

**School of Science
Department of Chemistry**

**Organic Geochemistry of the Paleoproterozoic Here's Your
Chance Pb/Zn/Ag Deposit**

Alexander I Holman

**This thesis is presented for the Degree of
Doctor of Philosophy
of
Curtin University**

January 2014

Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Alexander I Holman

Perth, 25th September 2014

Abstract

The Barney Creek Formation (BCF) is a 1.64 Ga marine shale deposited in the McArthur Basin, Northern Territory, Australia. Immature sections of the formation contain some of the best-preserved known Proterozoic biomarkers; hence the area has been extensively used in paleoenvironmental reconstructions of the middle Proterozoic. The BCF is host to the Here's Your Chance (HYC) deposit, the largest of the sediment-hosted Pb/Zn/Ag deposits in Northern Australia. The deposit was formed by the action of a metal-rich hydrothermal fluid, and sedimentary organic matter (OM) at the deposit has been highly affected by hydrothermal alteration. It has also been proposed that a significant quantity of OM was carried with the mineralising fluid and deposited at HYC, overprinting the signal of indigenous OM.

The precipitation of base metal sulfide deposits requires large amounts of reduced sulfur. It was generally believed that formation of these deposits during the middle Proterozoic was linked to the global development of euxinic oceans. Recent evidence suggests however that ferruginous conditions may have predominated during this period, and that euxinia may have been limited to localised areas such as restricted basins. The analysis of sedimentary OM is a powerful tool for the detection of ocean euxinia. The organic products of sulfate-reducing bacteria and phototrophic sulfur bacteria persist in sediments after diagenesis, providing reliable evidence for euxinic conditions. Such evidence has been found in unmineralised sediments from the BCF, but has not been detected in the mineralised zones of HYC due to the hydrothermal alteration that occurred during deposition.

The aim of this PhD project is to apply novel organic geochemical techniques with the potential to characterise sedimentary OM impacted by hydrothermal alteration to the HYC deposit. The non-traditional techniques used were required to detect organic evidence of the microbial environment in which the deposit was formed. OM extracted from within the kerogen / mineral matrix (Bitumen II) was analysed for preserved hydrocarbons indigenous to the deposit. $\delta^{34}\text{S}$ of elemental sulfur (S^0) and organic sulfur were also measured as reduced sulfur species are sensitive indicators of depositional conditions. The effects of hydrothermal alteration on OM in mineral deposits were also investigated. Maturity parameters based on polycyclic aromatic hydrocarbons (PAHs) were used to compare the thermal histories of freely-extracted

and mineral-bound hydrocarbons. Micro-Scale Sealed Vessel pyrolysis (MSSVpy) was employed to simulate the effects of hydrothermal alteration on an immature, organic-rich sediment from the BCF.

Freely-extractable organics (Bitumen I) from HYC were strongly affected by alteration or migration. Organics preserved within the kerogen / mineral matrix (Bitumen II) are believed to be resistant to these effects and may therefore more accurately reflect the depositional environment. If Bitumen I was not fully extracted before acid digestion, the remainder would contaminate Bitumen II and render the results invalid. In **Chapter 2** a Soxhlet extraction of Bitumen I from a HYC sample was broken into a number of time periods, with the extract from each period quantified separately and compared with Bitumen II isolated from the same sample pit. PAH maturity parameters show a decrease with successive extractions, as the more stable β isomers are extracted slightly more efficiently leaving the residual with more α isomers. It was found that over 99.8 % of phenanthrene and methylphenanthrenes were extracted after 72 hours, so these compounds are not expected to remain after extraction to contaminate Bitumen II. Further, PAH maturity parameters determined for the final extraction stages were significantly different from Bitumen II. PAHs with four or more aromatic rings were extracted more slowly, but after 72 hours 90 % of coronene and 95 % of all other PAHs were removed. It was concluded that Bitumen II isolated from HYC contained a negligible amount of residual Bitumen I and can thus be reliably interpreted as originating from within the kerogen / mineral matrix.

In **Chapter 3** Bitumen II was analysed from five HYC sample pits as well as the underlying W-Fold Shale Formation. Bitumen II contained a highly distinctive distribution of long-chain *n*-alkanes up to C₃₇ or C₃₈, and three samples showed a predominance of even carbon numbers. These features were not observed in Bitumen I, which had a maximum range up to *n*-C₃₂ and no carbon number predominance. The $\delta^{13}\text{C}$ of Bitumen II *n*-alkanes ranged from -32 to -34 ‰, which is 4 to 7 ‰ depleted compared to Bitumen I *n*-alkanes. Comparison with $\delta^{13}\text{C}$ of isolated kerogen strongly suggested that Bitumen II *n*-alkanes are indigenous to HYC. The long-chain, isotopically-light *n*-alkanes with even-over-odd predominance were interpreted as evidence for the presence of sulfate-reducing bacteria and phototrophic sulfur bacteria, indicating that the deposit was formed under euxinic conditions that

extended into the photic zone. The thermal maturities of Bitumens I and II were compared by evaluating PAH maturity parameters. Bitumen II contained a greatly-reduced proportion of methylphenanthrene isomers compared to Bitumen I, so parameters based on both phenanthrene and methylphenanthrenes were lower in Bitumen II than Bitumen I. It was hypothesised that as Bitumen II is occluded within the kerogen / mineral matrix it may be less able to exchange methyl groups with other aromatic hydrocarbons. The methylphenanthrene ratio parameter, which is based solely on methylphenanthrene isomers, is similar for both Bitumens I and II.

Chapter 4 details the use of MSSVpy to simulate the hydrothermal alteration experienced by sedimentary OM during the deposition of HYC. A low-maturity, unmineralised sample from the Glyde River region of the BCF was pyrolysed at 300, 330 and 360 °C for 72 hours. The pyrolysis resulted in the destruction of aliphatic biomarkers and the formation of PAHs with up to six aromatic rings. The values of PAH maturity parameters consistently increased with higher pyrolysis temperatures. The MPI-1 parameter was lower than observed at HYC due to a reduced proportion of methylated isomers in the pyrolysate, possibly due to cracking of the alkyl-aromatic bond during pyrolysis. High-molecular weight PAHs were formed in increasing abundances at higher pyrolysis temperatures, but even at 360 °C the amounts produced were far below those at HYC. The pyrolysis time or applied temperatures may not have been sufficient to simulate the full production of these compounds. To assess the effect of abundant sulfide minerals on organic maturation, the pyrolysis experiments were repeated with the addition of pure PbS or ZnS. The sulfide minerals had a considerable effect on the behaviour of PAH ratios, causing a slight increase at 300 °C and a large decrease at 360 °C. It is hypothesised that the sulfide mineral surfaces may cause a retardation of methylation and demethylation reactions, although the mechanism is currently unknown.

In **Chapter 5** the $\delta^{34}\text{S}$ of S^0 and organic sulfur in kerogen were measured to complement previous $\delta^{34}\text{S}$ analyses of pyrite, sphalerite and galena from the deposit. Both S^0 and organic sulfur were enriched by 6 to 7 ‰ compared to the first generation of HYC sulfide minerals. This enrichment is broadly consistent with measurements of co-existing S^0 , organic sulfur and sulfide minerals from a range of recent and ancient samples. It is believed that S^0 and organic sulfur were formed contemporaneously with the first generation of sulfide minerals at HYC and share a

common sulfur source. A simplified model of the sulfur cycle during the deposition of HYC was proposed in which sulfate originating from seawater was reduced to sulfide with $\delta^{34}\text{S}$ between 0 and +5 ‰. This sulfide reacted with abundant metal ions to form the base metal sulfides. Oxidation of the remaining sulfide produced S^0 , along with polysulfides that were incorporated into sedimentary OM. The $\delta^{34}\text{S}$ of organic sulfur increased from +5 to +8 ‰ along the flow path of the mineralising fluid, suggesting that the sulfate transported with the fluid was progressively enriched through the process of Rayleigh distillation.

This PhD project has explored new aspects of the organic geochemistry of the HYC Pb/Zn/Ag deposit. Bitumen II has revealed evidence of sulfate-reducing bacteria and phototrophic sulfur bacteria in highly mineralised and thermally-altered samples. Together with $\delta^{34}\text{S}$ measurements of kerogen and S^0 , this evidence suggests that the HYC deposit was formed under euxinic conditions. MSSVpy of an unmineralised BCF sample has closely simulated the effects of hydrothermal alteration, and revealed that sulfide minerals may significantly affect the behaviour of sedimentary OM during thermal maturation. This project has demonstrated that novel organic geochemical techniques have great potential in the study of ore deposits.

Acknowledgements

This project seems to have been both a long and exhausting journey and an incredibly quick and exciting one. I've learnt so much during my PhD, not just about organic geochemistry and ore deposits but about myself as well. A very sincere thanks to all those that have helped me along the way.

Firstly of course to my supervisor Prof. Kliti Grice: for her wisdom and guidance in all areas of this project, for her patience and willingness to take the time when I needed help, for her endless enthusiasm and scientific curiosity, for pushing me out of my comfort zone and giving me some amazing opportunities to travel and present at conferences all around Australia and the world, for giving me great freedom and encouragement to explore my own ideas, and for her warmth and kindness throughout these three years. I knew very little about organic geochemistry when I started, but Kliti must have recognised some potential in me. With her help I think I've produced some good work and had a great time in the process!

Thanks also to my co-supervisors Drs. Caroline Jaraula, Katy Evans and Chris Yeats. I thank Caroline for help in the laboratory at the start of my project, and for always being a friendly face and a great source of advice. I am very grateful to Katy for her heroic efforts in teaching this chemistry student the ins and outs of geology, and for always providing a fresh and interesting perspective in scientific discussions. As my CSIRO co-supervisor, Chris has given helpful scientific advice and great support throughout the project.

Sincere thanks to A/Prof. Paul Greenwood, who has been something of an unofficial supervisor. Paul has provided great help with the pyrolysis and sulfur isotope studies as well as in the preparation of this thesis, and has always been ready with a friendly word and good advice. I am most grateful to the two examiners of this thesis; Dr. Linda Stalker and Prof. Pierre Adam, for their time and effort in providing detailed and helpful reviews.

The WA-OIGC is not only a great centre of research but a fun and friendly place to work, thanks to the many wonderful people with whom I've shared my time here.

These include Dr. Lyndon Berwick, Dr. Alison Blyth, Hendrik Grotheer, Siyu 'Shirley' Hu, Mojgan Ladjavardi, Dr. Sabine Lengger, Dr. Robert Lockhart, Ines Melendez, Dr. Sebastian Naeher, Anais Pages, Chloe Plet, Aileen Robert, A/Prof. Kate Trinajstic, Dr. Svenja Tulipani and Dr. Martijn Woltering, plus visitors Dr. Melissa Burke and Kate Thompson. Special mention must go to Dr. Jeff Dick for accompanying me on a number of exciting trips and being a great room-mate, as well as a source of scientific inspiration. I am exceedingly grateful to Geoff Chidlow for his tireless technical support with GC-MS, pyrolysis and general laboratory matters, and for remaining patient and helpful in the face of my endless problems and questions. Thanks also to Dr. Steve Clayton for assistance with compound-specific isotope analysis, and to Tanya Chambers, Alicia Harrison, Marija Predojevic and the other administrative staff for all their support.

It has been a privilege to collaborate with some brilliant researchers from around the world. Sincere thanks to A/Prof. Arndt Schimmelmann for the opportunity to visit the beautiful Indiana University and work in his laboratory, and for his support in and out of the laboratory. Thanks also to Dr. Peter Sauer, Ling Gao, Agnieszka Furmann and Katarina Topalov for their help and friendship during my time there, and also to Mojgan Ladjavardi for travelling with me and helping to make the trip a very enjoyable one.

I thank A/Prof. Jochen Brocks for kindly providing the sample from the Barney Creek Formation, for the chance to visit his laboratory at ANU, and for his scientific advice throughout my project. I would also like to thank Prof. Michael Böttcher for $\delta^{34}\text{S}$ analyses and for sharing his vast experience with sulfur isotopes, Dr. John Walshe for his thoughtful suggestions on the same paper, Dr. Greg Skrzypek for $\delta^{13}\text{C}$ measurements of kerogen and Robert Herman for his support with HPLC.

The funding for my project has been provided by the CSIRO Organic Geochemistry of Mineral Systems Cluster, directed by Jonathan Law. As part of the Cluster I have attended some productive and thought-provoking workshops and had valuable discussions with researchers from a variety of fields. Apart from those already acknowledged, these include Drs. Robert Hough, James Cleverley and Louise Fisher from CSIRO, Prof. Campbell McCuaig from UWA and Dr. John Moreau from the University of Melbourne. I have been fortunate to have had valuable discussions with

international collaborators Profs. Lorenz Schwark, Roger Summons and David Leach, and have greatly benefitted from their collective wisdom and experience.

Completing a PhD is not only about laboratory experiments and writing papers. Thanks to my fellow chemistry PhD students Amanda, Patrick, Rhys, Mark, Krish, How, Vassy and Dan for providing entertainment, distraction and occasional free food. Thanks also to my friends in the 'real world' for keeping me sane and reminding me that there is a life outside of chemistry.

The final words go to my family. This project is in many ways a culmination of my many years of education, and through it all you have always been there to support and guide me. I could never have achieved all that I have without your patience, understanding and love.

Primary publications

This thesis is assembled from publications in international peer-reviewed journals, which form the individual chapters as listed below.

Chapter 2

Holman A.I., Grice K., Jaraula C.M.B., Schimmelmann A., Brocks J.J., 2012. Efficiency of extraction of polycyclic aromatic hydrocarbons from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag ore deposit and implications for a study of Bitumen II. *Organic Geochemistry* **52**, 81-87 (impact factor 2.828).

Chapter 3

Holman A.I., Grice K., Jaraula C.M.B., Schimmelmann A., 2014. Bitumen II from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag deposit: implications for the analysis of depositional environment and thermal maturity of hydrothermally-altered sediments. *Geochimica et Cosmochimica Acta* **139**, 98-109 (impact factor 4.250).

Chapter 4

Holman A.I., Greenwood P.F., Brocks J.J., Grice K. Effects of sulfide minerals on aromatic maturity parameters: laboratory investigation using micro-scale sealed vessel pyrolysis. *Organic Geochemistry* in press 2014 (impact factor 2.828).

Chapter 5

Holman A.I., Grice K., Greenwood P.F., Böttcher M.E., Walshe, J.L., Evans, K.A. New aspects of sulfur biogeochemistry during ore deposition from $\delta^{34}\text{S}$ of elemental sulfur and organic sulfur from the Here's Your Chance Pb/Zn/Ag deposit. *Chemical Geology* **387**, 126-132 (impact factor 3.482).

Statement of contributions of others

The work presented in this thesis was primarily designed, conducted, interpreted and written by the first author (Alex Holman). Contributions by co-authors are detailed below.

Chapter 2

Kliti Grice provided the sample. Arndt Schimmelmann designed the acid digestion procedure. Alex Holman, Kliti Grice and Jochen Brocks designed the sequential extraction experiment. Acid digestions, Soxhlet extractions, fractionation of organic extracts and GC-MS analysis of organic extracts were conducted by Alex Holman. Arndt Schimmelmann provided analytical facilities and laboratory support for the acid digestion procedure. Kliti Grice provided all other analytical facilities. Caroline Jaraula provided laboratory support for the sequential extraction experiment. Alex Holman was the primary author of the manuscript with contributions from all co-authors. Funding was provided by the CSIRO Organic Geochemistry of Mineral Systems Cluster.

Chapter 3

All samples were provided by Kliti Grice. Arndt Schimmelmann designed the acid digestion procedure. Alex Holman and Kliti Grice designed the GC-MS and compound-specific isotope experiments. Acid digestions, Soxhlet extractions, fractionation of organic extracts, GC-MS and GC-irMS analyses of organic extracts were conducted by Alex Holman. Arndt Schimmelmann provided analytical facilities and laboratory support for the acid digestion procedure. Kliti Grice provided all other analytical facilities. Caroline Jaraula provided laboratory support for extraction and fractionation procedures. Alex Holman was the primary author of the manuscript with contributions from all co-authors. Funding was provided by the CSIRO Organic Geochemistry of Mineral Systems Cluster.

Chapter 4

Jochen Brocks provided the sample from the Barney Creek Formation. Alex Holman, Kliti Grice and Paul Greenwood designed the pyrolysis experiments. Alex Holman prepared the sample tubes and conducted the pyrolysis and GC-MS analyses. Paul Greenwood provided laboratory support for the pyrolysis experiments. All analytical facilities were provided by Kliti Grice. Alex Holman was the primary author of the manuscript with contributions from all co-authors. Funding was provided by the CSIRO Organic Geochemistry of Mineral Systems Cluster.

Chapter 5

The samples were provided by Kliti Grice. Alex Holman, Kliti Grice and Paul Greenwood designed the experiments. Sample preparation, extraction and quantification of elemental sulfur, and isolation of kerogen were conducted by Alex Holman. Michael Böttcher measured the $\delta^{34}\text{S}$ of elemental sulfur and kerogen. Kliti Grice provided all other analytical facilities. Alex Holman was the primary author of the manuscript with contributions from all co-authors. Funding was provided by the CSIRO Organic Geochemistry of Mineral Systems Cluster.

Secondary publications

Manuscripts and abstracts based on work that was conducted during this PhD project.

Peer-reviewed journal articles not part of this thesis

Dick J.M., Evans K.A., **Holman A.I.**, Jaraula C.M.B., Grice K., 2013. Estimation and application of the thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature. *Geochimica et Cosmochimica Acta* **122**, 247-266 (impact factor 4.250).

Dick J.M., Evans K.A., **Holman A.I.**, Leach D., Grice K. Combined sulfur, carbon and redox budget constraints on genetic models for the Here's Your Chance Pb-Zn deposit, Australia. *GeoResJ*, accepted 2014.

Peer-reviewed book chapters not part of this thesis

Greenwood P.F., Amrani A., Sessions A., Raven M.R., **Holman A.I.**, Dror G., Grice K., McColloch M.T., Adkins, J.F., 2015. Development and initial biogeochemical applications of compound specific sulfur isotope analysis. In: *Principles and Practice of Analytical Techniques in Geosciences* (ed. Grice K.). Royal Society of Chemistry, Oxford. pp 285-312.

Conference presentations

* directly related to this thesis

***Holman A.**, Grice K., Jaraula C., Schimmelmann A., 2011. Organic geochemistry of entrapped bitumen within kerogen/mineral matrix of an Australian Late Paleoproterozoic lead-zinc-silver deposit. 25th International Meeting on Organic Geochemistry, Interlaken (poster presentation).

- Pages A., Grice K., Lockhart R., **Holman A.**, Melendez I., van Kranendonk M., Jaraula C., 2011. Biomarkers of sulfate reducing bacteria from a variety of different aged samples including a modern microbial mat. 44th American Geophysical Union Fall Meeting, San Francisco.
- Dick J., Evans K., **Holman A.**, Jaraula C., Grice K. 2012. Thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature. 22nd V.M. Goldschmidt Conference, Montreal.
- ***Holman A.**, Grice K., Jaraula C., Dick J., Schimmelmann A., Evans K., 2012. Organic geochemical insights into the formation of the Here's Your Chance lead-zinc-silver deposit. 22nd V.M. Goldschmidt Conference, Montreal (oral presentation).
- Dick J., Evans K., **Holman A.**, Jaraula C., Grice K., 2012. Thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature. 34th International Geological Congress, Brisbane.
- ***Holman A.**, Grice K., Jaraula C., Dick J., Schimmelmann A., Evans K., Yeats C. 2012. Additional insight into ore formation from biological markers in the kerogen-mineral matrix of the Here's Your Chance lead-zinc-silver deposit. 34th International Geological Congress, Brisbane (oral presentation).
- ***Holman A.I.**, Grice K., Jaraula C.M.B., Dick J.M., Evans K.A., Schimmelmann A., Brocks J.J., Greenwood P.F., 2012. Analysis of organic matter preserved within the kerogen-mineral matrix of the Paleoproterozoic Here's Your Chance Pb-Zn-Ag deposit. 17th Australian Organic Geochemistry Conference, Sydney (oral presentation).
- Greenwood P., McCulloch M., Grice K., **Holman A.**, Sessions A., Hong L., Ling H., Jin S., 2013. Compound specific $\delta^{34}\text{S}$ analysis – development and applications. 26th International Meeting on Organic Geochemistry, Tenerife.
- ***Holman A.I.**, Grice K., Jaraula C.M.B., Evans K.A., Greenwood P.F., Schimmelmann A., Brocks J.J., Bottcher M.E., Walshe J.L., Yeats C. J., 2014. Organic geochemistry of the Paleoproterozoic 'Here's Your Chance' Pb/Zn/Ag deposit. 24th V.M. Goldschmidt Conference, Sacramento (oral presentation).

Dick J., Evans K., **Holman A.**, Leach D., Grice K., 2014. Combined sulfur, carbon and redox budget constraints on genetic models for clastic-dominated base-metal sulfide deposits. Examples from the Here's Your Chance Pb-Zn deposit, Australia. 24th V.M. Goldschmidt Conference, Sacramento.

Table of contents

Declaration	ii
Abstract	iii
Acknowledgements	vii
Primary publications	x
Statement of contributions of others	xi
Secondary publications	xiii
Table of contents	xvi
List of figures	xxii
List of tables	xxvii
Abbreviations	xxix

Chapter 1

Introduction	1
Organic geochemistry	1
The carbon cycle	1
Sedimentary OM	2
Biomarkers	4
Polycyclic aromatic hydrocarbons	6
Organic geochemistry of mineral deposits	8
Stable isotopes	9
Stable isotope ratios and measurement techniques	9
Stable carbon and hydrogen isotopes	11
Organic sulfur isotopes	13
The Barney Creek Formation and the Here's Your Chance deposit	14
Geological setting	14

Environment and ecosystem of the Barney Creek Formation and wider McArthur Basin	15
Formation of the HYC deposit.....	17
Organic geochemistry of the HYC deposit.....	19
Aims of this thesis.....	20
Chapter 2	21
Chapter 3	21
Chapter 4	22
Chapter 5	22
References	23
Appendix 1	40

Chapter 2

Efficiency of extraction of Polycyclic Aromatic Hydrocarbons from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag ore deposit and implications for a study of Bitumen II	42
Abstract	43
Introduction	44
Materials and methods.....	45
Sample description	45
Sequential extraction.....	46
Extraction of Bitumen II.....	47
Gas chromatography – mass spectrometry (GC-MS)	48
Results and discussion.....	48
Saturate fractions.....	48
Aromatic fractions.....	48
Bitumen II.....	52

Implications for ore formation.....	54
Conclusions.....	55
Acknowledgements.....	56
References	56
Appendix 2	61

Chapter 3

Bitumen II from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag deposit: implications for the analysis of depositional environment and thermal maturity of hydrothermally-altered sediments.....	62
Abstract	63
Introduction	64
Materials and methods.....	65
The Barney Creek Formation and the Here's Your Chance deposit.....	65
Extraction and separation of Bitumen II	67
Isolation of kerogen.....	67
Gas chromatography mass spectrometry (GC-MS)	68
Stable carbon isotope analysis	68
Results	69
Bitumen II saturated hydrocarbons	69
Stable carbon isotope analysis	69
Bitumen II aromatic hydrocarbons	70
Discussion	72
Sources of saturated compounds.....	72
Aromatic hydrocarbons in Bitumens I and II	76
Conclusions.....	81
Acknowledgements.....	82

References	82
Appendix 3	89
Chapter 4	
Effects of sulfide minerals on aromatic maturity parameters: laboratory investigation using micro-scale sealed vessel pyrolysis.....	90
Abstract	91
Introduction	92
Materials and methods.....	94
Sample site and description	94
Sample preparation.....	95
Pure metal sulfides	95
Micro-scale sealed vessel pyrolysis and GC-MS analysis	96
Correction factors.....	97
Simulated maturation of Barney Creek sediment by MSSVpy.....	98
Overall product distribution.....	98
Methylated phenanthrene ratios.....	99
High MW PAHs.....	102
Effects of metal sulfides on simulated thermal maturation.....	104
Methylated phenanthrene ratios.....	104
High-MW PAHs	106
Conclusions.....	108
Acknowledgements.....	108
References	109
Appendix 4	117

Chapter 5

New aspects of sulfur biogeochemistry during ore deposition from $\delta^{34}\text{S}$ of elemental sulfur and organic sulfur from the Here's Your Chance Pb/Zn/Ag deposit	119
Abstract	120
Introduction	121
Materials and methods.....	123
Geologic setting	123
Sample storage and preparation.....	123
Quantification of S^0	124
Isolation of kerogen and S^0 for isotopic measurements	124
Measurement of sulfur isotopic composition	124
Results and discussion.....	125
Distribution of sulfur species in HYC sediments	125
$\delta^{34}\text{S}$ of kerogen and S^0	127
Model of sulfur transformations at HYC	131
Conclusions.....	135
Acknowledgements.....	135
References	136

Chapter 6

Conclusions	145
 Depositional environment and sulfur biogeochemistry of HYC	146
 Effects of hydrothermal alteration on HYC OM.....	147
 Application of novel organic geochemical techniques to ore deposit studies	148
 Limitations and future work	149

Bibliography..... 151
Appendix 181

List of figures

Chapter 1

Figure 1.1: Summary of the biogeochemical carbon cycle. Figure modified from Killops and Killops (2005).....	2
Figure 1.2: Simplified model of the biogeochemical sulfur cycle illustrating the formation of biosynthetic and diagenetic organic sulfur, along with elemental sulfur and metal sulfides. SOB: sulfide-oxidising bacteria. Figure modified from Canfield (2001).	4
Figure 1.3: Approximate range of $\delta^{13}\text{C}$ from a variety of carbon sources, primary producers and fossil fuels. SRB: sulfate-reducing bacteria. Data from Peters et al. (2005), Schidlowski (1988), Londry et al. (2004) and Melendez et al. (2013).	12
Figure 1.4: Map of northern Australia showing the HYC deposit and other major Pb/Zn deposits, plus stratigraphy of HYC showing the distribution of the eight ore bodies. Figure modified from Ireland et al. (2004a) and Williford et al. (2011).	15
Figure 1.5: Genetic model for the HYC deposit. Mineralising fluids flowed through the Tawallah Group and Wologorang Formation, leaching base metals and generating PAHs. They then flowed upwards through the Emu fault to the BCF. The inserts depict (A) a replacement model where sulfides are deposited between sedimentary layers, and (B) exhalative mineralisation where sulfides precipitate in a euxinic ocean. Figure modified from Greenwood et al. (2013).	18
Figure 1.6: Location of the five sample pits of the HYC deposit following the estimated flow path of the mineralising fluid (red arrows). Figure modified from Williford et al. (2011).....	20
Figure A1.1: Structures referred to in the text.....	40

Chapter 2

- Figure 2.1:** Cumulative extraction efficiency of individual PAHs in Bitumen I (as % of total amount extracted after 144 hours). Low MW PAHs show higher extraction efficiency than high MW PAHs. *n*-Alkanes are almost 100 % extracted within the first four hours.....50
- Figure 2.2:** Selected PAH ratios for sequential extraction and Bitumen II. Solid lines track instantaneous value of the PAH ratio for each sequential extraction step. Dashed line is the value for Bitumen II. The ratios are: (A) MPI-1, (B) MPR, (C) phenanthrene / methylphenanthrenes, (D) chrysene / phenanthrene, (E) benzo[*ghi*]perylene / phenanthrene and (F) coronene / phenanthrene.51
- Figure 2.3:** Cumulative extraction efficiency of phenanthrene and methylphenanthrenes in Bitumen I (as % of total amount extracted after 144 hours). The parent PAH is extracted with the highest efficiency. The β isomers 2- and 3-methylphenanthrene are extracted with slightly higher efficiency than the α isomers (MP - methylphenanthrene).52
- Figure 2.4:** Residual PAH ratios for sequential extraction and Bitumen II. Solid lines show the value of the PAH ratio for the bitumen remaining after the specified time. The dashed line is the value for Bitumen II. The ratios are: (A) MPI-1, (B) MPR, (C) phenanthrene / methylphenanthrenes, (D) chrysene / phenanthrene, (E) benzo[*ghi*]perylene / phenanthrene and (F) coronene / phenanthrene.54
- Figure A2.1:** Structures referred to in the text.....61

Chapter 3

- Figure 3.1:** Total ion chromatograms of (A) pit 1 Bitumen II saturate fraction, (B) pit 3 Bitumen II saturate fraction and (C) pit 1 Bitumen II aromatic fraction. *n*-Alkanes in (A) and (B) are marked with red circles and even carbon numbers are labelled. Labels in (C) are a: phenanthrene, b: methylphenanthrenes, c: pyrene, d: chrysene + triphenylene, e: benzo[*e*]pyrene, f: benzo[*ghi*]perylene and g: coronene.....73

- Figure 3.2:** $\delta^{13}\text{C}$ of *n*-alkanes from Bitumen I (carbon number range C_{18} to C_{21}), Bitumen II (ranges $\text{C}_{16} + \text{C}_{18}$ and C_{24} to C_{32}) and bulk $\delta^{13}\text{C}$ of isolated kerogen from HYC sample pits. Bitumen I data was taken from Williford et al. (2011). Error bars are one standard deviation. The box labelled WFS refers to the W-Fold Shale unit, which underlies the mineralised sections of the deposit.75
- Figure 3.3:** Selected PAH ratios calculated for Bitumens I and II. (A) methylphenanthrene index (MPI-1) and (B) methylphenanthrene ratio (MPR). Equations of MPI-1 and MPR are shown in Appendix 3. Bitumen I data was taken from Williford et al. (2011). The boxes labelled WFS refer to the W-Fold Shale unit, which underlies the mineralised sections of the deposit.77
- Figure 3.4:** Relative proportion of phenanthrene (P) and methylphenanthrenes (MP) for (A) Bitumen I and (B) Bitumen II. Bitumen I data was taken from Williford et al. (2011).79
- Figure A3.1:** Structures of PAHs discussed in the text. Positions of methylation are indicated for naphthalene and phenanthrene. Equations of the methylphenanthrene index (MPI-1) and methylphenanthrene ratio (MPR) are taken from Radke et al. (1982). Equation of the carbon preference index (CPI) is taken from Marzi et al. (1993). Equation of the Average Chain Length (ACL) is adapted from Poynter & Eglinton (1990).89

Chapter 4

- Figure 4.1:** Total ion chromatogram from MSSVpy of the BCF sample, pyrolysed at 300 °C for 72 hours, with no added metal sulfides. Labelled peaks are listed in Table 4.3.99
- Figure 4.2:** Summed m/z 202 + 228 + 252 + 276 chromatograms from MSSVpy of the BCF sample at each pyrolysis temperature, with no added metal sulfides. Pyrolysis temperatures are (A): 300 °C, (B): 330 °C, (C): 360 °C. Fla: fluoranthene, Pyr: pyrene, BaAn: benzo[*a*]anthracene, Chry: chrysene,

Tpn: triphenylene, BePy: benzo[*e*]pyrene, BaPy: benzo[*a*]pyrene, BPerly: benzo[*ghi*]perylene. 103

- Figure 4.3:** Selected PAH ratios from MSSVpy. (A) methylphenanthrene index 1 (MPI-1), (B) methylphenanthrene ratio (MPR), (C) methylphenanthrene index 3 (MPI-3) and (D) ratio of four to six ring PAHs over phenanthrene (PAH / P). Data points are the average of duplicate measurements, error bars show the range of measurement. Shaded areas in A to C represent the range from the HYC deposit, reported by Williford et al. (2011). The range of PAH / P reported by Williford et al. (2011) is 2.2 to 7.9..... 107
- Figure A4.1:** Structures referred to in the text..... 117

Chapter 5

- Figure 5.1:** $\delta^{34}\text{S}$ of kerogen and S^0 from the five HYC sample pits. Error bars indicate uncertainty of 0.3 ‰..... 127
- Figure 5.2:** $\delta^{34}\text{S}$ of kerogen from the five HYC sample pits (error bars indicate uncertainty of 0.3 ‰), plotted against average $\delta^{13}\text{C}$ of PAHs (reported by Williford et al., 2011). The input of ^{13}C -enriched, non-indigenous PAHs decreases from pits 1 to 5 (page 129). 128
- Figure 5.3:** Box-and-whisker plots of $\delta^{34}\text{S}$ data for kerogen and S^0 from HYC (this study) and previously-reported $\delta^{34}\text{S}$ of sulfide minerals from HYC and the McArthur Basin. Whiskers show the full range of reported $\delta^{34}\text{S}$, boxes represent the middle 50 % of the data (first to third quartiles). Estimated isotopic composition of Paleoproterozoic seawater sulfate (+20 to +25 ‰: Strauss, 1993) is indicated by the lightly shaded area. 1 Eldridge et al. (1993), 2 Ireland et al. (2004), 3 Johnston et al. (2008), 4 Shen et al. (2002)..... 130
- Figure 5.4:** Proposed scheme for the formation of organic sulfur, S^0 and sulfide minerals at HYC. Details of the scheme are discussed on pages 131-134. Boxes represent the $\delta^{34}\text{S}$ of the various sulfur species (vertical axis is not to scale), and arrows represent predicted fractionations during transformation processes. $\delta^{34}\text{S}$ values in bold were measured either in this

study (S^0 and organic sulfur) or by previous researchers. $\delta^{34}S$ values in italics are predictions calculated from the measured values and fractionations reported in previous studies. 1 Strauss (1993), 2 Canfield (2001a), 3 Shen et al. (2002), 4 Machel et al. (1995), 5 Eldridge et al. (1993), 6 Ireland et al. (2004), 7 Zerkle et al. (2009), 8 Amrani et al. (2006), 9 Amrani and Aizenshtat (2004), 10 Anderson and Pratt (1995)..... 133

List of tables

Chapter 1

Table 1.1: The average atomic abundances (%) of stable isotopes of common elements relevant in organic geochemistry. Data from Berglund and Wieser (2011).....	9
-----------------------------------------------------------------------------------------------------------------------------------------------------------------------	---

Chapter 2

Table 2.1: Mass of extracted PAHs (ng g ⁻¹ extracted rock powder) and PAH ratios for sequential extracts and Bitumen II.	49
-------------------------------------------------------------------------------------------------------------------------------------------------	----

Chapter 3

Table 3.1: Average chain length (ACL) and carbon preference index (CPI) for Bitumen II <i>n</i> -alkanes, plus stable carbon isotope ratios ($\delta^{13}\text{C}$) of <i>n</i> -alkanes and isolated kerogen. $\delta^{13}\text{C}$ is given as the average of repeated analyses, with one standard deviation shown in parentheses and the number of analyses in superscript. CPI was calculated using the generalised formula of Marzi et al. (1993), with $n = 7$ and $m = 17$. WFS – W-Fold Shale unit.	70
----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	----

Table 3.2: Quantification of selected PAHs present in Bitumen II aromatic fractions, plus calculated PAH ratios for Bitumens I and II. Bitumen I ratios were calculated from data presented by Williford et al. (2011).	71
-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	----

Chapter 4

Table 4.1: Precise weights of BCF sample and metal sulfides for the mixtures sub-sampled for MSSVpy experiments.	96
------------------------------------------------------------------------------------------------------------------------------	----

Table 4.2: Diagnostic ions and mass spectral correction factors for major PAH products. Data used in calculation of correction factors are shown in Table A4.1.....	97
----------------------------------------------------------------------------------------------------------------------------------------------------------------------------	----

Table 4.3: Major products from MSSVpy of the BCF sample at 300 °C for 72 hours, with no added metal sulfides.....	100
--------------------------------------------------------------------------------------------------------------------------	-----

Table 4.4: PAH ratios measured from MSSVpy analyses. Values are reported as the average of duplicate measurements, with the range of measurement in parentheses. 104

Table A4.1: Data used in the calculation of mass spectral correction factors for major PAH products. Correction factors were determined by calculating the correlation between abundances from total ion chromatograms (TIC) and extracted ion chromatograms (EIC) for each compound. 118

Chapter 5

Table 5.1: $\delta^{34}\text{S}$ of kerogen and S^0 for the five HYC sample pits (error is $\pm 0.3\text{‰}$), plus masses of sulfur contained in kerogen and S^0 in the five HYC sample pits, reported in μg of sulfur per g of rock. Average masses of sulfur in sulfide minerals were calculated from data reported by Huston et al. (2006) for ZnS and PbS, and Lambert and Scott (1973) for FeS_2 126

Abbreviations

ACL.....	average chain length
BACQ.....	branched alkanes with quaternary carbons
BCF.....	Barney Creek Formation
BSR.....	bacterial sulfate reduction
CD.....	clastic-dominated deposit
CPI.....	Carbon Preference Index
CSIA.....	compound-specific isotope analysis
DBT.....	dibenzothiophene
DCM.....	dichloromethane
EIC.....	extracted ion chromatogram
GC-MS.....	gas chromatography-mass spectrometry
HYC.....	Here's Your Chance
IAEA.....	International Atomic Energy Agency
ICP-MS.....	inductively-coupled plasma mass spectrometry
irMS.....	isotope ratio mass spectrometry
MeOH.....	methanol
MSSVpy.....	Micro-Scale Sealed Vessel pyrolysis
MP.....	methylphenanthrene
MPI.....	methylphenanthrene index
MPR.....	methylphenanthrene ratio
MW.....	molecular weight
OM.....	organic matter

Abbreviations

P	phenanthrene
PAH	polycyclic aromatic hydrocarbon
PSB	phototrophic sulfur bacteria
PZE	photic zone euxinia
R ₀	vitrinite reflectance
S ⁰	elemental sulfur
SEDEX	sedimentary-exhalative deposit
SRB	sulfate-reducing bacteria
TIC	total ion chromatogram
T _m	17 α -22,29,30-trisnorhopane
TOC	total organic carbon
T _s	18 α -22,29,30-trisnorneohopane
TSR	thermochemical sulfate reduction
VCDT	Vienna Cañon Diablo Troilite
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water

Chapter 1

Introduction

Organic geochemistry

The carbon cycle

Organic geochemistry studies the transformations undergone by organic matter (OM) in the Earth system. As such it considers the geological fate of carbon, which is an essential element for all life on Earth. Organic carbon is strongly linked to inorganic carbon, as the majority of organic carbon is produced from atmospheric CO₂ by photosynthesis (Falkowski, 2012).

Figure 1.1 shows a simplified representation of the biogeochemical carbon cycle. The major sources and sinks of carbon are: atmospheric CO₂, animal and plant biomass, sedimentary OM (including fossil fuels), carbonate minerals, marine HCO₃⁻ and carbon in deeply buried metamorphic rocks and the mantle (Des Marais, 1997; Killops and Killops, 2005). Major processes of carbon transfer between these pools have occurred since the Archean, but the relative importance of different processes

has been strongly influenced by changes in atmospheric and oceanic redox conditions and the concurrent evolution of life (Des Marais, 1997).

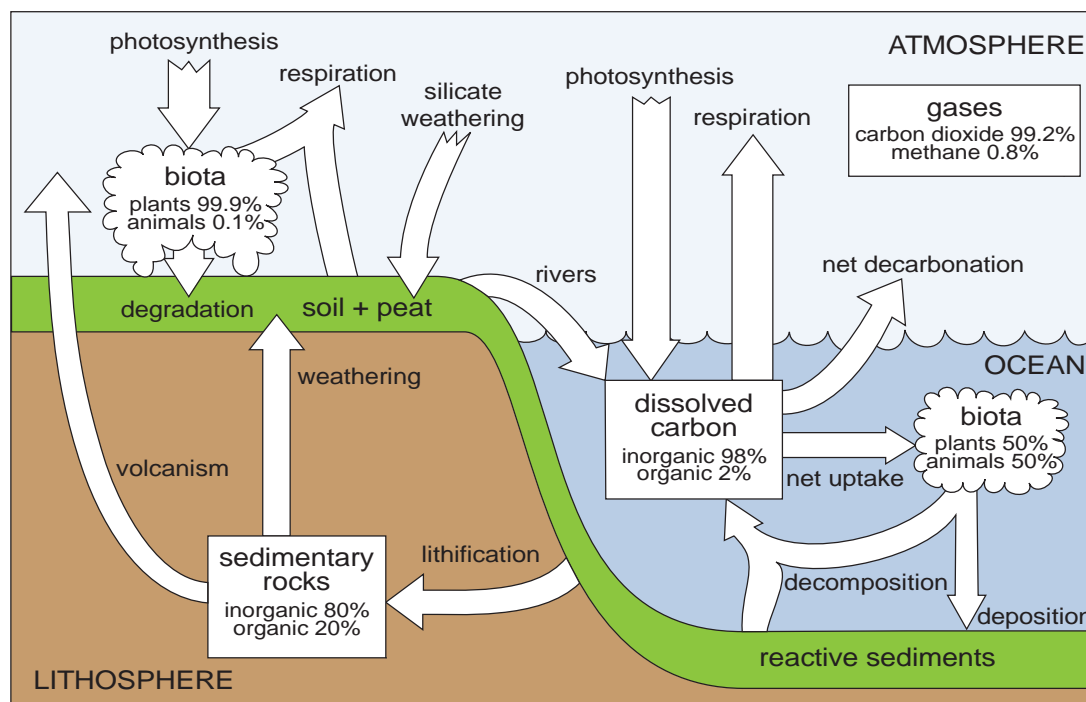


Figure 1.1: Summary of the biogeochemical carbon cycle. Figure modified from Killops and Killops (2005).

