washing and evaporation) and biodegradation by native bacterial communities as a function of both depth in the sediment column and time of exposure.

Intact polar lipids and isotopic signatures of photosynthetic microbial mats from Shark Bay, Western Australia

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Photosynthetic microbial mats and living stromatolites at Shark Bay are significant microbial niches which resemble traces of life forms that are preserved in rocks of some 3.5 billion years in age. At Shark Bay, the distribution and growth of morphologically different microbial mats across the hypersaline coastal plain is attributed to a complex network of physicochemical factors, such as strong insolation, high salinity, wave energy and daily variability in the chemistry (Logan *et al.*, 1974). Mat morphologies may be linked to the interplay of different microbial consortia and their metabolic pathways that influence mat geochemistry and lithification (Allen *et al.*, 2009). With a multidisciplinary approach, we link different mat morphotypes with stable isotopes, their organic and inorganic geochemistry to understand the regional occurrence of different mats while enhancing our geological interpretation of these modern analogues of ancient carbonate systems.

Using LC-MS techniques, we observe profiles of intact polar lipids (IPLs) that are typical of photosynthetic microbial mats (phospho- and glycolipids, N- and S-containing IPLs). Differences occur amongst mat types sampled from four diverse embayments mainly influenced by salinity. Distinct IPL profiles indicate variable contributions of oxygenic and anoxygenic phototrophs including sulphur-cycling bacteria. The analysis of phospholipid fatty acids (PLFAs) is in good accordance with the profiles of IPL acyl side chains (range: C_{14:0} to C_{19:1} fatty acids) and allow insight into metabolic strategies via stable isotope analysis. $\delta^{13}\text{C}$ values of C_{17-n}-alkanes attributed to cyanobacteria support differences between mat types (range: -18.6 to -31.2 ‰ vs. VPDB), whereas discrete mat morphotypes (e.g. smooth mats) reflect similarities across the embayments (-18.6 to -23.5 ‰ vs. VPDB). Isotopic values of bulk organic matter (-10.6 to -30.0 ‰ vs. VPDB) and porewater of the mats (-9 to -19 ‰ vs. VPDB) are consistent with rising salinity levels between the embayments (40-80 ‰). The understanding of geochemical signatures within the microbial deposits at Shark Bay is important as they serve as a modern analogue of carbonate systems of

the Neoproterozoic-Mesozoic from which significant commercial oil and gas reservoirs have been identified (e.g. offshore Brazil).

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Using radiocarbon (^{14}C) to monitor atmospheric CO_2 storage

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Biogenic CO_2 and fossil CO_2 have very distinct radiocarbon ratios. Fossil carbon sources (natural gas, coal, oil) do not contain radioactive ^{14}C anymore due to their age. Biogenic carbon sources have easily measurable amounts of ^{14}C that equate to the time period the organism lived. This makes radiocarbon a useful tracer for monitoring the uptake or release of CO_2 in the environment. Radiocarbon has also been used to validate the fossil and biogenic fraction of CO_2 plant emissions greenhouse gas emission monitoring and carbon trading.

As an example we will show that ultramafic tailings produced by some mining operations capture atmospheric CO_2 . This mineralization of CO_2 within Mg-carbonate minerals can occur on a scale large enough to be a significant sink of greenhouse gas emissions from the mine. Traditionally stable carbon and oxygen isotope data have been used to examine this trapping effect, however in two of our study sites (Mount Kieth Nickel Mine, Australia, Daivik Diamond Mine, Canada) the stable isotope data reflects the processes of carbon cycling and not its provenance. By using ^{14}C we can obtain an unambiguous measure of the amount of modern atmospheric CO_2 sequestered by the carbonate minerals. Using this method we determined that >90% of the carbon mineralised in secondary Mg-carbonate at Mount Kieth and Daivik was trapped from the modern atmosphere.

Gas Stable Isotope Analysis – Sample containment and $\delta^{13}\text{C}$ stability

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Gas composition and stable carbon isotope analyses are two of the many tools used to assist in the evaluation of the quality and origin of gas samples. The cost attributed to obtaining samples through drilling and subsequent analysis is typically in the thousands of dollars, growing exponentially for remote sample locations. The decisions resulting from interpretation of the analytical data shape drilling programs, exploration plays and further research avenues. If samples are not carefully collected, stored appropriately and the data not quality controlled, the decisions being made may inadvertently impact on the overall interpretation and investment of a program.

Gas samples can be contained in many types of vessels and over time we have become aware that some sample vessels are better suited to retaining samples. While we have a good understanding of the residence time of samples in the laboratory, we have no control over how long these samples take to be dispatched from the source, or the conditions under which they are stored prior to analysis in our laboratory. To investigate which sample vessels maintain sample integrity, stable carbon isotope composition of methane and carbon dioxide over time was analysed from sub-samples of a known gas standard.

The six most common sample vessels are, stainless steel cylinders, aluminium cylinders, pre-evacuated glass vials (originally designed for blood collection), aluminium and plastic bladders designed for wine storage, tedlar bags and aluminium 5 layer bonded bags. These vessel types were filled according to manufacturers' specifications with a gas mixture of methane and carbon dioxide (50/50 %). The gas mixture was of a known isotopic composition and the vessels were sampled regularly over a 115 day sampling period.

Table 1 demonstrates the difference between stable carbon isotope results obtained on day 0 and the last day of sampling. The results show that the stainless steel cylinders, aluminium cylinders and the aluminium 5 layer bags showed the least amount of change over the > 100 day testing period. Although molecular composition was not analysed, the stability of the carbon isotope results suggest that the composition of the compounds are most likely stable.

Sampling from the glass vials and the wine bladders was terminated once it became obvious that the samples had become isotopically fractionated. The cause for isotopic fractionation within each type of vessel will vary. Causes may include leaking septa,

vessel not designed for gas storage, gas diffusion through the vessel wall, worn valves and vessel deterioration. Repeated sampling over time from the one vessel may exacerbate fractionation for the reasons mentioned above, therefore multiple vessels were left untouched for longer time periods prior to testing to reduce this risk.

Table 1: Difference of carbon isotope results between the first and the last day of sampling for CH₄ and CO₂.

Vessel	Difference between day 0 and day x, $\delta^{13}\text{CH}_4$ (‰ VPDB)	Difference between day 0 and day x, $\delta^{13}\text{CO}_2$ (‰ VPDB)	Time (days)	x	No. of times vessel was sampled during period
Stainless Steel Cylinder	0.1	0.1	115		59
Aluminium Cylinder	0.5	0.3	115		65
Glass Vial	20.9	6.7	23		16
Aluminium Wine Bladder	2.4	2.0	72		31
Tedlar Bag	0.8	9.4	113		51
Aluminium 5 layer Bag	0.1	0.0	113		53

Reusing sample vessels is another point of quality control that researchers and field researchers can manage to ensure that the sample integrity is maintained. Whilst most of the vessels are recommended as once use only, in reality these vessels are commonly used repeatedly. Experiments examining sample carryover and the measures employed to reduce sample carryover will be different for each vessel and in some cases it may be advisable to not reuse the vessel at all.

By understanding the limitations of the sample vessels and the importance of careful sampling technique, analysts can supply information on the constraints of the data generated and researchers can make decisions that allow their hard won samples to have high integrity such that high quality results over time can be generated.