Sedimentary OM

Sedimentary rocks are composed of particulate matter, both mineral and organic, that are produced by erosion and transported and deposited by water or wind. OM in sediments can be either autochthonous (originating from organisms that lived within the sediment) or allochthonous (carried to the sediment, generally by water). The vast majority of detrital OM in marine environments is either recycled by co-existing organisms or re-mineralised back to CO₂. Only a small proportion (typically 0.1 %) of OM is preserved in oxic environments (Moodley et al., 2005). In anoxic, reducing environments this proportion can increase to greater than 5 % (Peters et al., 2005).

OM that is buried in sedimentary rocks is altered over geological time by temperature and pressure. This process is also known as maturation. The maturation of OM is most commonly measured by the vitrinite reflectance parameter (R_0). Vitrinite is a maceral derived from lignin and cellulose produced by vascular plants (Mukhopadhyay, 1994), and is ubiquitous in Phanerozoic sedimentary rocks. Vitrinite becomes increasingly reflective with increasing maturity and so R_0 is a

reliable indicator of maturity (Dow, 1977). Ratios of the abundances of biomarker isomers are also used as maturity parameters and are particularly useful for oils or amorphous sediments where no vitrinite can be identified. For example, steranes (**I**) are converted to diasteranes (**II**) by a combination of maturation and acid catalysis, hence the ratio of diasteranes / steranes is an indicator of maturity as well as depositional environment (Moldowan et al., 1986). Likewise the 18α -22,29,30-trisnorneohopane (Ts, **III**) is more stable during catagenesis than the 17α -22,29,30-trisnorhopane (Tm, **IV**), and the ratio of Ts / (Ts + Tm) is a common maturity parameter (Seifert and Moldowan, 1978). A range of maturity parameters are based on the methylated isomers of polycyclic aromatic hydrocarbons (PAHs), as discussed on page 7.

The first stage of maturation is diagenesis, which typically occurs at $R_0 < 0.6$ % (Mukhopadhyay, 1994). Condensation and defunctionalisation reactions during diagenesis result in the formation of kerogen, macromolecular OM which is insoluble in organic solvents (Vandenbroucke and Largeau, 2007). Above R_0 values of 0.6 % kerogen begins to break down to form petroleum in a process called catagenesis (Killops and Killops, 2005). The term bitumen is used to refer to the liquid hydrocarbons in petroleum which are soluble in organic solvents. Bitumen typically makes up 10 % or less of sedimentary OM, with the rest consisting of kerogen (Killops and Killops, 2005).

Sedimentary OM may contain a significant amount of sulfur, with some sulfur-rich kerogens containing in excess of 10 wt. % sulfur (Orr, 1986). Organic sulfur is the second-largest reservoir of reduced sulfur in the environment, after pyrite (Werne et al., 2008). Sulfur is incorporated into living cells through assimilatory sulfate reduction, in which dissolved sulfate is reduced to sulfide (Canfield, 2001). This biogenic sulfur is essential to life, and is most abundant in the sulfur-containing amino acids cysteine and methionine. It is estimated that biogenic sulfur generally makes up 10-25 % of organic sulfur in marine sediments (Anderson and Pratt, 1995; Werne et al., 2003). The majority of sedimentary organic sulfur is incorporated into OM during diagenesis, and the diagenetic incorporation of sulfur has been identified as an important pathway in the preservation of OM during diagenesis (Sinninghe Damsté and de Leeuw, 1990; Melendez et al., 2013). The mechanisms by which sulfur is incorporated into OM are complex. One major pathway may involve

polysulfide ions (S_x^{-2}), which are formed by the oxidation of dissolved sulfide and rapidly react with organic functional groups (Sinninghe Damsté and de Leeuw, 1990; Amrani and Aizenshtat, 2004; Werne et al., 2008). Other reduced sulfur species may also be incorporated into OM, including dissolved H_2S (Hebting et al., 2006; Melendez et al., 2013) and elemental sulfur (S^0) (Asif et al., 2009). A model of the biogeochemical sulfur cycle is presented in Figure 1.2.

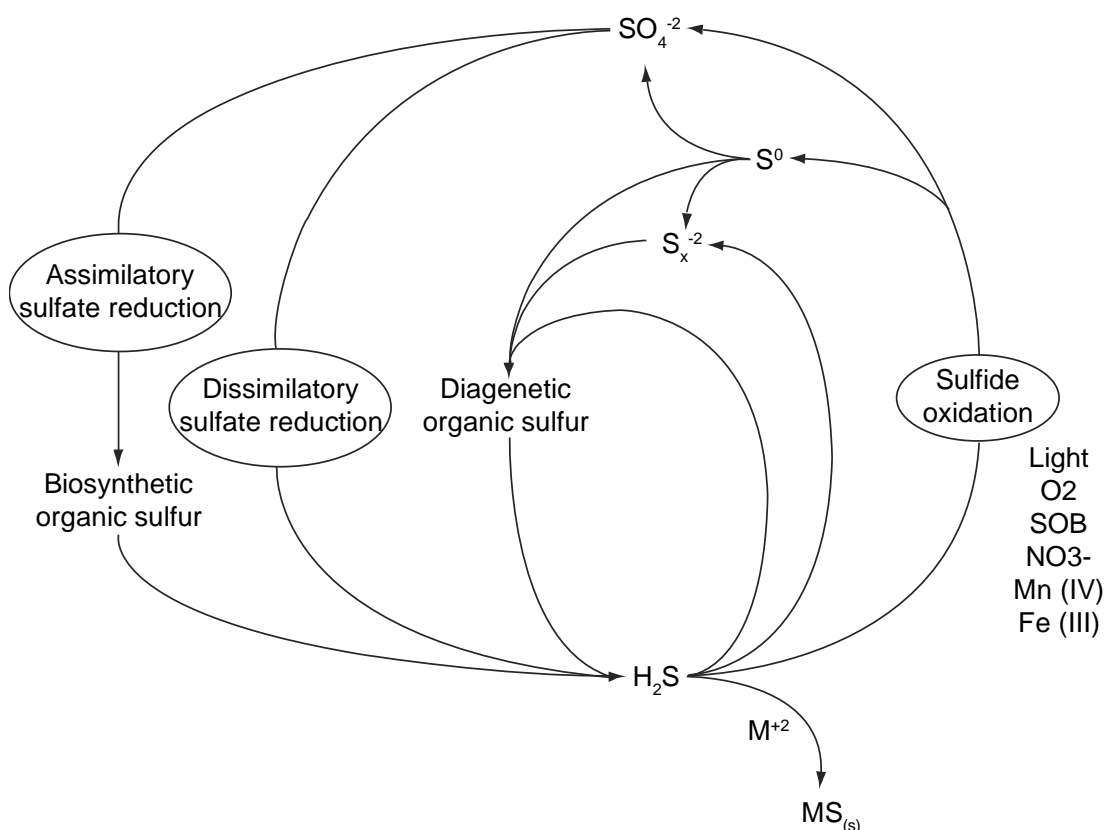


Figure 1.2: Simplified model of the biogeochemical sulfur cycle illustrating the formation of biosynthetic and diagenetic organic sulfur, along with elemental sulfur and metal sulfides. SOB: sulfide-oxidising bacteria. Figure modified from Canfield (2001).

Biomarkers

Bitumen is derived from natural organic molecules; hence the molecular structure of bitumen is determined by the structure of the original OM. Diagenesis and catagenesis result in changes to the structure of biomolecular precursors, such as the removal of functional groups and unsaturation, but the carbon skeleton of some compounds may be preserved. In some cases this skeleton can be linked to the original biomolecule, and these molecules are referred to as biomarkers or molecular fossils (Peters et al., 2005; Brocks and Grice, 2011). For example, okenane (**V**) has a

carbon skeleton that has only been identified in the carotenoid pigment okenone (**VI**), which is produced exclusively by the purple sulfur bacteria Chromatiaceae (Brocks et al., 2005). Okenone is therefore a biomarker for the presence of Chromatiaceae. Conversely the β -carotane skeleton (**VII**) is common to hundreds of carotenoids that occur throughout all domains of life, so β -carotane is not considered a diagnostic biomarker and is not useful as an indicator of any specific organism without additional information (Brocks and Grice, 2011). Compound-specific stable isotope analysis (CSIA, discussed on page 10) is one technique that can assist in the interpretation of biomarkers.

A wide variety of organic compounds are useful as biomarkers. Bacterial hopanoids (**VIII**) are some of the most common biomarkers in sediments. They are derived from bacteriohopanepolyols (**IX**) which are believed to act as membrane modifiers (Kannenberg and Poralla, 1999). Another common class are steranes (**I**), derived from sterols which are essential membrane components in eukaryotes (Volkman, 2003). *n*-Alkanes are the most abundant natural products in sediments, and their biological precursors are long chain fatty acids found in almost all organisms (Brocks and Summons, 2003). The distribution of *n*-alkanes can indicate specific organisms or environmental conditions, especially when combined with CSIA. For example long-chain *n*-alkanes (C₂₇ and higher) with an odd-number predominance are indicative of plant waxes (Eglinton and Hamilton, 1967), while *n*-alkanes with an even-number predominance have been attributed to phototrophic sulfur bacteria (Logan et al., 1999; Melendez et al., 2013). A number of molecular parameters have been developed to quantify the distribution of *n*-alkanes. The Carbon Preference Index (CPI) measures the ratio of odd-numbered over even-numbered *n*-alkanes (Marzi et al., 1993). A CPI greater than one results from a predominance of odd-numbered *n*-alkanes which commonly indicates input from terrestrial plants, while a CPI approximately equal to one may suggest marine input or significant thermal maturation (Bray and Evans, 1961; Eglinton and Hamilton, 1967).

Derivatives of carotenoid pigments can be highly specific indicators of photic zone euxinia (PZE), where anoxic and sulfidic conditions occur within the photic zone of the water column. Isorenieratane (**X**) and chlorobactane (**XI**) are derived from isorenieratene (**XII**), chlorobactene (**XIII**) and hydroxychlorobactene (**XIV**), produced by green and brown pigmented Chlorobiaceae (Overmann, 2006; Vogl et

al., 2006; Brocks and Grice, 2011). Chlorobiaceae are anaerobic phototrophs which require H₂S or another reduced sulfur source as electron donors, hence their presence is interpreted as a marker of PZE (Grice et al., 1996; Brocks et al., 2005).

Biomarkers are invaluable in the study of early life. For example biomarkers extracted from Precambrian sediments have been used as evidence for the Archean evolution of eukaryotes (Waldbauer et al., 2009) and for the reconstruction of Proterozoic marine environments (Brocks et al., 2005; Pawlowska et al., 2013). Interpretation of Precambrian biomarkers however must be done with caution. Sediments of this age have generally experienced significant degrees of thermal alteration and often contain very low levels of extractable OM. Care must be taken to ensure that the biomarkers in these sediments are not overprinted by anthropogenic contamination. Samples may be contaminated by petroleum-based drilling fluids (Brocks et al., 2008), or through storage in plastic sample bags (Grosjean and Logan, 2007). A thorough system of procedural blanks is required to ensure the reliability of biomarker analyses. Removal of the outer surfaces of samples may be required if they have received significant contamination during drilling or sample handling (Brocks et al., 2008). In addition to the freely-extractable hydrocarbons that are traditionally analysed in organic geochemistry, a second fraction of extractable OM can be obtained by dissolving carbonate and silicate minerals in hydrochloric and hydrofluoric acids respectively. This technique liberates a fraction of bitumen that was occluded within the kerogen / mineral matrix, which is referred to as Bitumen II. The freely-extractable bitumen is likewise called Bitumen I. Due to its close association with the kerogen / mineral matrix Bitumen II is believed to be shielded from anthropogenic contamination, as well as from the migration of younger hydrocarbons into the sediment after deposition (Sherman et al., 2007). A recent study of sediments from the Permian / Triassic boundary suggested that Bitumens I and II show different values for common aliphatic and aromatic maturity parameters, suggesting that Bitumen II may be less susceptible to thermal maturation (Nabbefeld et al., 2010b).

Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are highly condensed aromatic molecules consisting of two or more benzene rings. PAHs such as naphthalene (**XV**) and

phenanthrene (**XVI**) are almost ubiquitous in sediments but are not produced by living organisms. They are generated through diagenetic alteration of triterpenoid compounds (Wakeham et al., 1980b; Grice et al., 2007; Grice et al., 2009) or by combustion processes (Wakeham et al., 1980a; Venkatesan and Dahl, 1989; Nabbefeld et al., 2010c). They are also important products of hydrothermal alteration, and have been detected in marine hydrothermal vents (Kawka and Simoneit, 1990, 1994) and mineral deposits (Püttmann et al., 1989; Chen et al., 2003; Williford et al., 2011). PAHs in hydrothermal systems are formed by the addition of C_2 or C_2H_4 units to existing aromatic molecules (Stein, 1978).

PAHs with (poly)methyl or other alkyl groups are commonly found in sediments. The alkylation patterns of some compounds are traceable to biological precursors; for example retene (**XVII**) is a marker for terrestrial plants (Nabbefeld et al., 2010c). Biological precursors do not account for the occurrence in sediments of the full range of alkylated isomers. It has been proposed that methylation and demethylation reactions occur readily in sediments to generate all possible methylated isomers (Smith et al., 1995). Such reactions have been demonstrated to occur in pyrolysis experiments at temperatures of 100 to 400 °C (Alexander et al., 1985; Smith et al., 1995; van Aarssen et al., 1999). Sedimentary methylation is most likely to occur at α positions (Alexander et al., 1995; Le Métayer et al., 2014). However PAHs that are methylated in β positions are more thermodynamically stable than those methylated in α positions (Szczerba and Rospondek, 2010). Therefore during maturation the proportion of β isomers increases compared to α isomers. Various ratios of β isomers to α isomers are commonly used to indicate the relative maturity of sedimentary OM.

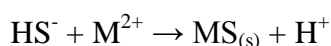
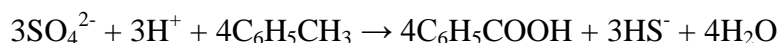
The most commonly-used PAH parameters are based on methylated naphthalenes (Radke et al., 1982b; Alexander et al., 1985; Radke et al., 1986) and phenanthrenes (Radke et al., 1982a; Radke et al., 1982b; Kvalheim et al., 1987). Two of the most commonly used are the methylphenanthrene ratio (MPR; Radke et al., 1982b) and methylphenanthrene index (MPI-1; Radke et al., 1982a). Others have been proposed based on higher molecular weight PAHs (Garrigues et al., 1988) and heteroatomic compounds such as dibenzothiophene (DBT, **XVIII**) (Radke et al., 1986). PAH maturity parameters are generally effective at higher maturities than aliphatic biomarker ratios, which often reach end point at R_0 values between 0.7 % and 1.0 %, before the main part of the oil window (van Graas, 1990). In contrast MPI-1 and

MPR have shown strong correlations with R_0 beyond 1.4 % (Radke, 1988). They are also useful in Precambrian systems where maturity is often high, aliphatic biomarkers are absent or in low abundance and vitrinite reflectance is not applicable (George and Ahmed, 2002).

Organic geochemistry of mineral deposits

It has long been recognised that several major classes of mineral deposit are closely associated with sedimentary OM. These include Mississippi Valley-type (MVT) Pb/Zn deposits (Gizè and Barnes, 1987; Spangenberg and Macko, 1998), hydrothermal gold deposits (Gatellier and Disnar, 1989), stratiform copper deposits (Ho et al., 1990; Rieger et al., 2008) and sedimentary uranium deposits (Landais, 1996). Extensive studies have been made of several deposits including the Permian Kupferschiefer (Püttmann et al., 1989; Schwark and Püttmann, 1990; Grice et al., 1996, 1997) and the Paleoproterozoic Here's Your Chance (HYC) deposit (reviewed on page 19).

One of the most significant potential roles of OM in base metal sulfide deposits is as a reducing agent at the site of metal deposition. Rieger et al. (2008) proposed the following general reaction scheme, in which toluene represents the reactant OM and benzoic acid is the oxidation product. Dissolved sulfate is reduced to sulfide, which reacts with metal cations to precipitate metal sulfides.



A similar scheme was proposed for the HYC deposit (Logan et al., 2001), although there is evidence that at least some sulfide involved in base metal formation was bacterially generated (Ireland et al., 2004b). Oxidation of OM was noted in mineralised sections of the Kupferschiefer deposit in southwest Poland, and was attributed to the reaction of OM with an oxidising, metal-rich fluid during deposition (Püttmann et al., 1989). OM has been recognised as a potential reducing agent in sediment-hosted lead-zinc (Spangenberg and Macko, 1998), uranium (Spirakis, 1996) and copper (Ho et al., 1990) deposits.

Another potential role of OM in ore deposition is as a transporting agent for metal species, in the form of soluble metal-organic complexes. This possibility was

considered by Gize and Barnes (1994), who noted that organic compounds involved in metal transport would have to be thermally stable at 200 °C or more, be able to support metals at a +2 or +3 oxidation state and survive for the order of 10⁶ years. The authors suggested acetate as a potential ligand. The complexation of uranium with fulvic and humic acids has been demonstrated in laboratory experiments (Munier-Lamy et al., 1986). Fulvic acids, especially those with high sulfur contents, have also been shown to solubilise gold *via* the formation of gold-fulvic acid complexes (Bowell et al., 1993). However there has been no unequivocal evidence of a deposit where organic complexes have been shown to play a major role in metal transport. Polar organic ligands, which are the most likely to form stable complexes with metal cations, are also the most susceptible to destruction during burial and maturation (Peters et al., 2005) hence are unlikely to be detected in lithified sediments. Organic complexes have often been considered to play only a minor role in the transport of Pb and Zn (e.g. Sicree and Barnes, 1996; Giordano, 2002). It has been predicted that inorganic complexes (e.g. chloride) are able to transport sufficient lead and zinc to form large base metal deposits such as HYC (Cooke et al., 2000). The most likely role of OM in these systems seems to be as a reducing agent during deposition.

Stable isotopes

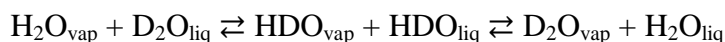
Stable isotope ratios and measurement techniques

The measurement of stable isotope ratios is a valuable tool in many fields of geochemistry. Stable isotopes do not decay; hence the ratio remains relatively constant over geological time.

Table 1.1: The average atomic abundances (%) of stable isotopes of common elements relevant in organic geochemistry. Data from Berglund and Wieser (2011).

Carbon	Hydrogen	Oxygen	Sulfur	Nitrogen
¹² C (98.938)	¹ H (99.989)	¹⁶ O (99.757)	³² S (94.993)	¹⁴ N (99.636)
¹³ C (1.078)	² H/D (0.012)	¹⁷ O (0.038)	³³ S (0.752)	¹⁵ N (0.364)
		¹⁸ O (0.205)	³⁴ S (4.252)	

Each stable isotope of an element has different properties due to the slight difference in mass. Stable isotopes can fractionate due to temperature-dependent equilibrium effects: e.g. closed system exchange of hydrogen isotopes between liquid water and water vapour (Grice and Brocks, 2011):



Kinetic fractionation occurs during chemical reactions. Chemical bonds formed by light isotopes are weaker than those formed by heavier isotopes (Hoefs, 2009). Molecules containing light isotopes will react more readily; hence a greater proportion of light isotopes will be incorporated into the products. Conversely the remaining reactants will be depleted in light isotopes.

Stable isotope composition is expressed in δ notation, as the ratio of the heavy isotope to the light isotope relative to a standard. It is generally expressed in *per mil* (‰, parts per thousand):

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}$$

Where R is the abundance ratio of the heavy isotope to the light isotope (e.g. $^{13}\text{C}/^{12}\text{C}$ or D/H) in the sample or standard. Measurements are expressed relative to the isotopic composition of international standards. Stable carbon isotope measurements are expressed relative to the Vienna Pee Dee Belemnite (VPDB) scale, defined by the International Atomic Energy Agency (IAEA) based on the original Pee Dee Belemnite carbonate standard that is now exhausted (Werner and Brand, 2001). The IAEA has also defined reference scales for other elements. The Vienna Standard Mean Ocean Water (VSMOW) scale is used for hydrogen and oxygen measurements (Werner and Brand, 2001) and sulfur is reported according to the Vienna Cañon Diablo Troilite (VCDT) scale (Krouse and Coplen, 1997).

Bulk analytical methods such as elemental analysis combined with isotope ratio mass spectrometry (irMS; Gehre and Strauch, 2003; Skrzypek and Paul, 2006) measure the average isotopic composition of milligram-sized samples. Elemental analysis is particularly suitable for solid samples that are not amenable to GC-MS, e.g. $\delta^{13}\text{C}$ or δD of kerogen (Sauer et al., 2009; Nabbefeld et al., 2010a). The measurement of isotope ratios of individual compounds in complex mixtures (CSIA) became possible with the development of the GC-irMS, in which a gas chromatograph is linked to a

specialised mass spectrometer *via* a combustion interface (Matthews and Hayes, 1978). The original instruments measured carbon isotopes (Hayes et al., 1990), and have been extended to hydrogen, nitrogen and oxygen (Sessions et al., 1999; Dawson et al., 2004; Sessions, 2006). Compound-specific sulfur isotopes have recently been measured by the coupling of a GC to a multi-collector ICP-MS (Amrani et al., 2009). The general requirements for CSIA are injection of analytes without fractionation, baseline separation of chromatographic peaks, conversion of analytes into a simple molecular form (e.g. CO₂, H₂) and precise measurement of isotopic abundance of the analytes (Sessions, 2006).

Stable carbon and hydrogen isotopes

The stable carbon isotopic composition of sedimentary OM is determined by three factors: 1) the isotopic composition of the carbon source; 2) the carbon isotope fractionation during biosynthesis; and 3) fractionation during secondary alteration of the OM. Carbon in plants and animal lipids is sourced from atmospheric CO₂ that is fixed by plants during photosynthesis (Falkowski, 2012). Isotopic fractionation during photosynthesis produces organic carbon which is depleted in ¹³C compared to the carbon source. Bacteria have a wide variety of carbon sources depending on their environment and pathway of carbon uptake. Biolipids are formed by a range of pathways, and each have an associated carbon isotopic fractionation (e.g. Melzer and Schmidt, 1987; Hayes, 2001; Chikaraishi et al., 2004) resulting in differences in $\delta^{13}\text{C}$ of up to 20 ‰ within an individual organism. The range of $\delta^{13}\text{C}$ of common carbon sources is summarised in Figure 1.3.

Secondary reworking of plant OM produces little carbon fractionation in modern sediments (Freeman, 2001), but in the Proterozoic the lack of faecal pellet production resulted in slowly sinking OM that was extensively reworked in the water column, with a significant isotopic depletion of kerogen compared to co-existing *n*-alkanes (Logan et al., 1995). Secondary processes during maturation of OM have been found to increase the $\delta^{13}\text{C}$ of sedimentary lipids due to the loss of isotopically light bitumen (Clayton, 1991), however this increase is generally small (< 4 ‰). Compound-specific $\delta^{13}\text{C}$ measurements have shown great utility in a wide variety of organic geochemical studies. For instance, they have been used to reconstruct past marine environments (Freeman, 2001), trace the evolution of the biogeochemical carbon

cycle (Logan et al., 1995) and distinguish between migrated and indigenous OM (Williford et al., 2011).

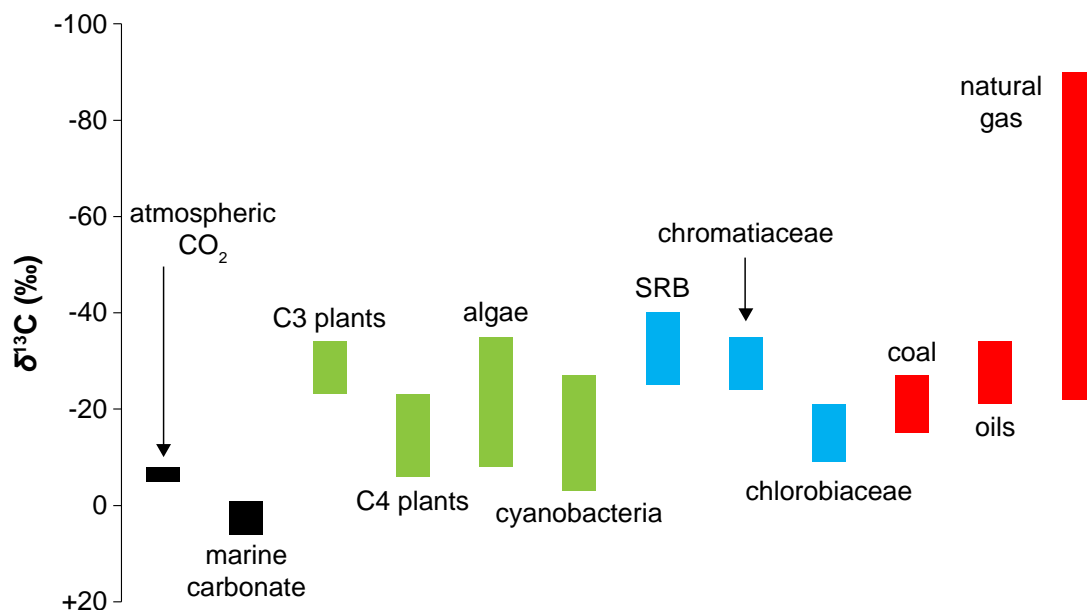


Figure 1.3: Approximate range of $\delta^{13}\text{C}$ from a variety of carbon sources, primary producers and fossil fuels. SRB: sulfate-reducing bacteria. Data from Peters et al. (2005), Schidlowski (1988), Londry et al. (2004) and Melendez et al. (2013).

Hydrogen is the other major component of biolipids. This element has the greatest relative mass difference between the two stable isotopes (D having double the atomic mass of ^1H) so isotopic fractionations of hydrogen are significantly larger than other elements (Hoefs, 2009). The main source of hydrogen in biological systems is water, and thus the isotopic composition of the source water is a major control on the δD value of OM. Water vapour that is evaporating from a body of water is depleted in D due to kinetic fractionation. Meteoric water is therefore depleted in D compared to the oceans. The extent of fractionation depends on temperature, resulting in latitude and temperature fractionation effects whereby lipids from plants growing in cool, high-latitude environments are significantly D-depleted compared to those from low-latitude tropical climates (Dawson et al., 2004). As for carbon, hydrogen is subject to fractionation during the synthesis of biolipids (Sessions et al., 1999; Hayes, 2001).

The hydrogen isotopic composition of sedimentary OM is strongly affected by thermal maturity. Hydrogen atoms at certain positions within molecules are highly susceptible to exchange with external hydrogen atoms. Aromatic hydrogen appears

to exchange on a timescale of 10^3 to 10^6 years at 100 °C, while highly acidic hydrogen atoms in hydroxyl or carboxyl groups can exchange almost instantaneously (Schimmelmann et al., 2006). Hydrogen atoms bonded to tertiary carbon atoms within isoprenoid molecules are also susceptible to exchange, giving rise to a significant difference in the δD of isoprenoids and co-occurring *n*-alkanes which increases with thermal maturity (Dawson et al., 2005; Maslen et al., 2013). Measurement of δD has also been used to identify hydrogen exchange caused by interaction with enriched, evaporitic waters in the formation of mineral systems (Williford et al., 2011).

Organic sulfur isotopes

The isotopic composition of organic sulfur is fundamentally linked to the inorganic sulfur cycle. Large fractionations are produced by the reduction of seawater sulfate to sulfide by sulfate-reducing bacteria. When sulfate is abundant (> 1 mM) bacterial sulfate reduction (BSR) produces sulfide significantly reduced in $\delta^{34}S$ by up to 70 ‰ (Wortmann et al., 2001). In low-sulfate environments (< 1 mM) the majority of sulfate that enters the cell may be reduced, in which case fractionations will be negligible (e.g. Shen et al., 2002).

Dissolved sulfide can undergo a variety of reactions. The formation of metal sulfides (e.g. pyrite) from dissolved sulfide involves minimal fractionation (Böttcher et al., 1998; Canfield, 2001), so the $\delta^{34}S$ of sulfide minerals can be taken to match that of the parent dissolved sulfide. Up to 90 % of sulfide produced in some settings may be reoxidised back to sulfate or intermediate oxidation products (Canfield, 2001), by biological or non-biological means. Phototrophic oxidation by green sulfur bacteria produces elemental sulfur (S^0), which is enriched in ^{34}S by 1 to 3 ‰ from the parent sulfide (Zerkle et al., 2009). In a wide-ranging review of reported $\delta^{34}S$ values from Jurassic to recent sediments, Anderson and Pratt (1995) found that organic sulfur is enriched in ^{34}S compared to co-existing sulfide minerals by an average of 10 ‰. The recent development of compound-specific $\delta^{34}S$ instruments has the potential to reveal detailed information on the processes affecting organic sulfur (Amrani et al., 2009). For example an enrichment in the $\delta^{34}S$ of benzothiophene (**XIX**) compared to dibenzothiophene (**XVIII**) was found to be an indicator of thermochemical sulfate

reduction (TSR), an abiotic process in which dissolved sulfate is reduced to sulfide coupled with the oxidation of OM (Amrani et al., 2012).

The Barney Creek Formation and the Here's Your Chance deposit

Geological setting

The Barney Creek Formation (BCF) is located in the McArthur Basin, a 5 to 15 km-thick carbonate, siliciclastic and volcanic succession in the Northern Territory of Australia, deposited between 1815 and 1450 Ma (Plumb, 1979). The deposition of the BCF was dated at 1639 ± 2 Ma based on zircon Pb/U geochronology (Page and Sweet, 1998; Page et al., 2000). The formation was previously described as a shallow lacustrine or sabkha setting (Jackson et al., 1988) but is now considered to represent deposition in a marine environment below the wave base (Bull, 1998; McGoldrick et al., 2010). The Barney Creek Formation contains abundant black shales which generally contain 0.2 to 2 % total organic carbon (TOC), with some sections containing greater than 7 % TOC (Powell et al., 1987).

The Here's Your Chance (HYC) deposit is the largest of the Proterozoic sediment-hosted Pb/Zn/Ag deposits of Northern Australia (Large et al., 2005). The deposit contains a total endowment of 227 Mt, with a composition of 9.2 % Zn, 4.1 % Pb and 40 g/t Ag (Huston et al., 2006). The HYC deposit is hosted in the McArthur Group within the BCF, adjacent to the Emu fault zone (Bull, 1998). Mineralised rocks are comprised of dark, carbonaceous siltstones and fine-grained pyrite, sphalerite and galena (Croxford and Jephcott, 1972). Mineralisation occurs within eight separate ore bodies, spread within a depth of ~ 80 m (Large et al., 1998). Figure 1.4 shows the location and stratigraphy of the HYC deposit. The non-mineralised W-Fold Shale unit lies directly underneath the HYC deposit, and is composed of tuffaceous shales and siltstones (Lambert and Scott, 1973). The HYC deposit is relatively unmetamorphosed and considered to be remarkably well-preserved for a deposit of Proterozoic age (Croxford and Jephcott, 1972; Large et al., 2005).

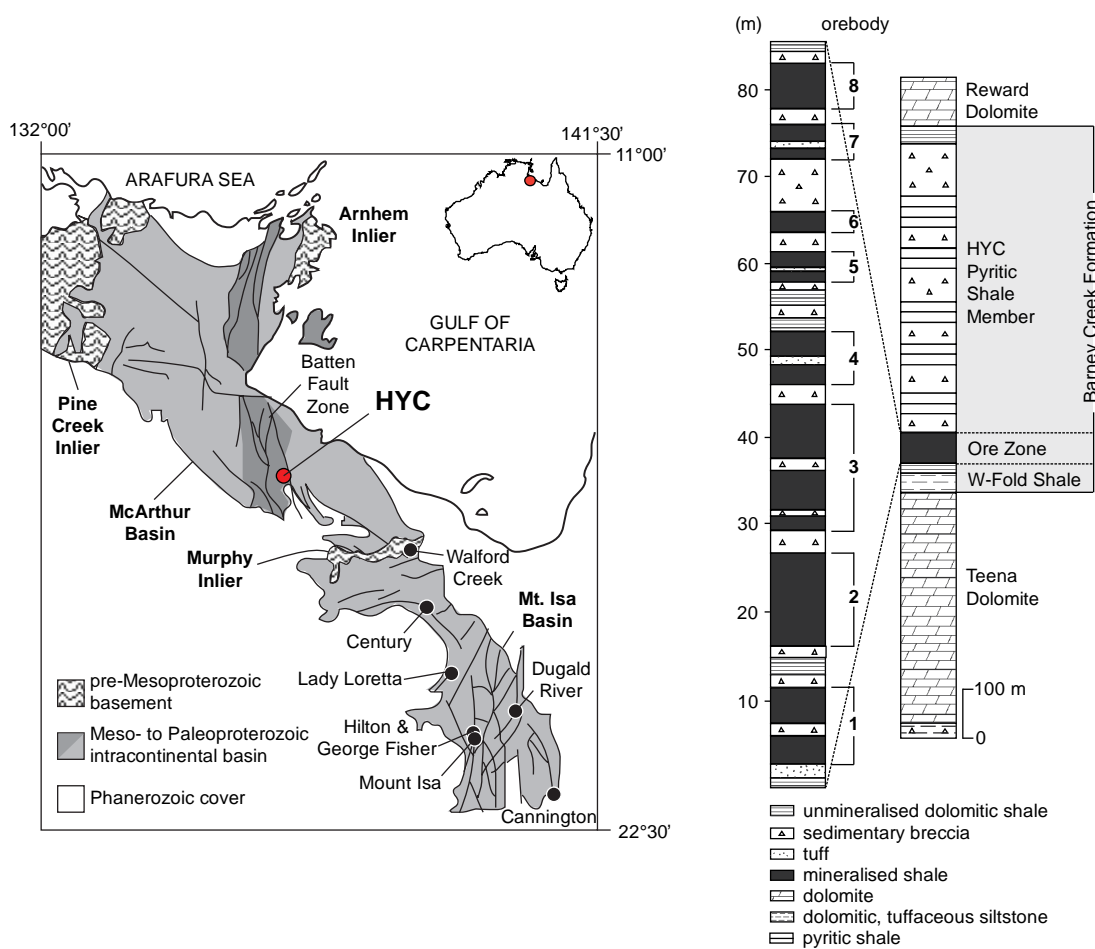


Figure 1.4: Map of northern Australia showing the HYC deposit and other major Pb/Zn deposits, plus stratigraphy of HYC showing the distribution of the eight ore bodies. Figure modified from Ireland et al. (2004a) and Williford et al. (2011).

Environment and ecosystem of the Barney Creek Formation and wider McArthur Basin

The McArthur Basin is one of the best-preserved Proterozoic sedimentary basins in the world, having experienced only low-grade metamorphism (Jackson et al., 2000; Rawlings et al., 2004). It has therefore become a classic location for biogeochemical studies of the middle Proterozoic (Johnston et al., 2008). Carbonate $\delta^{13}\text{C}$ values from 1.7 to 1.5 Ga are exceptionally stable ($-0.6 \pm 2 \text{‰}$) indicating a period of prolonged stability in ocean chemistry, planetary climate and tectonic activity (Brasier and Lindsay, 1998; Lindsay and Brasier, 2000). Samples from the McArthur Basin have provided evidence for anoxic and euxinic oceans from Mo isotopes (Arnold et al., 2004; Kendall et al., 2009) and sulfur isotopes (Shen et al., 2002; Johnston et al., 2008), supporting the prediction of Canfield (1998) for widespread ocean euxinia

during the middle Proterozoic. Recent evidence however demonstrates that ferruginous conditions may have predominated in the McArthur Basin (Planavsky et al., 2011), which are incompatible with widespread ocean euxinia as dissolved iron would have rapidly precipitated out of a sulfide-rich ocean. This suggests that euxinia may have been restricted to localised settings, possibly developing as a result of increased sulfate supply to restricted sub-basins (Poulton et al., 2010).

Several sections of the McArthur Basin contain rocks of low maturity that have been investigated as potential petroleum source rocks (Crick et al., 1988; Jackson et al., 1988). These include the Mesoproterozoic Velkerri Formation (Summons et al., 1994; George and Ahmed, 2002). Black shales from the 1730 Ma Wollgorang Formation (in the underlying Tawallah Group) contain up to 6% TOC (Donnelly and Jackson, 1988), but intrusions related to volcanic activity have caused extensive alteration and likely destroyed indigenous biomarkers (Brocks et al., 2008).

The best-preserved biomarkers from the McArthur Basin are in sediments from the Glyde River region of the BCF (Summons et al., 1988; Brocks et al., 2005). The Glyde sub-basin is located 80 km south of the HYC deposit, and is considered to be stratigraphically equivalent to the deposit (Davidson and Dashlooty, 1993). Sediments from the Glyde region contain a wide variety of intact carotenoid pigments and carotenoid breakdown products. These include isorenieratane (**X**) from brown-pigmented Chlorobiaceae, chlorobactane (**XI**) from green-pigmented Chlorobiaceae and okenane (**V**) from the purple sulfur bacteria Chromatiaceae (Brocks et al., 2005; Brocks and Schaeffer, 2008). These bacteria live only in environments where euxinic conditions extend into the photic zone (Imhoff, 2006; Overmann, 2006). Their presence confirms that conditions of PZE occurred during deposition of the BCF (e.g. Steenbergen and Korthals, 1982; Grice et al., 1996, 1997; Grice et al., 2005). Diagnostic eukaryotic steroids were below detection limits in BCF bitumen, but a high abundance of C₄-methylated triaromatic steroids and 3 β -methylhopanes indicates a high abundance of type I methanotrophic bacteria (Brocks et al., 2005). These bacteria thrive in low sulfate conditions (less than 0.5 mM) where the activity of sulfate-reducing bacteria is suppressed (Kristjansson et al., 1982).

Formation of the HYC deposit

Stratiform sediment-hosted Pb/Zn/Ag deposits such as HYC are commonly referred to as sedimentary-exhalative (SEDEX) deposits, although the exhalative origin of many of these deposits is disputed (see page 18 for further discussion) and the term clastic-dominated (CD) has been proposed as an alternative (Leach et al., 2010). The general characteristics of these deposits are laminated Pb/Zn/Ag sulfide mineralisation hosted in sedimentary basins and limited or no association with volcanic rocks (Leach et al., 2005). McArthur-type deposits are believed to have formed from oxidised (sulfide-poor) fluids (Cooke et al., 2000), hence the formation of these deposits has been strongly linked to the evolution of ocean chemistry and the development of euxinic conditions (Lyons et al., 2006). HYC was formed during the maximum period for CD deposit formation (1800-1600 Ma), when it is believed that increased oxidation of surface sulfides after the Great Oxidation Event greatly increased the transport of sulfate into the ocean, resulting in euxinic conditions caused by abundant bacterial sulfate reduction (Leach et al., 2010). However recent evidence that ferruginous conditions were predominant in mid-Proterozoic oceans (e.g. Planavsky et al., 2011) suggests that Proterozoic ocean chemistry may have been more varied than previously thought.

Although there is disagreement on the timing and mechanism of deposition, it is generally agreed that HYC was formed by the action of a metal-rich hydrothermal brine (Huston et al., 2006). The mineralising fluid likely originated in volcanic aquifers in the Tawallah Group (Cooke et al., 1998), and rocks from this group show evidence of significant hydrothermal alteration (Donnelly and Jackson, 1988; Kendall et al., 2009). It is generally agreed that the deposit formed at low to moderate temperatures of up to 200 °C (Large et al., 1998; Cooke et al., 2000). Mathematical modelling suggests that heat flow typical of the continental crust is sufficient to produce these temperatures, hence an additional heat source such as a volcanic intrusion is not required (Garven et al., 2001). Base metal depletion in volcanic rocks of the Tawallah Group suggests that Pb and Zn were sourced from these rocks (Cooke et al., 1998).

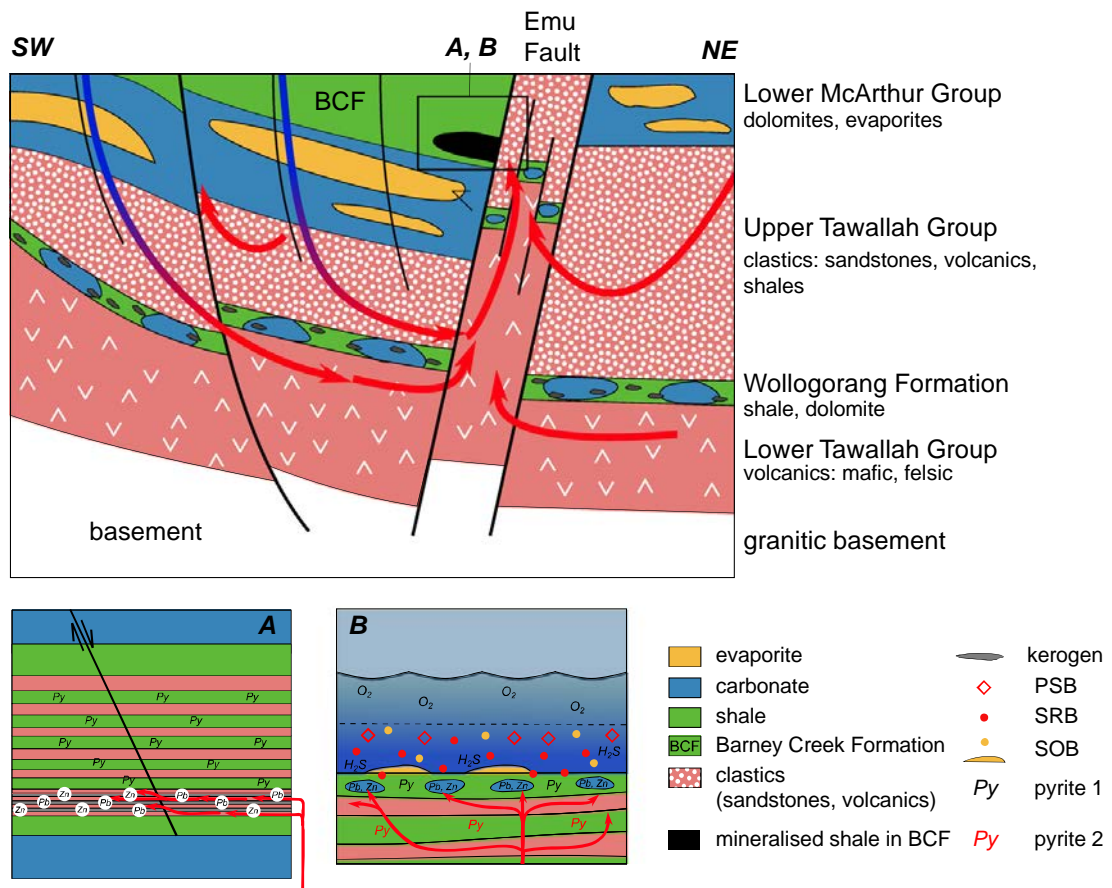


Figure 1.5: Genetic model for the HYC deposit. Mineralising fluids flowed through the Tawallah Group and Wollgorang Formation, leaching base metals and generating PAHs. They then flowed upwards through the Emu fault to the BCF. The inserts depict (A) a replacement model where sulfides are deposited between sedimentary layers, and (B) exhalative mineralisation where sulfides precipitate in a euxinic ocean. Figure modified from Greenwood et al. (2013).

Two models have been proposed for ore deposition at HYC (presented in Figure 1.5): an exhalative model where the mineralising fluid was exhaled into euxinic deep waters, and a replacement model in which metal sulfide precipitation occurred in sedimentary layers below the sea floor. Early workers favoured the exhalative model based on the fine-grained, layered sulfide textures (Croxford and Jephcott, 1972). More recent studies have also favoured the exhalative model based on ore textures (Large et al., 1998) and the presence of ore clasts (Ireland et al., 2004a). The replacement model was proposed by Williams (1978) and refined by Hinman (1996), who noted that fine-grained ore textures can also be formed by replacement of sedimentary laminations. The formation of a late, isotopically distinct pyrite phase, and textural evidence that pyrite formation had ceased before base metal deposition

began, support the replacement mode (Eldridge et al., 1993). Arguments for and against both models are summarised by Huston et al. (2006).

Organic geochemistry of the HYC deposit

A number of organic geochemical studies have explored the formation of HYC. Logan et al. (2001) studied saturated hydrocarbons from the highly-mineralised upper ore body 2 and from non-mineralised host sediments. The study found distributions of *n*-alkanes, monomethyl branched alkanes and alkylcyclohexanes indicative of marine bacteria and branched alkanes typical of cyanobacteria. Ore body 2 showed a strong predominance of even-numbered *n*-alkanes and methyl alkanes which were attributed to sulfide-oxidising bacteria (Logan et al., 2001). A subsequent investigation Grosjean and Logan (2007) has noted the occurrence in these samples of branched alkanes with quaternary carbon atoms (BACQs), which are known anthropogenic contaminants from plastic sample bags, so the other hydrocarbon data from this study should be interpreted with caution.

OM in the mineralised zones of HYC has been heavily affected by hydrothermal alteration from the mineralising fluid. Hydrogen isotopic analysis showed that *n*-alkanes from mineralised zones were 50 to 60 ‰ enriched in D compared to those from non-mineralised BCF sediments (Williford et al., 2011). This was interpreted as evidence that *n*-alkanes at HYC experienced significant hydrogen exchange with a D-enriched fluid, which likely originated in an evaporitic basin. T_{\max} and estimated vitrinite reflectance values are significantly higher within the deposit than is expected from the burial trend (Crick et al., 1988; Logan et al., 2001; Mackenzie et al., 2008). The mineralised zones contain high abundances of 3- to 7-ringed PAHs, believed to be generated by hydrothermal alteration from the hot mineralising fluid (Chen et al., 2003; Williford et al., 2011). The distribution of high-molecular weight PAHs was interpreted by Chen et al. (2003) to reflect a mineralisation temperature of 250 to 400 °C, contradicting previous studies predicting a temperature of less than 200 °C (e.g. Cooke et al., 2000; Garven et al., 2001). The study of Williford et al. (2011) attempted to resolve this discrepancy by measuring $\delta^{13}\text{C}$ of PAHs and co-existing kerogen. PAHs (-29.8 ± 0.6 ‰) were enriched in ^{13}C by 3 ‰ on average compared to kerogen (-33.2 ± 0.2 ‰), but similar to the $\delta^{13}\text{C}$ of kerogen from the underlying Wollogorang Formation (-27.9 to -31.6 ‰). It was proposed that PAHs were not

indigenous to HYC, but were instead generated in the Wollgorang Formation at temperatures above 250 °C and transported by the mineralising fluid to HYC (Williford et al., 2011).

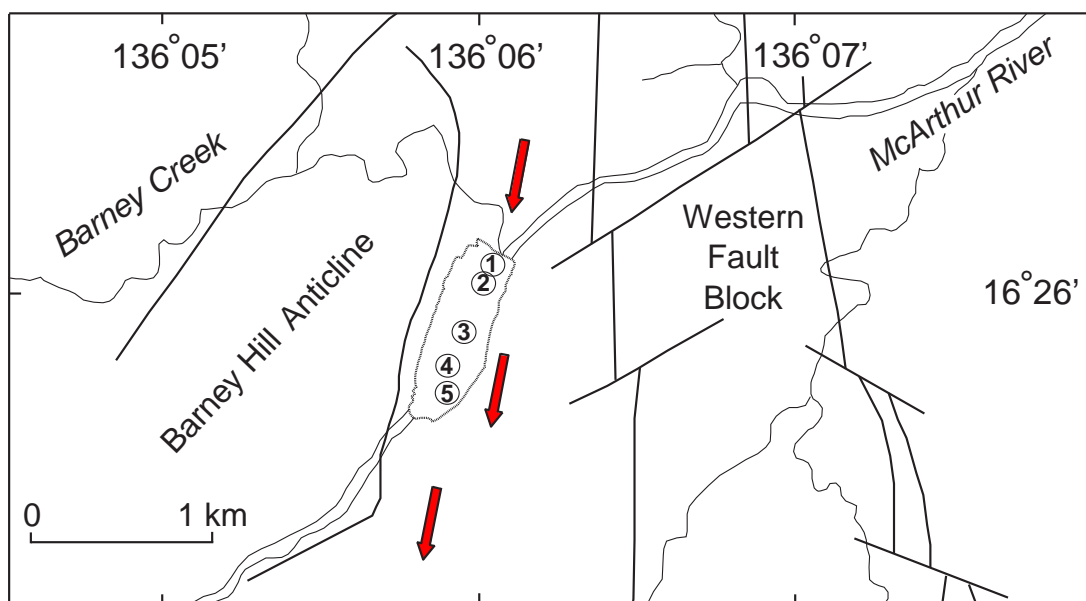


Figure 1.6: Location of the five sample pits of the HYC deposit following the estimated flow path of the mineralising fluid (red arrows). Figure modified from Williford et al. (2011).

The samples studied by Williford et al. (2011) were collected from five sample pits following the estimated flow path of the mineralising fluid (shown in Figure 1.6). It was therefore expected that the samples would follow a gradient of decreasing hydrothermal alteration, with pit one being the most altered and pit five the least. The maturity parameters MPI-1 and MPR showed a generally decreasing trend from pits one to five, while the concentrations of high molecular weight PAHs decreased over the gradient of alteration (Williford et al., 2011).

Aims of this thesis

Although the HYC deposit has been extensively studied (pages 14 to 20), questions still remain about many aspects of its formation. Analysis of OM has the potential to help answer a number of these questions, such as the temperature of mineralising fluid, the characteristics of the depositional environment, and the relative importance of BSR and TSR to ore deposition. The sedimentary OM at HYC has been characterised by a number of studies, the findings of which are summarised on page

19 and 20. These studies have been limited due to the extensive hydrothermal alteration of the OM during ore deposition (Chen et al., 2003; Williford et al., 2011), as well as the potential overprinting of OM with non-indigenous hydrocarbons carried by the mineralising fluid (Williford et al., 2011). This PhD project attempted to ‘look behind’ the alteration and migration through the analyses of well-preserved OM indigenous to the deposit. To this end, Bitumen II (page 6) was isolated from the samples of Williford et al. (2011) and analysed to determine the depositional conditions and thermal maturity of the deposit. Artificial maturation of an immature, unmineralised sediment from the same region was used to assess the effect of sulfide minerals on organic maturation. Due to the important control of some sulfur species on the formation of deposits such as HYC, $\delta^{34}\text{S}$ of organic and elemental sulfur was measured to investigate their behaviour during deposition and their role in the ore formation process.

Chapter 2

Extractable OM that is occluded within the kerogen / mineral matrix (Bitumen II) is believed to be shielded from the migration of non-indigenous hydrocarbons (Sherman et al., 2007) and also possibly against thermal maturation (Nabbefeld et al., 2010b). The freely-extractable hydrocarbons (Bitumen I) must be thoroughly removed before the better-preserved Bitumen II can be analysed in isolation. The aim of **Chapter 2** was to validate the isolation of Bitumen II from the HYC samples. A Soxhlet extraction of Bitumen I from a highly-mineralised HYC sample was monitored over 144 hours to assess the time taken for various aliphatic and aromatic compounds to be totally extracted. PAH ratios were compared against Bitumen II separately isolated from the same sample pit, to ensure that Bitumen II is not significantly affected by residual Bitumen I.

Chapter 3

Sediment-hosted Pb/Zn ore deposits such as HYC have been generally thought to form in periods of widespread ocean euxinia (Lyons et al., 2006). Recent evidence that ferruginous conditions were prevalent in the middle Proterozoic (Planavsky et al., 2011) suggests however that euxinia may have been a localised condition. The analysis of immature sedimentary OM can provide strong evidence of euxinic

conditions, however OM at HYC has been strongly affected by hydrothermal alteration and possible migration of non-indigenous hydrocarbons (Williford et al., 2011). In **Chapter 3** we address these challenges by isolating Bitumen II from five HYC sample pits as well as from the underlying W-Fold Shale formation. Molecular parameters (CPI, average chain length) and $\delta^{13}\text{C}$ of *n*-alkanes were measured to examine the microbial community present during ore deposition, and carbon isotopes of kerogen were measured to confirm the syngeneity of Bitumen II. To investigate the proposal that Bitumen II may be less affected by thermal maturation (Nabbefeld et al., 2010b), PAH maturity parameters were calculated to assess the relative maturities of Bitumen I and Bitumen II.

Chapter 4

OM associated with sedimentary Pb/Zn deposits has often been significantly affected by hydrothermal alteration. The assessment of thermal maturity is common practice in organic geochemistry (e.g. through the use of molecular maturity parameters), however the high abundance of sulfide minerals in these deposits may alter the behaviour of OM during maturation (Gizé, 1999). MSSV pyrolysis was used in **Chapter 4** to simulate the hydrothermal alteration that occurred during the formation of the HYC deposit. A thermally well-preserved sample from the Glyde River region of the BCF was used as an analogue of the HYC host rocks before deposition. The behaviour of PAH maturity parameters and the formation of high molecular weight PAHs were monitored over three pyrolysis temperatures applied for the same time period (72 hours). The same series of thermal treatments were then applied following the addition of pure PbS or ZnS to assess the effect of sulfide minerals on organic maturation.

Chapter 5

The formation of sedimentary Pb/Zn deposits is significantly controlled by the cycling and redox state of sulfur species. Previous sulfur isotope studies of these deposits have revealed important information on the mechanisms of deposition (e.g. Ireland et al., 2004b) as well as on the broader evolution of the global sulfur cycle (Lyons et al., 2006). However such studies have largely neglected elemental sulfur and organic sulfur, which often accumulate in significant quantities. In **Chapter 5**

$\delta^{34}\text{S}$ of elemental sulfur and organic sulfur in kerogen was measured for the five HYC sample pits. The measured isotopic values were combined with previously measurements from McArthur Basin sulfide minerals to construct a simplified model of the sulfur cycle during the deposition of HYC.

References

- Alexander R., Bastow T.P., Fisher S.J., Kagi R.I., 1995. Geosynthesis of organic compounds: II. Methylation of phenanthrene and alkylphenanthrenes. *Geochimica et Cosmochimica Acta* **59**, 4259-4266.
- Alexander R., Kagi R.I., Rowland S.J., Sheppard P.N., Chirila T.V., 1985. The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalenes in some Ancient sediments and petroleums. *Geochimica et Cosmochimica Acta* **49**, 385-395.
- Amrani A., Aizenshtat Z., 2004. Mechanisms of sulfur introduction chemically controlled: $\delta^{34}\text{S}$ imprint. *Organic Geochemistry* **35**, 1319-1336.
- Amrani A., Deev A., Sessions A.L., Tang Y., Adkins J.F., Hill R.J., Moldowan J.M., Wei Z., 2012. The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction. *Geochimica et Cosmochimica Acta* **84**, 152-164.
- Amrani A., Sessions A.L., Adkins J.F., 2009. Compound-specific $\delta^{34}\text{S}$ analysis of volatile organics by coupled GC/multicollector-ICPMS. *Analytical Chemistry* **81**, 9027-9034.
- Anderson T.F., Pratt L.M., 1995. Isotopic evidence for the origin of organic sulfur and elemental sulfur in marine sediments. In *Geochemical Transformations of Sedimentary Sulfur* (eds. Vairavamurthy M.A., Schoonen M.A.A.). American Chemical Society, Washington, D.C. pp 378-396.
- Arnold G.L., Anbar A.D., Barling J., Lyons T.W., 2004. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304**, 87-90.
- Asif M., Alexander R., Fazeelat T., Pierce K., 2009. Geosynthesis of dibenzothiophene and alkyl dibenzothiophenes in crude oils and sediments by carbon catalysis. *Organic Geochemistry* **40**, 895-901.

- Berglund M., Wieser M.E., 2011. Isotopic compositions of the elements 2009 (IUPAC Technical Report). *Pure and Applied Chemistry* **83**, 397-410.
- Böttcher M.E., Smock A.M., Cypionka H., 1998. Sulfur isotope fractionation during experimental precipitation of iron(II) and manganese(II) sulfide at room temperature. *Chemical Geology* **146**, 127-134.
- Bowell R.J., Gize A.P., Foster R.P., 1993. The role of fulvic acid in the supergene migration of gold in tropical rain forest soils. *Geochimica et Cosmochimica Acta* **57**, 4179-4190.
- Brasier M.D., Lindsay J.F., 1998. A billion years of environmental stability and the emergence of eukaryotes: new data from northern Australia. *Geology* **26**, 555-558.
- Bray E.E., Evans E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* **22**, 2-15.
- Brocks J.J., Grice K., 2011. Biomarkers (molecular fossils). In *Encyclopedia of Geobiology* (eds. Reitner J., Thiel V.). Springer, Dordrecht, The Netherlands. pp 147-167.
- Brocks J.J., Grosjean E., Logan G.A., 2008. Assessing biomarker syngeneity using branched alkanes with quaternary carbon (BAQCs) and other plastic contaminants. *Geochimica et Cosmochimica Acta* **72**, 871-888.
- Brocks J.J., Love G.D., Summons R.E., Knoll A.H., Logan G.A., Bowden S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866-870.
- Brocks J.J., Schaeffer P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. *Geochimica et Cosmochimica Acta* **72**, 1396-1414.
- Brocks J.J., Summons R.E., 2003. Sedimentary hydrocarbons, biomarkers for early life. In *Treatise on Geochemistry Volume 8 - Biogeochemistry* (ed. Schlesinger W.H.). Elsevier-Pergamon, Oxford. pp 63-115.
- Bull S.W., 1998. Sedimentology of the Palaeoproterozoic Barney Creek formation in DDH BMR McArthur 2, southern McArthur basin, Northern Territory. *Australian Journal of Earth Sciences* **45**, 21-31.

- Canfield D.E., 1998. A new model for Proterozoic ocean chemistry. *Nature* **396**, 450-453.
- Canfield D.E., 2001. Biogeochemistry of sulfur isotopes. *Reviews in Mineralogy and Geochemistry* **43**, 607-636.
- Chen J., Walter M.R., Logan G.A., Hinman M.C., Summons R.E., 2003. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: organic geochemistry and ore genesis. *Earth and Planetary Science Letters* **210**, 467-479.
- Chikaraishi Y., Naraoka H., Poulson S.R., 2004. Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. *Phytochemistry* **65**, 1369-1381.
- Clayton C.J., 1991. Effect of maturity on carbon isotope ratios of oils and condensates. *Organic Geochemistry* **17**, 887-899.
- Cooke D.R., Bull S.W., Donovan S., Rogers J.R., 1998. K-metasomatism and base metal depletion in volcanic rocks from the McArthur Basin, Northern Territory; implications for base metal mineralization. *Economic Geology* **93**, 1237-1263.
- Cooke D.R., Bull S.W., Large R.R., McGoldrick P.J., 2000. The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb-Zn (sedex) deposits. *Economic Geology* **95**, 1-18.
- Crick I.H., Boreham C.J., Cook A.C., Powell T.G., 1988. Petroleum geology and geochemistry of middle Proterozoic McArthur Basin, Northern Australia II: assessment of source rock potential. *AAPG Bulletin* **72**, 1495-1514.
- Croxford N.J.W., Jephcott S., 1972. The McArthur lead-zinc-silver deposit, N.T. *Proceedings: Australasian Institute of Mining and Metallurgy* **243**, 1-26.
- Davidson G.J., Dashlooty S.A., 1993. The Glyde Sub-basin: a volcanoclastic-bearing pull-apart basin coeval with the McArthur River base-metal deposit, Northern Territory. *Australian Journal of Earth Sciences* **40**, 527-543.
- Dawson D., Grice K., Alexander R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Organic Geochemistry* **36**, 95-104.

- Dawson D., Grice K., Wang S.X., Alexander R., Radke J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. *Organic Geochemistry* **35**, 189-197.
- Des Marais D.J., 1997. Long-term evolution of the biogeochemical carbon cycle. *Reviews in Mineralogy and Geochemistry* **35**, 429-448.
- Donnelly T.H., Jackson M.J., 1988. Sedimentology and geochemistry of a mid-Proterozoic lacustrine unit from northern Australia. *Sedimentary Geology* **58**, 145-169.
- Dow W.G., 1977. Kerogen studies and geological interpretations. *Journal of Geochemical Exploration* **7**, 79-99.
- Eglinton G., Hamilton R.J., 1967. Leaf epicuticular waxes. *Science* **156**, 1322-1335.
- Eldridge C.S., Williams N., Walshe J.L., 1993. Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe SHRIMP: II. A study of the H.Y.C. deposit at McArthur River, Northern Territory, Australia. *Economic Geology* **88**, 1-26.
- Falkowski P.G., 2012. The global carbon cycle: biological processes. In *Fundamentals of Geobiology* (eds. Knoll A.H., Canfield D.E., Konhauser K.O.). Blackwell Publishing Ltd., Chichester. pp 5-19.
- Freeman K.H., 2001. Isotopic biogeochemistry of marine organic carbon. *Reviews in Mineralogy and Geochemistry* **43**, 579-605.
- Garrigues P., De Sury R., Angelin M.L., Bellocq J., Oudin J.L., Ewald M., 1988. Relation of the methylated aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta. *Geochimica et Cosmochimica Acta* **52**, 375-384.
- Garven G., Bull S.W., Large R.R., 2001. Hydrothermal fluid flow models of stratiform ore genesis in the McArthur Basin, Northern Territory, Australia. *Geofluids* **1**, 289-311.
- Gatellier J.-P., Disnar J.-R., 1989. Organic matter and gold-ore association in a hydrothermal deposit, France. *Applied Geochemistry* **4**, 143-149.

- Gehre M., Strauch G., 2003. High-temperature elemental analysis and pyrolysis techniques for stable isotope analysis. *Rapid Communications in Mass Spectrometry* **17**, 1497-1503.
- George S.C., Ahmed M., 2002. Use of aromatic compound distributions to evaluate organic maturity of the Proterozoic middle Velkerri Formation, McArthur Basin, Australia. In *The Sedimentary Basins of Western Australia 3: Proceedings of the Petroleum Exploration Society of Australia Symposium 2002* (eds. Keep M., Moss S.J.). Petroleum Exploration Society of Australia, Perth. pp 253-270.
- Giordano T.H., 2002. Transport of Pb and Zn by carboxylate complexes in basinal ore fluids and related petroleum-field brines at 100 °C: the influence of pH and oxygen fugacity. *Geochemical Transactions* **3**, 56-72.
- Gizé A.P., 1999. Organic alteration in hydrothermal sulfide ore deposits. *Economic Geology* **94**, 967-979.
- Gizé A.P., Barnes H.L., 1987. The organic geochemistry of two Mississippi Valley-type lead-zinc deposits. *Economic Geology* **82**, 457-470.
- Gizé A.P., Barnes H.L., 1994. Organic contributions to Mississippi Valley-type lead-zinc genesis - a critical assessment. In *Sediment-hosted Zn-Pb ores - Special publication no. 10 of the Society for Geology Applied to Mineral Deposits* (eds. Fontboté L., Boni M.). Springer-Verlag, Berlin. pp 13-26.
- Greenwood P.F., Brocks J.J., Grice K., Schwark L., Jaraula C.M.B., Dick J.M., Evans K.A., 2013. Organic geochemistry and mineralogy. I. Characterisation of organic matter associated with metal deposits. *Ore Geology Reviews* **50**, 1-27.
- Grice K., Brocks J.J., 2011. Biomarkers (organic, compound-specific isotopes). In *Encyclopedia of Geobiology* (eds. Reitner J., Thiel V.). Springer, Dordrecht, The Netherlands. pp 167-182.
- Grice K., Cao C., Love G.D., Böttcher M.E., Twitchett R.J., Grosjean E., Summons R.E., Turgeon S.C., Dunning W., Jin Y., 2005. Photic zone euxinia during the Permian-Triassic superanoxic event. *Science* **307**, 706-709.

- Grice K., Lu H., Atahan P., Asif M., Hallmann C., Greenwood P.F., Maslen E., Tulipani S., Williford K., Dodson J., 2009. New insights into the origin of perylene in geological samples. *Geochimica et Cosmochimica Acta* **73**, 6531-6543.
- Grice K., Nabbefeld B., Maslen E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. *Organic Geochemistry* **38**, 1795-1803.
- Grice K., Schaeffer P., Schwark L., Maxwell J.R., 1996. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. *Organic Geochemistry* **25**, 131-147.
- Grice K., Schaeffer P., Schwark L., Maxwell J.R., 1997. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Lower Rhine Basin, northwest Germany) inferred from molecular and isotopic compositions of biomarker components. *Organic Geochemistry* **26**, 677-690.
- Grosjean E., Logan G.A., 2007. Incorporation of organic contaminants into geochemical samples and an assessment of potential sources: examples from Geoscience Australia marine survey S282. *Organic Geochemistry* **38**, 853-869.
- Hayes J.M., 2001. Fractionation of carbon and hydrogen isotopes in biosynthetic processes. *Reviews in Mineralogy and Geochemistry* **43**, 225-277.
- Hayes J.M., Freeman K.H., Popp B.N., Hoham C.H., 1990. Compound-specific isotopic analyses: a novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochemistry* **16**, 1115-1128.
- Hebting Y., Schaeffer P., Behrens A., Adam P., Schmitt G., Schneckenburger P., Bernasconi S.M., Albrecht P., 2006. Biomarker evidence for a major preservation pathway of sedimentary organic carbon. *Science* **312**, 1627-1631.
- Hinman M.C., 1996. Constraints, timing and processes of stratiform base metal mineralisation at the HYC Ag-Pb-Zn deposit, McArthur River. In *MIC '96 extended conference abstracts: New developments in metallogenic research:*

- The McArthur, Mount Isa, Cloncurry Minerals Province* (eds. Baker T., Rotherham J.F., Richmond J.M., Mark G., Williams P.J.). James Cook University of North Queensland Economic Geology Research Unit, Townsville. pp 56-59.
- Ho E.S., Meyers P.A., Mauk J.L., 1990. Organic geochemical study of mineralization in the Keweenawan Nonesuch Formation at White Pine, Michigan. *Organic Geochemistry* **16**, 229-234.
- Hoefs J., 2009. *Stable Isotope Geochemistry*. Springer, Berlin.
- Huston D.L., Stevens B., Southgate P.N., Muhling P., Wyborn L., 2006. Australian Zn-Pb-Ag ore-forming systems: a review and analysis. *Economic Geology* **101**, 1117-1157.
- Imhoff J.F., 2006. The Chromatiaceae. In *The Prokaryotes Volume 6: Proteobacteria: Gamma Subclass* (eds. Dworkin M., Falkow S., Rosenberg E., Schleifer K.-H., Stackebrandt E.). Springer, New York. pp 846-873.
- Ireland T., Bull S.W., Large R.R., 2004a. Mass flow sedimentology within the HYC Zn-Pb-Ag deposit, Northern Territory, Australia: evidence for syn-sedimentary ore genesis. *Mineralium Deposita* **39**, 143-158.
- Ireland T., Large R.R., McGoldrick P., Blake M., 2004b. Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore textures in the McArthur River (HYC) Zn-Pb-Ag deposit, Northern Territory, Australia. *Economic Geology* **99**, 1687-1709.
- Jackson M.J., Southgate P.N., Winefield P.R., Barnett K., Zeilinger I., 2000. Revised sub-division and regional correlation of the McArthur Basin succession based on NABRE's 1995-8 sequence stratigraphic studies. Australian Geological Survey Organization Record 2000/03, Canberra.
- Jackson M.J., Sweet I.P., Powell T.G., 1988. Studies on petroleum geology and geochemistry, middle Proterozoic, McArthur Basin northern Australia I: petroleum potential. *The APEA Journal* **28**, 283-302.
- Johnston D.T., Farquhar J., Summons R.E., Shen Y., Kaufman A.J., Masterson A.L., Canfield D.E., 2008. Sulfur isotope biogeochemistry of the Proterozoic McArthur Basin. *Geochimica et Cosmochimica Acta* **72**, 4278-4290.

- Kannenber E.L., Poralla K., 1999. Hopanoid biosynthesis and function in bacteria. *Naturwissenschaften* **86**, 168-176.
- Kawka O.E., Simoneit B.R.T., 1990. Polycyclic aromatic hydrocarbons in hydrothermal petroleum from the Guaymas Basin spreading center. *Applied Geochemistry* **5**, 17-27.
- Kawka O.E., Simoneit B.R.T., 1994. Hydrothermal pyrolysis of organic matter in Guaymas Basin: I. Comparison of hydrocarbon distributions in subsurface sediments and seabed petroleum. *Organic Geochemistry* **22**, 947-978.
- Kendall B., Creaser R.A., Gordon G.W., Anbar A.D., 2009. Re–Os and Mo isotope systematics of black shales from the Middle Proterozoic Velkerri and Wollongorang Formations, McArthur Basin, northern Australia. *Geochimica et Cosmochimica Acta* **73**, 2534-2558.
- Killops S., Killops V., 2005. *Introduction to Organic Geochemistry*. Blackwell Publishing, Oxford.
- Kristjansson J.K., Schönheit P., Thauer R.K., 1982. Different K_s values for hydrogen of methanogenic bacteria and sulfate reducing bacteria: an explanation for the apparent inhibition of methanogenesis by sulfate. *Archives of Microbiology* **131**, 278-282.
- Krouse H.R., Coplen T.B., 1997. Reporting of relative sulfur isotope-ratio data (Technical Report). *Pure and Applied Chemistry* **69**, 293-295.
- Kvalheim O.M., Christy A.A., Telnæs N., Bjørseth A., 1987. Maturity determination of organic matter in coals using the methylphenanthrene distribution. *Geochimica et Cosmochimica Acta* **51**, 1883-1888.
- Lambert I.B., Scott K.M., 1973. Implications of geochemical investigations of sedimentary rocks within and around the McArthur zinc-lead-silver deposit, Northern Territory. *Journal of Geochemical Exploration* **2**, 307-330.
- Landais P., 1996. Organic geochemistry of sedimentary uranium ore deposits. *Ore Geology Reviews* **11**, 33-51.
- Large R.R., Bull S.W., Cooke D.R., McGoldrick P.J., 1998. A genetic model for the HYC deposit, Australia: based on regional sedimentology, geochemistry, and sulfide-sediment relationships. *Economic Geology* **93**, 1345-1368.

- Large R.R., Bull S.W., McGoldrick P.J., Walters S., Derrick G.M., Carr G.R., 2005. Stratiform and strata-bound Zn-Pb-Ag deposits in Proterozoic sedimentary basins, Northern Australia. In *Economic Geology 100th Anniversary Volume* (eds. Hedenquist J.W., Thompson J.F.H., Goldfarb R.J., Richards J.P.). Society of Economic Geologists, Littleton, Colorado. pp 931-963.
- Le Métayer P., Grice K., Chow C.N., Caccetta L., Maslen E., Dawson D., Fusetti L., 2014. The effect of origin and genetic processes of low-molecular-weight aromatic hydrocarbons in petroleum on their stable carbon isotopic compositions. *Organic Geochemistry*, *in press*.
- Leach D.L., Bradley D.C., Huston D., Pisarevsky S.A., Taylor R.D., Gardoll S.J., 2010. Sediment-hosted lead-zinc deposits in Earth history. *Economic Geology* **105**, 593-625.
- Leach D.L., Sangster D.F., Kelly K.D., Large R.R., Garven G., Allen C.R., Gutzmer J., Walters S., 2005. Sediment-hosted lead-zinc deposits: a global perspective. In *Economic Geology 100th Anniversary Volume* (eds. Hedenquist J.W., Thompson J.F.H., Goldfarb R.J., Richards J.P.). Society of Economic Geologists, Littleton, Colorado. pp 561-607.
- Lindsay J.F., Brasier M.D., 2000. A carbon isotope reference curve for ca. 1700-1575 Ma, McArthur and Mount Isa Basins, Northern Australia. *Precambrian Research* **99**, 271-308.
- Logan G.A., Calver C.R., Gorjan P., Summons R.E., Hayes J.M., Walter M.R., 1999. Terminal Proterozoic mid-shelf benthic microbial mats in the Centralian Superbasin and their environmental significance. *Geochimica et Cosmochimica Acta* **63**, 1345-1358.
- Logan G.A., Hayes J.M., Hieshima G.B., Summons R.E., 1995. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* **376**, 53-56.
- Logan G.A., Hinman M.C., Walter M.R., Summons R.E., 2001. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. *Geochimica et Cosmochimica Acta* **65**, 2317-2336.

- Londry K.L., Jahnke L.L., Des Marais D.J., 2004. Stable carbon isotope ratios of lipid biomarkers of sulfate-reducing bacteria. *Applied and Environmental Microbiology* **70**, 745-751.
- Lyons T.W., Gellatly A.M., McGoldrick P.J., Kah L.C., 2006. Proterozoic sedimentary exhalative (SEDEX) deposits and links to evolving global ocean chemistry. *Geological Society of America Memoirs* **198**, 169-184.
- Mackenzie K.L., Marshall C.P., Walter M.R., 2008. Regional organic geochemistry of host sediments of Palaeoproterozoic McArthur River Ore deposit, Australia. *Theoretical Chemistry Accounts* **119**, 143-153.
- Marzi R., Torkelson B.E., Olson R.K., 1993. A revised carbon preference index. *Organic Geochemistry* **20**, 1303-1306.
- Maslen E., Grice K., Dawson D., Wang S., Horsfield B., 2013. Stable hydrogen isotopes of isoprenoids and *n*-alkanes as a proxy for estimating the thermal history of sediments through geological time. In *Analyzing the Thermal History of Sedimentary Basins: Methods and Case Studies* (eds. Harris N.B., Peters K.E.). Society for Sedimentary Geology Special Publication No. 103, Tulsa, Oklahoma.
- Matthews D.E., Hayes J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. *Analytical Chemistry* **50**, 1465-1473.
- McGoldrick P., Winefield P., Bull S., Selley D., Scott R., 2010. Sequences, synsedimentary structures, and sub-basins: the where and when of SEDEX zinc systems in the southern McArthur Basin, Australia. In *The Challenge of Finding New Mineral Resources: Global Metallogeny, Innovative Exploration, and New Discoveries. Volume II: Zinc-Lead, Nickel-Copper-PGE, and Uranium* (eds. Goldfarb R.J., Marsh E.E., Monecke T.). Society of Economic Geologists Special Publication Number 15, Littleton, Colorado. pp 367-389.
- Melendez I., Grice K., Trinajstić K., Ladjavardi M., Greenwood P., Thompson K., 2013. Biomarkers reveal the role of photic zone euxinia in exceptional fossil preservation: an organic geochemical perspective. *Geology* **41**, 123-126.

- Melzer E., Schmidt H.L., 1987. Carbon isotope effects on the pyruvate dehydrogenase reaction and their importance for relative carbon-13 depletion in lipids. *Journal of Biological Chemistry* **262**, 8159-8164.
- Moldowan J.M., Sundararaman P., Schoell M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. *Organic Geochemistry* **10**, 915-926.
- Moodley L., Middelburg J.J., Herman P.M.J., Soetaert K., de Lange G.J., 2005. Oxygenation and organic-matter preservation in marine sediments: direct experimental evidence from ancient organic carbon-rich deposits. *Geology* **33**, 889-892.
- Mukhopadhyay P.K., 1994. Vitrinite reflectance as maturity parameter. In *Vitrinite Reflectance as a Maturity Parameter* (eds. Mukhopadhyay P.K., Dow W.G.). American Chemical Society, Washington, D.C. pp 1-24.
- Munier-Lamy C., Adrian P., Berthelin J., Rouiller J., 1986. Comparison of binding abilities of fulvic and humic acids extracted from recent marine sediments with UO₂²⁺. *Organic Geochemistry* **9**, 285-292.
- Nabbefeld B., Grice K., Schimmelmann A., Sauer P.E., Böttcher M.E., Twitchett R.J., 2010a. Significance of δD (kerogen), $\delta^{13}C$ (kerogen) and $\delta^{34}S$ (pyrite) from several Permian/Triassic (P/Tr) sections. *Earth and Planetary Science Letters* **295**, 21-29.
- Nabbefeld B., Grice K., Schimmelmann A., Summons R.E., Troitzsch U., Twitchett R.J., 2010b. A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks. *Organic Geochemistry* **41**, 78-87.
- Nabbefeld B., Grice K., Summons R.E., Hays L.E., Cao C., 2010c. Significance of polycyclic aromatic hydrocarbons (PAHs) in Permian/Triassic boundary sections. *Applied Geochemistry* **25**, 1374-1382.
- Orr W.L., 1986. Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils. *Organic Geochemistry* **10**, 499-516.

- Overmann J., 2006. The family Chlorobiaceae. In *The Prokaryotes Volume 7: Proteobacteria: Delta, Epsilon Subclass* (eds. Dworkin M., Falkow S., Rosenberg E., Schleifer K.-H., Stackebrandt E.). Springer, New York. pp 359-378.
- Page R.W., Jackson M.J., Krassay A.A., 2000. Constraining sequence stratigraphy in north Australian basins: SHRIMP U–Pb zircon geochronology between Mt Isa and McArthur River. *Australian Journal of Earth Sciences* **47**, 431-459.
- Page R.W., Sweet I.P., 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences* **45**, 219-232.
- Pawlowska M.M., Butterfield N.J., Brocks J.J., 2013. Lipid taphonomy in the Proterozoic and the effect of microbial mats on biomarker preservation. *Geology* **41**, 103-106.
- Peters K.E., Walters C.C., Moldowan J.M., 2005. *The Biomarker Guide Volume 1 - Biomarkers and Isotopes in the Environment and Human History*. Cambridge University Press, Cambridge.
- Planavsky N.J., McGoldrick P., Scott C.T., Li C., Reinhard C.T., Kelly A.E., Chu X., Bekker A., Love G.D., Lyons T.W., 2011. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448-451.
- Plumb K.A., 1979. Structure and tectonic style of the Precambrian shields and platforms of northern Australia. *Tectonophysics* **58**, 291-325.
- Poulton S.W., Fralick P.W., Canfield D.E., 2010. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geoscience* **3**, 486-490.
- Powell T.G., Jackson M.J., Sweet I.P., Crick I.H., Boreham C.J., Summons R.E., 1987. Petroleum geology and geochemistry, Middle Proterozoic McArthur Basin. Australia Bureau of Mineral Resources, Geology and Geophysics, record 1987/48.
- Püttmann W., Merz C., Speczik S., 1989. The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland. *Applied Geochemistry* **4**, 151-161.

- Radke M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology* **5**, 224-236.
- Radke M., Welte D.H., Willsch H., 1982a. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* **46**, 1-10.
- Radke M., Welte D.H., Willsch H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. *Organic Geochemistry* **10**, 51-63.
- Radke M., Willsch H., Leythaeuser D., Teichmüller M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* **46**, 1831-1848.
- Rawlings D.J., Korsch R.J., Goleby B.R., Gibson G.M., Johnstone D.W., Barlow M., 2004. The 2002 Southern McArthur Basin Seismic Reflection Survey, Geoscience Australia record 2004/17, Canberra.
- Rieger A., Schwark L., Cisternas M.-E., Miller H., 2008. Genesis and evolution of bitumen in Lower Cretaceous lavas and implications for strata-bound copper deposits, North Chile. *Economic Geology* **103**, 387-404.
- Sauer P.E., Schimmelmann A., Sessions A.L., Topalov K., 2009. Simplified batch equilibration for D/H determination of non-exchangeable hydrogen in solid organic material. *Rapid Communications in Mass Spectrometry* **23**, 949-956.
- Schidlowski M., 1988. A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* **333**, 313-318.
- Schimmelmann A., Sessions A.L., Mastalerz M., 2006. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Sciences* **34**, 501-533.
- Schwark L., Püttmann W., 1990. Aromatic hydrocarbon composition of the Permian Kupferschiefer in the Lower Rhine Basin, NW Germany. *Organic Geochemistry* **16**, 749-761.
- Seifert W.K., Moldowan J.M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochimica et Cosmochimica Acta* **42**, 77-95.

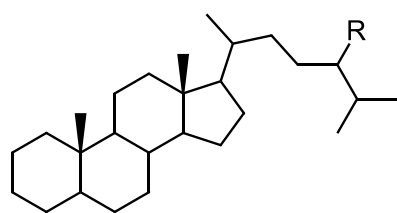
- Sessions A.L., 2006. Isotope-ratio detection for gas chromatography. *Journal of Separation Science* **29**, 1946-1961.
- Sessions A.L., Burgoyne T.W., Schimmelmann A., Hayes J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochemistry* **30**, 1193-1200.
- Shen Y., Canfield D.E., Knoll A.H., 2002. Middle Proterozoic ocean chemistry: evidence from the McArthur Basin, northern Australia. *American Journal of Science* **302**, 81-109.
- Sherman L.S., Waldbauer J.R., Summons R.E., 2007. Improved methods for isolating and validating indigenous biomarkers in Precambrian rocks. *Organic Geochemistry* **38**, 1987-2000.
- Sicree A.A., Barnes H.L., 1996. Upper Mississippi Valley district ore fluid model: the role of organic complexes. *Ore Geology Reviews* **11**, 105-131.
- Sinninghe Damsté J.S., de Leeuw J.W., 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: state of the art and future research. *Organic Geochemistry* **16**, 1077-1101.
- Skrzypek G., Paul D., 2006. $\delta^{13}\text{C}$ analyses of calcium carbonate: comparison between the GasBench and elemental analyzer techniques. *Rapid Communications in Mass Spectrometry* **20**, 2915-2920.
- Smith J.W., George S.C., Batts B.D., 1995. The geosynthesis of alkylaromatics. *Organic Geochemistry* **23**, 71-80.
- Spangenberg J.E., Macko S.A., 1998. Organic geochemistry of the San Vicente zinc-lead district, eastern Pucará Basin, Peru. *Chemical Geology* **146**, 1-23.
- Spirakis C.S., 1996. The roles of organic matter in the formation of uranium deposits in sedimentary rocks. *Ore Geology Reviews* **11**, 53-69.
- Steenbergen C.L.M., Korthals H.J., 1982. Distribution of phototrophic microorganisms in the anaerobic and microaerophilic strata of Lake Vechten (The Netherlands). Pigment analysis and role in primary production. *Limnology and Oceanography* **27**, 883-895.