Fluorescein: analysis and geochemical application in CO2CRC Otway Project

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The CO2CRC Otway Site in southwestern Victoria is Australia primary demonstration site for the geological storage of CO₂. Phase 1 of the project involved the injection of a CO₂-rich (~80:20 CO₂:CH₄) supercritical fluid into a depleted natural gas field at a depth of ~2 km. The project reached a major milestone late last year with the cessation of injection and the emplacement of around 65,000 tonnes of the supercritical fluid. Phase 2 of the project is set to commence in early 2011 with the injection a few 100 tonnes of pure CO₂ into a saline aquifer at ~1.5 km depth. Critical to the project was the drilling of the CRC-1 and CRC-2 wells, with both being used as injection wells. During drilling of each well, fluorescein dye was added to the drilling mud with the intention to maintain a concentration of 5 ppm w/v. The role of fluorescein was to 1) quantify the degree of drilling fluid contamination that may accompany autochthonous formation waters recovered with the multiple dynamic testing (MDT) tool, and 2) provide a measure of the depth of drilling mud penetration into the recovered cores in order to provide pristine material for microbiological studies.

During drilling, varying amounts of a concentrated fluorescein solution were added to the drilling mud at least twice per day (over 18 days for CRC-1 and 7 days for CRC-2) based on the fluorescein analyses performed on the filtered drilling fluid on-site using a Hach spectrophotometer. Invariably the fluorescein concentration in the drilling mud (soluble fluorescein; SF) was considerably less than the calculated amount based on the weight of fluorescein added and the total volume of drilling fluid within circulation (total fluorescein; TF). For CRC-1, the former averaged 4.7 ppm w/v while the latter gave a calculated average of 11.9 ppm w/v, giving a TF1/SF1 = 2.5. This compares to a similar fluorescein drilling mud content of 5.4 ppm w/v for CRC-2 but now the calculated value is much higher at 26.3 ppm w/v, resulting in a TF2/ SF2 ratio of 4.9. The rock successions in both wells are very similar and the reason for the greater fluorescein loss at CRC-2 is being investigated further. However, the 1.9 fold increase in fluorescein loss between CRC-2 and CRC-1 is similar to the 1.6 fold increase in the well cross-sectional areas (CRC-2 and CRC-1 wells' ID = 8½" and 6¾", respectively), suggesting that surface area of the suspended rock fragments may have a strong influence on fluorescein sorption (loss).

For the fluorescein penetration tests, selected recovered cores were washed with distilled water to remove drilling mud cake and wrapped in Al-foil and plastic wrap. Back in the laboratory, core plugs (1" OD) were air-drilled through representative

rock lithologies ranging from unconsolidated sandstone to claystone. Successive 2–3 mm layers either to the centre of the core or for the complete core were removed with a metal rasp or a dremal drill disc. The recovered rock material was powdered in a mortar and pestle and water solution of pH12 was added in a 2:1 v/w ratio, then the solution was sonicated, filtered and fluorescein concentration was measured using a Perkin-Elmer LS50B Luminescence Spectrometer. Figure 1 displays the fluorescein concentration for a claystone (Figure 1a) and a sandy claystone (Figure 1b) showing the variable decline in fluorescein concentration from the outside to the centre of the core from CRC-2. For microbiological studies, only approx 4–5 mm of the outer core would need to be removed to leave claystone virtually free of drilling mud contamination, whereas a 2 cm thick layer of core is required for the more permeable sandy claystone.

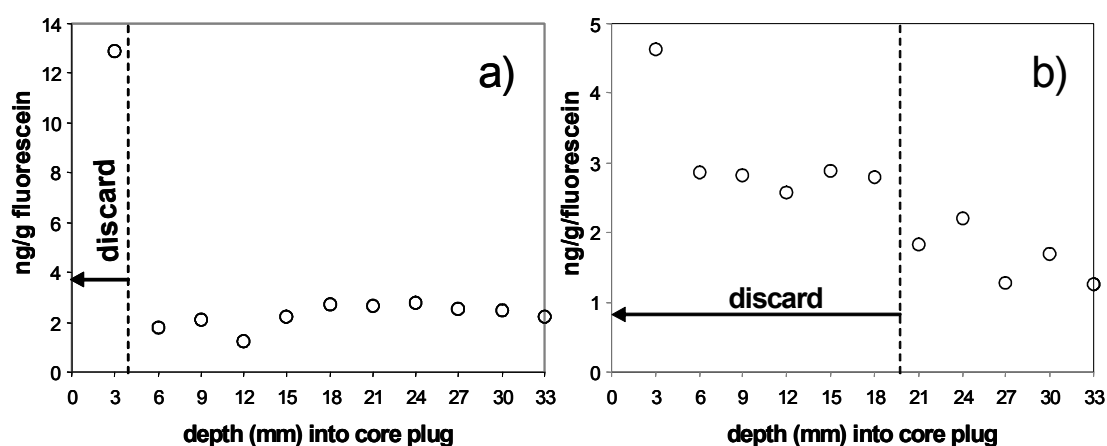


Figure 1: The fluorescein concentration (ng/g rock) versus depth (mm) from the outside of the core plug for a) claystone and b) sandy claystone.

Biogeochemical Evolution in Neoproterozoic Oceans: The search for a ‘turbid ocean’

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The fossil record indicates that the first morphologically-complex animal phyla appear in the Ediacaran (630-542 Ma) and rapidly diversify during the ‘Cambrian Explosion’ after 542 Ma (Xiao and Laflamme, 2009). Chemical, geological and isotopic evidence demonstrate that the oceans in the late Neoproterozoic (800 – 542 Ma) were subject to significant environmental and chemical change. Relationships between ocean chemistry and the evolution of organisms in the Neoproterozoic remain largely unclear. The aim of our study is to resolve some of the relationships between ocean chemistry and evolutionary events by testing the hypothesis of organically-loaded ‘Turbid Oceans’.

Logan *et al.* (1995) noticed a distinctive shift of biomarker assemblages as well as preservation of organic material across the Precambrian-Cambrian boundary. Bacterial biomarkers isolated from Proterozoic sediments appear unusually highly biodegraded indicating reworking in a stagnant organically-loaded water column. These conditions are thought to have dominated the carbon cycle for a quarter of Earth history between 1,800 – 580 Myr ago (Fike *et al.*, 2006; Logan *et al.*, 1995; Rothman *et al.*, 2003). In Phanerozoic sediments, preservation of algal lipids greatly improves due to rapidly sinking organic material due to larger organism size and the evolution of organisms which produce fecal pellets. This process is termed the ‘biological pump’ and was also thought to have facilitated oxygenation of the deeper ocean (Fike *et al.*, 2006).

A turbid ocean would firstly be populated by high levels of picoplankton-sized (0.2 -2 μm in size) bacteria thought to dominate the Neoproterozoic oceans due to the absence of predators before the late Ediacaran (Butterfield, 2009). Secondly, organic material in the turbid ocean would be highly biodegraded due to constant microbial reworking of material sinking slowly through the water column. Finally, the ocean state would be anoxic, or possibly euxinic (anoxic and sulfidic) or ferruginous, due to the lack of oxygen dissolved in the ocean at depth. At present, there is no direct geological evidence to suggest that such an ocean with suspended organic material existed. In this study we are using the above characteristics to test for the presence of a ‘Turbid Ocean’ using samples from the Centralian Superbasin, Australia and searching for evidence for a transition to a clear water, ventilated ocean state expected to coincide with the ‘Shuram excursion’ ~560 – 570 Ma (Fike *et al.*, 2006).

In this presentation, we will show newly acquired iron and sulfur speciation data and complementary biomarker assemblages from Neoproterozoic sections of the Centralian Superbasin. Our data indicate that the Neoproterozoic oceans in Australia were anoxic and ferruginous. In contrast to previous biomarker studies, our recent work has shown that Neoproterozoic molecular fossils are not as abundant as initially thought. The majority of biomarkers found in this study were contaminants from drilling fluids and diesel oil. In this study we found that samples older than 635 Ma did not have detectable amounts of indigenous steranes in the interior fraction, however they were abundant on the exterior surfaces of the drill core. Furthermore, indigenous steranes from samples dated between 635 Ma and the Precambrian-Cambrian boundary (~542 Ma) contained sterane ratios fundamentally different to those in the Phanerozoic (542 Ma - present).

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Biomarker distributions and stable isotopes (C, H) establish the age and palaeoenvironmental conditions spanning the Permian/Triassic in the northern onshore Perth Basin

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The Perth Basin is located in southwest Western Australia (WA). It is a deep, north to south trending basin, extending over 1,000 km from Geraldton to the north of WA (how far north is this?). The Perth Basin sediments comprise of rocks of Permian–Early Cretaceous in age. The Perth Basin petroleum system has been intermittently explored for the last few decades, resulting in the production of gas and oil from several onshore fields (e.g. Summons *et al.*, 1995). The perception that the area is gas prone has been challenged with the recent discovery of the near-shore Cliff Head oil field. The premier effective source rock for petroleum in the Perth Basin is the marine Kockatea Shale, with the hydrogen-richest interval being the Sapropelic Unit of the Hovea Member (use either a Thomas or Barber reference here). As well as being central to the petroleum prospectivity of the Perth Basin, particularly the lateral extent offshore of the Kockatea Shale, deposition of the Kockatea Shale was intimately associated with events spanning the Permo-Triassic mass extinction. Therefore, this study continues our focused research into better defining the age, organic facies and deposition conditions associated with this World class source rock and their link with the global system over this confined time interval.

The Perth Basin sediments used in this study are from the Senecio-1 drill core, which is located approximately 15.5 km from the north of Dongara (is this the distance from the town or the gas field?). In the present study bulk geochemical, biomarker and compound specific isotopic analysis (CSIA) of biomarkers will be used to further constrain the age and palaeoenvironmental conditions spanning the Permian/Triassic in the northern onshore Perth Basin and to compare these results with the Hovea-3 drill core ‘type-section’ (Grice *et al.*, 2005a). In particular, stable carbon and hydrogen isotopic composition of biomarkers measured by CSIA has been shown to be an effective tool for establishing biogeochemical changes across the Permian/Triassic boundary (Grice *et al.*, 2005a). For this purpose 31 samples from

the Senecio-1 cored interval were selected at 1 m spacing. The ages of the samples have been assessed by conodont biostratigraphy (can you expand on this?). Rock-Eval & TOC analysis have been carried out to identify the type and maturity of organic matter and to assess petroleum potential. The samples were then analysed following the methodology of Grice *et al.* [(2005b)]. Briefly, each sample was ground to a fine powder and extracted using an Accelerated solvent extractor. The extracts were separated into 6 fractions by liquid chromatography. Saturate and aromatic hydrocarbon fractions and were characterised by GC-MS. The saturated hydrocarbon fractions were separated from branched and cyclic hydrocarbons by treating with 5A molecular sieves and CSIA of biomarkers was performed for these fractions. Bulk stable isotopic compositions were measured on the kerogens isolated from the extracted powders. The results will be presented at the conference.

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Nature, origin, and precursor evolution of Indian fossil resins

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Resins are plant exudates which harden on atmospheric contact. They can occur as lumps in sediments or coal, or at a microscopic scale as the maceral resinite within coal and due to their non-degraded nature can be well-preserved for hundreds of millions of years. However, during the late stage diagenesis or an early stage catagenesis resins can make important contribution to crude oils by releasing several saturated and aromatic products. Fossil resins are ubiquitous in Indian coal and sediments; occur from Cretaceous to Miocene age. The Eocene resins have been collected from Cambay, Kutch Basins; Miocene resins are sourced from Kerala-Konkan, and Cauvery Basins, while the Cretaceous resin has been collected from Meghalaya (Assam-Arakan Basin). The major pyrolysis products of both Eocene and Miocene resins are cadalene based C₁₅ bicyclic sesquiterpenoids and their dimers bicadinanes (Figure 1a) identifying them as angiosperm Dipterocarpaceae-sourced dammar resins (Dutta *et al.*, 2009; Mallick *et al.*, 2009, Dutta *et al.*, 2010).

The main products of Cretaceous resin are diterpenoids of abietane type with significant amount of labdane derivatives (Figure 1b). These biomarkers are consistent with conifer (Gymnosperms) source (Langenheim, 1995) which contrasts the angiosperm (i.e., Dipterocarpaceae) origin of Cenozoic resins. The exclusive occurrence of abietane and labdane diterpenoid products suggests Pinaceae as a probable source.

The wide occurrence of sesquiterpenoids in SE Asian oils suggests dammar resins may be a significant regional precursor of petroleum hydrocarbons, and these may be important biomarkers for exploration purposes (i.e., source rock–oil and oil–oil correlations) in Indian sedimentary basins.