- Stein S.E., 1978. On the high temperature chemical equilibria of polycyclic aromatic hydrocarbons. *The Journal of Physical Chemistry* **82**, 566-571.
- Summons R.E., Powell T.G., Boreham C.J., 1988. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. *Geochimica et Cosmochimica Acta* **52**, 1747-1763.
- Summons R.E., Taylor D., Boreham C.J., 1994. Geochemical tools for evaluating petroleum generation in Middle Proterozoic sediments of the McArthur Basin, Northern Territory, Australia. *The APEA Journal* **34**, 692-706.
- Szczerba M., Rospondek M.J., 2010. Controls on distributions of methylphenanthrenes in sedimentary rock extracts: critical evaluation of existing geochemical data from molecular modelling. *Organic Geochemistry* **41**, 1297-1311.
- van Aarssen B.G.K., Bastow T.P., Alexander R., Kagi R.I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Organic Geochemistry* **30**, 1213-1227.
- van Graas G.W., 1990. Biomarker maturity parameters for high maturities: calibration of the working range up to the oil/condensate threshold. *Organic Geochemistry* **16**, 1025-1032.
- Vandenbroucke M., Largeau C., 2007. Kerogen origin, evolution and structure. *Organic Geochemistry* **38**, 719-833.
- Venkatesan M.I., Dahl J., 1989. Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary. *Nature* **338**, 57-60.
- Vogl K., Glaeser J., Pfannes K., Wanner G., Overmann J., 2006. *Chlorobium chlorochromatii* sp. nov., a symbiotic green sulfur bacterium isolated from the phototrophic consortium "Chlorochromatium aggregatum". *Archives of Microbiology* **185**, 363-372.
- Volkman J.K., 2003. Sterols in microorganisms. *Applied Microbiology and Biotechnology* **60**, 495-506.

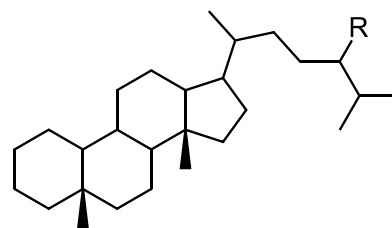
- Wakeham S.G., Schaffner C., Giger W., 1980a. Polycyclic aromatic hydrocarbons in Recent lake sediments—I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta* **44**, 403-413.
- Wakeham S.G., Schaffner C., Giger W., 1980b. Polycyclic aromatic hydrocarbons in Recent lake sediments—II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta* **44**, 415-429.
- Waldbauer J.R., Sherman L.S., Sumner D.Y., Summons R.E., 2009. Late Archean molecular fossils from the Transvaal Supergroup record the antiquity of microbial diversity and aerobiosis. *Precambrian Research* **169**, 28-47.
- Werne J.P., Lyons T.W., Hollander D.J., Formolo M.J., Sinninghe Damsté J.S., 2003. Reduced sulfur in euxinic sediments of the Cariaco Basin: sulfur isotope constraints on organic sulfur formation. *Chemical Geology* **195**, 159-179.
- Werne J.P., Lyons T.W., Hollander D.J., Schouten S., Hopmans E.C., Sinninghe Damsté J.S., 2008. Investigating pathways of diagenetic organic matter sulfurization using compound-specific sulfur isotope analysis. *Geochimica et Cosmochimica Acta* **72**, 3489-3502.
- Werner R.A., Brand W.A., 2001. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Communications in Mass Spectrometry* **15**, 501-519.
- Williams N., 1978. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: I. The Cooley and Ridge deposits. *Economic Geology* **73**, 1005-1035.
- Williford K.H., Grice K., Logan G.A., Chen J., Huston D., 2011. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters* **301**, 382-392.
- Wortmann U.G., Bernasconi S.M., Böttcher M.E., 2001. Hypersulfidic deep biosphere indicates extreme sulfur isotope fractionation during single-step microbial sulfate reduction. *Geology* **29**, 647-650.
- Zerkle A.L., Farquhar J., Johnston D.T., Cox R.P., Canfield D.E., 2009. Fractionation of multiple sulfur isotopes during phototrophic oxidation of

sulfide and elemental sulfur by a green sulfur bacterium. *Geochimica et Cosmochimica Acta* **73**, 291-306.

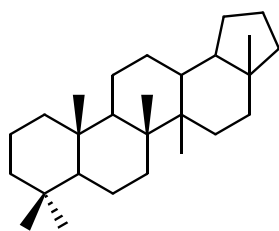
Appendix 1



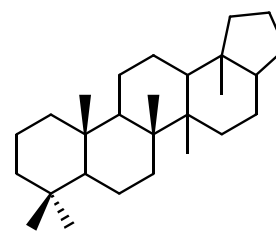
steranes (I)
R = H, CH₃, C₂H₅, C₃H₇



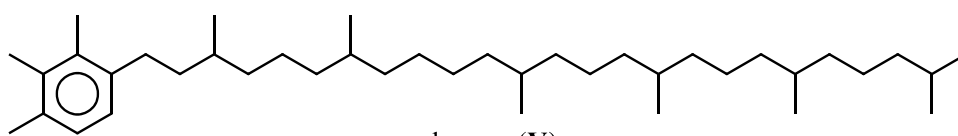
diasteranes (II)
R = H, CH₃, C₂H₅, C₃H₇



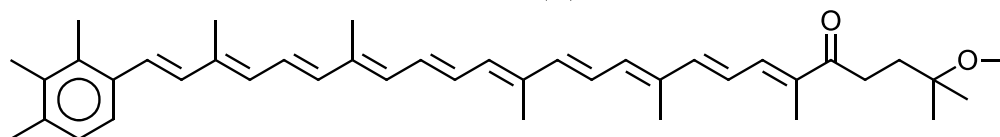
Ts (III)



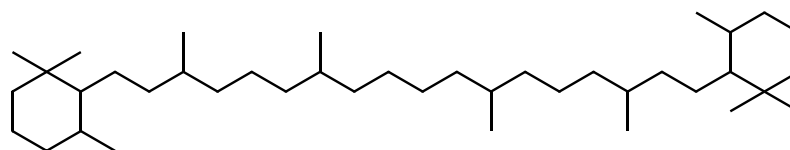
Tm (IV)



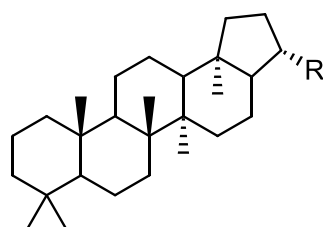
okenane (V)



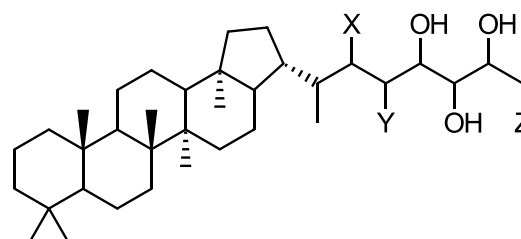
okenone (VI)



β -carotane (VII)



hopanes (VIII)
R = H, CH₃, C₂H₅ ... C₇H₁₅



bacteriohopanepolyols (IX)
X, Y = H, OH
Z = OH, OR, NHR

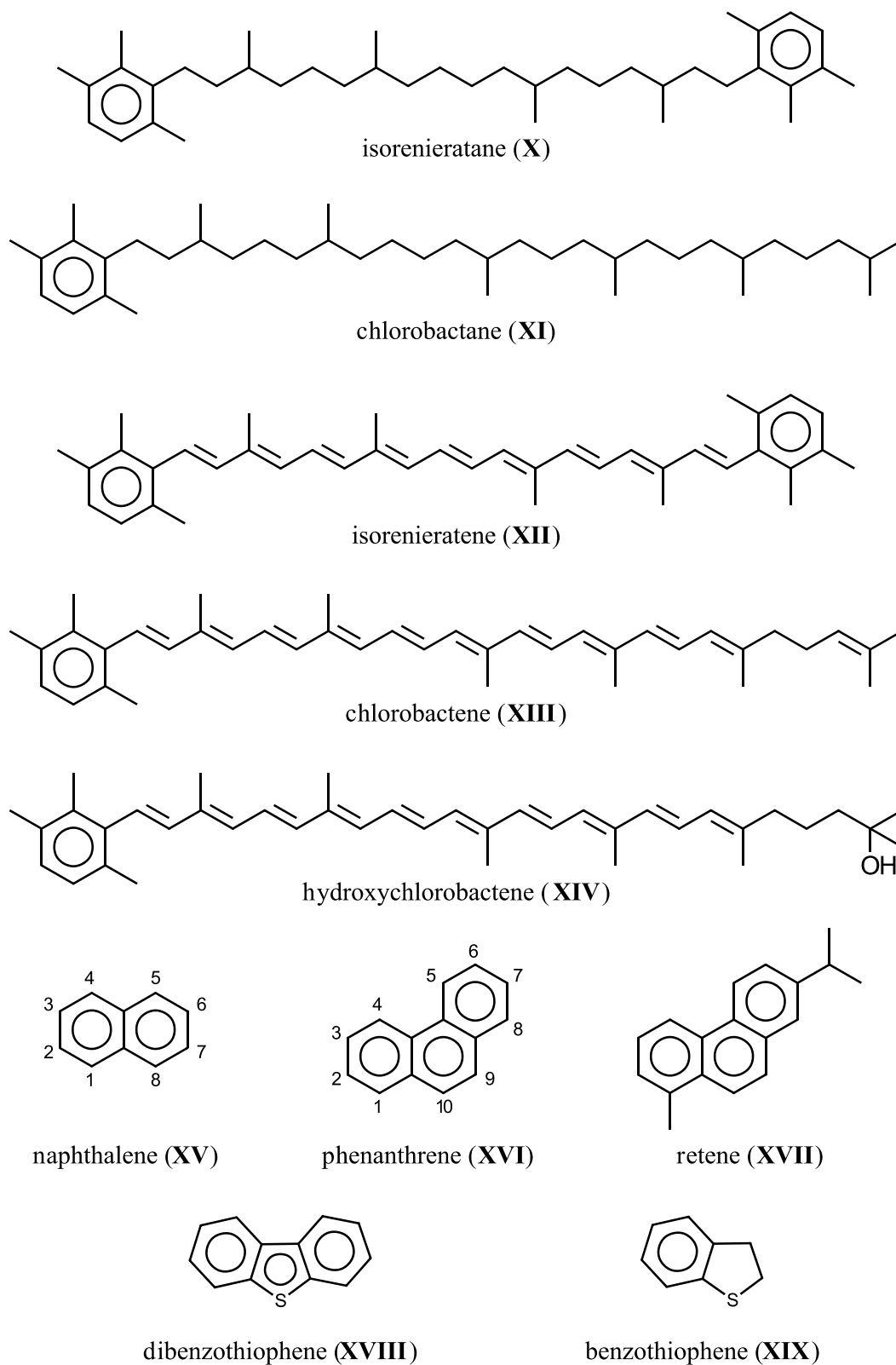


Figure A1.1: Structures referred to in the text.

Chapter 2

**Efficiency of extraction of Polycyclic Aromatic
Hydrocarbons from the Paleoproterozoic Here's
Your Chance Pb/Zn/Ag ore deposit and implications
for a study of Bitumen II**

**Alex I. Holman, Kliti Grice, Caroline M. B. Jaraula, Arndt Schimmelmann and
Jochen J. Brocks**

Organic Geochemistry **52**, 81-87 (2012)

Abstract

Demineralisation of a sedimentary rock with HF liberates a fraction of extractable organic matter (OM) that is not accessible by standard extraction techniques, which is known as Bitumen II. This fraction displays lower maturity parameters than the free extractable OM (Bitumen I). Studies of successive conventional extraction have found that the later extraction steps show a decrease in maturity similar to that observed in Bitumen II. We aim to investigate if Bitumen II is simply the result of residual Bitumen I left over from the initial extraction.

A series of successive Soxhlet extraction steps was performed on a highly-mineralised sample from the Paleoproterozoic Here's Your Chance (HYC) Pb/Zn/Ag deposit in the Northern Territory of Australia. The study shows that the extraction efficiency for polycyclic aromatic hydrocarbons (PAHs) decreases with increasing molecular weight. Maturity parameters based on methyl phenanthrenes generally decrease with successive extractions. This is because the more thermodynamically stable β isomers are preferentially extracted over α isomers, so later extraction steps contain a greater proportion of α isomers.

Bitumen II was prepared from a previously-studied sample from the same sample pit. It showed a decrease in maturity parameters relative to Bitumen I, but the distribution of PAHs did not match those of the later Bitumen I extraction steps. We conclude that Bitumen II did not result from incomplete extraction of Bitumen I. As Bitumen II is preserved within the kerogen / mineral matrix, it has great potential for tracing the migration and maturation history of ancient or thermally altered systems.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in sediments. Those methylated at β positions are thermodynamically more stable than those methylated at α positions (van Aarssen et al., 1999; Szczerba and Rospondek, 2010). Ratios of β to α isomers are thus dependent on maturity and are commonly used as maturity parameters (Radke et al., 1982a; Radke, 1988). PAH-derived maturity parameters are especially useful for Proterozoic sediments where measurements such as vitrinite reflectance are not applicable and aliphatic biomarkers are often in low abundance (George and Ahmed, 2002). Many common aromatic maturity parameters are based on the methyl naphthalenes (MNs) and methyl phenanthrenes (MPs). Examples include the methyl naphthalene ratio (MNR, 2-MN/1-MN) (Radke et al., 1982b), methyl phenanthrene ratio (MPR, 2-MP/1-MP) (Radke et al., 1982b) and methyl phenanthrene index (MPI-1), defined by Radke et al. (1982a) as $1.5 \times (2\text{-MP} + 3\text{-MP}) / (P + 1\text{-MP} + 9\text{-MP})$.

Demineralisation of rock samples with HF is a standard technique for kerogen isolation (Saxby, 1970; Marshall et al., 2007) but may also liberate OM occluded in the kerogen / mineral matrix and thus inaccessible to conventional solvent extraction. Bitumen recovered through this technique is termed Bitumen II, whereas the solvent extract from undigested rock powder is known as Bitumen I. Bitumen II is considered less likely to be overprinted by migrated OM by virtue of its close association with, and shielding by, the kerogen / mineral matrix (Sherman et al., 2007). Nabbefeld et al. (2010b) compared aliphatic and aromatic maturity parameters in Bitumen I and Bitumen II for a variety of marine sediments spanning the Permian / Triassic boundary. It was found that the common aromatic maturity parameters MPI-1 and MNR are generally lower for Bitumen II than Bitumen I, and that the magnitude of the difference is greater with increasing clay / total organic carbon (TOC) ratio.

Several studies have explored the use of multiple extraction steps to recover hydrocarbons beyond those extracted with conventional methods such as Soxhlet extraction. Wilhelms et al. (1996) performed three extraction steps with increasingly polar solvent to analyse successive oil charges in reservoir rocks. Schwark et al. (1997) analysed oils from pore spaces in reservoir sandstones using successive extraction in a high pressure cell. Both observed lower maturity from final extracts of

some samples, which was interpreted as evidence that the final extracts came from oil residing in fine pores made accessible after initial extraction (Schwark et al., 1997). Price and Clayton (1992) performed successive Soxhlet extraction steps on unground source rocks using the same solvent system, and observed reduced aromatic maturity ratios and increased proportion of high molecular weight (MW) aromatics with successive extraction steps. The results were attributed to heterogeneous distribution of hydrocarbons within the rock. Mueller and Philp (1998) showed that high-MW hydrocarbons ($> C_{40}$) are resistant to conventional Soxhlet extraction, and can be recovered via subsequent ultrasonic extraction with *p*-xylene.

Separate studies of both Bitumen II and successive conventional extraction steps have demonstrated a decrease in molecular maturity ratios. We aim to determine whether the liberation of Bitumen II merely releases the fraction of Bitumen I that is more strongly adsorbed to the mineral and kerogen surfaces and thus resistant to extraction, rather than releasing organic compounds physically trapped within the kerogen / mineral matrix. Bitumen II was prepared from a Paleoproterozoic basin-hosted mineral deposit and compared with sequential Soxhlet extraction steps on Bitumen I from the same deposit, to investigate the effect of sequential extraction on PAH maturity parameters and to examine the source of Bitumen II.

Materials and methods

Sample description

This study is a part of a larger investigation of the HYC Pb/Zn/Ag deposit, carried out under the CSIRO Organic Geochemistry of Mineral Systems Cluster project. The deposit is located within the Barney Creek Formation (BCF), a 1640 Myr, carbonaceous marine shale in the Northern Territory of Australia (Page and Sweet, 1998). The BCF contains some of the best preserved Proterozoic biomarkers (Summons et al., 1988; Brocks et al., 2005). HYC is one of the world's largest sediment-hosted Pb/Zn/Ag deposits. A total of eight ore bodies are hosted in the 90 m deep ore zone (Large et al., 1998). It is generally held that HYC was formed by the interaction of low-temperature (100-240 °C) sulfate-rich fluids with BCF sediments (Huston et al., 2006) and hence the deposit has been studied as an example

of hydrothermal alteration of ancient OM (Logan et al., 2001; Chen et al., 2003; Williford et al., 2011). It has been proposed that the ore fluid carried aromatic hydrocarbons generated in the underlying Wollongorang Formation into HYC (Williford et al., 2011). It is hoped that Bitumen II has been protected from this migration and thus will more closely reflect the original environment prior to ore formation.

Five samples of several kg each were collected from surface exposures along the western edge of ore body five by the McArthur River Mining Company. The samples were taken along a north-south line following the estimated path of the hydrothermal fluid (Williford et al., 2011). Approximately 1 kg of each sample was extracted and analysed by Williford et al. (2011), with the remainder being wrapped in aluminium foil and stored in reserve. A 50 g piece was broken off from the reserve of sample pit 1 for use in this study. On visual inspection the 50 g piece was similar in appearance to the rest of the rock, being composed of finely laminated light-coloured mineralised layers throughout the darker shale. Pit 1 is the northernmost pit and was expected to show the highest degree of hydrothermal alteration (Williford et al., 2011). The sample was surface extracted (30 min) with 9:1 (v/v) dichloromethane (DCM): MeOH to remove external contaminants and ground to powder in a RockLabs bench top ring mill with a Zr head. The mill had been cleaned beforehand by grinding ($\times 3$) annealed sand. The final batch of sand was extracted after grinding and showed no significant contaminants.

Sequential extraction

Sequential extraction of Bitumen I followed the procedure of Williford et al. (2011). Powdered rock (ca. 21 g) was placed in an annealed and pre-extracted (9:1 DCM: MeOH v/v; 24 hours) glass fibre thimble and extracted in a Soxhlet apparatus with 9:1 DCM: MeOH v/v. Activated Cu turnings (ca. 50 g) were added to the round bottomed flask to remove elemental S. The solvent was periodically removed and the extraction continued with fresh solvent and Cu turnings. The extraction was thus split into a number of time intervals: 0-4, 4-8, 8-24, 24-48, 48-96 and 94-144 hours. The extract from each interval was evaporated to dryness and weighed.

The total extracts were adsorbed onto a minimum amount of activated silica and added to the top of a small column (5.5 cm \times 0.5 cm i.d.) of activated (overnight at

160 °C) silica. Saturate, aromatic and polar fractions were eluted with hexane, 30 % DCM in hexane and 1:1 (v/v) DCM: MeOH respectively. Aromatic fractions were semi-quantified using an internal standard of deuterated *p*-terphenyl.

Extraction of Bitumen II

Bitumen II was isolated as part of a study of the effect of hydrothermal alteration on the OM from the HYC deposit. The sample used to prepare Bitumen II had been previously studied by Williford et al. (2011). As discussed on page 46 this sample was broken off from the same large piece of rock as the one used for the sequential extraction. To remove Bitumen I the sample was extracted in a large Soxhlet apparatus (9:1 DCM:MeOH v/v, 72 hours); for full details see Williford et al. (2011).

Bitumen II was prepared using a modification of the HF-BF₃ procedure (Robl and Davis, 1993), previously used by Nabbefeld et al. (Nabbefeld et al., 2010a; 2010b). Pre-extracted rock powder was decarbonated with 1 M HCl. The sample was digested with a mixture of concentrated HF (48 %) and an equal volume of Milli-Q purified water in clean 50 mL polyethylene centrifuge vials (ca. 37 g sample spread over six vials). The vials were left (1-2 hours) in an ice bath to minimise build-up of pressure from the exothermic reaction and were regularly shaken. The liquid was decanted and fresh acid/water mixture was added and left (3-4 hours) at room temperature with occasional shaking to dissolve any re-precipitated minerals. In the original Robl and Davis method the first acid digestion was followed by the addition of H₃BO₃ to prevent the precipitation of insoluble fluoride salts. The second acid digestion was found to be equally as effective as the addition of H₃BO₃, with the advantage of increased simplicity and reduction in the number of chemicals that could potentially introduce contamination. After acid digestion the sample was washed (×3) with Milli-Q water to remove any residual acid and freeze-dried. The mass of the sample had decreased to ca. 20 g, comprising Bitumen II, kerogen, HF-insoluble minerals such as pyrite, and any fluoride minerals re-precipitated during digestion. The acid-digested rock powder was Soxhlet extracted (9:1 DCM: MeOH v/v, 72 hours), followed by small-column chromatography to separate the extract into saturate, aromatic and polar fractions as described on page 46.

Gas chromatography – mass spectrometry (GC-MS)

Saturate and aromatic fractions were analysed with a Hewlett Packard (HP) 5973 mass selective detector coupled to a HP 6890 GC instrument. Samples in *n*-hexane were injected via the HP 6890 autosampler into a split-splitless injector using pulsed-splitless mode. A DB5-MS column (Agilent Technologies, 60 m x 0.250 mm i.d., 0.25 µm film thickness) was used with He as carrier gas. The GC oven temperature was increased from 40 to 310 °C (held 30 min) at 3 °C min⁻¹. Data were acquired in full scan mode (*m/z* 50-550).

Results and discussion

Saturate fractions

The saturate fractions from the Bitumen I sequential extraction predominantly contained straight chain and branched alkanes. The straight chain alkanes C₁₅ to C₃₀ were found in all extracts. Shorter chain alkanes C₁₁ to C₁₃ were only observed in the 0-4 hours extract. There are no reports of aliphatic biomarkers such as steranes or hopanes in HYC saturate fractions, and none were found here. With respect to the total amount extracted after 144 hours, it is estimated that > 99 % of *n*-alkanes from C₁₅ to C₂₅ were extracted in the first 4 hours (based on comparison of peak areas). Only trace amounts were found in extracts from 8 hours onwards.

Aromatic fractions

The masses of individual PAHs extracted in each time period are shown in Table 2.1. Naphthalene and methyl naphthalenes were detected only in the first extraction, so are not included. Figure 2.1 shows the cumulative amount of individual PAHs extracted over time as a proportion of the total amount extracted after 144 hours. It can be seen that extraction proceeds more slowly with increasing MW. Phenanthrene, the lowest MW PAH considered, was extracted almost instantly, with 99 % recovery in the first 4 hours. In contrast 90 % of benzo[*ghi*]perylene and just 51 % of coronene were extracted in the same period. After a typical extraction period of 48 hours, phenanthrene and methyl phenanthrenes were extracted with > 99.8 % efficiency, but coronene was only extracted with 94 % efficiency. Adsorption energy

Table 2.1: Mass of extracted PAHs (ng g^{-1} extracted rock powder) and PAH ratios for sequential extracts and Bitumen II.

	0-4 hours	4-8 hours	8-24 hours	24-48 hours	48-96 hours	96-144 hours	Bitumen II
<i>Mass (ng g^{-1} rock)</i>							
Phenanthrene	222.00	0.63	0.58	0.03	0.12	0.08	4.86
3-Methylphenanthrene	261.54	1.28	1.50	0.07	0.18	0.24	3.35
2-Methylphenanthrene	284.80	1.39	1.51	0.07	0.19	0.31	3.79
9-Methylphenanthrene	167.47	0.94	1.14	0.06	0.14	0.25	2.83
1-Methylphenanthrene	210.00	1.20	1.55	0.07	0.18	0.37	2.83
Pyrene	53.72	0.44	0.71	0.02	0.09	0.15	3.09
Chrysene	66.78	0.87	1.45	0.07	0.25	0.29	2.59
Benzo[e]pyrene	75.72	1.45	2.42	0.17	0.48	0.62	6.10
Benzo[ghi]perylene	14.09	0.46	0.73	0.06	0.14	0.12	2.83
Coronene	0.62	0.17	0.32	0.03	0.04	0.04	0.80
Sum	1356.73	8.83	11.91	0.66	1.81	2.47	33.05
<i>PAH ratios</i>							
MPI-1	1.4	1.4	1.4	1.3	1.2	1.2	1.0
MPR	1.4	1.2	1.0	1.0	1.0	0.8	1.3
P/MPs	0.2	0.1	0.1	0.1	0.2	0.1	0.4
Chry/Phen	0.3	1.4	2.5	2.2	2.1	3.5	0.5
BePery/Phen	0.1	0.7	1.3	2.0	1.2	1.5	0.6
Coro/Phen	0.0	0.3	0.5	0.8	0.3	0.4	0.2

generally rises with increased aromaticity (Carlson and Chamberlain, 1986). Heavier aromatics are therefore preferentially retained in the rock over lighter compounds. Organic facies and mineral composition have a large effect on extraction yield and efficiency; so the numbers reported here are not universally applicable. Nevertheless, any researcher investigating high MW PAHs should be aware that higher MW compounds are not extracted at the same rate as lower MW ones. High MW PAHs such as coronene are important markers of burning events (Venkatesan and Dahl, 1989; Killops and Massoud, 1992; Grice et al., 2005; Nabbefeld et al., 2010c) and hydrothermal alteration (Kawka and Simoneit, 1994; Simoneit et al., 2004). Maturity parameters based on methylchrysene and methylpyrene isomers have also been proposed (Garrigues et al., 1988), although they have not come into general use. Short extraction times may cause the proportion of high MW PAHs to be underestimated. It is recommended that extraction times of 96 hours or more be used if such compounds are of importance to a study.

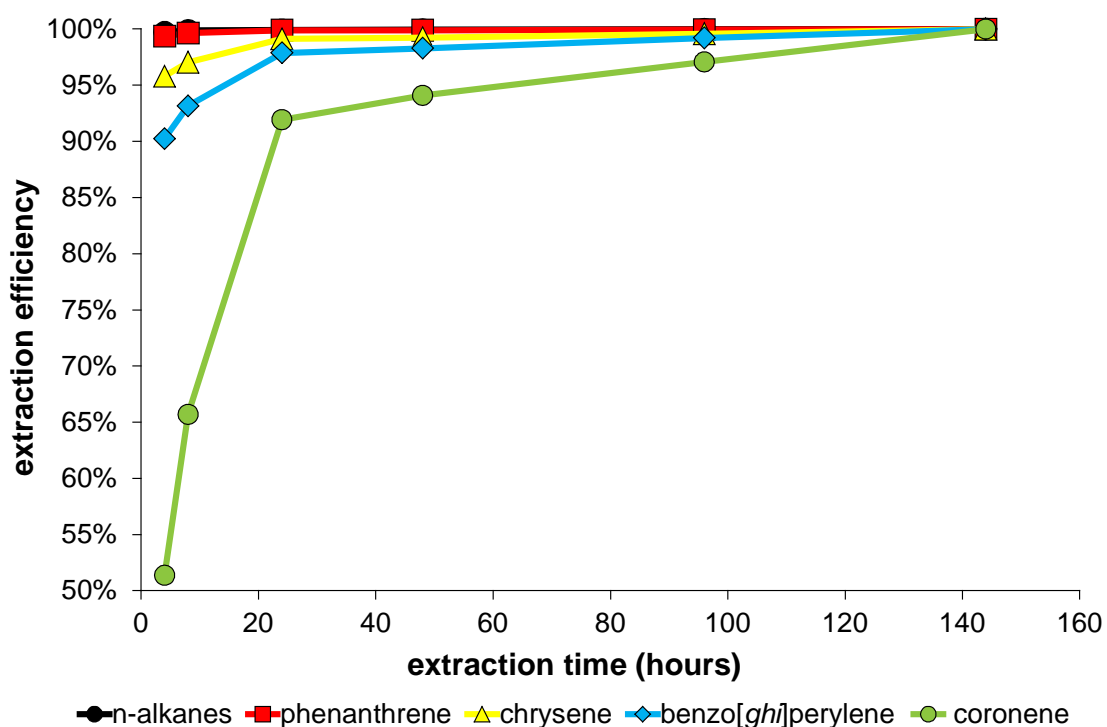


Figure 2.1: Cumulative extraction efficiency of individual PAHs in Bitumen I (as % of total amount extracted after 144 hours). Low MW PAHs show higher extraction efficiency than high MW PAHs. *n*-Alkanes are almost 100 % extracted within the first four hours.

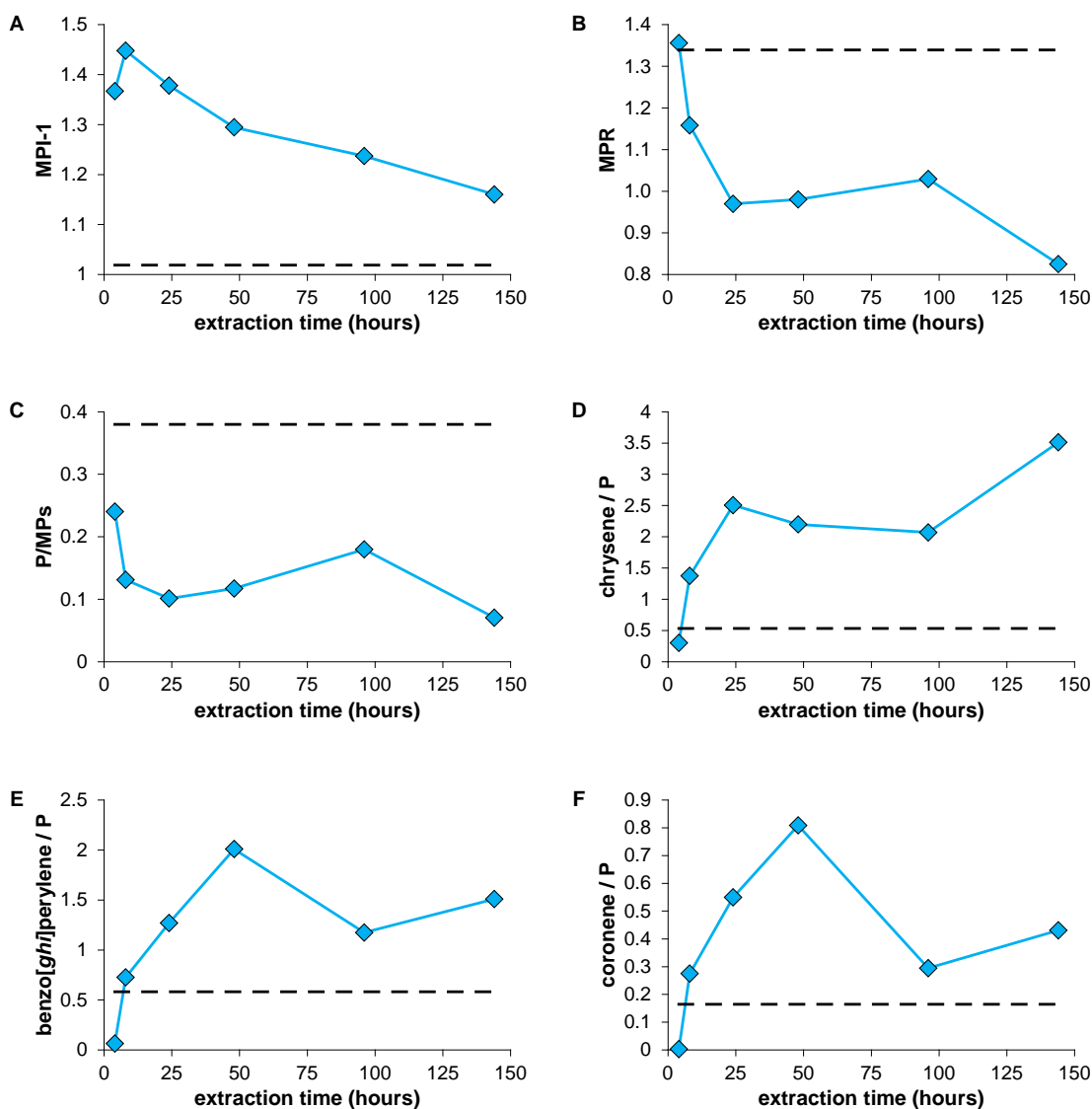


Figure 2.2: Selected PAH ratios for sequential extraction and Bitumen II. Solid lines track instantaneous value of the PAH ratio for each sequential extraction step. Dashed line is the value for Bitumen II. The ratios are: (A) MPI-1, (B) MPR, (C) phenanthrene / methylphenanthrenes, (D) chrysene / phenanthrene, (E) benzo[ghi]perylene / phenanthrene and (F) coronene / phenanthrene.

Several PAH ratios are plotted against extraction time in Figure 2.2. The commonly used maturity parameters MPI-1 and MPR generally decrease with extended extraction time, consistent with previous observations from sequential extraction experiments (Price and Clayton, 1992; Wilhelms et al., 1996; Schwark et al., 1997). In Figure 2.3 it is shown that the more stable β isomers (2- and 3-methylphenanthrene) are extracted preferentially to α isomers. Later extracts hence contain proportionally more α isomers, leading to lower maturity ratios. The phenanthrene / methylphenanthrenes ratio decreases to less than one third of its

original value, as the lower MW PAH is extracted more quickly than its methylated counterparts. This is consistent with the relative adsorption energies of parent and alkylated phenanthrenes observed in adsorption experiments on shales (Brocks, 2011). Conversely, the concentrations of higher MW PAHs increase relative to phenanthrene with successive extraction.

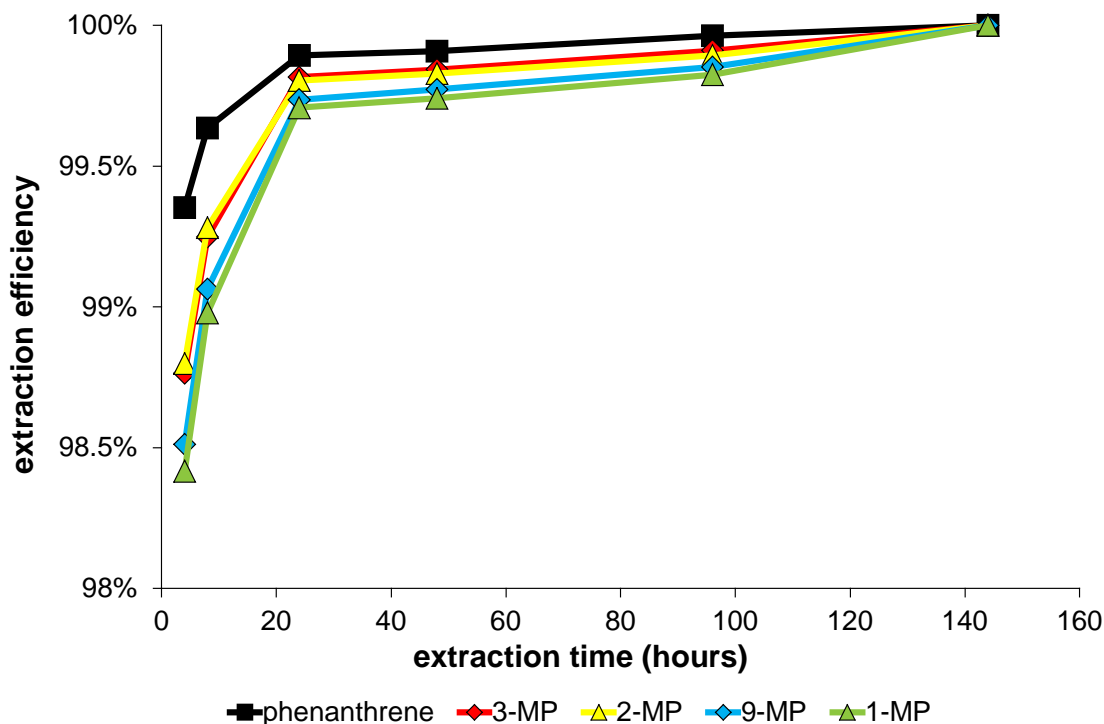


Figure 2.3: Cumulative extraction efficiency of phenanthrene and methylphenanthrenes in Bitumen I (as % of total amount extracted after 144 hours). The parent PAH is extracted with the highest efficiency. The β isomers 2- and 3-methylphenanthrene are extracted with slightly higher efficiency than the α isomers (MP - methylphenanthrene).

Bitumen II

Aromatic maturity parameters for Bitumen II are shown in Table 2.1 alongside the sequential Bitumen I extraction. It is important to note that Bitumen II was not prepared from the same rock sample as the sequential extraction sample due to safety restrictions on the use of large quantities of HF. Care was taken to ensure that extracts from the two samples were comparable. The sample from which Bitumen II was prepared was broken off from the same large rock as that used for the sequential extraction and was extracted using the same conditions (pages 45 to 47). Aromatic maturity parameters for Bitumen I prepared from this rock have been reported by Williford et al. (2011). They can be compared to those calculated for the first of the sequential extraction step (0-4 hours), which contains the majority of the extractable

PAHs and almost all of the phenanthrene and methylphenanthrenes. The methylphenanthrene ratios are identical to one decimal place, demonstrating that the two samples are comparable.

Results indicate that Bitumen II cannot be attributed to biomarkers left over from incomplete extraction of Bitumen I. Methyl phenanthrene maturity ratios for Bitumen II are generally lower than those for Bitumen I, following the trend observed by Nabbefeld et al. (2010b). The phenanthrene / methylphenanthrenes ratio decreases in the final extraction steps but is significantly higher in Bitumen II, indicating that the more stable parent PAH is preferentially preserved in the kerogen / mineral matrix. Ratios of higher MW PAHs to phenanthrene are roughly equivalent for Bitumen I and II but much higher in the final sequential extraction steps.

Figure 2.4 shows the calculated aromatic maturity parameters for the residual Bitumen I left after extraction for various time periods. These were calculated by subtracting the amount of each compound extracted at each time period from the total amount extracted after 144 hours, and represent the composition of Bitumen I that would have been left over if extraction had been stopped at that time. If Bitumen II contained a significant contribution from un-extracted Bitumen I then the Bitumen II maturity parameters would be close to the residual Bitumen I values. It can be seen in Figure 2.4 that this is not the case; in fact for all parameters except MPI-1 the difference between Bitumen II and the residual Bitumen I increases with extraction time. It is clear that the composition of Bitumen II is highly distinct from that of the residual Bitumen I.

Semi-quantification of Bitumen II (Table 2.1) shows a total of just over 33 ng parent PAHs and methyl phenanthrenes per gram of extracted rock powder, far greater than that in any of the sequential extraction steps after the initial 4 hours. This amount does not include methyl naphthalenes, which were not present in the sequential extraction but occur in moderate abundance in Bitumen II. The residual Bitumen I after the 72 hours extraction by Williford et al. (2011) could contribute no more than 10 % of the total aromatics in Bitumen II. The majority of aromatic maturity parameters are based on methylated naphthalenes and phenanthrene (George and Ahmed, 2002), which are absent from, or significantly depleted in, the residual Bitumen I. The contribution from residual Bitumen I to these parameters will be minimal; hence they can be used with confidence in studies of Bitumen II.

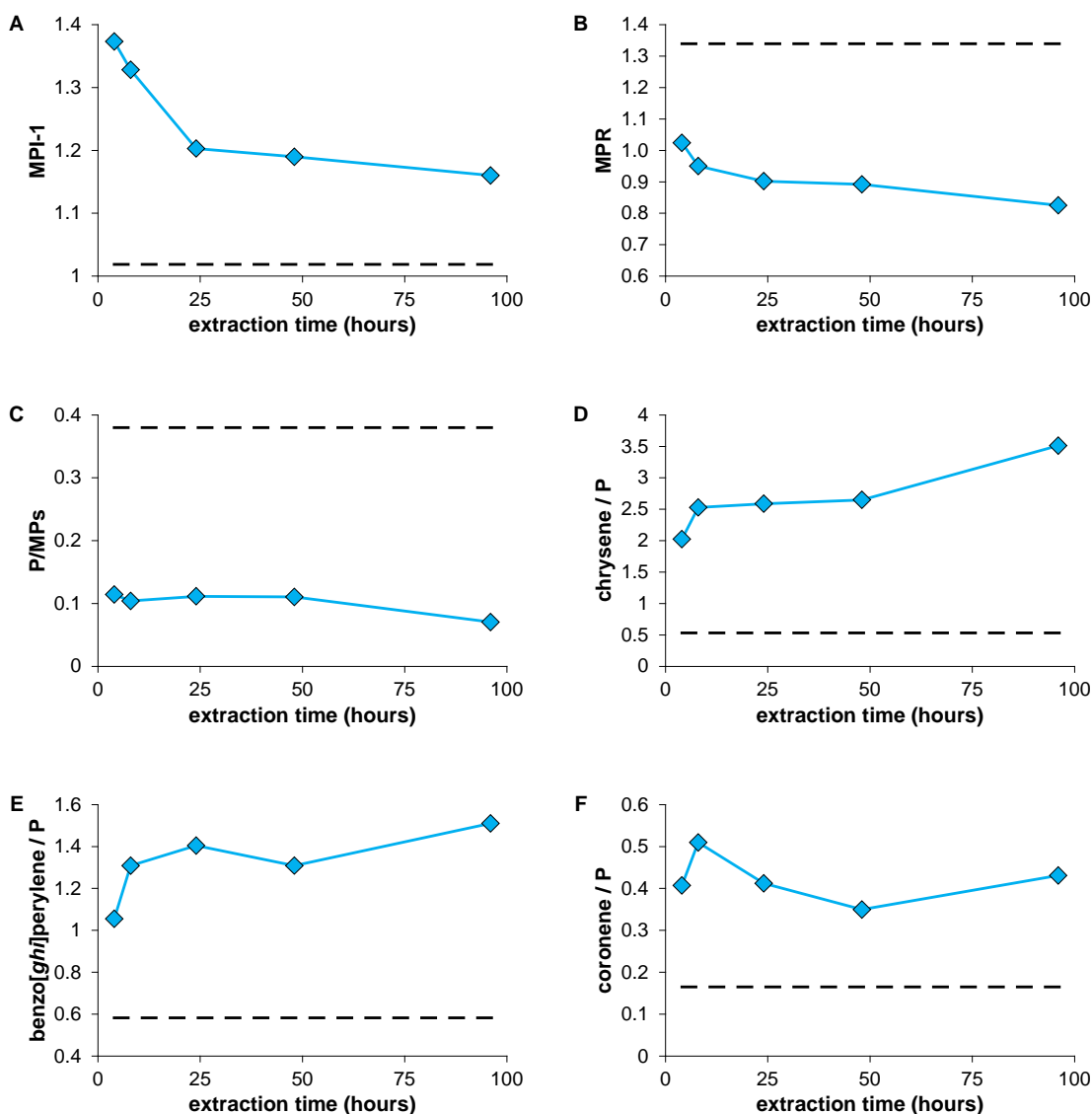


Figure 2.4: Residual PAH ratios for sequential extraction and Bitumen II. Solid lines show the value of the PAH ratio for the bitumen remaining after the specified time. The dashed line is the value for Bitumen II. The ratios are: (A) MPI-1, (B) MPR, (C) phenanthrene / methylphenanthrenes, (D) chrysene / phenanthrene, (E) benzo[ghi]perylene / phenanthrene and (F) coronene / phenanthrene.