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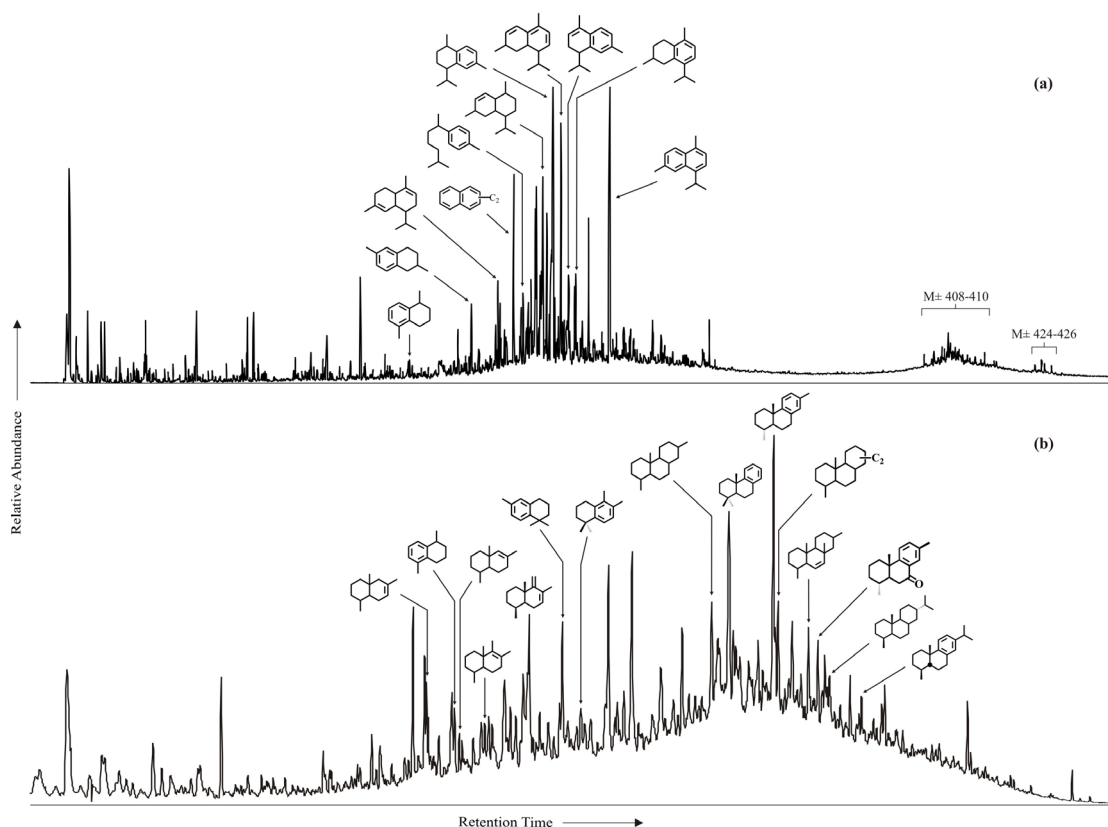


Figure 1: Total Ion Chromatograms of (a) Cenozoic resin sample from Vastan lignite mine, Cambay Basin; (b) Cretaceous resin sample from Meghalaya, Assam-Arakan Basin resulting from Pyrolysis-Gas Chromatography-Mass Spectrometry.

Genesis and Biogeochemical Evolution of Hydrocarbons in the Neo-Mesoproterozoic Sediments of the Yanshan Basin, North China

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The Yanshan Basin is located on the northern margin of the North China Plate and is bounded on the north by the greater Xing'an-Mongolian Orogenic Belt and on the south side by the Inner North China Plate and the Bohai Bay. It can be divided into the Jibei, Xuanlong and Liaoxi major depressions. Since 1977 oil seeps have been found in the Jibei Depression, and these are extensive in the Xiamaling and Tieling Formation of the Neo-Mesoproterozoic, which are thus regarded as effective petroleum systems. However, for Precambrian organic matter, there are significant difficulties doing oil-source rock correlations because of the likely high thermal maturity of the sedimentary organic matter, the sometimes low organic matter abundance, the small amount of geochemical information, and problems of contamination and over-printing. One solution is the geochemical analysis of the oil trapped in fluid inclusions (FI), which is a powerful technique for understanding the evolution of petroleum within a reservoir. Thus, oil-bearing FIs hosted in vein calcite of a limestone sample from the Tieling Formation and in quartz of a bitumen-bearing sandstone from the Xiamaling Formation were chosen for detailed analyses by the Molecular Composition of Inclusions (MCI) protocols. In addition, twenty samples from the reservoirs have been sequentially extracted as a supplement to the MCI analysis. In order to get more reliable geochemical information on high thermal maturity potential source sequences, three outcrop source rocks were sampled from the Hongshuizhuang and Gaoyuzhuang Formation and kerogen catalytic hydrogenation (HyPy) was performed.

Hopanes, tricyclic terpanes and bicyclic sesquiterpanes are abundant in the FI oils and most samples from the reservoir sequences, and their ratios suggest dominantly microbial input under a reducing deep water environment. However, steranes were below detection limit in the FI oils, and also in the source rocks of the Hongshuizhuang Formation which was deposited under anoxic conditions. The distribution of monomethylalkanes in the reservoir sequence FI oils and most reservoir extracts correlate well with the organic-rich marine Hongshuizhuang Formation and is different from the Gaoyuzhuang Formation. Maturity parameters based on biomarkers, alkanes and aromatic hydrocarbons indicate that the FI oils and most reservoir sequential extracts have reached the peak stage of the oil generation window, indicating that the Hongshuizhuang Formation is the main source rock of this area, according to its maturity in the oil window. Furthermore, some specific 13 α -tricyclic terpanes which were only detected in the FI oils (see [Table 1](#)), most reservoir extracts and the Hongshuizhuang Formation also supports this deduction. However, some reservoir sequential extracts contain different geochemical signatures, including higher 2 α (H)-methylhopanes, less abundant 3 β -methylhopanes and rich steranes, which indicate cyanobacterial and algal

input. In association with other parameters, such as a lower gammacerane index and a higher R_c (%) (based on MPI_1) and $C_{30} \alpha\beta/(\alpha\beta+\beta\alpha)$ ratios, these data suggest that these extracts are derived from the Gaoyuzhuang Formation, which was deposited in a shallow water oxic environment and which has experienced high thermal maturity. Following these oil-source correlations, and combined with the geological background, the history of this palaeo-oil reservoir accumulation has been reconstructed. In particular, the region received early petroleum charge that was possibly from the Gaoyuzhuang Formation source rock before dolerite intrusion (ca. 1327Ma). A late oil charge occurred during the Yanshan movement when the Hongshuizhuang Formation source rock generated and expelled mature oil. This has a more significant oil contribution in terms of its large oil generation potential and tectonic dynamics.

Table 1: Semi-quantitative Analysis of hydrocarbons

Sample details Compounds	Reservoir rock EOMs, Oil seeps/Bitumen							Source Rock EOMs				
	Xiamaling			Tieling			Hongshuizhuang	Wumishan	Hongshuizhuang		Gaoyuzhuang	
	JQ2-16 EOM-3	KC-HP- 3 EOM-3	PQ-SD- 21 FI oil	JQ2-22 EOM-3	JQ2-24 EOM-4	KC-TS- 9 FI oil	JQ2-29 EOM-4	JQ1-w-3 EOM-3	JQ1-H- 48	KC2-5 _CH	JQ3- 191	GR151- 1 _CH
2+3-Methylalkanes (C_{14} - C_{20})	0000000	0000000	0000000	0000000	0000000	0000000	0000000	0000000	0000000	000000	000	0000
7+8+9-Melthy C_{17}	0000000	0000000	0000	0000000	0000000	000	0000000	0000	000	000	o	oo
Pregnane+ homopregnane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	tr.	o
C_{27} - C_{29} Sterane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	tr.	oo
C_{29} Sterane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	tr.	o
$C_{14} \alpha\beta$ bi-sesquiterpanes	oo	o	o	ooo	oo	ooo	o	o	ooo	o	n.d.	n.d.
$C_{15} \alpha\beta$ bi-sesquiterpanes	oo	oo	o	ooo	oo	ooo	oo	o	ooo	oo	o	o
Drimane + HomoDrimane	ooo	ooo	oo	oooo	oo	oooo	oo	oo	oooo	oooo	o	oo
C_{19} 13 α (H) tri-terpane	oo	ooo	o	oooo	oo	ooo	oo	oo	ooo	oooo	n.d.	n.d.
C_{19} + C_{20} tri-terpanes	ooo	ooo	o	ooo	ooo	ooo	oo	ooo	ooo	ooo	o	o
Tri-terpanes	ooo	oooo	oo	oooo	oooo	oooo	ooo	ooo	oooo	ooo	oo	oo
Hopanes	ooo	ooo	o	ooo	ooo	ooo	ooo	oo	oo	oo	o	o
C_{24} tetra-terpane	oo	ooo	o	ooo	ooo	oo	oo	ooo	oo	oo	o	o
$C_{29} \alpha\beta$ hopane	ooo	ooo	o	ooo	ooo	ooo	oo	o	oo	o	o	o
$C_{30} \alpha\beta$ hopane	ooo	ooo	o	ooo	ooo	ooo	ooo	o	oo	oo	o	oo
C_{31} 2 α - methylhopane	o	o	o	o	o	o	o	o	tr.	o	o	o
C_{31} 3 β -methylhopane	o	o	o	o	o	o	o	o	tr.	o	o	o
Ts	oo	ooo	o	oo	ooo	ooo	ooo	ooo	oo	oo	o	o
C_{29} Ts	oo	ooo	o	oo	ooo	ooo	ooo	oo	oo	oo	o	o
C_{29}^*	oo	oo	o	o	oo	oo	oo	o	oo	o	o	o
C_{30}^*	oo	oo	o	oo	ooo	oo	ooo	o	oo	oo	o	o
Gammacerane	o	o	o	o	o	o	o	o	tr.	o	n.d.	tr.
DBT	0000000	000000	oo	0000	ooo	oo	ooo	0000	ooo	o	oo	ooo
DBF	0000000	0000	o	ooo	ooo	o	ooo	00000	oo	o	o	ooo