Implications for ore formation

This study has shown that Bitumen II prepared from the HYC samples is not composed of residual Bitumen I left over after extraction, and hence must contain OM preserved within the kerogen / mineral matrix. The potential role of OM in ore formation processes has received increasing attention in the past 20 years (Disnar and Sureau, 1990; Püttmann et al., 1991; Gizè, 1999; Logan et al., 2001; Rieger et al., 2008). In the case of HYC the situation is complicated by the likely presence of significant migrated OM from an underlying formation (Williford et al., 2011) and

alteration of the OM by warm hydrothermal brines (Chen et al., 2003). Bitumen II is closely associated with the kerogen / mineral matrix and is less likely to be contaminated by migrated OM (Sherman et al., 2007). Now that Bitumen II has been shown to be genuine, it has great potential to distinguish between indigenous and migrated OM in the HYC system. Further detailed studies of HYC conducted as part of the CSIRO Organic Geochemistry of Mineral Systems Cluster will make use of Bitumen II.

Conclusions

Sequential Soxhlet extractions were performed on a highly mineralised sample from the HYC lead/zinc/silver deposit of the Northern Territory of Australia. The majority of saturated compounds were extracted within a few hours, such that only trace amounts of straight chain and branched alkanes remained after 8 hours extraction. The low MW PAHs were also extracted quickly, with > 99 % of phenanthrene and methyl phenanthrenes extracted after 48 hours. Extraction efficiency decreased with increasing MW, such that only 94 % of coronene was extracted after 48 hours. The extraction rate for different samples will differ due to organic facies and mineral composition, but the results highlight the effect of MW on extraction efficiency. Insufficient extraction time may lead to underestimation of the abundance of high MW PAHs. Extraction times of 96 hours or more may be required if high MW PAHs are to be quantified accurately.

Aromatic maturity ratios generally decrease with successive extraction steps. The more stable β isomers are extracted more quickly than α isomers, so later extraction steps yield decreased maturity parameters. Bitumen II from a sample from the same pit also shows lower maturity ratios, but distinct from the final Bitumen I extract in many molecular parameters. Bitumen II has a high phenanthrene / methylphenanthrenes ratio, suggesting that the parent PAH is preferentially incorporated in the kerogen / mineral matrix, whereas the final Bitumen I extract has a higher proportion of the heavier methyl phenanthrenes. The amount of extract left after a 72 hour Soxhlet extraction amounts to 10 % or less of Bitumen II. As the residual Bitumen I is depleted in low MW PAHs, the contribution to aromatic

maturity parameters will be minimal. It is implausible to interpret the low maturity of Bitumen II as a result of unextracted Bitumen I.

Acknowledgements

The authors thank G. Chidlow for GC-MS technical support. A.H. thanks Curtin University for an Australian Postgraduate Award scholarship and the CSIRO for a PhD top up scholarship. All authors acknowledge the CSIRO Flagship Collaboration Fund Cluster for Organic Geochemistry of Mineral Systems led by Curtin University. Additional funding was provided by WA-OIGC, The Institute for Geoscience Research (TIGeR) and the John de Laeter Centre for Isotope Research. K. Evans, J. Dick and two anonymous reviewers provided helpful comments which greatly improved this manuscript.

References

- Brocks J.J., 2011. Millimeter-scale concentration gradients of hydrocarbons in Archean shales: live-oil escape or fingerprint of contamination? *Geochimica et Cosmochimica Acta* **75**, 3196-3213.
- Brocks J.J., Love G.D., Summons R.E., Knoll A.H., Logan G.A., Bowden S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866-870.
- Carlson R.M.K., Chamberlain D.E., 1986. Steroid biomarker-clay mineral adsorption free energies: implications to petroleum migration indices. *Organic Geochemistry* **10**, 163-180.
- Chen J., Walter M.R., Logan G.A., Hinman M.C., Summons R.E., 2003. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: organic geochemistry and ore genesis. *Earth and Planetary Science Letters* **210**, 467-479.
- Disnar J.R., Sureau J.F., 1990. Organic matter in ore genesis: progress and perspectives. *Organic Geochemistry* **16**, 577-599.

- Garrigues P., De Sury R., Angelin M.L., Bellocq J., Oudin J.L., Ewald M., 1988. Relation of the methylated aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta. *Geochimica et Cosmochimica Acta* **52**, 375-384.
- George S.C., Ahmed M., 2002. Use of aromatic compound distributions to evaluate organic maturity of the Proterozoic middle Velkerri Formation, McArthur Basin, Australia. In *The Sedimentary Basins of Western Australia 3: Proceedings of the Petroleum Exploration Society of Australia Symposium 2002* (eds. Keep M., Moss S.J.). Petroleum Exploration Society of Australia, Perth. pp 253-270.
- Gizè A.P., 1999. A special issue on organic matter and ore deposits; interactions, applications, and case studies: introduction. *Economic Geology* **94**, 963-965.
- Grice K., Backhouse J., Alexander R., Marshall N., Logan G.A., 2005. Correlating terrestrial signatures from biomarker distributions, $\delta^{13}\text{C}$, and palynology in fluvio-deltaic deposits from NW Australia (Triassic–Jurassic). *Organic Geochemistry* **36**, 1347-1358.
- Huston D.L., Stevens B., Southgate P.N., Muhling P., Wyborn L., 2006. Australian Zn-Pb-Ag ore-forming systems: a review and analysis. *Economic Geology* **101**, 1117-1157.
- Kawka O.E., Simoneit B.R.T., 1994. Hydrothermal pyrolysis of organic matter in Guaymas Basin: I. Comparison of hydrocarbon distributions in subsurface sediments and seabed petroleums. *Organic Geochemistry* **22**, 947-978.
- Killops S.D., Massoud M.S., 1992. Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient sediments: evidence for Jurassic vegetation fires. *Organic Geochemistry* **18**, 1-7.
- Large R.R., Bull S.W., Cooke D.R., McGoldrick P.J., 1998. A genetic model for the HYC deposit, Australia: based on regional sedimentology, geochemistry, and sulfide-sediment relationships. *Economic Geology* **93**, 1345-1368.
- Logan G.A., Hinman M.C., Walter M.R., Summons R.E., 2001. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments,

- Northern Territory, Australia. *Geochimica et Cosmochimica Acta* **65**, 2317-2336.
- Marshall C.P., Love G.D., Snape C.E., Hill A.C., Allwood A.C., Walter M.R., Van Kranendonk M.J., Bowden S.A., Sylva S.P., Summons R.E., 2007. Structural characterization of kerogen in 3.4 Ga Archaean cherts from the Pilbara Craton, Western Australia. *Precambrian Research* **155**, 1-23.
- Mueller E., Philp R.P., 1998. Extraction of high molecular weight hydrocarbons from source rocks: an example from the Green River Formation, Uinta Basin, Utah. *Organic Geochemistry* **28**, 625-631.
- Nabbefeld B., Grice K., Schimmelmann A., Sauer P.E., Böttcher M.E., Twitchett R.J., 2010a. Significance of δD (kerogen), $\delta^{13}C$ (kerogen) and $\delta^{34}S$ (pyrite) from several Permian/Triassic (P/Tr) sections. *Earth and Planetary Science Letters* **295**, 21-29.
- Nabbefeld B., Grice K., Schimmelmann A., Summons R.E., Troitzsch U., Twitchett R.J., 2010b. A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks. *Organic Geochemistry* **41**, 78-87.
- Nabbefeld B., Grice K., Summons R.E., Hays L.E., Cao C., 2010c. Significance of polycyclic aromatic hydrocarbons (PAHs) in Permian/Triassic boundary sections. *Applied Geochemistry* **25**, 1374-1382.
- Page R.W., Sweet I.P., 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences* **45**, 219-232.
- Price L.C., Clayton J.L., 1992. Extraction of whole versus ground source rocks: fundamental petroleum geochemical implications including oil-source rock correlation. *Geochimica et Cosmochimica Acta* **56**, 1213-1222.
- Püttmann W., Fermont W.J.J., Speczik S., 1991. The possible role of organic matter in transport and accumulation of metals exemplified at the Permian Kupferschiefer formation. *Ore Geology Reviews* **6**, 563-579.

- Radke M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology* **5**, 224-236.
- Radke M., Welte D.H., Willsch H., 1982a. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* **46**, 1-10.
- Radke M., Willsch H., Leythaeuser D., Teichmüller M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* **46**, 1831-1848.
- Rieger A., Schwark L., Cisternas M.-E., Miller H., 2008. Genesis and evolution of bitumen in Lower Cretaceous lavas and implications for strata-bound copper deposits, North Chile. *Economic Geology* **103**, 387-404.
- Robl T.L., Davis B.H., 1993. Comparison of the HF-HCl and HF-BF₃ maceration techniques and the chemistry of resultant organic concentrates. *Organic Geochemistry* **20**, 249-255.
- Saxby J.D., 1970. Isolation of kerogen in sediments by chemical methods. *Chemical Geology* **6**, 173-184.
- Schwark L., Stoddart D., Keuser C., Spitthoff B., Leythaeuser D., 1997. A novel sequential extraction system for whole core plug extraction in a solvent flow-through cell — application to extraction of residual petroleum from an intact pore-system in secondary migration studies. *Organic Geochemistry* **26**, 19-31.
- Sherman L.S., Waldbauer J.R., Summons R.E., 2007. Improved methods for isolating and validating indigenous biomarkers in Precambrian rocks. *Organic Geochemistry* **38**, 1987-2000.
- Simoneit B.R.T., Lein A.Y., Peresykin V.I., Osipov G.A., 2004. Composition and origin of hydrothermal petroleum and associated lipids in the sulfide deposits of the Rainbow Field (Mid-Atlantic Ridge at 36°N). *Geochimica et Cosmochimica Acta* **68**, 2275-2294.
- Summons R.E., Powell T.G., Boreham C.J., 1988. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. *Geochimica et Cosmochimica Acta* **52**, 1747-1763.

- Szczerba M., Rospondek M.J., 2010. Controls on distributions of methylphenanthrenes in sedimentary rock extracts: critical evaluation of existing geochemical data from molecular modelling. *Organic Geochemistry* **41**, 1297-1311.
- van Aarssen B.G.K., Bastow T.P., Alexander R., Kagi R.I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Organic Geochemistry* **30**, 1213-1227.
- Venkatesan M.I., Dahl J., 1989. Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary. *Nature* **338**, 57-60.
- Wilhelms A., Horstad I., Karlsen D., 1996. Sequential extraction—a useful tool for reservoir geochemistry? *Organic Geochemistry* **24**, 1157-1172.
- Williford K.H., Grice K., Logan G.A., Chen J., Huston D., 2011. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters* **301**, 382-392.

Appendix 2

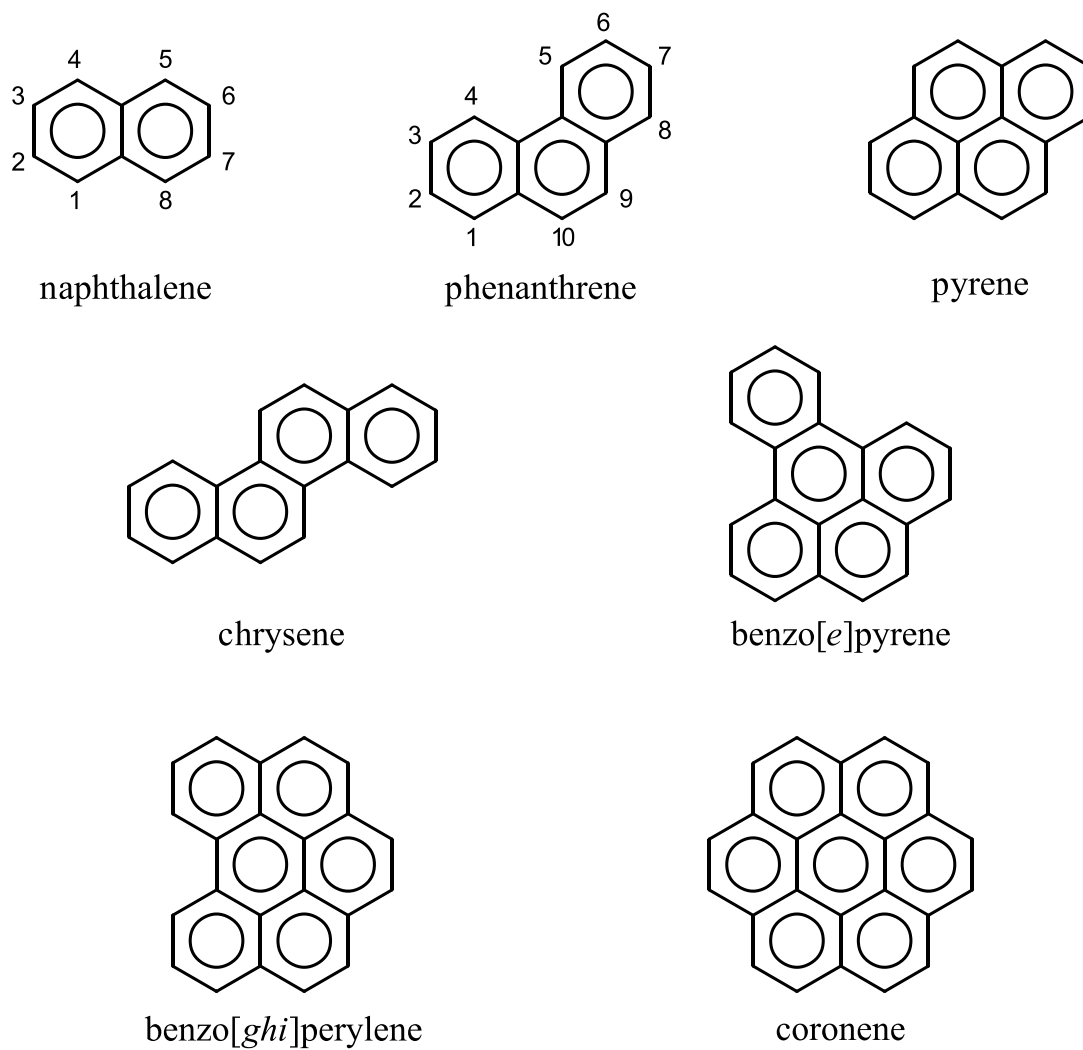


Figure A2.1: Structures referred to in the text.

Chapter 3

Bitumen II from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag deposit: implications for the analysis of depositional environment and thermal maturity of hydrothermally-altered sediments

Alex I. Holman, Kliti Grice, Caroline M. B. Jaraula and Arndt Schimmelmann

Geochimica et Cosmochimica Acta, **139**, 98-109 (2014)

Abstract

The formation of sedimentary-exhalative (SEDEX) Pb/Zn deposits is linked to ocean euxinia, but recent evidence suggests that ferruginous conditions may have dominated the deep ocean during the Middle Proterozoic, a maximum period for SEDEX distribution. Biomarkers of sulfate-reducing and sulfide-oxidising bacteria are valuable indicators of euxinic conditions in such settings. Organic matter (OM) from SEDEX deposits is often affected by alteration or migration, but OM entrapped within the kerogen / mineral matrix (Bitumen II) may be less affected than the freely-extractable OM (Bitumen I). We analysed Bitumen II from the Paleoproterozoic Here's Your Chance (HYC) Pb/Zn/Ag deposit to find evidence of euxinic conditions in the depositional environment. *n*-Alkane distributions in Bitumen II are markedly distinct from previously-reported Bitumen I. Bitumen II contains long-chain *n*-alkanes (up to C₃₆ or C₃₈) and a strong even-over-odd distribution in a number of samples, which are 4 to 7 ‰ depleted in ¹³C compared to *n*-alkanes in Bitumen I and verified as indigenous by comparison with δ¹³C of isolated kerogen. These features are interpreted as evidence of sulfate-reducing bacteria and phototrophic sulfur bacteria, confirming that HYC was deposited under euxinic conditions. Bitumen II has the potential to reveal information from OM that is degraded and/or overprinted in Bitumen I. Commonly-used methylphenanthrene maturity ratios give conflicting information as to the relative maturity of Bitumens I and II. Bitumen I contains a far higher proportion of methylated phenanthrenes than Bitumen II. As Bitumen II is sequestered within the kerogen / mineral matrix it may have experienced restricted access to the 'methyl pool' of organic compounds that can donate methyl groups to aromatic hydrocarbons. Parameters that include both phenanthrene and methylphenanthrenes do not appear suitable to compare maturity of Bitumen I and II; hence there is no clear evidence that Bitumen II is of lower thermal maturity than Bitumen I.

Introduction

Sedimentary-exhalative (SEDEX) deposits are stratiform, sediment-hosted Pb/Zn ore bodies dominated by sulfide minerals. The genetic models of these deposits are complex and have been extensively reviewed (e.g. Large et al., 2005); the general aspects are deposition of Pb and Zn from a hydrothermal brine in rifted sedimentary basins. The occurrence of major SEDEX mineralisation from *ca* 1800 Ma has been linked to the development of widespread oceanic euxinia during the middle Proterozoic (Lyons et al., 2006). Recent evidence however shows that ferruginous conditions may have dominated in the deep ocean during this period, with euxinia being restricted to isolated basins and mid-depth coastal waters (Poulton et al., 2010; Planavsky et al., 2011). Organic biomarkers are a reliable proxy for the presence of euxinic conditions. For example the breakdown products of carotenoid pigments produced by green and purple sulfur bacteria indicate photic zone euxinia in ancient marine systems (Brocks et al., 2005; Grice et al., 2005).

Organic compounds are also useful as indicators of thermal maturity, providing a valuable indication of fluid temperature for deposits which lack fluid inclusions (e.g. Large et al., 2005). SEDEX and other deposits often contain high abundances of polycyclic aromatic hydrocarbons (PAHs) (Püttmann et al., 1989; Williford et al., 2011), highly condensed aromatic compounds made up of two or more benzene rings. Low-molecular-weight PAHs such as naphthalene and phenanthrene are almost ubiquitous in sediments. They can be formed through diagenetic alteration of natural organic precursors (e.g. Wakeham et al., 1980b; Grice et al., 2007; Grice et al., 2009) or by combustion of biomass (Venkatesan and Dahl, 1989; Nabbefeld et al., 2010b) and fossil fuels (Wakeham et al., 1980a). High-molecular-weight PAHs are found in high abundance in high-temperature (> 300 °C) marine hydrothermal vents (Kawka and Simoneit, 1990), where they are generated by the addition of C₂ or C₂H₄ units to existing aromatic compounds (Stein, 1978). Methylated PAHs are produced by geosynthetic methylation reactions in sediments (Voigtmann et al., 1994). PAHs methylated in β positions are more thermodynamically stable than those in α positions (Szczerba and Rospondek, 2010), and hence the ratios of β to α isomers are frequently used as indicators of thermal maturity. Ratios of methylphenanthrene (MP) isomers include the methylphenanthrene index (MPI-1)

and methylphenanthrene ratio (MPR) (Radke et al., 1982, see Appendix 3 for equations).

The Mt. Isa-McArthur basin system of Northern Australia is host to five supergiant Proterozoic SEDEX deposits; the most significant accumulation of Pb and Zn in the world (Large et al., 2005). The largest of these deposits is the Here's Your Chance (HYC) deposit, hosted in unmetamorphosed carbonaceous shales and siltstones of the Barney Creek Formation (BCF). Organic matter (OM) from HYC has been strongly affected by hydrothermal alteration from the mineralising fluid (see page 66) and diagnostic biomarkers have been degraded and possibly overprinted by non-indigenous OM. Traditional extraction techniques can therefore give only limited information on the depositional environment and thermal maturity. Removal of silicate minerals from extracted rock powder by digestion with hydrofluoric acid (HF) liberates a second fraction of extractable OM, which is likely to be protected from migration and alteration (Sherman et al., 2007; Nabbefeld et al., 2010a). This fraction is referred to as Bitumen II, whereas the first extract is called Bitumen I. The methods used in this study for the extraction of Bitumen II have been previously reported and validated in **Chapter 2**. In this study we isolate and analyse Bitumen II from a range of HYC samples in an attempt to distinguish between indigenous and migrated OM and reveal evidence that the deposit was formed in a euxinic environment. A previous report has found that PAH maturity ratios in Bitumen II show different values than those in Bitumen I (Nabbefeld et al., 2010a), so we also evaluate PAH ratios to determine whether Bitumen II has been protected from thermal alteration.

Materials and methods

The Barney Creek Formation and the Here's Your Chance deposit

The 1640 Ma (Page and Sweet, 1998) carbonaceous, pyritic and tuffaceous shales and siltstones of the Barney Creek Formation (BCF) in the McArthur Basin, Northern Territory, Australia were originally interpreted as a deep marine succession deposited in a reducing environment below the wave base (Bull, 1998). More recently, it has been recognised that these sediments are part of a facies mosaic of time-equivalent shelf, slope and deep-water sediments deposited in a series of

tectonically controlled sub-basins (McGoldrick et al., 2010). The BCF has been widely studied as it contains possibly the most well-preserved Proterozoic organic matter (OM) (Summons et al., 1988). BCF black shales generally contain 0.2 to 2 wt. % total organic carbon, and locally greater than 7 wt. % (Powell et al., 1987). Previous studies of low-maturity shales from the Glyde River region of the BCF have found biomarkers of the sulfide-oxidising green and purple sulfur bacteria Chlorobiaceae and Chromatiaceae (Brocks et al., 2005; Brocks and Schaeffer, 2008). These bacteria are known to thrive in marine systems where euxinic conditions persist in the photic zone of the water column (e.g. Summons and Powell, 1987; Grice et al., 2005).

The BCF is host to the HYC Pb/Zn/Ag deposit, one of the largest sediment-hosted base metal deposits in the world. The HYC deposit has a total resource of 227 Mt, at 9.25 wt. % Zn, 4.1 wt. % Pb and 41 ppm Ag contained in eight discrete ore lenses (Walker et al., 1977; Large et al., 2005). The deposit is generally considered to have been formed by exhalation of a metal-rich hydrothermal brine into the water column (Croxford, 1968; Ireland et al., 2004a; Large et al., 2005). The OM at HYC has been strongly affected by hydrothermal alteration, but several studies have used OM to investigate the conditions of deposition (Logan et al., 2001; Chen et al., 2003; Williford et al., 2011). HYC *n*-alkanes are enriched in deuterium by 50 to 60 ‰ compared to those from the unmineralised BCF, indicating isotopic exchange with a D-enriched evaporitic brine (Williford et al., 2011). Williford et al. also presented carbon isotopic data which suggest that a significant quantity of aromatic hydrocarbons were generated in the underlying Wollongorang Fm and transported to the deposit within the mineralising fluid.

The samples used were collected and analysed by Williford et al. (2011). Five samples of Pb/Zn/Ag sulfide ore were taken from the highly mineralised upper ore body 5 of the deposit (referred to as sample pits 1 to 5), plus one non-mineralised shale sample from the underlying W-Fold Shale member, a sequence of red-green shales and siltstones at the basal 10 to 15 meters of the BCF at and around the area of the mine (Walker et al., 1977).

Extraction and separation of Bitumen II

The extraction of Bitumen II followed a procedure modified from Robl and Davis (1993) and Nabbefeld et al. (2010a), as detailed in **Chapter 2** for the pit 1 sample. The other samples were prepared using the same method. HCl and HF were cleaned prior to use by shaking with dichloromethane (DCM) to remove organic contaminants from the acids. GC-MS analysis (page 68) revealed that saturate and aromatic contaminants were below the limit of detection after cleaning.

Extracted rock powder was digested with HCl (1 M) to remove carbonates then placed into clean 50 mL polyethylene centrifuge tubes (5-6 g of sample per tube). Equal volumes of concentrated HF (48 wt. %) and Milli-Q purified water were added to the tubes and left to digest (1-2 hours) in an ice bath with regular shaking. The supernatant liquid was then decanted and a second volume of acid-water mixture was added. The tubes were left at room temperature (3-4 hours) with occasional shaking to complete the digestion. The solid residue was then washed ($\times 3$) with Milli-Q water and freeze dried. The samples had decreased in mass by ca. 50 %.

After the acid digestion the samples were extracted in a Soxhlet apparatus (72 hours) with 9:1 (v:v) DCM: methanol (MeOH) to extract Bitumen II, replicating the conditions used by Williford et al. (2011) to isolate Bitumen I. Copper turnings (rinsed with DCM and activated with dilute HCl) were added to the flask to remove elemental sulfur. The extract was evaporated to dryness under a stream of warm N_2 , dissolved in a minimum amount of DCM and added to the top of a small column (5.5 cm \times 0.5 cm i.d.) of silica gel (activated at 160 °C for 24 hours). The total extract was separated into saturate, aromatic and polar fractions by elution with *n*-hexane, 30 vol. % DCM in *n*-hexane and 1:1 DCM:MeOH respectively. Semi-quantitative analysis of aromatic fractions was done using an internal standard of deuterated *p*-terphenyl.

Isolation of kerogen

Following the extraction of Bitumen II a fraction of each sample was taken for the isolation of kerogen, following the procedure of Nabbefeld et al. (2010a). A small amount of sample was placed into glass centrifuge tubes (< 1 g per tube) and shaken with 2-3 mL of saturated aqueous zinc bromide solution ($\rho \approx 2.4$ g mL⁻¹). After centrifugation (2000 RPM, 5 minutes) the acid-insoluble minerals settled to the

bottom of the vial while the isolated kerogen remained floating on or suspended in the ZnBr solution. The liquid was then decanted and diluted with Milli-Q water to allow the kerogen to settle. The kerogen was washed with Milli-Q water ($\times 3$) and freeze-dried. 30-50 mg of kerogen was isolated for each sample from 3-5 g of acid-digested rock powder.

Gas chromatography mass spectrometry (GC-MS)

Saturate and aromatic fractions were analysed by GC-MS using a Hewlett Packard (HP) 6890 gas chromatograph coupled to a HP 5973 mass selective detector, following the procedure described in **Chapter 2**. Fractions were dissolved in *n*-hexane and injected into a split-splitless injector in pulsed splitless mode. A DB5-MS column (Agilent Technologies, 60 m length, 0.25 mm i.d., 0.25 μm film thickness) was used with He as the carrier gas. The GC oven temperature was increased from 40 to 310 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$ then held isothermally for 30 min. Data were acquired in full scan mode (m/z 50–550).

Stable carbon isotope analysis

Compound-specific stable carbon isotope ratios ($\delta^{13}\text{C}$) of the saturate fractions were measured using a HP 6890 gas chromatograph coupled to a Micromass Isoprime isotope ratio monitoring mass spectrometer (irmMS). The GC oven was held at 50 $^{\circ}\text{C}$ for 1 min, increased to 310 $^{\circ}\text{C}$ at 3 $^{\circ}\text{C min}^{-1}$ then held isothermally for 20 min. The GC column was the same as that described on page 68. $\delta^{13}\text{C}$ values are reported relative to CO_2 reference gas calibrated to the Vienna Pee Dee Belemnite (VPDB) scale. Samples were analysed 2 to 5 times each, and standard deviations for measured compounds ranged from 0.2 to 0.5 ‰. The instrument was calibrated daily with a mixture of compounds of known $\delta^{13}\text{C}$ to monitor the precision and accuracy of analysis. The aromatic fractions were of insufficient quantities to perform compound-specific isotope analysis.

Bulk stable carbon isotope ratios of isolated kerogens were measured using a Delta V Plus mass spectrometer connected to a Thermo Flush 1112 elemental analyser via a ConFlo IV (Thermo-Finnigan/Germany).

Results

Bitumen II saturated hydrocarbons

Total ion chromatograms (TICs) of Bitumen II saturated hydrocarbon fractions from sample pits 1 and 3, which together exemplify the most important features of all the samples, are displayed in Figure 3.1. Samples from pits 1, 5 and the W-Fold Shale show a significant predominance of *n*-alkanes with even carbon numbers, while this pattern is less pronounced in ore from pits 2, 3 and 4. Long-chain *n*-alkanes up to *n*-C₃₆ are present in all samples, with *n*-C₃₇ and *n*-C₃₈ present only in pits 1 and 5. These distributions are characterised by Average Chain Length (ACL) and Carbon Preference Index (CPI), which are presented in Table 3.1. The ACL in Bitumen II ranges from 25.4 to 26.9, which is greater than the Bitumen I ACL of roughly 18 (Williford et al., 2011). Equations of ACL and CPI are presented in Figure A3.1.

CPI measures the ratio of *n*-alkanes with odd carbon numbers over those with even carbon numbers, and is calculated here using the formula of Marzi et al. (1993). The Bitumen I *n*-alkanes reported by Williford et al. (2011) show no predominance of odd or even carbon numbers and hence the CPI will approximately equal one. The CPI of Bitumen II from pits 1, 5 and the W-Fold Shale samples range from 0.59 to 0.83, showing a strong prevalence of even-numbered *n*-alkanes that is seen in Figure 3.1A. The remaining samples have CPI values much closer to one and show no obvious carbon number preference (Figure 3.1B).

Stable carbon isotope analysis

Compound-specific stable carbon isotope ratios for Bitumen II *n*-alkanes and isolated kerogen are listed in Table 3.1. Values are reported in the ranges C₁₆ and C₁₈, and C₂₄ to C₃₂, as these were the compounds that were of sufficient abundance to measure $\delta^{13}\text{C}$. The $\delta^{13}\text{C}$ values of Bitumen II *n*-alkanes (-34.4 to -31.6 ‰) are 4 to 7 ‰ lower than those in Bitumen I (Williford et al., 2011). Within Bitumen II the long chain *n*-alkanes (C₂₄ to C₃₂) are generally 1 to 3 ‰ lighter than to C₁₆ and C₁₈, although the two values are within error for pit 1 and there was insufficient abundance of *n*-C₁₆ and *n*-C₁₈ from pit 2 to measure their isotopic composition. Bulk kerogen $\delta^{13}\text{C}$ ranges from -37.0 to -34.2 ‰, which is 1 to 4 ‰ lower than Bitumen II long-chain alkanes.

No consistent trend in $\delta^{13}\text{C}$ is observed between samples for either *n*-alkanes or kerogen (Figure 3.2).

Table 3.1: Average chain length (ACL) and carbon preference index (CPI) for Bitumen II *n*-alkanes, plus stable carbon isotope ratios ($\delta^{13}\text{C}$) of *n*-alkanes and isolated kerogen. $\delta^{13}\text{C}$ is given as the average of repeated analyses, with one standard deviation shown in parentheses and the number of analyses in superscript. CPI was calculated using the generalised formula of Marzi et al. (1993), with $n = 7$ and $m = 17$. WFS – W-Fold Shale unit.

	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5	WFS
<i>Distance from pit 1 (m)</i>	0	104	372	553	710	-
<i>Molecular parameters</i>						
ACL	26.3	26.9	26.7	25.6	25.4	25.6
CPI	0.67	0.91	0.98	0.94	0.83	0.59
$\delta^{13}\text{C}$						
C16+C18	-32.2 (0.3) ⁵	-	-32.5 (0.2) ²	-32.1 (0.4) ⁴	-32.4 (0.3) ²	-31.6 (0.5) ⁴
C24-C32	-32.3 (0.3) ⁵	-31.7 (0.2) ²	-34.2 (0.2) ²	-34.0 (0.3) ⁴	-33.4 (0.5) ²	-34.4 (0.5) ⁴
Kerogen	-35.5 (0.1)	-36.3 (0.1)	-35.6 (0.1)	-37.0 (0.1)	-34.2 (0.1)	-35.5 (0.1)

Bitumen II aromatic hydrocarbons

Quantification of selected PAHs in Bitumen II (reported in ng of compound per g of TOC) is presented in Table 3.2 along with selected ratios of aromatic compounds. Data from pit 1 have been previously reported (**Chapter 2**). Several methylphenanthrene ratios are also included from Bitumen I, calculated from data reported by Williford et al. (2011). The amounts of aromatic compounds measured in Bitumen II are commonly 5 to 15 % that of Bitumen I. As in Bitumen I there is no clear trend in PAH concentrations from pits 1 to 5.

The methylphenanthrene ratios MPI-1 and MPR are plotted for Bitumens I and II in Figure 3.3. Both parameters are designed to be a measure of maturity (Radke et al., 1982), however the relationships between the parameters in Bitumens I and II are distinct. MPI-1 for Bitumen I is consistently significantly higher than in Bitumen II (Figure 3.3A), whereas the MPR is generally higher in Bitumen II than Bitumen I (Figure 3.3B). These differences may be explained by the increased ratio of phenanthrene to methylphenanthrenes (P/MPs) in Bitumen I (Table 3.2), indicating

that Bitumen I contains a greater proportion of methylated isomers (see pages 78 to 80 for discussion).

Table 3.2: Quantification of selected PAHs present in Bitumen II aromatic fractions, plus calculated PAH ratios for Bitumens I and II. Bitumen I ratios were calculated from data presented by Williford et al. (2011).

	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5	WFS
<i>Compounds (ppb/TOC)</i>						
Phenanthrene	615	327	379	1156	334	231
3-Methylphenanthrene	424	190	263	754	232	249
2-Methylphenanthrene	479	283	339	948	274	250
9-Methylphenanthrene	358	181	247	616	243	277
1-Methylphenanthrene	358	174	260	689	263	315
Pyrene	391	192	156	558	160	202
Chrysene	327	125	356	481	273	477
Benzo[e]pyrene	772	180	830	490	658	1025
Benzo[ghi]perylene	358	111	266	185	254	317
Coronene	101	-	57	-	42	27
<i>Bitumen II PAH ratios</i>						
MPI-1	1.02	1.04	1.02	1.04	0.90	0.91
MPR	1.34	1.62	1.31	1.38	1.04	0.79
MP/P	2.63	2.53	2.93	2.60	3.03	4.72
BePyr/Pyr	1.97	0.94	5.33	0.88	4.11	5.08
BePyr/Chry	2.36	1.44	2.33	1.02	2.41	2.15
Chry/Phen	0.53	0.38	0.94	0.42	0.82	2.06
BePery/Phen	0.58	0.34	0.70	0.16	0.76	1.37
BePery/Pyr	0.92	0.58	1.71	0.33	1.59	1.57
BePery/Chry	1.09	0.89	0.75	0.38	0.93	0.66
BePery/BePyr	0.46	0.61	0.32	0.38	0.39	0.31
<i>Bitumen I PAH ratios</i>						
MPI-1	1.38	1.41	1.26	1.49	1.34	1.25
MPR	1.37	1.32	1.21	1.35	1.12	1.26
MP/P	5.00	6.26	5.31	7.05	9.32	4.67

Discussion

Sources of saturated compounds

The Bitumen II *n*-alkanes reported in this study differ from those previously found in Bitumen I in three main aspects: a marked predominance of even carbon numbers in three out of six samples (Figure 3.1), the presence of long-chain *n*-alkanes up to C₃₈, and reduced $\delta^{13}\text{C}$ values of -34 to -31 ‰ (Figure 3.2). These features have not previously been observed together in samples from HYC. *n*-Alkane distributions previously reported from HYC Bitumen I have been limited to C₃₂ or C₃₃, with $\delta^{13}\text{C}$ between -30 and -27 ‰ (Logan et al., 2001; Williford et al., 2011). Logan et al. (2001) observed *n*-alkanes with a strong even-over-odd distribution in highly mineralised samples from ore body 2, however there is evidence that these samples were contaminated with hydrocarbons from plastic sample bags (Grosjean and Logan, 2007) and thus results from this study should be treated with caution.

The significant differences between the *n*-alkanes in Bitumens I and II may be due to a different source of OM, a difference in the response to hydrothermal alteration, or a combination of both. *n*-Alkanes from Proterozoic sediments are typically enriched 2 to 3 ‰ in ^{13}C compared to the source kerogen (Logan et al., 1995). Carbon isotopic data (Table 3.1) shows that *n*-alkanes in HYC Bitumen II bear this exact relationship with the isolated kerogens from HYC. These data strongly suggest that Bitumen II *n*-alkanes are indigenous to HYC, in accordance with the contention that Bitumen II is less likely to be overprinted by migrated OM (Sherman et al., 2007). It was proposed by Williford et al. (2011) that aromatic hydrocarbons in Bitumen I were transported to HYC from the underlying Wollogorang Fm. The similar $\delta^{13}\text{C}$ of aromatics and *n*-alkanes in Bitumen I (Williford et al., 2011) suggest that saturated compounds may also have been transported. The migration of non-indigenous *n*-alkanes would obscure the even-over-odd distribution, resulting in the more typical Proterozoic distribution of Bitumen I.

A strong even-over-odd preference of *n*-alkanes is uncommon in the geological record, but has been observed in a variety of marine sediments (e.g. Dembicki Jr et al., 1976; Simoneit, 1994). George et al. (1994) studied solid bitumens from the ca 1400 Ma Roper Group in the McArthur Basin. Several of these samples displayed a

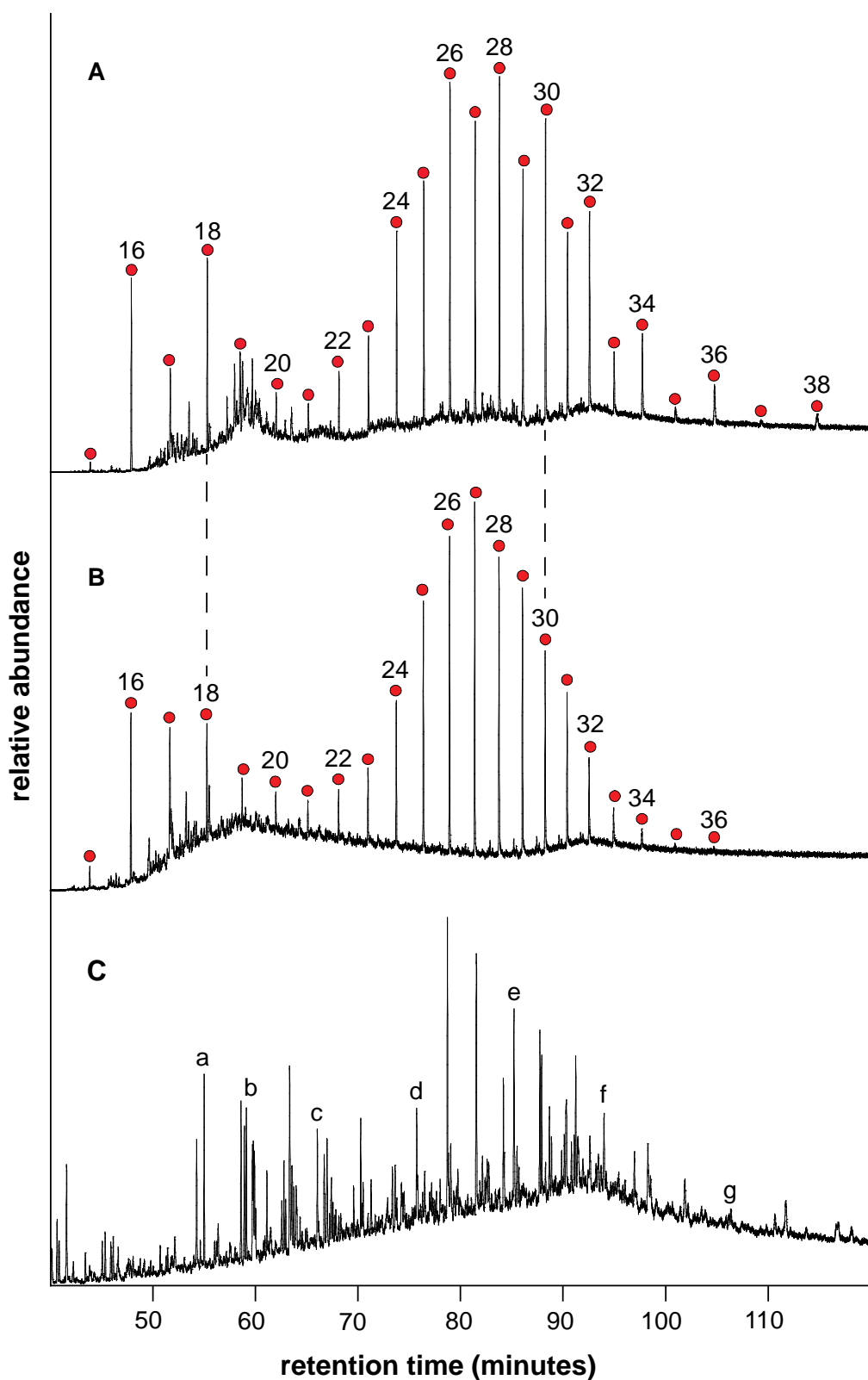


Figure 3.1: Total ion chromatograms of (A) pit 1 Bitumen II saturate fraction, (B) pit 3 Bitumen II saturate fraction and (C) pit 1 Bitumen II aromatic fraction. *n*-Alkanes in (A) and (B) are marked with red circles and even carbon numbers are labelled. Labels in (C) are a: phenanthrene, b: methylphenanthrenes, c: pyrene, d: chrysene + triphenylene, e: benzo[*e*]pyrene, f: benzo[*ghi*]perylene and g: coronene.

slight even-over-odd *n*-alkane predominance. These alkanes were also depleted in ^{13}C compared to those which did not show an even-over-odd distribution. It was concluded that solid bitumens in the Roper Group incorporate multiple sources of organic input, including one which is isotopically light and contains a high proportion of even-numbered alkanes (George et al., 1994). Possible origins of this input were not discussed in detail, but a number of studies have connected similar *n*-alkane distributions with the presence of sulfate-reducing and sulfide-oxidising bacteria. For instance, a strong predominance of isotopically light even-numbered *n*-alkanes in microbial mat facies of the Neoproterozoic Centralian Super-basin was ascribed to the activity of purple or colourless sulfur bacteria (Logan et al., 1999). A recent report of a 380 Ma fossil invertebrate preserved within a carbonate concretion in the Canning Basin, Western Australia also showed *n*-alkanes with a pronounced even-over-odd distribution in the desulfurised fossil extract, along with ^{13}C -depleted long-chain *n*-alkanes in the fossil nucleus and carbonate matrix (Melendez et al., 2013). Biomarker and isotopic evidence revealed the strong activity of sulfate-reducing bacteria and green sulfur bacteria (*Chlorobi*) in conditions of photic zone euxinia at the time the fossil was preserved.