Note: Sample name with FI oil based on MCI, EOM based on sequential extraction, CH based on HyPy; n.d. , not detectable; tr., trace; o, <15 ng/g; oo, 15~50 ng/g; ooo, 50~200 ng/g; oooo, 200~300 ng/g; ooooo, 300~800 ng/g; 800~2500 ng/g; >2500 ng/g

Application of Biological markers to Characterize Petroleum and source rocks of Southern Indus Basin of Pakistan

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Biomarkers are important constituents of petroleum source rocks, oils and coal. They represent diagenetically defunctionalised product of specific natural product precursors. The most effective biomarkers have high taxonomic specificity, potential for preservation, and limited number of well defined sources and recalcitrant against geochemical changes. Therefore these compounds are highly specific for a given source and depositional environment. The distribution and relative abundance of these compounds permit information on the key geological issues like source, depositional environment, maturity of organic matter, possible pathway and relative migration distance, extent of biodegradation, basin modeling and oil-source correlation.

In Southern Indus Basin, sediments from Triassic to Quaternary age are characterised by significant variations in lithofacies, organic matter input and depositional environments. These variations are likely to produce petroleum with different geochemical characteristics. The information regarding the existence of source rocks and their potential to generate oil or gas, timing and temperature of hydrocarbon expulsion is obtained from pyrolysis experiments, biomarker and stable isotopic analyses. Application of source rock maturity and timing of oil/gas expulsion will be used to identify source rock characteristics, petroleum systems and their geographic boundaries within Southern Indus Basin, using techniques like Rock Eval, GCMS, GC-IRMS. 21 oil samples from various oil fields of Southern Indus Basin will be studied. Many of these are condensates with high API values. 20 sediment samples of different formations of Pasahki Deep-1 are selected. Laki and Ranikot Formation shales of Tertiary age have good TOC values and hydrocarbon generating potential and thermally immature according to rock Eval data. Cretaceous sequence is dominant in the area and Upper Goru, Lower Goru and Sembar Formations show good TOC values. Sembar and some parts of the lower Goru are considered as the major source rocks with kerogen belonging to a mixture of type II and III. Jurassic sequence consists of Chilton and Datta Formations. Chilton lime stones have poor TOC values and hydrocarbon generating potential. Organic matter will be extracted from the sediment samples for further studies. Quantitative and qualitative potential of source rocks will be reported on the basis of distribution of biomarker and non-biomarker parameters. Petroleum rich sites from different geological ages and

formations will be indicated for exploration prospectuses. The study will assist exploration geoscientists in locating new horizons for oil and gas in Pakistan.

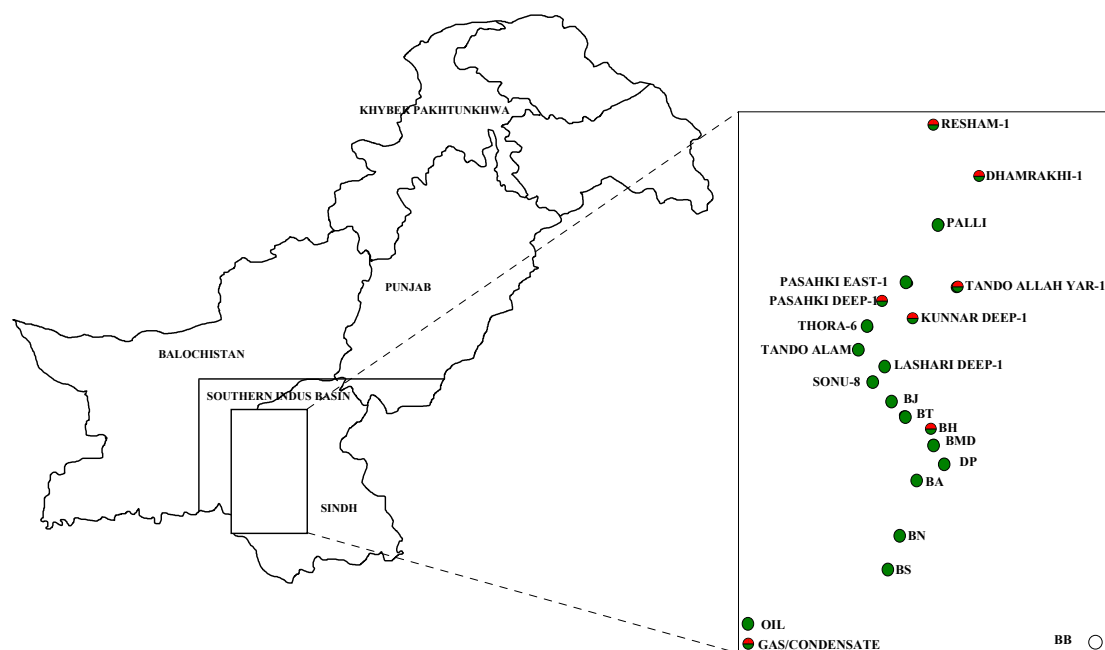


Figure 1: Sampling locations

Laser micropyrolysis GCMS of hydrocarbon bearing fluid inclusions and petroleum source rocks

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An advanced laser micropyrolysis GCMS facility has been established at the Wuxi Institute of Petroleum Geology for the primary objective of analysing oil bearing fluid inclusions. Special features of this instrument include an Eximer pulsed laser source tuned to an output of 193 nm and a newly designed laser-GC inlet system. UV wavelengths of the order of 193 nm were able to drill through the sedimentary quartz in which the oil inclusions typically occur. The purpose built inlet which interfaces the laser microprobe to an Agilent 6890II/5975C GC-MSD system comprises a simplistic single section 1/8# glass line SS tubing with dual zone temperature regulation (up to 350°C) to allow the laser pyrolysates to be cryo-focussed onto an isolated zone, whilst using very high carrier gas flows to efficiently transfer the pyrolysates from the moderately heated sample chamber (e.g. 120°C).

A wide molecular weight range of gaseous to liquid hydrocarbon products have been successfully detected from the analysis of selected fluid inclusions with this facility. GCMS data from the laser micropyrolysis of blue and yellow fluorescing fluid inclusions in calcites from the Tarim Basin, Xin Jiang Province China are shown in Figure 1:

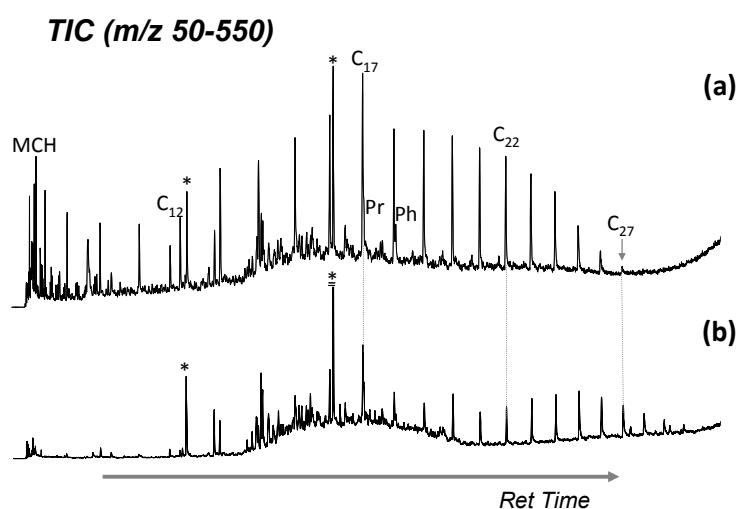


Figure 1: Laser pyrolysis GCMS analysis of (a) blue; and (b) yellow fluid inclusions from the Tarim basin. MCH= methylcyclohexane, C_n =n-alkane, Pr=pristane; Ph=phytane; *=analytical artefact.

The data shown represents the combined hydrocarbon content of a few large sized (~50 µm) inclusions separately opened by the laser. The total ion chromatogram (TIC) is dominated by n-alkanes ranging from below C10 up to C27. The high MW end represents a significant improvement on the ~C19 limit of previously reported data from the laser micropyrolysis GCMS analyses of hydrocarbon bearing fluid inclusions (Greenwood *et al.*, 1998; Volk *et al.*, 2009). A large range of alkyl aromatics and higher MW PAHs were also detected. These and a distinctive unresolved complex mixture were more significant in the TIC of the yellow inclusions. Conversely, the n-alkanes and low MW cycloalkane and alkene gases were of higher relative abundance in the blue inclusions. Further analyses are underway to more robustly assess the relationship between fluid inclusion colour and hydrocarbon composition. The high quality of these data increases optimism for the potential petroleum exploration value of the GCMS analysis of laser selected inclusions.

Whereas pulsed 193 nm is the optimal irradiation source for quartz hosted fluid inclusions, it proved less ideal for analysis of consolidated sediments, which was attributed to the pulsed Q-Switch mode of operation. Much higher pyrolysate concentrations were obtained by CW laser irradiation (532 nm, 1064 nm) of source rocks than Q-switch pulsed irradiation (1064 nm, 266 nm) at several different wavelengths. The high peak-power of the Q-switched pulses might be overly efficient at dissociating organic compounds to a basic elemental level. Alternatively, smaller fragments may reassemble into large molecules unamenable to GC detection – e.g., previous laser ablation studies of coal showed the almost exclusive production of fullerene ions (Greenwood *et al.*, 1994).

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Using organically preserved soft tissue to explore the evolution and preservation of the unique fauna from the Gogo Formation, Western Australia

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Fossilization is usually a rather destructive process involving loss of soft tissues and distortion of hard tissues, but a few exceptional localities provide fully three-dimensional specimens with preserved soft anatomy. Some of the finest examples come from the 380 million year old (Devonian) Gogo Formation of Western Australia, which yields primitive fossil fishes and arthropods containing 3D musculature and abdominal organs (Long *et al.*, 2010). The Devonian reef complexes are exposed over 350km with the fossils preserved in carbonate nodules that occur in the basinal shales between the reefal outcrops. The fossils have become the nucleus of a rapidly-formed fine-grained limestone concretion. The rapid formation of the concretion is demonstrated by the 3-dimensional preservation of the fossils prior to compaction by sedimentary pile weight, and the fact that even the most delicate structures like perichondral tubes around cartilage are preserved intact and often in articulation. Fossils are revealed through acetic acid digestion but this has recently been demonstrated to destroy the majority of the soft tissue preserved. While the original bone hydroxyapatite remains, the muscle tissues have phosphatised (apatite crystals). Initially only small pieces of phosphatised body wall musculature was recovered, most likely preserved through bacterially mediated phosphatisation (Trinajstić *et al.*, 2007). However, recent field work has yielded many specimens with extensive soft tissues preserved. The rate at which microbes gain access to the tissues is controlled by the rate of decay. In the fossil fish the best preservation is when soft tissues is pressed against plates or scales of the body creating a local anoxic compartment which is more favourable to rapid phosphatisation.

In addition to muscle tissue the Gogo Formation preserves the earliest known vertebrate organs including a gut, liver and heart. These are suspended in light and dark calcite cements. The internal organs have been replaced by sparry calcite and in rare instances by barite. In some fishes the liver is consistently replaced by barite. The barite is dendritic and its interrelationship with the calcite indicates that the two minerals were co-precipitated. It is here suggested that original preservation was by bacterial action on decaying sulfur- containing organic matter under reducing

conditions and that this has been secondarily oxidised to barite and calcium sulfate. $\delta^{34}\text{S}$ value of a sulfate bearing mineral (-3 per mil) in the abdominal region clearly supports a microbially-reduced sulfur source. Trace element contents are also been used to reconstruct the composition of the solution involved.

Through off-line pyrolysis and on-line pyrolytic and gas chromatography-mass spectrometry (GCMS) analyses of fossil muscle and muscle tissue from extant fishes, a direct comparison between the macromolecules present in fossil and extant taxa can be done for the first time. The structural analysis by pyrolysis-gas chromatography mass spectrometry of ancient fish scales (Devonian) has revealed a series of aliphatic components (alkenes and alkanes) and a series of low-molecular-weight aromatic hydrocarbons ranging up to C_{16} (including phenol) representative of the biopolymer selectively preserved. These are comparable to modern fish scales.

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New molecular marker and spectroscopic tools for reconstructing wildfire history from sedimentary records

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The wildfire regimes of Australia have been changing during the late Quaternary under the influence of changing climate and vegetation, and by anthropogenic impact. Wildfires are an important parameter in the biosphere-climate system and affect the carbon cycling. Thus, reconstructing their history helps to understand palaeoenvironmental conditions and is essential to project future biosphere-climate interactions and associated carbon cycles.