Analyses of lipids from microbial cultures have shown that the phototrophic sulfur bacterium *Chlorobi* produces *n*-alkanes with a marked even-over-odd distribution over the range C_{15} to C_{28} , while the sulfate-reducing bacterium *Desulfovibrio Hildenborough* produces a similar but less pronounced distribution over the range C_{19} to C_{31} (Han and Calvin, 1969). Sulfate-reducing bacteria are known to generate long-chain lipids: *D. desulfuricans* produces *n*-alkanes predominantly in the range C_{25} - C_{35} (Ladygina et al., 2006), while long chain fatty acids up to C_{34} were found in *Desulfotomaculum* (Řezanka et al., 1990). Both sulfate-reducing bacteria and phototrophic sulfur bacteria produce lipids that are significantly depleted in ^{13}C compared to the biomass. Lipids from sulfate-reducing bacteria were found to be depleted 4 to 17 ‰ (Londry et al., 2004) and lipids from purple sulfur bacteria were depleted by up to 20 ‰ (Madigan et al., 1989).

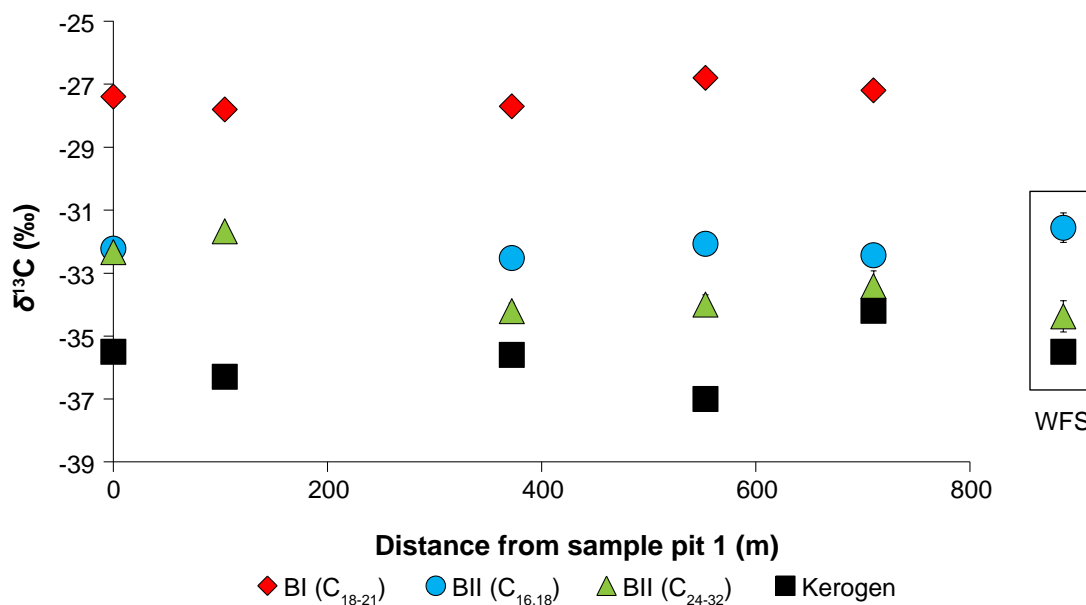


Figure 3.2: $\delta^{13}\text{C}$ of *n*-alkanes from Bitumen I (carbon number range C_{18} to C_{21}), Bitumen II (ranges $\text{C}_{16} + \text{C}_{18}$ and C_{24} to C_{32}) and bulk $\delta^{13}\text{C}$ of isolated kerogen from HYC sample pits. Bitumen I data was taken from Williford et al. (2011). Error bars are one standard deviation (often obscured by the markers). The box labelled WFS refers to the W-Fold Shale unit, which underlies the mineralised sections of the deposit.

The distinctive even-over-odd distribution of *n*-alkanes in Bitumen II was likely generated by phototrophic sulfur bacteria, while the ^{13}C -depleted long-chain *n*-alkanes in Bitumen II indicate sulfate-reducing bacteria. Their presence in Bitumen II, closely associated with the kerogen / mineral matrix, implies that these bacteria were present at the time of ore deposition. This evidence is consistent with deposition under euxinic conditions, as required for the formation and preservation of large-scale sulfide deposits (Lyons et al., 2006). The extent of euxinia into the photic zone is evidenced by the presence of phototrophic sulfur bacteria. The results fit the generally-held model in which a metal-rich hydrothermal brine was vented into the basin, reacting with bacterially-produced sulfide to form fine-grained base metal sulfides (Ireland et al., 2004b; Large et al., 2005). Recent findings of widespread ferruginous conditions in the McArthur Basin (Planavsky et al., 2011) suggest that euxinia was restricted to localised settings, such as the HYC sub-basin (McGoldrick et al., 2010) and the Glyde River region studied by Brocks et al. (2005). An increased supply of sulfate to a basin would promote euxinia over ferruginous conditions (Poulton et al., 2010). Sulfate carried by the oxidised hydrothermal fluid

(Cooke et al., 2000) may have contributed to the development of euxinic conditions during the deposition of HYC. It is notable that the evidence of euxinia is seen only in Bitumen II; the distinctive features from sulfate-reducing and sulfide-oxidising bacteria have been removed from Bitumen I by the actions of hydrothermal alteration and migration of non-indigenous OM.

Aromatic hydrocarbons in Bitumens I and II

The aromatic fractions of both Bitumens I and II are dominated by PAHs. The distribution of PAHs (Figure 3.1C) follows the most thermodynamically favourable pathway for the creation of condensed aromatic molecules (Stein, 1978) and is typical of those found in hydrothermal systems (e.g. Kawka and Simoneit, 1990). The high abundance of PAHs indicates that Bitumen II, like Bitumen I, has experienced significant hydrothermal alteration. The quantity of PAHs in Bitumen II (Table 3.2) is much lower than found in Bitumen I (Williford et al., 2011). This could indicate that Bitumen II has been partially shielded from alteration, although it also likely reflects the small amounts of OM available within the kerogen / mineral matrix.

A variety of parameters have been developed to evaluate thermal maturity based on the ratios of various methylated isomers of PAHs. Ratios based on methylphenanthrene (MP) isomers have been found in a study of the McArthur Basin to be sensitive to changes in maturity throughout the oil window (George and Ahmed, 2002). Two common MP ratios, MPI-1 and MPR are shown in Figure 3.3 for both Bitumens I and II. The value of MPI-1 in Bitumen I exceeds that of Bitumen II in every sample. If MPI-1 is taken to be a true indicator of maturity this would indicate that Bitumen I is of higher maturity than Bitumen II, suggesting that Bitumen II has been protected from thermal alteration. A different relationship however is observed for MPR. The values for Bitumens I and II are similar, and in some samples Bitumen II exceeds Bitumen I. Both parameters are expected to be indicative of maturity (Radke et al., 1982) but it is apparent that other factors are affecting the behaviour of these two ratios. Williford et al. (2011) proposed that PAHs in Bitumen I were generated at high temperatures (> 250 °C) in the underlying Wologorang Fm, whereas Bitumen II is likely indigenous to HYC and has experienced temperatures of less than 200 °C (Cooke et al., 2000; Large et al., 2005).

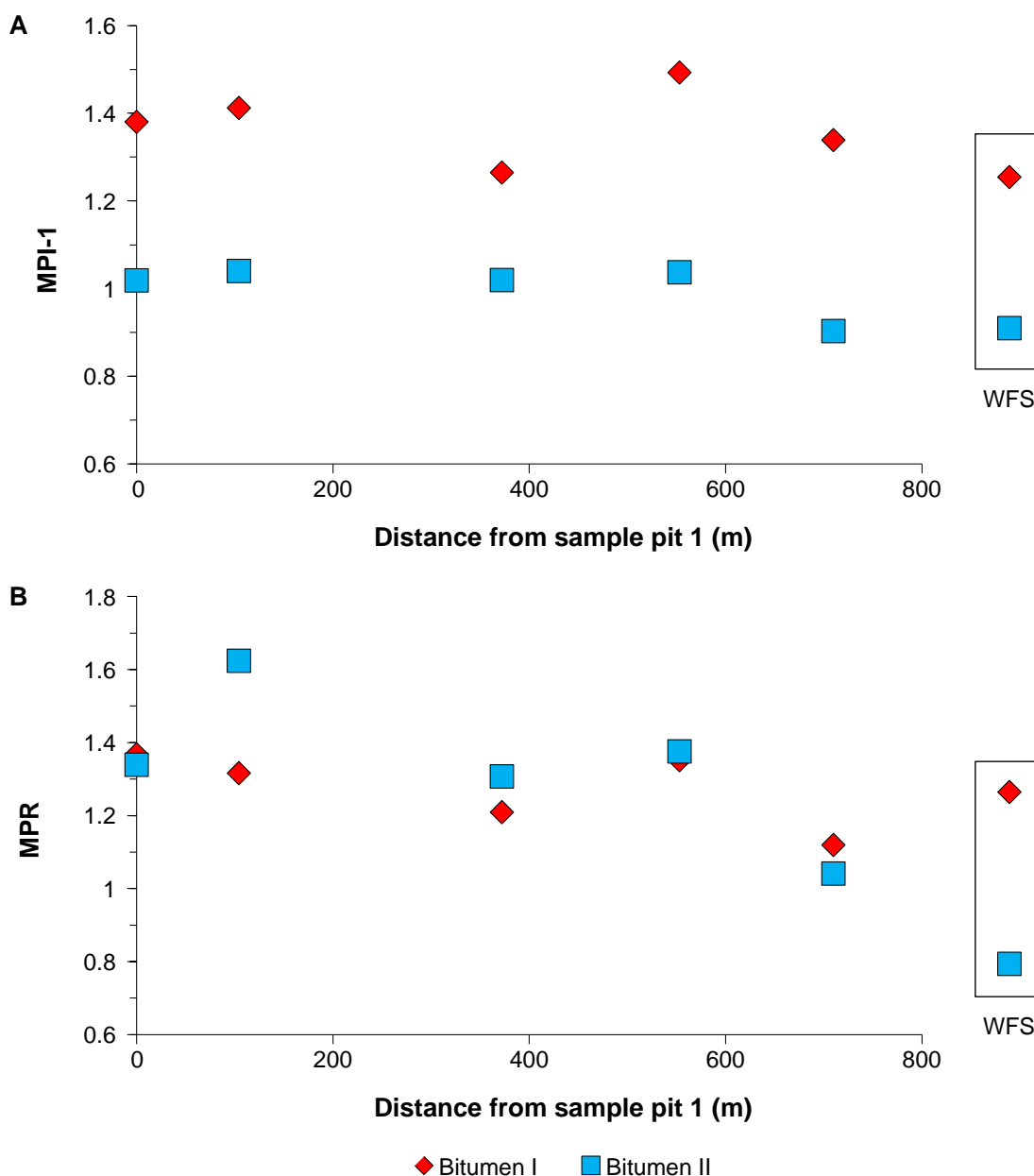


Figure 3.3: Selected PAH ratios calculated for Bitumens I and II. (A) methylphenanthrene index (MPI-1) and (B) methylphenanthrene ratio (MPR). Equations of MPI-1 and MPR are shown in Appendix 3. Bitumen I data was taken from Williford et al. (2011). The boxes labelled WFS refer to the W-Fold Shale unit, which underlies the mineralised sections of the deposit.

The different thermal histories are consistent with the increased MPI-1 values in Bitumen I but cannot explain why MPR is often greater in Bitumen II. Notably this is not the first study that has reported such behaviour. In a study of marine sediments from multiple locations spanning the Permian/Triassic boundary by Nabbefeld et al. (2010a) the same relationships were found. MPI-1 is consistently greater in Bitumen I but the β/α MP ratio, which is similar to MPR but includes all four isomers rather

than only 2- and 1-MP, is frequently greater in Bitumen II. The samples analysed by Nabbefeld et al. are of greatly different age and thermal history to those from this study, hence it appears that the relationships between MPI-1 and MPR are not unique to HYC but rather are a result of fundamental differences between Bitumens I and II.

The major difference between MPI-1 and the MPR or β/α MP ratio is that the unmethylated phenanthrene is included in the denominator of MPI-1 but does not appear in the other ratios. Figure 3.4 shows that Bitumen II contains far higher proportions of phenanthrene than Bitumen I. Phenanthrene is more abundant than the MPs in Bitumen II for all samples except the W-Fold Shale, but in Bitumen I it is less abundant than most or all of the MP isomers. The inclusion of phenanthrene in the denominator of MPI-1 causes this ratio to give much lower values for Bitumen II. Higher proportions of phenanthrene in Bitumen II were reported by Nabbefeld et al. (2010a), who also observed that Bitumen II contained a greater proportion of β methylated isomers compared to Bitumen I. The relationship between β and α isomers is less consistent in HYC, and the proportion of β to α isomers appears similar in Bitumens I and II.

The increased proportion of phenanthrene in Bitumen II from multiple locations and maturities implies that the cause of the increase is unrelated to location or thermal history. Nabbefeld et al. (2010a) suggest that phenanthrene is preferentially preserved in Bitumen II as it is more stable than the MPs, just as the more stable β isomers are preserved over the α isomers. Comparisons of thermodynamic properties of both phenanthrene and MPs, either experimental or theoretical, are rare, and the relative stabilities are strongly dependant on redox conditions (Püttmann et al., 1989; Dick et al., 2013). Regardless of their relative stabilities it is not clear why phenanthrene should be preferentially retained in Bitumen II over the MPs. Evidence for the retention of the more stable β MPs is limited in HYC, but is seen to a greater extent in the results of Nabbefeld et al. (2010a). Previous studies have explained the retention of β isomers in coals not by thermodynamic stability but by a 'molecular sieve' effect whereby larger molecules are trapped by pores in the coal structure (Vahrman and Watts, 1972). This effect does not explain the retention of the less bulky unmethylated molecule. In a study of the chromatographic behaviour of organic compounds moving through a column of montmorillonite clay, Brothers et al. (1991) found that 2-MP appears to be more strongly adsorbed to the clay than

phenanthrene. This is the opposite effect to that seen in Bitumen II. Studies of the relative adsorption behaviour of phenanthrene and MP are limited, but the available evidence does not seem to support the preferential retention of phenanthrene within the kerogen / mineral matrix.

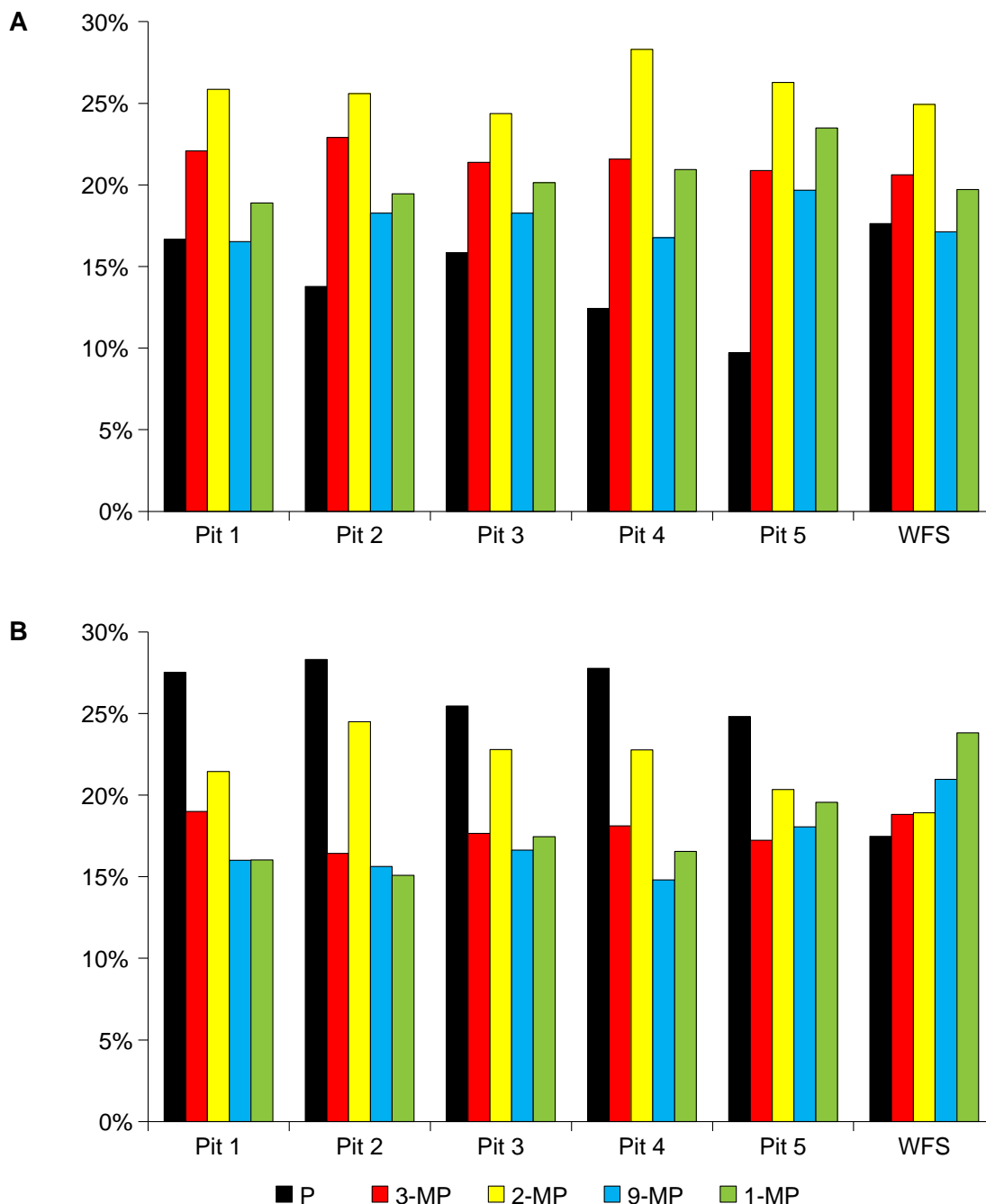


Figure 3.4: Relative proportion of phenanthrene (P) and methylphenanthrenes (MP) for (A) Bitumen I and (B) Bitumen II. Bitumen I data was taken from Williford et al. (2011).

An alternative explanation for the high proportion of phenanthrene in Bitumen II is that the MP isomers are prevented from forming within the kerogen / mineral matrix. MPs in sediments are generated by geosynthetic reactions in which methyl groups are added to unmethylated phenanthrene (Voigtman et al., 1994). Methylation of phenanthrene has been achieved in the laboratory under moderate temperature conditions in the presence of a clay catalyst, but requires the addition of a methyl donor such as methane (Voigtman et al., 1994) or existing methylated aromatic compounds (Alexander et al., 1995). A hydrous pyrolysis study found that phenanthrene alone does not undergo methylation even with prolonged heating, but significant methylation occurs with the addition of formic acid (McCollom et al., 1999). From these results it can be inferred that MPs will only form when other organic compounds are present that are able to donate methyl groups. This was recognised by van Aarssen et al. (1999) who proposed the concept of a 'methyl pool' that can be accessed by all aromatic compounds in the sediment. Compounds that are preserved within the kerogen / mineral matrix as part of Bitumen II may have experienced restricted access to the methyl pool and thus display reduced levels of methylation. It has been demonstrated that phenanthrene that is intercalated in clay minerals is significantly less available to biodegrading microorganisms (Theng et al., 2001), and it is feasible that it would experience reduced access to the methyl pool as well. This mechanism can explain the increased proportion of phenanthrene in Bitumen II from both this study and Nabbefeld et al. (2010a). Oxidation state can also affect the proportions of phenanthrene and MPs. A study of the Kupferschiefer deposit (southwest Poland) found increased proportions of phenanthrene in zones of higher oxidation state (Püttmann et al., 1989). PAHs in Bitumen I are believed to have been transported by a fluid that was likely oxidised (Cooke et al., 2000), hence the low proportions of phenanthrene in Bitumen I suggest that redox is not a significant control at HYC.

MPI-1 is commonly used to indicate thermal maturity, but results from this study have shown that the parameter can be heavily influenced by factors that affect the methylation of phenanthrene. Prior reports have noted that MPI-1 is also strongly influenced by demethylation reactions that occur at high temperatures (Garrigues et al., 1990). The inclusion of phenanthrene in the denominator of MPI-1 means that this ratio is not simply an indicator of maturity, but also reflects the source of OM

and the degree of methylation. As such MPI-1 is not a suitable parameter to compare the maturity of Bitumens I and II. Ratios such as MPR, which are based only on MP isomers, are perhaps better suited as indicators of maturity alone. As MPR from Bitumens I and II is generally similar it appears that the two extracts are of approximately equal maturity, and there is no conclusive evidence from MP ratios in this study that Bitumen II is significantly protected from thermal alteration. These results do not support a high-temperature origin for Bitumen I PAHs, as proposed by Chen et al. (2003), although the isotopic evidence for migration of hydrocarbons is strong (page 72).

Conclusions

Organic matter at HYC has experienced significant hydrothermal alteration, but Bitumen II may be protected from alteration and migration. Bitumen II prepared from HYC samples reveals highly distinct distributions of saturated and aromatic compounds. Bitumen II *n*-alkanes show a predominance of even carbon numbers, a preservation of long-chained *n*-alkanes up to C₃₈ and a marked depletion in ¹³C. These features are indicative of strong contributions from sulfate-reducing and sulfide-oxidising bacteria. Comparison with $\delta^{13}\text{C}$ of isolated kerogen confirms that *n*-alkanes in Bitumen II are indigenous to HYC, indicating that the deposit formed under euxinic conditions. This evidence supports the generally-held model whereby lead and zinc reacted in the water column with sulfide produced by bacterial sulfate reduction. Bitumen II appears useful in the study of environments that have experienced significant alteration and/or migration, where diagnostic features in Bitumen I have been destroyed or overprinted.

Bitumens I and II both contain high abundances of PAHs. The common maturity parameters MPI-1 and MPR display inconsistent results, with MPI-1 greater in Bitumen I but MPR often greater in Bitumen II. This behaviour is due to the greatly increased proportion of phenanthrene in Bitumen II compared to Bitumen I. We believe that this is a fundamental property of Bitumen II resulting from restricted access to the 'methyl pool' that contributes to methylation reactions. As MPI-1 is so heavily affected by access to the methyl pool it is not a suitable parameter for comparing the thermal maturity of Bitumens I and II.

Acknowledgements

All authors acknowledge the CSIRO Flagship Collaboration Fund Cluster for Organic Geochemistry of Mineral Systems led by Curtin University. A.H. thanks Curtin University for an Australian Postgraduate Award and CSIRO for a top-up scholarship. The Institute for Geoscience Research (TIGeR) and the John de Laeter Centre for Isotope Research provided additional funding. The authors thank Geoff Chidlow and Peter Sauer for GC-MS technical support, Stephen Clayton for GC-irMS technical support, and Grzegorz Skrzypek for bulk kerogen $\delta^{13}\text{C}$ measurements. Peter McGoldrick, an anonymous reviewer and Associate Editor Thomas Wagner provided helpful reviews, and Chris Yeats, Jochen Brocks and Katy Evans gave comments on earlier versions of the manuscript.

References

- Alexander R., Bastow T.P., Fisher S.J., Kagi R.I., 1995. Geosynthesis of organic compounds: II. Methylation of phenanthrene and alkylphenanthrenes. *Geochimica et Cosmochimica Acta* **59**, 4259-4266.
- Brocks J.J., Love G.D., Summons R.E., Knoll A.H., Logan G.A., Bowden S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866-870.
- Brocks J.J., Schaeffer P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. *Geochimica et Cosmochimica Acta* **72**, 1396-1414.
- Brothers L., Engel M.H., Krooss B.M., 1991. The effects of fluid flow through porous media on the distribution of organic compounds in a synthetic crude oil. *Organic Geochemistry* **17**, 11-24.
- Bull S.W., 1998. Sedimentology of the Palaeoproterozoic Barney Creek formation in DDH BMR McArthur 2, southern McArthur basin, Northern Territory. *Australian Journal of Earth Sciences* **45**, 21-31.
- Chen J., Walter M.R., Logan G.A., Hinman M.C., Summons R.E., 2003. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern

- Australia: organic geochemistry and ore genesis. *Earth and Planetary Science Letters* **210**, 467-479.
- Cooke D.R., Bull S.W., Large R.R., McGoldrick P.J., 2000. The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb-Zn (sedex) deposits. *Economic Geology* **95**, 1-18.
- Croxford N.J.W., 1968. A mineralogical examination of the McArthur lead-zinc-silver deposit. *Proceedings: Australasian Institute of Mining and Metallurgy* **226**, 97-108.
- Dembicki Jr H., Meinschein W.G., Hattin D.E., 1976. Possible ecological and environmental significance of the predominance of even-carbon number C₂₀-C₃₀ n-alkanes. *Geochimica et Cosmochimica Acta* **40**, 203-208.
- Dick J.M., Evans K.A., Holman A.I., Jaraula C.M.B., Grice K., 2013. Estimation and application of the thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature. *Geochimica et Cosmochimica Acta* **122**, 247-266.
- Garrigues P., Oudin J.L., Parlanti E., Monin J.C., Robcis S., Bellocq J., 1990. Alkylated phenanthrene distribution in artificially matured kerogens from Kimmeridge clay and the Brent Formation (North Sea). *Organic Geochemistry* **16**, 167-173.
- George S.C., Ahmed M., 2002. Use of aromatic compound distributions to evaluate organic maturity of the Proterozoic middle Velkerri Formation, McArthur Basin, Australia. In *The Sedimentary Basins of Western Australia 3: Proceedings of the Petroleum Exploration Society of Australia Symposium 2002* (eds. Keep M., Moss S.J.). Petroleum Exploration Society of Australia, Perth. pp 253-270.
- George S.C., Llorca S.M., Hamilton P.J., 1994. An integrated analytical approach for determining the origin of solid bitumens in the McArthur Basin, northern Australia. *Organic Geochemistry* **21**, 235-248.
- Grice K., Cao C., Love G.D., Böttcher M.E., Twitchett R.J., Grosjean E., Summons R.E., Turgeon S.C., Dunning W., Jin Y., 2005. Photic zone euxinia during the Permian-Triassic superanoxic event. *Science* **307**, 706-709.

- Grice K., Lu H., Atahan P., Asif M., Hallmann C., Greenwood P.F., Maslen E., Tulipani S., Williford K., Dodson J., 2009. New insights into the origin of perylene in geological samples. *Geochimica et Cosmochimica Acta* **73**, 6531-6543.
- Grice K., Nabbefeld B., Maslen E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. *Organic Geochemistry* **38**, 1795-1803.
- Grosjean E., Logan G.A., 2007. Incorporation of organic contaminants into geochemical samples and an assessment of potential sources: examples from Geoscience Australia marine survey S282. *Organic Geochemistry* **38**, 853-869.
- Han J., Calvin M., 1969. Hydrocarbon distribution of algae and bacteria, and microbiological activity in sediments. *Proceedings of the National Academy of Sciences of the United States of America* **64**, 436-443.
- Ireland T., Bull S.W., Large R.R., 2004a. Mass flow sedimentology within the HYC Zn-Pb-Ag deposit, Northern Territory, Australia: evidence for syn-sedimentary ore genesis. *Mineralium Deposita* **39**, 143-158.
- Ireland T., Large R.R., McGoldrick P., Blake M., 2004b. Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore textures in the McArthur River (HYC) Zn-Pb-Ag deposit, Northern Territory, Australia. *Economic Geology* **99**, 1687-1709.
- Kawka O.E., Simoneit B.R.T., 1990. Polycyclic aromatic hydrocarbons in hydrothermal petroleum from the Guaymas Basin spreading center. *Applied Geochemistry* **5**, 17-27.
- Ladygina N., Dedyukhina E.G., Vainshtein M.B., 2006. A review on microbial synthesis of hydrocarbons. *Process Biochemistry* **41**, 1001-1014.
- Large R.R., Bull S.W., McGoldrick P.J., Walters S., Derrick G.M., Carr G.R., 2005. Stratiform and strata-bound Zn-Pb-Ag deposits in Proterozoic sedimentary basins, Northern Australia. In *Economic Geology 100th Anniversary Volume* (eds. Hedenquist J.W., Thompson J.F.H., Goldfarb R.J., Richards J.P.). Society of Economic Geologists, Littleton, Colorado. pp 931-963.

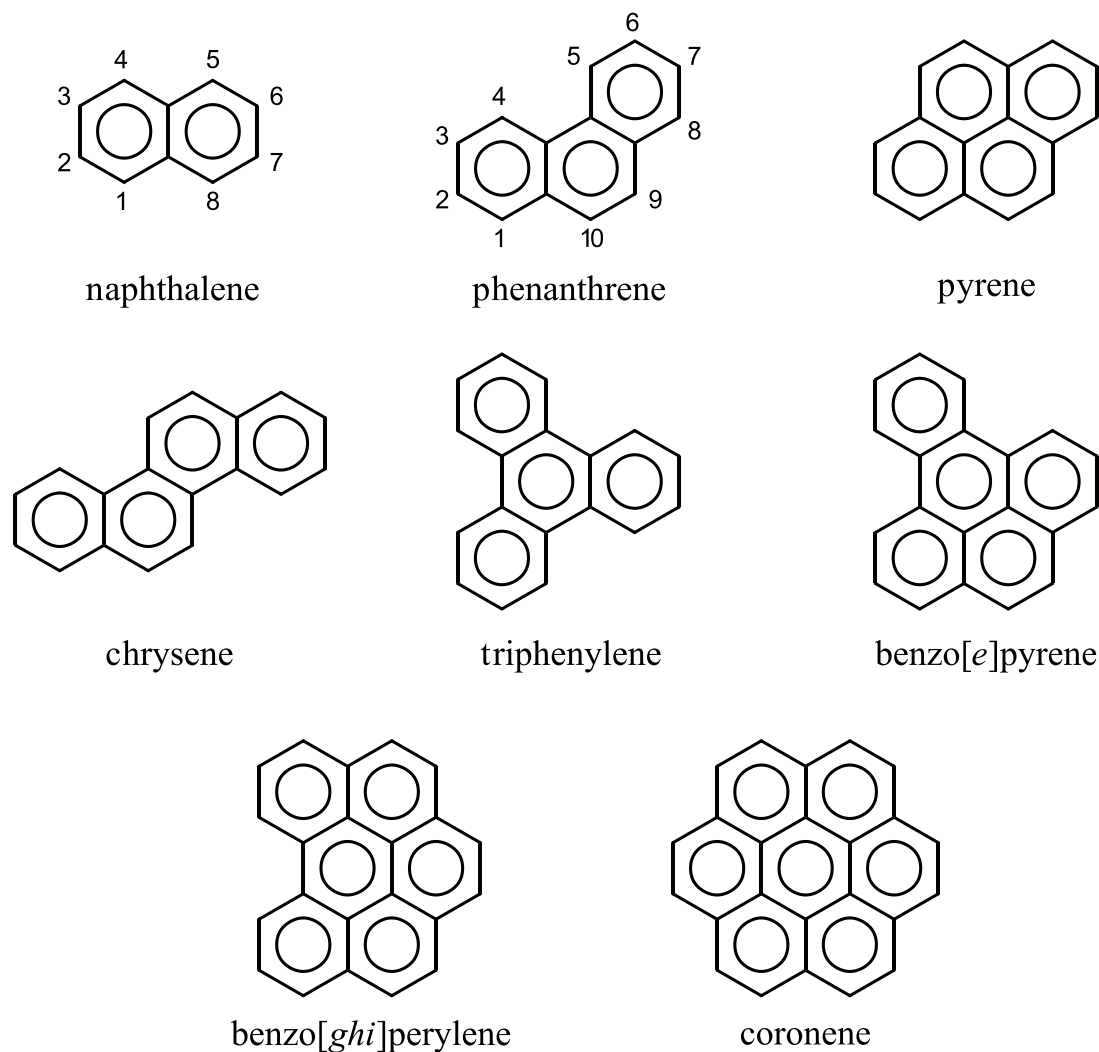
- Logan G.A., Calver C.R., Gorjan P., Summons R.E., Hayes J.M., Walter M.R., 1999. Terminal Proterozoic mid-shelf benthic microbial mats in the Centralian Superbasin and their environmental significance. *Geochimica et Cosmochimica Acta* **63**, 1345-1358.
- Logan G.A., Hayes J.M., Hieshima G.B., Summons R.E., 1995. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* **376**, 53-56.
- Logan G.A., Hinman M.C., Walter M.R., Summons R.E., 2001. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. *Geochimica et Cosmochimica Acta* **65**, 2317-2336.
- Londry K.L., Jahnke L.L., Des Marais D.J., 2004. Stable carbon isotope ratios of lipid biomarkers of sulfate-reducing bacteria. *Applied and Environmental Microbiology* **70**, 745-751.
- Lyons T.W., Gellatly A.M., McGoldrick P.J., Kah L.C., 2006. Proterozoic sedimentary exhalative (SEDEX) deposits and links to evolving global ocean chemistry. *Geological Society of America Memoirs* **198**, 169-184.
- Madigan M.T., Takigiku R., Lee R.G., Gest H., Hayes J.M., 1989. Carbon isotope fractionation by thermophilic phototrophic sulfur bacteria: evidence for autotrophic growth in natural populations. *Applied and Environmental Microbiology* **55**, 639-644.
- Marzi R., Torkelson B.E., Olson R.K., 1993. A revised carbon preference index. *Organic Geochemistry* **20**, 1303-1306.
- McCullom T.M., Simoneit B.R.T., Shock E.L., 1999. Hydrous pyrolysis of polycyclic aromatic hydrocarbons and implications for the origin of PAH in hydrothermal petroleum. *Energy & Fuels* **13**, 401-410.
- McGoldrick P., Winefield P., Bull S., Selley D., Scott R., 2010. Sequences, synsedimentary structures, and sub-basins: the where and when of SEDEX zinc systems in the southern McArthur Basin, Australia. In *The Challenge of Finding New Mineral Resources: Global Metallogeny, Innovative Exploration, and New Discoveries. Volume II: Zinc-Lead, Nickel-Copper-PGE, and*

- Uranium* (eds. Goldfarb R.J., Marsh E.E., Monecke T.). Society of Economic Geologists Special Publication Number 15, Littleton, Colorado. pp 367-389.
- Melendez I., Grice K., Trinajstić K., Ladjavardi M., Greenwood P., Thompson K., 2013. Biomarkers reveal the role of photic zone euxinia in exceptional fossil preservation: an organic geochemical perspective. *Geology* **41**, 123-126.
- Nabbefeld B., Grice K., Schimmelmann A., Summons R.E., Troitzsch U., Twitchett R.J., 2010a. A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks. *Organic Geochemistry* **41**, 78-87.
- Nabbefeld B., Grice K., Summons R.E., Hays L.E., Cao C., 2010b. Significance of polycyclic aromatic hydrocarbons (PAHs) in Permian/Triassic boundary sections. *Applied Geochemistry* **25**, 1374-1382.
- Page R.W., Sweet I.P., 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences* **45**, 219-232.
- Planavsky N.J., McGoldrick P., Scott C.T., Li C., Reinhard C.T., Kelly A.E., Chu X., Bekker A., Love G.D., Lyons T.W., 2011. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448-451.
- Poulton S.W., Fralick P.W., Canfield D.E., 2010. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geoscience* **3**, 486-490.
- Powell T.G., Jackson M.J., Sweet I.P., Crick I.H., Boreham C.J., Summons R.E., 1987. Petroleum geology and geochemistry, Middle Proterozoic McArthur Basin. Australia Bureau of Mineral Resources, Geology and Geophysics, record 1987/48.
- Poynter J., Eglinton G., 1990. Molecular composition of three sediments from hole 717C: The Bengal Fan. In *Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 116* (eds. Cochran J.R., Stow D.A.V.). Ocean Drilling Program, College Station, Texas. pp 155-161.

- Püttmann W., Merz C., Speczik S., 1989. The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland. *Applied Geochemistry* **4**, 151-161.
- Radke M., Willsch H., Leythaeuser D., Teichmüller M., 1982. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* **46**, 1831-1848.
- Řezanka T., Sokolov M.Y., Viden I., 1990. Unusual and very-long-chain fatty acids in Desulfotomaculum, a sulfate-reducing bacterium. *FEMS Microbiology Letters* **73**, 231-237.
- Robl T.L., Davis B.H., 1993. Comparison of the HF-HCl and HF-BF₃ maceration techniques and the chemistry of resultant organic concentrates. *Organic Geochemistry* **20**, 249-255.
- Sherman L.S., Waldbauer J.R., Summons R.E., 2007. Improved methods for isolating and validating indigenous biomarkers in Precambrian rocks. *Organic Geochemistry* **38**, 1987-2000.
- Simoneit B.R.T., 1994. Lipid/bitumen maturation by hydrothermal activity in sediments of Middle Valley, Leg 139. In *Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 139* (eds. Mottl M.J., Davis E.E., Fisher A.T., Slack J.F.). Ocean Drilling Program, College Station, Texas. pp 447-465.
- Stein S.E., 1978. On the high temperature chemical equilibria of polycyclic aromatic hydrocarbons. *The Journal of Physical Chemistry* **82**, 566-571.
- Summons R.E., Powell T.G., 1987. Identification of aryl isoprenoids in source rocks and crude oils: biological markers for the green sulphur bacteria. *Geochimica et Cosmochimica Acta* **51**, 557-566.
- Summons R.E., Powell T.G., Boreham C.J., 1988. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. *Geochimica et Cosmochimica Acta* **52**, 1747-1763.
- Szczerba M., Rospondek M.J., 2010. Controls on distributions of methylphenanthrenes in sedimentary rock extracts: critical evaluation of

- existing geochemical data from molecular modelling. *Organic Geochemistry* **41**, 1297-1311.
- Theng B.K.G., Aislabie J., Fraser R., 2001. Bioavailability of phenanthrene intercalated into an alkylammonium–montmorillonite clay. *Soil Biology and Biochemistry* **33**, 845-848.
- Vahrman M., Watts R.H., 1972. The smaller molecules obtainable from coal and their significance: Part 6. Hydrocarbons from coal heated in thin layers. *Fuel* **51**, 235-241.
- van Aarssen B.G.K., Bastow T.P., Alexander R., Kagi R.I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Organic Geochemistry* **30**, 1213-1227.
- Venkatesan M.I., Dahl J., 1989. Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary. *Nature* **338**, 57-60.
- Voigtmann M.F., Yang K., Batts B.D., Smith J.W., 1994. Evidence for synthetic generation of methylphenanthrenes in sediments. *Fuel* **73**, 1899-1903.
- Wakeham S.G., Schaffner C., Giger W., 1980a. Polycyclic aromatic hydrocarbons in Recent lake sediments—I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta* **44**, 403-413.
- Wakeham S.G., Schaffner C., Giger W., 1980b. Polycyclic aromatic hydrocarbons in Recent lake sediments—II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta* **44**, 415-429.
- Walker R.N., Logan R.G., Binnekamp J.G., 1977. Recent geological advances concerning the H.Y.C. and associated deposits, McArthur River, N.T. *Journal of the Geological Society of Australia* **24**, 365-380.
- Williford K.H., Grice K., Logan G.A., Chen J., Huston D., 2011. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters* **301**, 382-392.