Late Quaternary wildfire reconstruction has mainly been based on dated (^{14}C , ^{210}Pb , ^{137}Cs) lake sediment cores, where the number of microscopically detected charcoal particles (=fire residues) has served as the raw data for assessing the past fire frequency. Quantifying (microscopically) visible charcoal may reflect the relatively large and structurally sound charcoal particles from forest fires. However, this technique is less likely to quantify smaller charcoal fractions derived from grasses, for example – probably the main contributor of charcoal in Australia's vast savannas and open grassy woodlands (*Figure 1*).

Therefore, we are developing a new methodology to infer past wildfires from lacustrine sediments by using geochemical tools. Such geochemical methods could assess the whole size range of charred fire residues in sedimentary records and could yield additional information about the burned vegetation when only microscopically invisible fire residues are present. In particular, we are adapting a geochemical marker method (benzene polycarboxylic acids (BPCA)) for this task. BPCA have been used for almost a decade as unambiguous molecular markers for the presence of fire-derived organic matter in soil, and in a recent laboratory ring trial have been proven to be a robust tool for the quantification of charred fire residues. So far, however, this geochemical marker method has not been adapted to quantify fire residues in lake sediment cores.

In order to validate and calibrate the BPCA method for sedimentological fire reconstruction, we use two well characterized and dated (^{14}C , ^{210}Pb) lake sediment cores from Australia: Quincan Crater from the tropical north and Bega Swamp from the temperate south of the continent. They exhibit distinct vegetation (pollen) and wildfire histories (charcoal counting method) – data, that can be compared to the results of the BPCA method. In addition, we are examining these cores with MIR-PLS (Mid InfraRed spectroscopy coupled to a Partial Least Square analysis), which is another geochemical method that can detect charred organic material independent of

its particle size. We are using it as a screening method to locate interesting sections of the cores and it should provide another dataset of fire residue contents, to which the subsequent BPCA analysis can be compared. We will report preliminary results of this MIR-PLS analysis.

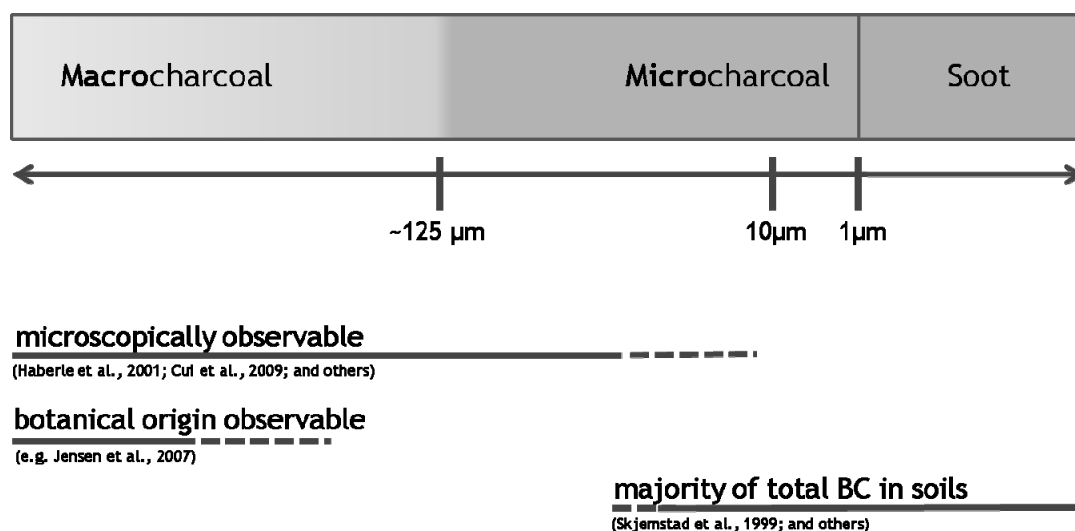


Figure 1: Charcoal size fractions and their microscopical observability. It is obvious that the majority of fire residues (=charcoal=Black Carbon=BC) in soils and probably also in sediments cannot be detected by microscopical methods. Therefore we are adapting a molecular marker method (BPCA) that could aid sedimentological fire reconstruction.

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Spatial and temporal variation of vegetation in the Nature Reserve of Macquarie Marshes (NSW, Australia) reflected by organic geochemical proxies

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The Macquarie Marshes, located in semi-arid central NSW, are a Ramsar wetland site renowned for its high biodiversity and role as a 'refuge' for flora and fauna. In the past 100 years, it has experienced dramatic decline due to the drought and anthropogenic river regulation.

In this study, 12 surface samples as well as 15 sections from one short core (70 cm in length) collected in the Nature Reserve of Macquarie Marshes were investigated. We aim to study the spatial and temporal variation of vegetation in this area and find out the cause of these changes. The analysis of organic geochemical proxies includes bulk organic carbon and nitrogen (TOC, TN, C/N ratio), carbon and nitrogen isotopes ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$), as well as some organic biomarkers (focusing on aliphatic hydrocarbons). Some modern plants (ferns, charophytes, reeds, *Eucalyptus*, etc.) and biota (black swan guano) samples, which were most abundant in the Macquarie Marshes, were also analysed for comparison with the sediment samples.

TOC values in surface samples range between 2 to 5% and are generally higher in the northern Marshes than in the southern Marshes, indicating more organic input. The TOC and TN curves exhibit similar trends along time, decreasing to only one tenth at the depth of 70 cm. The bulk $\delta^{13}\text{C}$ values of surface samples (less than 50 years old) vary from -23‰ to -26‰, falling within the range of values found in modern biota (-21.6‰) and plants (-27.0 to -31.5‰). The calculated C/N ratios range from 10 to 25, and together with $\delta^{13}\text{C}$ values suggests that the organic matter is mainly derived from terrestrial C_3 plants. The contribution of aquatic plants is shown by shifts to higher $\delta^{13}\text{C}$ values and lower C/N values in the core sections at 40 cm depth ([Figure 1](#)).

The aliphatic hydrocarbons in the sediments consist mainly of C_{14} – C_{31} *n*-alkanes with total absolute and organic C normalized concentrations ranging from 0.22 to 70.96 $\mu\text{g g}^{-1}$ and 0.24 to 147.91 $\mu\text{g g}^{-1}$ TOC. The *n*-alkanes data show differences in molecular profiles from C_{14} to C_{31} . However, the dominant component in the long-chain *n*-alkanes was either $n\text{-C}_{27}$ or C_{29} . The CPI_{25-31} (Carbon Preference Index) values are in the range of 1.05-5.81, indicating a strong odd-even carbon number predominance. The Pr/Ph (pristane:phytane) ratios are low (0.05-0.49, [Figure 1](#)), suggesting organic matter production under low-oxygen conditions in the Macquarie Marshes. The

temporal variation of proxies calculated by absolute aliphatic hydrocarbons concentrations in MMB3 core profile show that vegetation types in the watershed of the Macquarie Marshes has an obvious change at 40 cm depth, ~ 130 years ago (*Figure 1*). Grasses dominated in the watershed before 130 years ago, and trees dominated afterwards, suggesting the loss of wetland area in the Macquarie Marshes.