Appendix 3



$$\text{MPI-1} = 1.5 \frac{2\text{-MP} + 3\text{-MP}}{\text{P} + 1\text{-MP} + 9\text{-MP}}$$

$$\text{MPR} = \frac{2\text{-MP}}{1\text{-MP}}$$

$$\text{CPI} = \frac{(\sum_{i=n}^m C_{2i+1}) + (\sum_{i=n+1}^{m+1} C_{2i+1})}{2(\sum_{i=n+1}^{m+1} C_{2i})}$$

$$\text{ACL} = \frac{\sum C \times n}{\sum C}$$

Figure A3.1: Structures of PAHs discussed in the text. Positions of methylation are indicated for naphthalene and phenanthrene. Equations of the methylphenanthrene index (MPI-1) and methylphenanthrene ratio (MPR) are taken from Radke et al. (1982). Equation of the carbon preference index (CPI) is taken from Marzi et al. (1993). Equation of the average chain length (ACL) is adapted from Poynter and Eglinton (1990).

Chapter 4

Effects of sulfide minerals on aromatic maturity parameters: laboratory investigation using micro-scale sealed vessel pyrolysis

Alex I. Holman, Paul F. Greenwood, Jochen J. Brocks and Kliti Grice

Organic Geochemistry, in press 2014

Abstract

Sedimentary organic matter (OM) from the Here's Your Chance (HYC) Pb/Zn/Ag deposit (McArthur Basin, Northern Territory, Australia) displays increased thermal maturity compared to nearby non-mineralised sediments. Micro-scale sealed vessel pyrolysis (MSSVpy) of an immature organic-rich sediment from the host Barney Creek Formation (BCF) was used to simulate the thermal maturation of OM from the HYC deposit, and to assess the effect of sulfide minerals on organic maturation processes. MSSVpy at increasing temperatures (300, 330 and 360 °C) resulted in increased methylphenanthrene maturity ratios which were within the range reported for bitumen extracted from HYC sediments. The methylphenanthrene index ratio from MSSVpy of the BCF sample was lower than in HYC, due to a reduced proportion of methylated phenanthrenes. Polycyclic aromatic hydrocarbons with four to six rings were produced in increasing abundance as pyrolysis temperature increased, although they did not approach the levels reported from HYC. Addition of lead sulfide, zinc sulfide and pyrite to the MSSVpy experiments resulted in a reduced response of the methylphenanthrene maturity parameters, possibly due to retardation of methyl-shift and transmethylation reactions.

Introduction

Organic matter (OM) is thought to play an important role in the formation of many commercially viable ore bodies, hence there is significant interest in the use of organic geochemical techniques to investigate the formation history of ore deposits (Greenwood et al., 2013). OM can be significantly altered by interaction with ore-forming fluids. For example, major hydrothermal events associated with the formation of sedimentary-exhalative (SEDEX) ore deposits have caused a marked increase in the thermal maturity of associated sedimentary OM (Gizè, 1999; Logan et al., 2001; Williford et al., 2011). Oxidised fluids which formed the Kupferschiefer deposit contributed to increased pristane / phytane ratios (Large and Gizè, 1996) and lower abundances of methylated aromatics (Püttmann et al., 1989). The high abundance of sulfide minerals in such environments may be a major influence on the behaviour of OM during alteration, such that traditional assumptions and interpretations largely based on petroleum organic geochemistry may not apply (Gizè, 1999). Although sulfide minerals have been found to catalyse abiotic organic reactions important to the early origins of life (Cody et al., 2004; Cleaves et al., 2012) their effect on the thermal maturation of OM has been largely unexplored.

A wide range of molecular parameters have been developed to assess the thermal maturity of source rocks and petroleum hydrocarbons, summarised by Peters et al. (2005). Parameters based on polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and phenanthrene are widely used due to the ubiquity of these compounds in sediments and their high thermal stability compared to aliphatic biomarkers (Price, 1993). Methylated PAHs readily undergo isomerisation reactions during maturation, with the β substituted isomers being more thermodynamically stable than the α isomers (Nabbefeld et al., 2010; Szczerba and Rospondek, 2010; Dick et al., 2013). A number of parameters have been developed based on the relative abundances of methylphenanthrene (MP) isomers, including the methylphenanthrene ratio $\text{MPR} = 2\text{-MP} / 1\text{-MP}$ (Radke et al., 1982b) and the methylphenanthrene indices $\text{MPI-1} = 1.5 (2\text{-MP} + 3\text{-MP}) / (\text{P} + 9\text{-MP} + 1\text{-MP})$ (Radke et al., 1982a) and $\text{MPI-3} = (2\text{-MP} + 3\text{-MP}) / (9\text{-MP} + 1\text{-MP})$ (Garrigues et al., 1988). Catalysis by clay mineral surfaces has been shown in different circumstances to promote methylation or demethylation of PAHs in shales and crude oils (Alexander et al., 1995; van Aarssen et al., 1999) and thus can influence the

values of aromatic maturity parameters (Nabbefeld et al., 2010). Larger PAHs with four or more aromatic rings are not generally used in maturity parameters, although they may be produced by burial metamorphism (Brocks et al., 2003) and have been detected in high abundances in submarine hydrothermal petroleum (Kawka and Simoneit, 1990; Simoneit, 1994; Simoneit et al., 2004). PAHs have been detected in a range of ore deposits including sediment-hosted lead-zinc (Chen et al., 2003; Williford et al., 2011), mercury (Blumer, 1975; Wise et al., 1986), copper-silver (Püttmann et al., 1989; Rospondek et al., 2007; Rospondek et al., 2009) and strata-bound copper sulfide (Rieger et al., 2008).

Microscale sealed vessel pyrolysis (MSSVpy) is a closed-system pyrolysis technique in which relatively small (mg) amounts of organic material are heated in a sealed glass tube. MSSVpy has been widely applied to simulate the catagenetic reactions of hydrocarbons and study the kinetics of petroleum generation (Horsfield et al., 1989; Schenk and Horsfield, 1993; Ladjavardi et al., 2013), as well as to characterise naturally-occurring OM (Greenwood et al., 2006; Berwick et al., 2010; Lockhart et al., 2013) and investigate the formation of specific organic products during diagenesis (Sinninghe Damsté et al., 1998). Another common technique for the artificial maturation of OM is hydrous pyrolysis, in which crushed or powdered rock is heated with water in sealed vessels (Lewan et al., 1979). Compared to MSSVpy, hydrous pyrolysis more holistically replicates the conditions of natural organic maturation due to the presence of water and the control of pressure, fluid composition and redox state (e.g. Landais et al., 1994; Lewan, 1997; Seewald, 2001). However the high pressures generated during hydrous pyrolysis require specialised laboratory equipment, while MSSVpy is easier to employ and generates similar products to natural organic maturation (Horsfield et al., 1989). Here we employ MSSVpy to simulate the thermal maturation of OM from the Here's Your Chance (HYC) Pb/Zn/Ag deposit, and to assess the effect of high abundances of sulfide minerals on aromatic maturity parameters.

Materials and methods

Sample site and description

The Barney Creek Formation (BCF) is a 1640 ± 3 Ma (Page and Sweet, 1998) marine shale deposited in the McArthur Basin (Northern Territory, Australia) under reduced, deep-water conditions (Bull, 1998). Detailed descriptions are presented by Brocks and Schaeffer (2008) and Greenwood et al. (2013). The BCF is host to the Here's Your Chance (HYC) Pb/Zn/Ag deposit, the largest of the Proterozoic deposits of the North Australian craton which is the world's richest Pb/Zn mineral province (Huston et al., 2006). The base metals in HYC are widely believed to have been deposited by a hydrothermal brine with a temperature of 100 to 200 °C (Huston et al., 2006; Williford et al., 2011), in a tectonically-controlled sub-basin (McGoldrick et al., 2010). A number of studies have investigated the organic geochemistry of HYC (Logan et al., 2001; Chen et al., 2003; Williford et al., 2011) and have found evidence of significant hydrothermal alteration of OM in mineralised sections. Mineralised sections of the deposit contain abundant fine-grained pyrite, sphalerite and galena (e.g. Large et al., 1998; Ireland et al., 2004).

The sample used in this study (referred to as the BCF sample) was taken from the Glyde Sub-basin, from drill core GR-7 at depth 94.69 to 94.81 m. The Glyde Sub-basin is located 80 km south of HYC, and is stratigraphically equivalent and morphologically similar to the deposit (Davidson and Dashlooty, 1993; McGoldrick et al., 2010). Sediments from the Glyde region often have low thermal maturity for samples of Paleoproterozoic age, with equivalent vitrinite reflectance of 0.6 to 0.8 % calculated from MPI-1 (Crick, 1992), and contain abundance biomarkers of phototrophic sulfur bacteria including intact carotenoid pigments (Brocks et al., 2005; Brocks and Schaeffer, 2008). Organic matter preserved within the kerogen-mineral matrix of HYC samples has shown evidence for the presence of these bacteria during ore formation (**Chapter 3**). The BCF sample was deposited in a similar environment to HYC and displays relatively low thermal maturity. While the sample is not an exact match of the HYC sediments prior to mineralisation, it is a suitable analogue to evaluate the effect of sulfide minerals on the organic maturation processes that occurred during the formation of the deposit.

Sample preparation

The BCF sample had been stored long-term in a Whirl-Pak plastic sample bag. Such plastic bags are potential sources of hydrocarbon contamination including branched alkanes with quaternary carbons (BAQCs; e.g. Grosjean and Logan, 2007; Greenwood et al., 2009). Before the sample was powdered, rock pieces were ultrasonically extracted (30 min) with a small amount of Milli-Q purified water to ablate the surfaces of the sample. The water and fine suspended particles were twice shaken with DCM in a separating funnel. The organic layer was reduced with a rotary evaporator and passed through a Pasteur pipette packed with MgSO₄ (Fisher Scientific, pre-rinsed with DCM). Three small pieces (1 × 1 cm) were cut from the sample bag with scissors (rinsed with DCM) and ultrasonically extracted for 15 minutes in DCM. Both extracts were analysed by GC-MS (instrumental conditions detailed in **Chapter 2**). Analysis of the *m/z* 99-85 extracted ion chromatogram from the sample bag extract revealed a series of 3,3-diethylalkanes with 21 to 35 carbon atoms, which are known contaminants from Whirl-Pak sample bags (Grosjean and Logan, 2007). These compounds were not detected in the surface washings from the BCF sample.

The sample was ground to a fine powder in a Rock Labs ring mill with a zirconia head. The mill was cleaned before use by repeated grinding of acid-washed, annealed sand. The final batch of ground sand was extracted with DCM, and GC-MS analysis showed no significant contamination.

Pure metal sulfides

Zinc sulfide (Purum, Riedel-de Haën, Sigma Aldrich) was received as a fine white powder. Lead sulfide (99.9 %, Aldrich) was in the form of aggregates that were crushed to a fine powder with a mortar and pestle. Pyrite (Alfa Aesar) was received as grains approximately 1.5 to 5 mm in length, which were powdered in a Rock-Labs ring mill with a zirconia head. Sulfides were cleaned by ultrasonic extraction (×3) with DCM. Analysis of the final extract by GC-MS showed no significant contaminants.

To examine the size distribution of the sulfides, particles were suspended in deionised water, transferred to microscope slides and imaged on an optical microscope under transmitted light. The sulfides consisted of fine particles, often

sub-micrometre in size, commonly aggregated into clusters ranging from ten to several hundred micrometres. Previous investigations of sulfide mineral textures in the HYC deposit have found that sulfide minerals occur in grains of one to ten micrometres, aggregated into clusters of twenty to two hundred micrometres (Eldridge et al., 1993; Ireland et al., 2004). The pure sulfides used in this study are therefore an adequate approximation of the sulfide minerals occurring in HYC.

Mixtures of BCF sample with approximately 5 wt. % and 20 wt. % metal sulfides were prepared and homogenised with a mortar and pestle. Precise weights for all mixtures are listed in Table 4.1.

Table 4.1: Precise weights of BCF sample and metal sulfides for the mixtures sub-sampled for MSSVpy experiments.

Sample name	BCF sample (mg)	Metal sulfide (mg)	Sulfide (wt. %)
5 % PbS	961.45	54.04	5.32 %
20 % PbS	865.98	216.57	20.01 %
5 % ZnS	968.86	50.96	5.00 %
20 % ZnS	783.12	196.76	20.08 %
5 % pyrite	945.88	49.26	4.91 %
20 % pyrite	796.24	196.90	19.83 %

Micro-scale sealed vessel pyrolysis and GC-MS analysis

MSSVpy followed a previously described procedure (Greenwood et al., 2006; Berwick et al., 2010). Extractable organic matter was not removed from the sample prior to pyrolysis. Glass tubes (5 cm × 5 mm i.d.) and glass beads (Alltech 60/80) were cleaned by heating overnight at 300 °C before use. Typically 6 to 10 mg of sample was loaded into the centre of the tube, and the void space above and below the sample was filled with glass beads. The tubes were flame sealed before heating in an oven for 72 hours at either 300, 330 or 360 °C. The tubes were then placed in a series II MSSV injector (held at 300 °C) mounted on a GC-MS (Agilent 6890 GC coupled to an Agilent 5973 MSD) and cracked with a plunger. Volatile products were transferred to the GC column (Agilent J&W DB5-MS, 60 m × 0.25 mm i.d., 0.25 µm film thickness) with He carrier gas at a constant pressure of 9 psi, and a split ratio of 20:1. The oven was held at 40 °C for 2 minutes while the column was immersed in liquid nitrogen to cryogenically focus the products. The oven

temperature was then increased from 40 to 320 °C at 4 °C per minute and held at 320 °C for 35 minutes. Mass spectra were acquired in full scan mode (m/z 25 to 550) with an ionisation energy of 70 eV. All samples were prepared and analysed in duplicate. Product assignments were based on GC retention time and mass spectral comparison with standards or library data.

Correction factors

Due to the online nature of MSSVpy the pyrolysates cannot be separated into saturate and aromatic fractions prior to GC-MS analysis. The GC chromatograms produced in this study contain products which fully or partially co-elute, and accurate integration of the total ion chromatogram (TIC) was often difficult for compounds of low abundance (see Figure 4.1 for a representative chromatogram). For this reason aromatic compounds were integrated from extracted ion chromatograms (EIC) of diagnostic ions. The selected ion makes up a different proportion of the total mass spectrum for each compound; hence ratios calculated from EIC cannot be directly compared to those from TIC. Correction factors were thus determined for each aromatic compound of interest by calculating the ratio of peak area from EIC to TIC from previous samples run on the GC-MS instrument. Only compounds free from co-elution were included in the calculations, and a range of peak areas were chosen to ensure linearity of the calibration. Calculated correction factors are listed in Table 4.2.

Table 4.2: Diagnostic ions and mass spectral correction factors for major PAH products. Data used in calculation of correction factors are shown in Table A4.1.

Compound	Diagnostic ion	Correction factor
Phenanthrene	178	0.45
Methylphenanthrenes	192	0.34
Pyrene	202	0.37
Chrysene + triphenylene	228	0.37
Benzo[<i>e</i>]pyrene	252	0.30
Benzo[<i>ghi</i>]perylene	276	0.46

Simulated maturation of Barney Creek sediment by MSSVpy

Overall product distribution

A representative chromatogram from MSSVpy of the BCF sample (300 °C) is shown in Figure 4.1. The most abundant products are listed in Table 4.3. Aliphatic products from MSSVpy were predominantly normal and methylated alkanes (marked with closed and open circles respectively). Low molecular weight alkanes (C₄ to C₉) displayed a higher proportion of methylation. *n*-Alkanes > C₁₀ displayed a unimodal distribution with a maximum at C₁₃, a long tail extending to C₃₁ and a reduced proportion of methylated isomers. Low-MW alkenes, cycloalkanes and ketones were present in relatively low abundances. The major aromatic products were benzenes and naphthalenes with one to five methyl groups. Phenanthrenes and high-MW PAHs with 4 to 7 aromatic rings were present in much lower abundance (see pages 100 to 103). Pyrolysis at higher temperatures gave similar results, with the most significant difference being an increase in the abundance of high-MW PAHs, consistent with the increase in PAH abundance observed across a thermal gradient at HYC (Chen et al., 2003) (see Figure 4.2 and page 102 for discussion).

Solvent-extracted bitumens from the BCF contain abundant aryl isoprenoids (Brocks et al., 2005; Brocks and Schaeffer, 2008), which are formed from the breakdown of microbial carotenoids (Summons and Powell, 1987; Grice et al., 1996; Koopmans et al., 1996; Grice et al., 1997). These were not detected in the MSSVpy experiments. Pyrolysis of long-chain alkylbenzenes has been shown to produce methylbenzene through cleavage of the alkyl C-C bond in the β position to the aromatic ring, a mechanism favoured by the high stability of the benzyl radical intermediate (Safarik and Strausz, 1997). Cleavage of the alkyl chain from the aryl isoprenoids present in the BCF bitumen would produce tetramethylbenzenes with a predominant 1,2,3,4 substitution pattern. Abundant 1,2,3,4-tetramethylbenzene was noted from flash pyrolysis of sedimentary organics from the Duverney Fm (Western Canada Basin), and was attributed to the breakdown of diaromatic carotenoids (Hartgers et al., 1994; Maslen et al., 2009). In the MSSVpy products from this study the mono-, di- and trimethylbenzenes were more abundant than the tetramethylbenzenes. It is likely they were produced by demethylation and methyl shift reactions (e.g. Szczerba and

Rospondek, 2010; Le Métayer et al., 2014) resulting in a larger suite of polymethylated products.

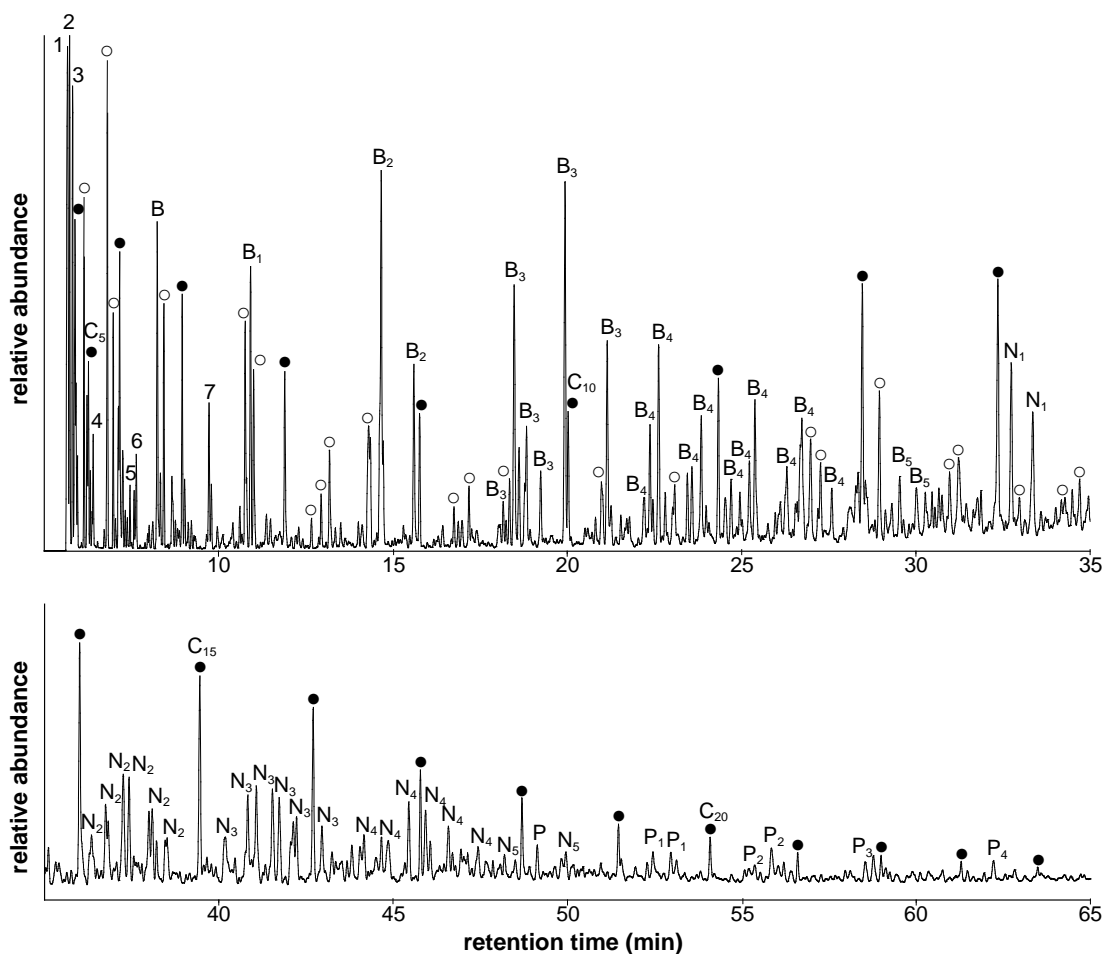


Figure 4.1: Total ion chromatogram from MSSVpy of the BCF sample, pyrolysed at 300 °C for 72 hours, with no added metal sulfides. Labelled peaks are listed in Table 4.3.

Methylated phenanthrene ratios

The average values for three commonly used methylphenanthrene (MP) maturity parameters (MPI-1, MPR and MPI-3) from the replicate MSSVpy experiments are listed in Table 4.4, with the range of replicate measurements in parentheses. The reproducibility was in most cases within 5 %. For the pure BCF sample, the maturity parameters increased with pyrolysis temperature, consistent with their behaviour during natural maturation (Radke et al., 1982a). The average MPI-1 values correspond to equivalent vitrinite reflectance values of 0.89 % at 300 °C to 1.16 % at 360 °C, using the calibration of Boreham et al. (1988).

The calculated MP ratios were compared to those from HYC bitumens reported by Williford et al. (2011), which are shown by the shaded areas in Figure 4.3A to 4.3C. The ratios using only MP isomers (MPR and MPI-3) display similar behaviours in comparison to HYC bitumen. The BCF sample pyrolysed at 300 °C gave values slightly below the minimum reported from HYC. At 330 °C the values lie towards the middle of the HYC range, while at 360 °C values significantly exceed the maximums reported for HYC.

Table 4.3: Major products from MSSVpy of the BCF sample at 300 °C for 72 hours, with no added metal sulfides.

Label	Compound	Label	Compound
1	CO ₂	B ₄	C ₄ benzenes
2	propene	B ₅	C ₅ benzenes
3	2-methylpropane	N	naphthalene
4	3-methylbut-1-ene	N ₁	methylnaphthalenes
5	methylpent-2-ene	N ₂	C ₂ naphthalenes
6	methylcyclopentane	N ₃	C ₃ naphthalenes
7	methylcyclohexane	N ₄	C ₄ -naphthalenes
•	<i>n</i> -alkanes	N ₅	C ₅ naphthalenes
○	methyl alkanes	P	phenanthrene
B	benzene	P ₁	methylphenanthrenes
B ₁	toluene	P ₂	C ₂ phenanthrenes
B ₂	C ₂ benzenes	P ₃	C ₃ phenanthrenes
B ₃	C ₃ benzenes	P ₄	C ₄ phenanthrenes

Unlike MPR and MPI-3, the MPI-1 ratio includes unmethylated phenanthrene as well as MP isomers. Whilst MPI-1 values similarly increased with higher pyrolysis temperatures they differed from the range reported for HYC (Figure 4.3A). MSSVpy at 300 and 330 °C gave MPI-1 values that were significantly lower than the minimum observed from HYC, and only the value at 360 °C was within the range of HYC. The MPI-1 values from MSSVpy were effectively lower than MPR and MPI-3 in comparison to the reported values from HYC.

The total abundances of the MP isomers relative to phenanthrene (referred to in this study as MP / P) is between 2.7 and 3.9 for all MSSVpy experiments, and generally decreased slightly from 300 °C to 360 °C pyrolysis temperature. For HYC the MP / P

ratio is between 5.0 and 9.3 (Williford et al., 2011). An increased proportion of phenanthrene in the MSSVpy experiments is responsible for a lowering of MPI-1 values. Pyrolysis can promote the cleavage of alkyl groups from aromatic molecules (Safarik and Strausz, 1997), which may account for the low abundances of MPs observed from MSSVpy experiments. Additionally, oxidation of OM during pyrolysis may result in a lowering of the MPI-1 and MP / P ratios. Phenanthrene has a higher average oxidation state of carbon than the MP isomers (-0.71 compared to -0.8). The values of MPI-1 and MP / P are therefore sensitive to changes in redox conditions as well as temperature, and oxidation of OM would be expected to decrease the MP / P ratio and lower the value of MPI-1 (Szczerba and Rospondek, 2010; Dick et al., 2013). A reduction in MPI-1 corresponding to a shift from reducing to oxidising conditions has been observed in the Kupferschiefer deposit (Püttmann et al., 1989; Sun, 1998). However, the use of glass beads to fill the majority of void space within the tube essentially renders the MSSVpy technique free of oxidation artefacts (Horsfield et al., 2015). Indeed the observed increase of MPI-1 with pyrolysis temperature (Figure 4.3A) shows that temperature is the major control on MPI-1 in these experiments.

Alternatively an additional mechanism that was not present in the MSSVpy experiments may have produced MPs at HYC. One potential explanation is the migration of aromatic hydrocarbons to HYC with the mineralising fluid. Williford et al. (2011) found that PAHs from HYC have similar $\delta^{13}\text{C}$ to kerogen from the underlying Wologorang Formation, and proposed that PAHs were generated in the Wologorang Formation by hydrothermal alteration and deposited in the BCF by the mineralising fluid. It is unclear however if these PAHs would have a greater ratio of MP / P than those produced by MSSVpy in this study. The Wologorang Formation has experienced extensive metamorphism from volcanic intrusions (Donnelly and Jackson, 1988), which has likely resulted in the destruction of all indigenous OM (Brocks et al., 2008). The composition of indigenous OM from this formation therefore remains uncertain, and the likelihood of this explanation cannot presently be evaluated.

High MW PAHs

PAHs with four to six aromatic rings (hereby collectively referred to as high-MW PAHs) were detected at low abundance in all MSSVpy experiments. Summed m/z 202 + 228 + 252 + 276 chromatograms for the three pyrolysis temperatures are shown in Figure 4.2. At 300 °C the four-ring PAHs fluoranthene and pyrene have lower abundance than other peaks in the m/z 202 chromatogram (mainly dimethyl- and trimethylphenanthrenes), while the five and six-ring PAHs are present only in trace amounts. At 330 and 360 °C the PAHs become far more prominent, implying increased production of high-MW PAHs at higher pyrolysis temperature. This is consistent with observations across a thermal gradient at HYC (Chen et al., 2003; Williford et al., 2011).

The summed abundance of the high-MW PAHs fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, triphenylene, benzo[*e*]pyrene, benzo[*a*]pyrene and benzo[*ghi*]perylene relative to the abundance of phenanthrene is defined here as PAH / P. This ratio increases with pyrolysis temperature, approximately doubling from 300 to 360 °C (see Table 4.4 and Figure 4.3D). Phenanthrene was reported to be totally stable during hydrous pyrolysis at 330 °C for up to 17 days (McCullom et al., 1999) and even persisted after pyrolysis at 400 °C for 30 days (Price, 1993), therefore destruction of the phenanthrene ring system is not expected to occur at the conditions used in this study. The increased PAH / P ratio is attributed to the increased production of high-MW PAHs at higher pyrolysis temperatures.

Bitumen isolated from the HYC deposit contains a high proportion of high-MW PAHs, with the samples from Williford et al. (2011) displaying PAH / P ratios from 2.2 to 7.9. In contrast all MSSVpy experiments showed PAH / P ratios of less than 1.0 (Figure 4.3D), due to the greatly reduced abundances of high-MW PAHs. It has been proposed that high-MW PAHs in hydrothermal systems are formed by the condensation of low-MW organic precursors (Kawka and Simoneit, 1990; Fetzer et al., 1996) through the addition of C₂ or C₄H₂ units to existing aromatic structures (Stein, 1978). There would likely be sufficient organic precursors present in the BCF sediment to form significant amounts of high-MW PAHs, suggesting that the low abundances of these compounds were due to the thermal conditions used during MSSVpy treatments. Higher temperatures or longer-term experiments may be required to generate large abundances of high-MW PAHs. Chen et al. (2003)

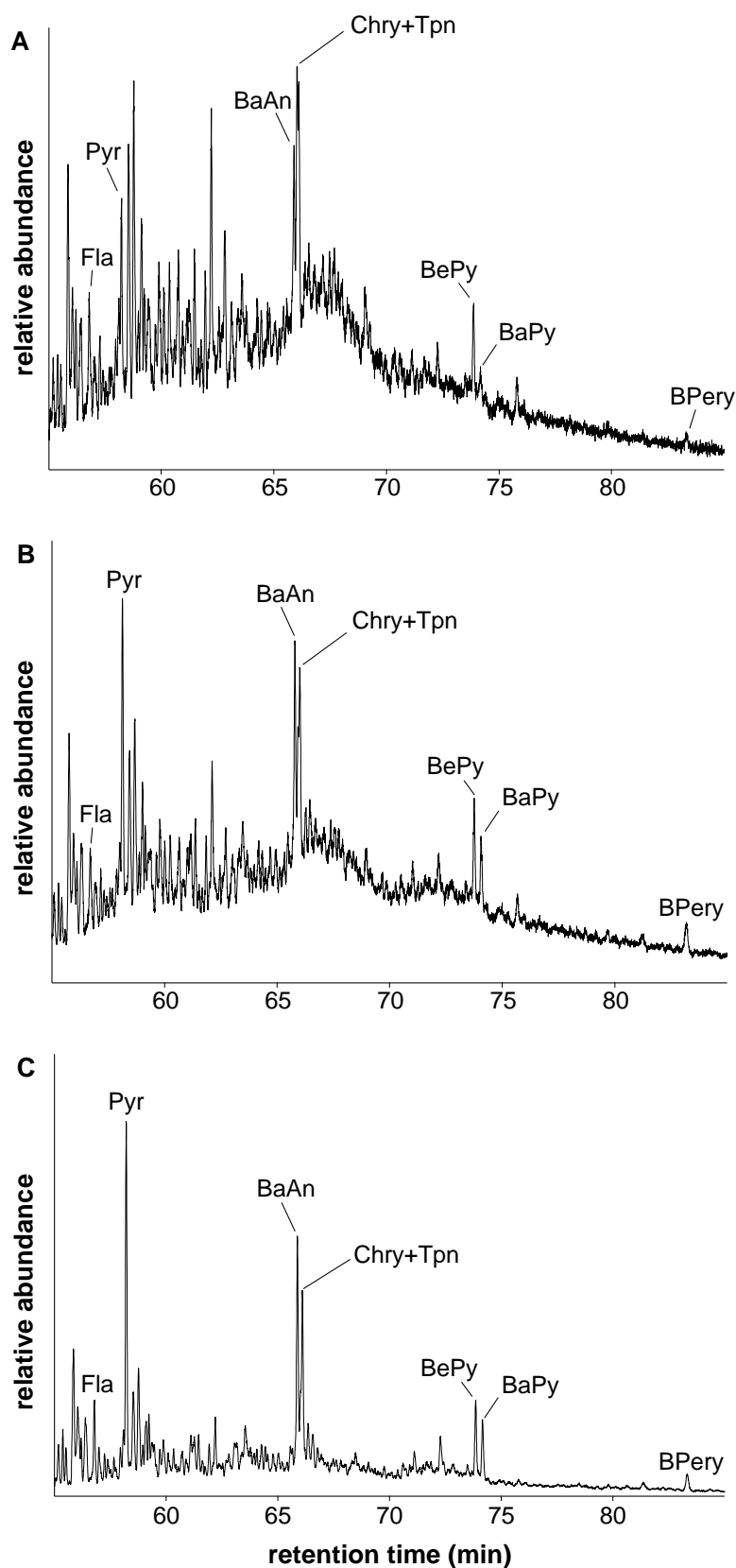


Figure 4.2: Summed m/z 202 + 228 + 252 + 276 chromatograms from MSSVpy of the BCF sample at each pyrolysis temperature, with no added metal sulfides. Pyrolysis temperatures are (A): 300 °C, (B): 330 °C, (C): 360 °C. Fla: fluoranthene, Pyr: pyrene, BaAn: benzo[*a*]anthracene, Chry: chrysene, Tpn: triphenylene, BePy: benzo[*e*]pyrene, BaPy: benzo[*a*]pyrene, BPery: benzo[*ghi*]perylene.

proposed that high-MW PAHs were concentrated at HYC by precipitation from hydrothermal fluid, due to the lower aqueous solubility of heavy aromatics compared to two- and three-ringed PAHs (Kawka and Simoneit, 1990). Such a mechanism may contribute to the increased abundances of high-MW PAHs at HYC compared to the MSSVpy experiments.

Effects of metal sulfides on simulated thermal maturation

Methylated phenanthrene ratios

The addition of PbS, ZnS and pyrite had a marked effect on all MP ratios (Figure 4.3A to 4.3C). At 300 °C pyrolysis temperature all ratios were higher than the pure BCF sample. At 330 °C the ratios were roughly equal with and without added metal sulfides, while at 360 °C the ratios were notably lower with added metal sulfides. Some samples also displayed a slight decrease in MP ratios from 300 to 330 °C, suggesting an inversion of the maturity parameters in this temperature range. MP maturity ratios from experiments with each sulfide mineral, and with 5 wt. % and 20 wt. % sulfide addition, were all generally within uncertainty.

Table 4.4: PAH ratios measured from MSSVpy analyses. Values are reported as the average of duplicate measurements, with the range of measurement in parentheses.

	300 °C	330 °C	360 °C
<i>BCF</i>			
MPI-1	0.96 (0.02)	1.07 (0.05)	1.34 (0.01)
MPR	1.07 (0.06)	1.24 (0.04)	1.69 (0.06)
MPI-3	1.05 (0.03)	1.15 (0.07)	1.58 (0.01)
MP / P	3.21 (0.01)	3.51 (0.04)	3.39 (0.02)
PAH / P	0.45 (0.01)	0.77 (0.04)	0.91 (0.02)
<i>BCF + 5 % PbS</i>			
MPI-1	1.04 (0.01)	0.98 (0.08)	1.17 (0.03)
MPR	1.15 (0.03)	1.23 (0.03)	1.52 (0.04)
MPI-3	1.11 (0.04)	1.08 (0.06)	1.34 (0.01)
MP / P	3.47 (0.13)	3.24 (1.07)	3.24 (0.16)
PAH / P	0.37 (0.05)	0.57 (0.29)	0.51 (0.31)

Table 4.4 (continued): PAH ratios measured from MSSVpy analyses. Values are reported as the average of duplicate measurements, with the range of measurement in parentheses.

	300 °C	330 °C	360 °C
<i>BCF + 20 % PbS</i>			
MPI-1	1.14 (0.06)	1.02 (0.04)	1.15 (0.01)
MPR	1.25 (0.05)	1.26 (0.03)	1.42 (0.04)
MPI-3	1.21 (0.03)	1.09 (0.08)	1.28 (0.01)
MP / P	3.75 (0.31)	3.47 (0.18)	3.42 (0.05)
PAH / P	0.24 (0.29)	0.43 (0.03)	0.69 (0.03)
<i>BCF + 5 % ZnS</i>			
MPI-1	1.06 (0.12)	1.06 (0.01)	1.16 (0.01)
MPR	1.21 (0.11)	1.24 (0.05)	1.49 (0.13)
MPI-3	1.2 (0.03)	1.13 (0.01)	1.38 (0.11)
MP / P	3.22 (0.72)	3.55 (0.09)	3.08 (0.42)
PAH / P	0.29 (0.24)	0.7 (0.16)	0.53 (0.19)
<i>BCF + 20 % ZnS</i>			
MPI-1	1.03 (0.12)	1.03 (0.01)	1.15 (0.01)
MPR	1.12 (0.03)	1.2 (0.01)	1.43 (0.01)
MPI-3	1.16 (0.01)	1.17 (0.01)	1.36 (0.01)
MP / P	3.19 (0.92)	3.09 (0.09)	3.07 (0.01)
PAH / P	0.3 (0.3)	0.35 (0.08)	0.57 (0.01)
<i>BCF + 5 % pyrite</i>			
MPI-1	1.21 (0.08)	1.14 (0.02)	1.3 (0.01)
MPR	1.31 (0.03)	1.22 (0.01)	1.51 (0.01)
MPI-3	1.29 (0.02)	1.21 (0.04)	1.47 (0.01)
MP / P	3.85 (0.85)	3.78 (0.13)	3.57 (0.01)
PAH / P	0.34 (0.19)	0.78 (0.13)	0.57 (0.01)
<i>BCF + 20 % pyrite</i>			
MPI-1	1.17 (0.04)	1.02 (0.08)	1.26 (0.01)
MPR	1.3 (0.08)	1.15 (0.01)	1.52 (0.01)
MPI-3	1.31 (0.15)	1.13 (0.08)	1.49 (0.01)
MP / P	3.45 (1.01)	3.17 (0.2)	3.21 (0.01)
PAH / P	0.36 (0.36)	0.73 (0.2)	0.54 (0.01)

MP maturity ratios may be influenced by the preferential adsorption of certain isomers onto the sulfide mineral surfaces. In **Chapter 2** it was found that the β MP isomers are more readily extracted with organic solvent than the α isomers. Preferential retention of α MP isomers by mineral surfaces would result in a decrease in apparent maturity. It is likely however that adsorption effects played only a minor role in the observed behaviour of the MP ratios in this study. Strong organic adsorption is generally observed on clay minerals (Lahav and Chang, 1976; Cleaves et al., 2012), not metal sulfides. Adsorption effects are expected to be proportional to mineral surface area (Cleaves et al., 2012), so it would be expected that experiments with 20 wt. % sulfide minerals added would display stronger effects than those with 5 wt. % sulfides. Figure 4.3 shows that this is not the case, with little difference being observed between 5 wt. % and 20 wt. % sulfides in most cases. This argues against the strong influence of adsorption effects.

Alternatively the metal sulfides may be acting to catalyse or retard the isomerisation of MPs. Transition metal sulfides are known to act as surface catalysts for a number of sedimentary organic reactions (Wächtershäuser, 1988; Cody et al., 2004). During thermal maturation MPs undergo a range of methyl-shift and transmethylation reactions (Szczerba and Rospondek, 2010) which may be retarded by the presence of metal sulfides. The overall effect on the MP maturity parameters will be determined by the kinetics of each individual isomerisation reaction, and will require more detailed studies to fully elucidate.

High-MW PAHs

The addition of sulfide minerals caused a decrease in the production of high-MW PAHs (Figure 4.3D). This is especially apparent at higher pyrolysis temperatures, where the average PAH / P ratio decreased from 0.91 for the pure BCF sample to between 0.51 and 0.69 when sulfide minerals were added. Further interpretation of this relationship is limited by the high degree of uncertainty in the analysis of several samples, with the PAH / P ratio of some replicates varying by greater than 50 %. Fluoranthene and chrysene / triphenylene are both significantly affected by co-eluting peaks even when integrated using the m/z 202 and 228 chromatograms, while five and six-ring PAHs were of such low abundance, especially at 300 °C pyrolysis temperature (Figure 4.2A), that they were difficult to integrate above the background

noise. Nevertheless the ratio of PAH / P for all MSSVpy experiments with added sulfide minerals were lower than those for the pure BCF sample. The reason for this reduction is currently unclear. The metal sulfide surfaces may inhibit the addition reactions by which high-MW PAHs are assembled from smaller aromatic units. As discussed on page 101, the MPI-1 and PAH / P ratios are sensitive to changes in redox conditions. Sulfide minerals are redox active and thus may influence the redox conditions of the MSSVpy experiments, however oxidation during pyrolysis is negligible due to the very low void space within the MSSV tubes (Horsfield et al., 2015).

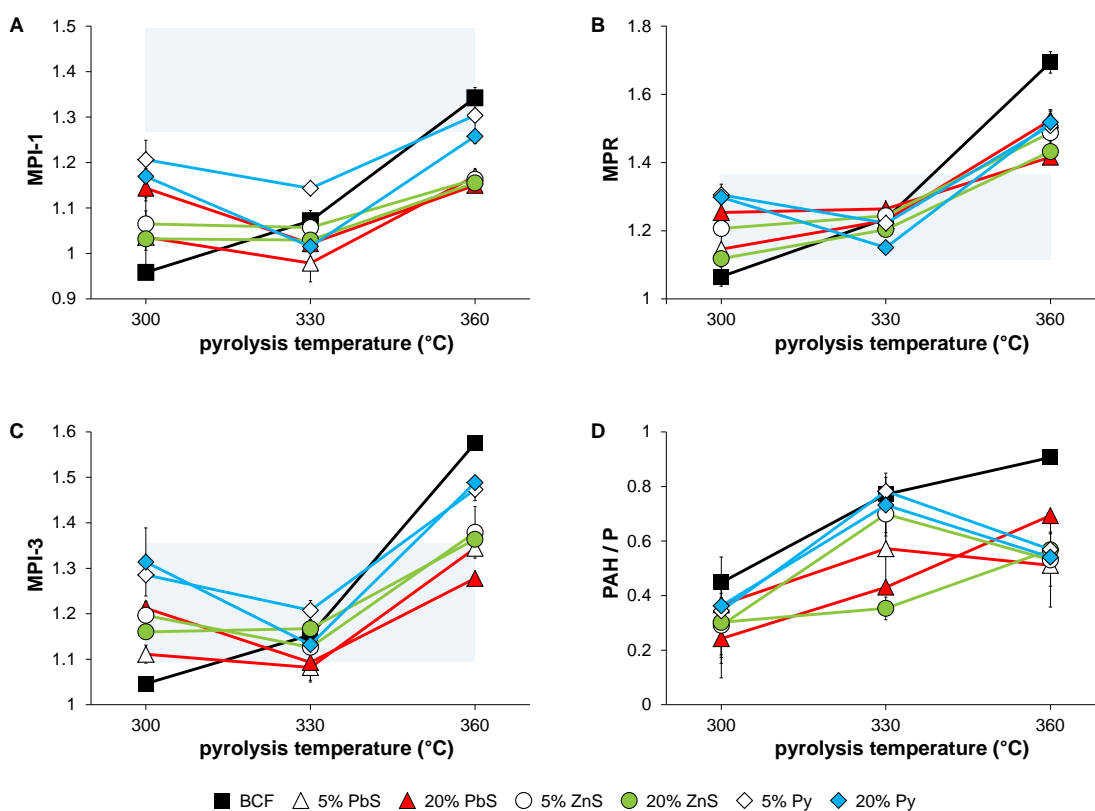


Figure 4.3: Selected PAH ratios from MSSVpy. (A) methylphenanthrene index 1 (MPI-1), (B) methylphenanthrene ratio (MPR), (C) methylphenanthrene index 3 (MPI-3) and (D) ratio of four to six ring PAHs over phenanthrene (PAH / P). Data points are the average of duplicate measurements, error bars show the range of measurement. Shaded areas in A to C represent the range from the HYC deposit, reported by Williford et al. (2011). The range of PAH / P reported by Williford et al. (2011) is 2.2 to 7.9.