In conclusion, these organic geochemical proxies indicate (1) Spatially, the northern Marshes are much better preserved than the Southern Marshes with more vegetation cover. (2) Temporally, the vegetation in the wetland system have an obvious change from grass dominance to tree dominance about 130 years ago, after the European arrival (perhaps water diverted for irrigation lead to the decline of the wetland ecosystem).

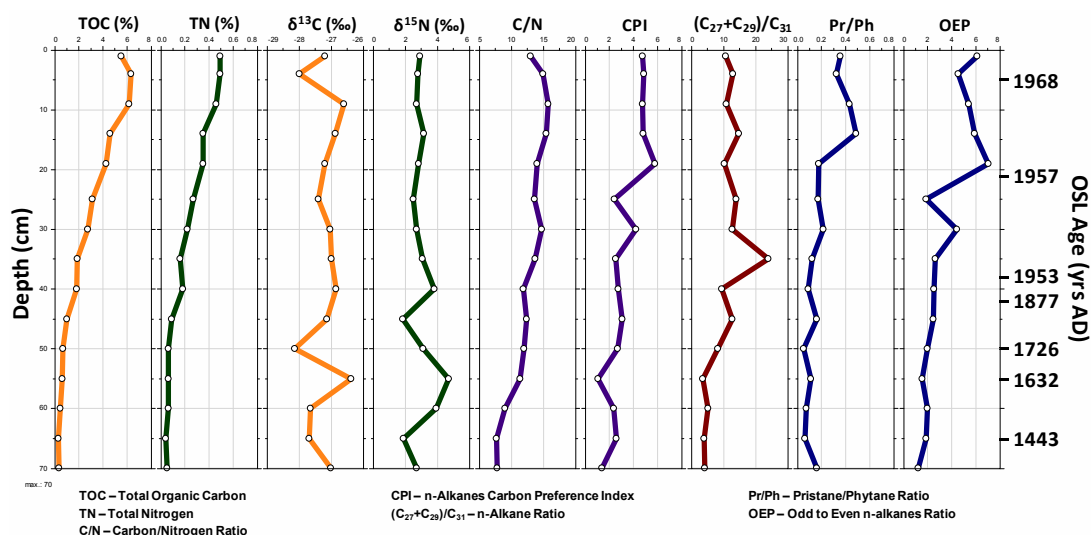


Figure 1: Organic Geochemical Proxies and Chronology of MMB3 Core Profile

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An extraction process appropriate for studies of hydrogen isotope fractionations during plant lipid biosynthesis

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The stable hydrogen isotopic composition of plant-derived lipids provide a valuable source of information on past growth environment (hence climate) reconstruction (Sachs *et al.*, 2009; Nabbefeld *et al.*, 2010; Schefuß *et al.*, 2003), plant photosynthetic mode discrimination (Chikaraishi *et al.*, 2004), metabolic pathways (Grice *et al.*, 2008; Zhou *et al.*, 2010) and status diagnosis (Zhang *et al.*, 2009). Understanding the isotopic fractionations at each and all steps leading to the synthesis of specific or groups of plant lipids is crucial for determining the contribution of the three immediate sources of hydrogen in lipid molecules (cellular water, precursor compounds and bioreductant NAD(P)H).

Compound-specific isotopic analysis of the hydrogen (CSIA-H) of lipid molecules isolated from higher plants will aid such an endeavour as it promises a molecular-level averaged isotopic measurement. In order to make meaningful CSIA-H, a few requisites need to be met: 1) significant concentrations of extractable lipids 2) no new or inhibition of normal metabolic intermediates and end products, i.e. no isolation-induced metabolic change or branching; 3) preservation of isotopic integrity, i.e., no isotopic fractionation as a result of chemical change such as functional group gain or loss (for example, the hydration of double bonds during heat-treatment of samples in aqueous medium, the dehydration of alcohol to form spurious unsaturations) or physical change such as drying (at ambient laboratory conditions, with heating, under vacuum or a N₂-stream) or as a result of physicochemical interaction accompanying partitioning of molecules between mobile and stationary phases when subjected to chromatographic separation (column chromatography or thin layer chromatography) during sample workup or during isotopic analysis by GC-IRMS; 4) if isotopic fractionation is unavoidable, it has to be demonstrated that correction can be made systematically.

Low molecular weight, unsaturated and functionalised lipids such as monoterpene and sesquiterpenoids (hydrocarbons, alcohols, and aldehydes) present the biggest challenge as they are volatile, susceptible to oxidation and other chemical changes upon exposure to air and light. In this abstract, we report a small scale method that streamlines extraction, chromatographic separation and drying of lipid molecules of interest under an oxygen-free environment. We will demonstrate that isotopic fractionation during sample workup can be avoided by a low-temperature process which does not use direct heating or chromatographic separation. The method is well suited to analyse volatile, unsaturated and functionalised lipids as well as other stable lipid molecules.

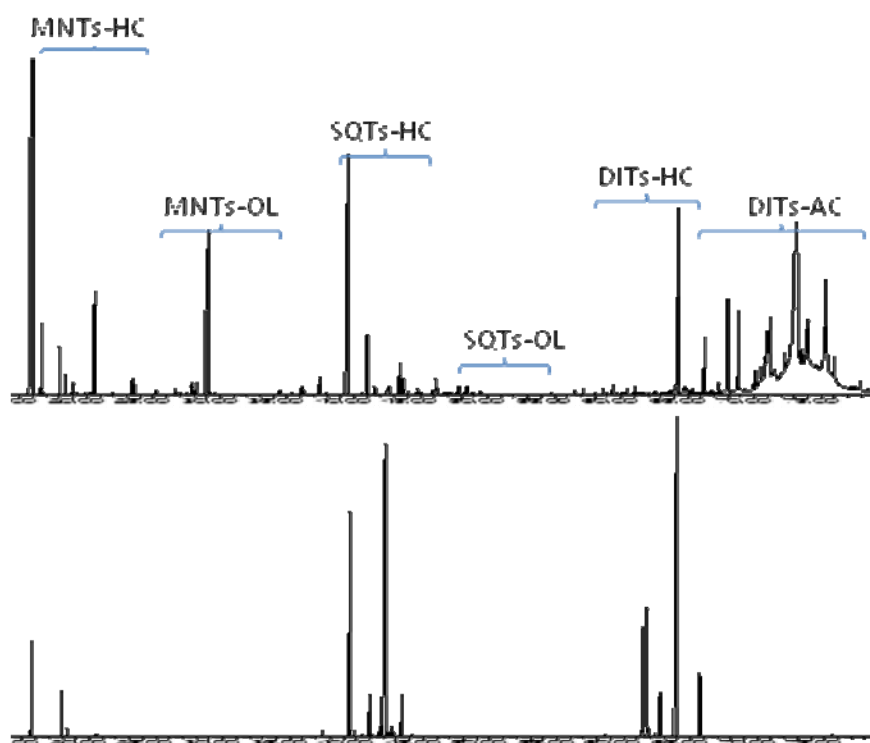


Figure 1: TIC highlighting monoterpenoids (MNTs), sesquiterpenoids (SQTs) and diterpenoid (DITs) hydrocarbons (HC), alcohols (OL) and acids (AC, analysed as free acids) from the GC/MS analysis of fresh needle (lower) and wood (upper) of field-grown *Pinus radiata*.

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