Conclusions

MSSVpy has been successfully used to simulate thermal maturation of OM from the BCF. MSSVpy of thermally immature sediment produced a distribution of hydrocarbon products including *n*-alkanes, two and three-ringed PAHs and their methylated isomers, typical of thermally mature organic sediments associated with mineralised regions of HYC. Methylphenanthrene maturity parameters measured from MSSVpy of BCF OM fell within the range previously reported from HYC, although the MPI-1 ratio was comparatively lower due to a greater proportion of unmethylated phenanthrene. PAHs with four to six aromatic rings were produced in increasing amounts at higher pyrolysis temperatures, but their relative abundance did not approach the levels reported at HYC. The temperature and time conditions used in this study may have been insufficient to form these compounds in high abundances. The increased maturity parameters and the production of high-MW PAHs were similar to those attributed to the hydrothermal alteration of sedimentary OM. The addition of metal sulfides consistently affected the values of MP maturity ratios, with an increase at 300 °C pyrolysis temperature and a decrease at 360 °C. It is hypothesised that MP isomerisation reactions may be moderated by the sulfide minerals.

Acknowledgements

This study was conducted as part of the CSIRO Flagship Collaboration Fund Cluster for Organic Geochemistry of Mineral Systems, led by Curtin University. A. H. thanks Curtin University for an Australia Postgraduate Award scholarship and CSIRO for a top-up scholarship. Geoff Chidlow and Lyndon Berwick provided technical support for MSSVpy and GC-MS analysis. Katy Evans is thanked for assistance with microscopy and for her insightful comments on the manuscript. Associate editor Geoffrey Abbott, Andrew Gize and an anonymous reviewer are acknowledged for their helpful reviews and patience with our subsequent response.

References

- Alexander R., Bastow T.P., Fisher S.J., Kagi R.I., 1995. Geosynthesis of organic compounds: II. Methylation of phenanthrene and alkylphenanthrenes. *Geochimica et Cosmochimica Acta* **59**, 4259-4266.
- Berwick L.J., Greenwood P.F., Smernik R.J., 2010. The use of MSSV pyrolysis to assist the molecular characterisation of aquatic natural organic matter. *Water Research* **44**, 3039-3054.
- Blumer M., 1975. Curtisite, idrialite and pendletonite, polycyclic aromatic hydrocarbon minerals: their composition and origin. *Chemical Geology* **16**, 245-256.
- Boreham C.J., Crick I.H., Powell T.G., 1988. Alternative calibration of the Methylphenanthrene Index against vitrinite reflectance: application to maturity measurements on oils and sediments. *Organic Geochemistry* **12**, 289-294.
- Brocks J.J., Buick R., Logan G.A., Summons R.E., 2003. Composition and syngeneity of molecular fossils from the 2.78 to 2.45 billion-year-old Mount Bruce Supergroup, Pilbara Craton, Western Australia. *Geochimica et Cosmochimica Acta* **67**, 4289-4319.
- Brocks J.J., Grosjean E., Logan G.A., 2008. Assessing biomarker syngeneity using branched alkanes with quaternary carbon (BAQCs) and other plastic contaminants. *Geochimica et Cosmochimica Acta* **72**, 871-888.
- Brocks J.J., Love G.D., Summons R.E., Knoll A.H., Logan G.A., Bowden S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866-870.
- Brocks J.J., Schaeffer P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. *Geochimica et Cosmochimica Acta* **72**, 1396-1414.
- Bull S.W., 1998. Sedimentology of the Palaeoproterozoic Barney Creek formation in DDH BMR McArthur 2, southern McArthur basin, Northern Territory. *Australian Journal of Earth Sciences* **45**, 21-31.
- Chen J., Walter M.R., Logan G.A., Hinman M.C., Summons R.E., 2003. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern

- Australia: organic geochemistry and ore genesis. *Earth and Planetary Science Letters* **210**, 467-479.
- Cleaves H.J., Michalkova Scott A., Hill F.C., Leszczynski J., Sahai N., Hazen R., 2012. Mineral-organic interfacial processes: potential roles in the origins of life. *Chemical Society Reviews* **41**, 5502-5525.
- Cody G.D., Boctor N.Z., Brandes J.A., Filley T.R., Hazen R.M., Yoder Jr H.S., 2004. Assaying the catalytic potential of transition metal sulfides for abiotic carbon fixation. *Geochimica et Cosmochimica Acta* **68**, 2185-2196.
- Crick I.H., 1992. Petrological and maturation characteristics of organic matter from the Middle Proterozoic McArthur Basin, Australia. *Australian Journal of Earth Sciences* **39**, 501-519.
- Davidson G.J., Dashlooty S.A., 1993. The Glyde Sub-basin: a volcanoclastic-bearing pull-apart basin coeval with the McArthur River base-metal deposit, Northern Territory. *Australian Journal of Earth Sciences* **40**, 527-543.
- Dick J.M., Evans K.A., Holman A.I., Jaraula C.M.B., Grice K., 2013. Estimation and application of the thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature. *Geochimica et Cosmochimica Acta* **122**, 247-266.
- Donnelly T.H., Jackson M.J., 1988. Sedimentology and geochemistry of a mid-Proterozoic lacustrine unit from northern Australia. *Sedimentary Geology* **58**, 145-169.
- Eldridge C.S., Williams N., Walshe J.L., 1993. Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe SHRIMP: II. A study of the H.Y.C. deposit at McArthur River, Northern Territory, Australia. *Economic Geology* **88**, 1-26.
- Fetzer J.C., Simoneit B.R.T., Budzinski H., Garrigues P., 1996. Identification of large PAHs in bitumens from deep-sea hydrothermal vents. *Polycyclic Aromatic Compounds* **9**, 109-120.
- Garrigues P., De Sury R., Angelin M.L., Bellocq J., Oudin J.L., Ewald M., 1988. Relation of the methylated aromatic hydrocarbon distribution pattern to the

- maturity of organic matter in ancient sediments from the Mahakam delta. *Geochimica et Cosmochimica Acta* **52**, 375-384.
- Gizé A.P., 1999. Organic alteration in hydrothermal sulfide ore deposits. *Economic Geology* **94**, 967-979.
- Greenwood P.F., Brocks J.J., Grice K., Schwark L., Jaraula C.M.B., Dick J.M., Evans K.A., 2013. Organic geochemistry and mineralogy. I. Characterisation of organic matter associated with metal deposits. *Ore Geology Reviews* **50**, 1-27.
- Greenwood P.F., Leenheer J.A., McIntyre C., Berwick L.J., Franzmann P.D., 2006. Bacterial biomarkers thermally released from dissolved organic matter. *Organic Geochemistry* **37**, 597-609.
- Greenwood P.F., Lengkeek N.A., Piggott M.J., Pierce K., 2009. Structural identification and mass spectral interpretation of C_{3n} highly branched alkanes in sediment and aquatic extracts and evidence for their anthropogenic origin. *Organic Geochemistry* **40**, 1055-1062.
- Grice K., Schaeffer P., Schwark L., Maxwell J.R., 1996. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. *Organic Geochemistry* **25**, 131-147.
- Grice K., Schaeffer P., Schwark L., Maxwell J.R., 1997. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Lower Rhine Basin, northwest Germany) inferred from molecular and isotopic compositions of biomarker components. *Organic Geochemistry* **26**, 677-690.
- Grosjean E., Logan G.A., 2007. Incorporation of organic contaminants into geochemical samples and an assessment of potential sources: examples from Geoscience Australia marine survey S282. *Organic Geochemistry* **38**, 853-869.
- Hartgers W.A., Sinninghe Damsté J.S., Requejo A.G., Allan J., Hayes J.M., Ling Y., Xie T.-M., Primack J., de Leeuw J.W., 1994. A molecular and carbon isotopic study towards the origin and diagenetic fate of diaromatic carotenoids. *Organic Geochemistry* **22**, 703-725.

- Horsfield B., Disko U., Leistner F., 1989. The micro-scale simulation of maturation: outline of a new technique and its potential applications. *Geologische Rundschau* **78**, 361-373.
- Horsfield B., Leistner F., Hall K., 2015. Microscale sealed vessel pyrolysis. In *Principles and Practice of Analytical Techniques in Geosciences* (ed. Grice K.). Royal Society of Chemistry, Oxford. pp 209-250.
- Huston D.L., Stevens B., Southgate P.N., Muhling P., Wyborn L., 2006. Australian Zn-Pb-Ag ore-forming systems: a review and analysis. *Economic Geology* **101**, 1117-1157.
- Ireland T., Large R.R., McGoldrick P., Blake M., 2004. Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore textures in the McArthur River (HYC) Zn-Pb-Ag deposit, Northern Territory, Australia. *Economic Geology* **99**, 1687-1709.
- Kawka O.E., Simoneit B.R.T., 1990. Polycyclic aromatic hydrocarbons in hydrothermal petroleums from the Guaymas Basin spreading center. *Applied Geochemistry* **5**, 17-27.
- Koopmans M.P., Köster J., van Kaam-Peters H.M.E., Kenig F., Schouten S., Hartgers W.A., de Leeuw J.W., Sinninghe Damsté J.S., 1996. Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia. *Geochimica et Cosmochimica Acta* **60**, 4467-4496.
- Ladjavardi M., Berwick L.J., Grice K., Boreham C.J., Horsfield B., 2013. Rapid offline isotopic characterisation of hydrocarbon gases generated by micro-scale sealed vessel pyrolysis. *Organic Geochemistry* **58**, 121-124.
- Lahav N., Chang S., 1976. The possible role of solid surface area in condensation reactions during chemical evolution: reevaluation. *Journal of Molecular Evolution* **8**, 357-380.
- Landais P., Michels R., Elie M., 1994. Are time and temperature the only constraints to the simulation of organic matter maturation? *Organic Geochemistry* **22**, 617-630.

- Large D.J., Gizè A.P., 1996. Pristane/phytane ratios in the mineralized Kupferschiefer of the Fore-Sudetic Monocline, southwest Poland. *Ore Geology Reviews* **11**, 89-103.
- Large R.R., Bull S.W., Cooke D.R., McGoldrick P.J., 1998. A genetic model for the HYC deposit, Australia: based on regional sedimentology, geochemistry, and sulfide-sediment relationships. *Economic Geology* **93**, 1345-1368.
- Le Métayer P., Grice K., Chow C.N., Caccetta L., Maslen E., Dawson D., Fusetti L., 2014. The effect of origin and genetic processes of low molecular weight aromatic hydrocarbons in petroleum on their stable carbon isotopic compositions. *Organic Geochemistry* **72**, 23-33.
- Lewan M.D., 1997. Experiments on the role of water in petroleum formation. *Geochimica et Cosmochimica Acta* **61**, 3691-3723.
- Lewan M.D., Winters J.C., McDonald J.H., 1979. Generation of oil-like pyrolyzates from organic-rich shales. *Science* **203**, 897-899.
- Lockhart R.S., Berwick L.J., Greenwood P., Grice K., Kraal P., Bush R., 2013. Analytical pyrolysis for determining the molecular composition of contemporary monosulfidic black ooze. *Journal of Analytical and Applied Pyrolysis* **104**, 640-652.
- Logan G.A., Hinman M.C., Walter M.R., Summons R.E., 2001. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. *Geochimica et Cosmochimica Acta* **65**, 2317-2336.
- Maslen E., Grice K., Gale J.D., Hallmann C., Horsfield B., 2009. Crocetane: a potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age. *Organic Geochemistry* **40**, 1-11.
- McCullom T.M., Simoneit B.R.T., Shock E.L., 1999. Hydrous pyrolysis of polycyclic aromatic hydrocarbons and implications for the origin of PAH in hydrothermal petroleum. *Energy & Fuels* **13**, 401-410.
- McGoldrick P., Winefield P., Bull S., Selley D., Scott R., 2010. Sequences, synsedimentary structures, and sub-basins: the where and when of SEDEX zinc systems in the southern McArthur Basin, Australia. In *The Challenge of*

- Finding New Mineral Resources: Global Metallogeny, Innovative Exploration, and New Discoveries. Volume II: Zinc-Lead, Nickel-Copper-PGE, and Uranium* (eds. Goldfarb R.J., Marsh E.E., Monecke T.). Society of Economic Geologists Special Publication Number 15, Littleton, Colorado. pp 367-389.
- Nabbefeld B., Grice K., Schimmelmann A., Summons R.E., Troitzsch U., Twitchett R.J., 2010. A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks. *Organic Geochemistry* **41**, 78-87.
- Page R.W., Sweet I.P., 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences* **45**, 219-232.
- Peters K.E., Walters C.C., Moldowan J.M., 2005. *The Biomarker Guide Volume 2 - Biomarkers and Isotopes in Petroleum Exploration and Earth History*. Cambridge University Press, Cambridge.
- Price L.C., 1993. Thermal stability of hydrocarbons in nature: limits, evidence, characteristics, and possible controls. *Geochimica et Cosmochimica Acta* **57**, 3261-3280.
- Püttmann W., Merz C., Speczik S., 1989. The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland. *Applied Geochemistry* **4**, 151-161.
- Radke M., Welte D.H., Willsch H., 1982a. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* **46**, 1-10.
- Radke M., Willsch H., Leythaeuser D., Teichmüller M., 1982b. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* **46**, 1831-1848.
- Rieger A., Schwark L., Cisternas M.-E., Miller H., 2008. Genesis and evolution of bitumen in Lower Cretaceous lavas and implications for strata-bound copper deposits, North Chile. *Economic Geology* **103**, 387-404.

- Rospondek M.J., Marynowski L., Chachaj A., Góra M., 2009. Novel aryl polycyclic aromatic hydrocarbons: phenylphenanthrene and phenylanthracene identification, occurrence and distribution in sedimentary rocks. *Organic Geochemistry* **40**, 986-1004.
- Rospondek M.J., Marynowski L., Góra M., 2007. Novel arylated polyaromatic thiophenes: Phenyl-naphtho[b]thiophenes and naphthylbenzo[b]thiophenes as markers of organic matter diagenesis buffered by oxidising solutions. *Organic Geochemistry* **38**, 1729-1756.
- Safarik I., Strausz O.P., 1997. The thermal decomposition of hydrocarbons. Part 2. Alkylaromatic hydrocarbons: alkylbenzenes. *Research on Chemical Intermediates* **23**, 63-99.
- Schenk H.J., Horsfield B., 1993. Kinetics of petroleum generation by programmed-temperature closed-versus open-system pyrolysis. *Geochimica et Cosmochimica Acta* **57**, 623-630.
- Seewald J.S., 2001. Aqueous geochemistry of low molecular weight hydrocarbons at elevated temperatures and pressures: constraints from mineral buffered laboratory experiments. *Geochimica et Cosmochimica Acta* **65**, 1641-1664.
- Simoneit B.R.T., 1994. Lipid/bitumen maturation by hydrothermal activity in sediments of Middle Valley, Leg 139. In *Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 139* (eds. Mottl M.J., Davis E.E., Fisher A.T., Slack J.F.). Ocean Drilling Program, College Station, Texas. pp 447-465.
- Simoneit B.R.T., Lein A.Y., Peresykin V.I., Osipov G.A., 2004. Composition and origin of hydrothermal petroleum and associated lipids in the sulfide deposits of the Rainbow Field (Mid-Atlantic Ridge at 36°N). *Geochimica et Cosmochimica Acta* **68**, 2275-2294.
- Sinninghe Damsté J.S., Kohnen M.E.L., Horsfield B., 1998. Origin of low-molecular-weight alkylthiophenes in pyrolysates of sulphur-rich kerogens as revealed by micro-scale sealed vessel pyrolysis. *Organic Geochemistry* **29**, 1891-1903.
- Stein S.E., 1978. On the high temperature chemical equilibria of polycyclic aromatic hydrocarbons. *The Journal of Physical Chemistry* **82**, 566-571.

- Summons R.E., Powell T.G., 1987. Identification of aryl isoprenoids in source rocks and crude oils: biological markers for the green sulphur bacteria. *Geochimica et Cosmochimica Acta* **51**, 557-566.
- Sun Y.-Z., 1998. Influences of secondary oxidation and sulfide formation on several maturity parameters in Kupferschiefer. *Organic Geochemistry* **29**, 1419-1429.
- Szczerba M., Rospondek M.J., 2010. Controls on distributions of methylphenanthrenes in sedimentary rock extracts: critical evaluation of existing geochemical data from molecular modelling. *Organic Geochemistry* **41**, 1297-1311.
- van Aarssen B.G.K., Bastow T.P., Alexander R., Kagi R.I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Organic Geochemistry* **30**, 1213-1227.
- Wächtershäuser G., 1988. Before enzymes and templates: theory of surface metabolism. *Microbiological Reviews* **52**, 452-484.
- Williford K.H., Grice K., Logan G.A., Chen J., Huston D., 2011. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters* **301**, 382-392.
- Wise S.A., Campbell R.M., West W.R., Lee M.L., Bartle K.D., 1986. Characterization of polycyclic aromatic hydrocarbon minerals curtisite, idrialite and pendletonite using high-performance liquid chromatography, gas chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy. *Chemical Geology* **54**, 339-357.

Appendix 4

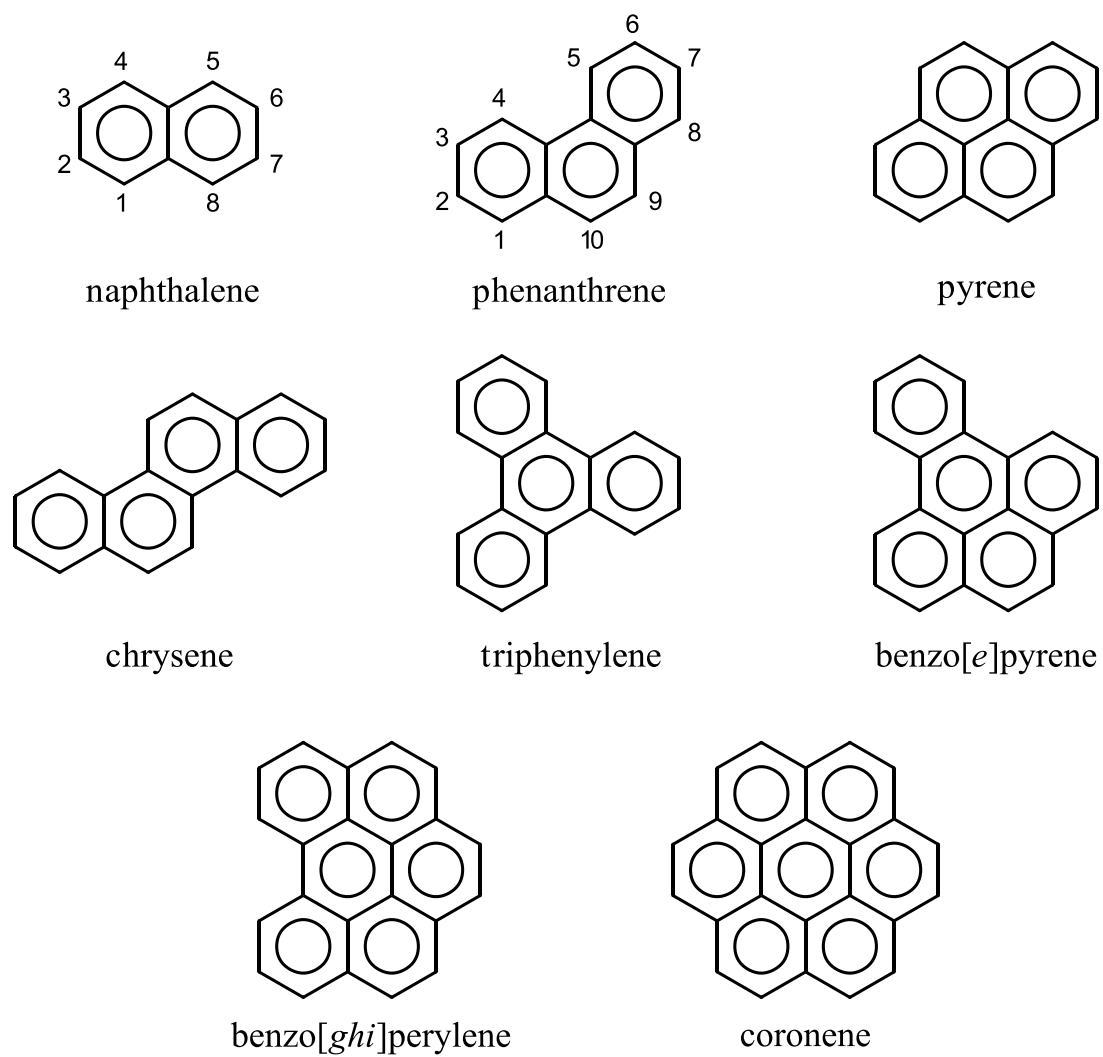


Figure A4.1: Structures referred to in the text.

Table A4.1: Data used in the calculation of mass spectral correction factors for major PAH products. Correction factors were determined by calculating the correlation between abundances from total ion chromatograms (TIC) and extracted ion chromatograms (EIC) for each compound.

Phenanthrene		Methylphenanthrenes		Pyrene		Chrysene		Benzo[<i>e</i>]pyrene		Benzo[<i>ghi</i>]perylene	
<i>TIC</i>	<i>EIC</i>	<i>TIC</i>	<i>EIC</i>	<i>TIC</i>	<i>EIC</i>	<i>TIC</i>	<i>EIC</i>	<i>TIC</i>	<i>EIC</i>	<i>TIC</i>	<i>EIC</i>
157922728	72851747	260393237	86811919	61756968	22181203	152443448	55532067	126537997	37307112	26611119	11939894
79150696	37123330	164693639	56923729	39719281	14630685	103362737	38568883	94315320	27414019	19063819	8345964
127894862	58734255	205403166	70564284	46095862	15162869	106025145	40555415	94125710	26800569	16174085	7150011
72553982	33859363	161853935	55727434	50924025	18557111	120733710	45478852	96033305	29258177	20034448	8110235
9049579	4056567	27747306	9589296	8482701	2459384	27361120	9875071	29361933	8658134	7222902	2669661
171954794	77073974	219190295	74564231	41837591	13526401	72578427	25310592	55138029	15177254	9413665	4206452
<i>Slope</i>	0.452	<i>Slope</i>	0.335	<i>Slope</i>	0.368	<i>Slope</i>	0.374	<i>Slope</i>	0.299	<i>Slope</i>	0.455
r^2	0.999	r^2	0.999	r^2	0.985	r^2	0.996	r^2	0.995	r^2	0.989

Chapter 5

**New aspects of sulfur biogeochemistry during ore
deposition from $\delta^{34}\text{S}$ of elemental sulfur and organic
sulfur from the Here's Your Chance Pb/Zn/Ag
deposit**

**Alex I. Holman, Kliti Grice, Paul F. Greenwood, Michael E. Böttcher, John L.
Walshe and Katy A. Evans**

Chemical Geology **387**, 126-132 (2014)

Abstract

Sulfur isotope studies of base metal sulfide deposits have mostly focussed on sulfide minerals, but elemental sulfur (S^0) and organic sulfur are also potentially significant components of the sulfur cycle during ore deposition. The $\delta^{34}S$ of S^0 and organic sulfur isolated from the Paleoproterozoic Here's Your Chance (HYC) Pb/Zn/Ag deposit (McArthur Basin, northern Australia) were measured to be between +5 and +8 ‰, approximately 6 to 7 ‰ heavier than the median values of first-generation HYC sulfides. S^0 and organic sulfur are thought to have been formed contemporaneously with the first generation of metal sulfides. The $\delta^{34}S$ of organic sulfur showed an increasing trend along the path of the mineralising fluid, as sulfate was progressively ^{34}S -enriched due to Rayleigh distillation. The $\delta^{34}S$ data support a model in which bacterial sulfate reduction produced dissolved sulfide with $\delta^{34}S$ of 0 to +5 ‰. The subsequent oxidation of sulfide produced reactive sulfur species such as polysulfide ions, which were then incorporated into organic matter.

Introduction

Base metal sulfide deposits are some of the largest and most economically significant mineral accumulations in the world (Huston et al., 2006). Stable sulfur isotopic studies on these deposits have revealed important information on the transport of metal-bearing fluids and precipitation mechanisms (e.g. Broadbent et al., 1998; Ireland et al., 2004). In addition, sulfur isotopes may reflect the evolution of the sulfur cycle and ocean chemistry (Canfield and Teske, 1996; Farquhar et al., 2010; Nabbefeld et al., 2010a; Nabbefeld et al., 2010c; Böttcher, 2011). Most sulfur isotope studies have however focussed on metal sulfides, and have often neglected elemental sulfur (S^0) and organic sulfur. The pool of elemental sulfur can be significant in anoxic sediments (Zhang and Millero, 1993; Zopfi et al., 2004; Zopfi et al., 2008; Yücel et al., 2010) and organic sulfur can also be a major sink of reduced sulfur in sediments (Sinninghe Damsté and de Leeuw, 1990; Anderson and Pratt, 1995; Brüchert and Pratt, 1996; Passier et al., 1999; Werne et al., 2003), yet the isotopic composition of S^0 and organic sulfur in ore deposits remains largely unexplored.

S^0 is one of the products of the oxidation of dissolved sulfide. It is produced by both phototrophic and non-phototrophic sulfur bacteria (Fossing et al., 1995; Zopfi et al., 2004; Zopfi et al., 2008) as well as by non-biological oxidation processes (Steger and Desjardins, 1980; Fry et al., 1988; Zhang and Millero, 1993). S^0 is considered a partially oxidised intermediate product in the sulfur cycle as it can undergo further oxidation, reduction and disproportionation processes in sediments (Canfield and Thamdrup, 1994; Böttcher et al., 2001; Jørgensen and Nelson, 2004) and can also form polysulfide ions (S_x^{-2}) through reaction with dissolved sulfide (Chen and Morris, 1972; Kamyshny and Ferdelman, 2010).

Organic sulfur is considered to be formed through two main pathways. Assimilatory sulfate reduction is the process by which microorganisms incorporate sulfate into the cell, where it is reduced to form essential sulfur-containing compounds such as amino acids (Canfield, 2001). This 'biosynthetic sulfur' is estimated to contribute up to 25 % of the organic sulfur in marine sediments (Anderson and Pratt, 1995; Passier et al., 1999; Werne et al., 2003). The second, more important pathway for the formation of organic sulfur is the incorporation of reduced sulfur during diagenesis. Reduced sulfur is produced from dissolved sulfate through dissimilatory sulfate reduction, also referred to as bacterial sulfate reduction (BSR) (Jørgensen, 1982;

Canfield, 2001). The mechanisms by which reduced sulfur is incorporated into organic matter (OM) are complex and not fully understood, but the reaction of polysulfide ions with functionalised organic moieties is thought to be a significant pathway in sediments (e.g. Sinninghe Damsté and de Leeuw, 1990; Aizenshtat et al., 1995; Werne et al., 2008). Other reduced sulfur species such as H₂S may also be incorporated into OM (Sinninghe Damsté and de Leeuw, 1990; Hebbing et al., 2006; Asif et al., 2009), and have been linked to the preservation of soft tissue associated with fossilised organisms within carbonate concretions (Melendez et al., 2013).

The isotopic composition of organic sulfur is primarily controlled by the isotopic composition of the source sulfur, most commonly dissolved seawater sulfate, as well as the isotopic fractionations associated with sulfate reduction and incorporation into OM. Assimilatory sulfate reduction produces minor fractionations of generally less than 2 ‰ (e.g. Kaplan and Rittenberg, 1964; Brüchert and Pratt, 1996), hence the $\delta^{34}\text{S}$ of biosynthetic sulfur will be close to that of the source sulfate. Diagenetic organic sulfur is derived from isotopically light dissolved sulfide produced by dissimilatory sulfate reduction, with $\delta^{34}\text{S}$ values up to 70 ‰ lower than the source sulfate under open system conditions (Wortmann et al., 2001; Sim et al., 2011). The magnitude of isotopic fractionation in sediments may be smaller than 70 ‰ due to reservoir effects (Brunner and Bernasconi, 2005; Böttcher, 2011). Conditions of severe sulfate depletion (< 200 μM dissolved sulfate) can reduce the isotopic fractionation to near zero, as almost all sulfates entering the cell are reduced (Habicht et al., 2002). The isotopic fractionations associated with the incorporation of sulfur into OM have not been extensively studied, however laboratory experiments performed on pure organic compounds have shown evidence of a ³⁴S-enrichment in the product (Amrani and Aizenshtat, 2004). In a review of marine sediments from recent to Jurassic age, Anderson and Pratt (1995) found that organic sulfur and S⁰ were enriched in ³⁴S by an average of 10 ‰ compared to co-existing pyrite.

Here we present $\delta^{34}\text{S}$ measurements of S⁰ and organic sulfur from a Paleoproterozoic massive sulfide deposit, to explore the mechanisms of formation of these sulfur species and the biogeochemistry and role of sulfur during ore deposition.

Materials and methods

Geologic setting

The field site of this study is the Paleoproterozoic Here's Your Chance (HYC) sediment-hosted Pb/Zn/Ag deposit located in the Barney Creek Formation (BCF), a 1.64 Ga black shale in the McArthur Basin, northern Australia (Page and Sweet, 1998). The geologic setting of HYC has been extensively described, and several models of formation have been proposed (e.g. Large et al., 1998; Logan et al., 2001; Williford et al., 2011). The deposit is hosted in a restricted sub-basin of the BCF (McGoldrick et al., 2010). Recent evidence has suggested that ferruginous conditions were widespread in the Paleoproterozoic McArthur Basin (Planavsky et al., 2011), however preserved *n*-alkane distributions from the deposit indicate the presence of sulfate-reducing and sulfide-oxidising bacteria, implying that the deposit was formed under euxinic conditions (detailed in **Chapter 3**). It is generally agreed that the formation of the deposit involved a hydrothermal fluid which leached base metals from underlying formations and transported them to the BCF (Cooke et al., 1998).

Sample storage and preparation

The samples used in this study were made available from the previous study of Williford et al. (2011). Samples were taken from five surface exposures of ore body five, and were labelled as pits 1 to 5. The samples follow the estimated flow path of the mineralising fluid from north-east to south-west, with pit 1 being the first deposited. At the conclusion of the Williford study the rock samples were wrapped in aluminium foil and stored in the dark at room temperature (for *ca* three years). Rock fragments were ground using a RockLabs ring mill with a zirconium head, and the powdered rock was stored in sealed glass jars in the dark at room temperature. Sulfide minerals that are exposed to atmosphere may be oxidised to produce a range of species including elemental sulfur (Chandra and Gerson, 2011). To mitigate this possibility, Soxhlet extractions for the analysis of elemental sulfur commenced no later than one week after the rock was powdered.

Quantification of S^0

S^0 was quantified using a method modified from Zopfi et al. (2004). 20 to 30 g of powdered rock sample was extracted with pure methanol (approximately 200 mL, 48 hours) in a Soxhlet apparatus. Each extract was made up to 250 mL with methanol and analysed by reverse-phase chromatography using an Agilent 1200 series HPLC with an Agilent pump (1260), a diode array detector and a Spherisorb S10 ODS2 column. Methanol (Mallinckrodt Chemicals, UltiMAR grade) was used as the mobile phase at a flow rate of 1 mL/min. S^0 was detected after 5.5 min at a wavelength of 265 nm. Standards of S^0 (Chem Supply 'sulfur powder', minimum 99.6 %) were prepared at concentrations of 1 to 1000 μ M and analysed to create an external calibration curve.

Isolation of kerogen and S^0 for isotopic measurements

The isolation of kerogen from HYC samples was a modification of the procedure described by Nabbefeld et al. (2010b), as detailed in **Chapter 3**. Briefly, removal of carbonates with 1 M HCl was followed by a two-stage digestion in 24 % hydrofluoric acid to remove silicate minerals. Kerogen was separated from acid-insoluble sulfide minerals by heavy liquid separation using a saturated zinc bromide solution.

S^0 for $\delta^{34}\text{S}$ analysis was obtained from Soxhlet extractions following the procedure described in **Chapter 2**. Powdered rock was extracted in a Soxhlet apparatus using dichloromethane / methanol (9:1 v/v, 96 hours). Activated copper turnings (VWR Chemicals, 1 hour sonication in 4 M HCl) were added to the collection flask to remove S^0 from the organic extract. Dissolved S^0 reacts with the activated copper to form solid copper sulfide, visible as a black layer on the surface of the copper. Additional copper was added to the collection flask after 24 hours, and the extraction continued for another 24 hours to ensure all S^0 was collected. Copper added after 48 hours showed no black colouration.

Measurement of sulfur isotopic composition

Copper sulfide was scraped from the surfaces of the activated copper for stable isotope measurements. Sulfur isotope measurements were carried out on both copper sulfide and kerogen by combustion-isotope monitoring ratio monitoring mass

spectrometry (C-irmMS). Samples were combusted with V_2O_5 added as a catalyst in Sn cups in a Thermo Flash elemental analyser coupled *via* a Thermo ConFlo split interface to a Thermo Finnigan Mat 253 gas mass spectrometer. Sulfur isotope ratios ($^{34}S/^{32}S$) are reported in conventional δ -notation with a precision of approximately ± 0.3 ‰, and were calibrated versus the Vienna Cañon Diablo Troilite (VCDT) scale according to Mann et al. (2009) using the international reference materials IAEA-S-1, -2 and -3.

Results and discussion

Distribution of sulfur species in HYC sediments

Table 5.1 shows the masses (μg per g sediment) of S^0 and kerogen sulfur isolated from the five HYC samples. Also listed are comparative amounts of sulfur in sphalerite, galena and pyrite, separately calculated from total endowments reported by Lambert and Scott (1973) and Huston et al. (2006). Over 98 % of total sulfur at HYC exists as sulfide minerals, reflecting the rapid and efficient scavenging of dissolved sulfide by highly abundant metal species (e.g. Canfield, 1989; Druschel et al., 2002). Organic sulfur incorporated into kerogen is the next most abundant fraction, and only minor amounts of S^0 are present. The amount of sulfur in HYC kerogens is higher than previous reports of non-mineralised McArthur Basin samples (Powell et al., 1987). A noticeable increase in organic sulfur appears to have accompanied mineralisation, indicating that whilst the majority of reduced sulfur is consumed by metal cations, some is also incorporated into OM.

Quantification of S^0 has not been reported for non-mineralised sediments from the McArthur Basin, but the amounts at HYC (2.5 to 11.8 $\mu\text{g/g}$) appear comparable to modern euxinic sediments (Henneke et al., 1997; Yücel et al., 2010). S^0 is known to be produced by phototrophic sulfur bacteria (Zerkle et al., 2009), which have been identified in the mineralised zones of HYC (**Chapter 3**) and also in unmineralised sections of the BCF (Brocks et al., 2005). These bacteria not only produce S^0 through the oxidation of dissolved sulfide, but also consume S^0 when the supply of sulfide is limited (Zerkle et al., 2009). During mineralisation the rapid reaction of sulfide with metal ions would have greatly reduced the availability of sulfide for phototrophic oxidation and may have forced the bacteria to consume S^0 . S^0 may also be consumed

by bacterial disproportionation reactions (Canfield and Thamdrup, 1994; Böttcher et al., 2001) or mobilised by reaction with dissolved sulfide to form polysulfide ions (Aizenshtat et al., 1995).

Table 5.1: $\delta^{34}\text{S}$ of kerogen and S^0 for the five HYC sample pits (error is ± 0.3 ‰), plus masses of sulfur contained in kerogen and S^0 in the five HYC sample pits, reported in μg of sulfur per g of rock. Average masses of sulfur in sulfide minerals were calculated from data reported by Huston et al. (2006) for ZnS and PbS, and Lambert and Scott (1973) for FeS_2 .

	Pit 1	Pit 2	Pit 3	Pit 4	Pit 5
<i>Distance from pit 1 (m)</i>	0	104	372	553	710
<i>$\delta^{34}\text{S}$ (‰)</i>					
Kerogen	4.9	8.5	6.2	6.5	8.0
S^0	7.3	7.9	6.0	7.1	7.0
<i>Kerogen sulfur (% dry wt.)</i>					
	26	8	23	28	25
<i>Mass ($\mu\text{g S/g rock}$)</i>					
Kerogen sulfur	2054	384	1104	1344	1400
S^0	2.9	8.4	2.5	11.8	10.7
	PbS	ZnS	FeS_2		
<i>Average mass ($\mu\text{g S/g rock}$)</i>	6345.9	45127.6	80390.3		

Extractable organic sulfur compounds such as dibenzothiophenes (DBTs) have been detected in only trace amounts in HYC sediments (Chen et al., 2003), hence are not considered significant to the sulfur cycle of the HYC mineral system (presented on page 131). DBTs may form through either the breakdown of sulfur-containing kerogen during thermal maturation (Aizenshtat et al., 1995) or the incorporation of sulfur into existing aromatic compounds (Fenton et al., 2007; Asif et al., 2009). The low abundance of DBTs in HYC bitumen suggests that these processes did not occur to a significant extent during mineralisation. It may also reflect the thermal cracking of DBTs to H_2 , H_2S and biphenyls, as has been demonstrated in pyrolysis experiments (Dartiguelongue et al., 2006).

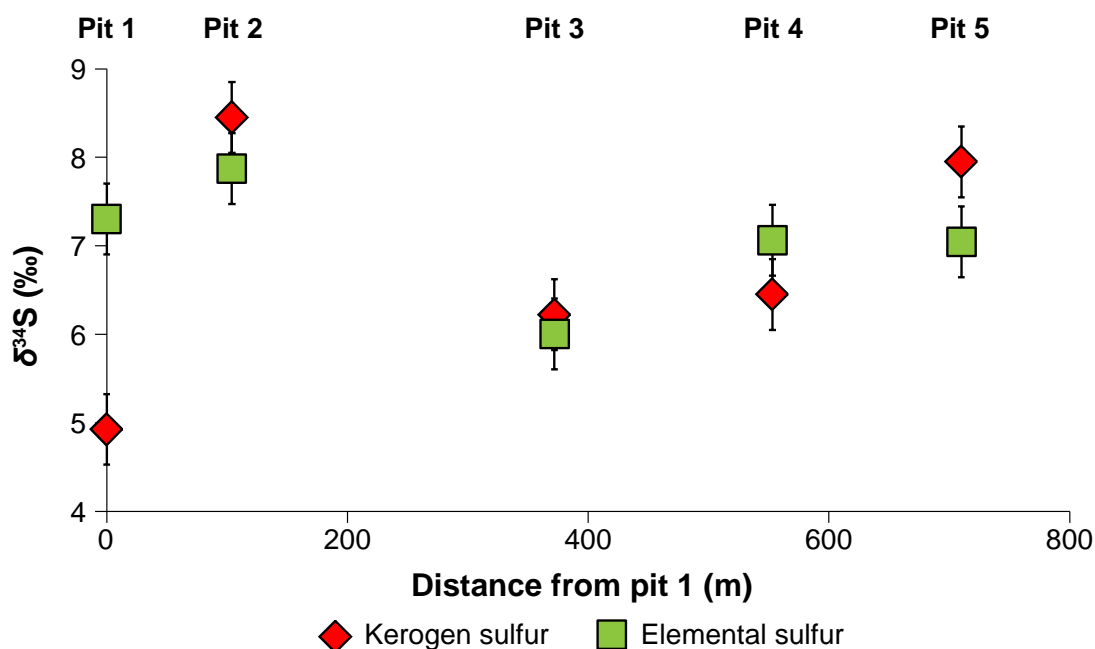


Figure 5.1: $\delta^{34}\text{S}$ of kerogen and S^0 from the five HYC sample pits. Error bars indicate uncertainty of 0.3 ‰.

$\delta^{34}\text{S}$ of kerogen and S^0

The $\delta^{34}\text{S}$ values of kerogen and S^0 from the five HYC sample pits are shown in Table 5.1. These were consistently between +6 and +8 ‰ except for pit 1 kerogen (+4.9 ‰). The $\delta^{34}\text{S}$ of kerogen and S^0 from each sample pit were within 1 ‰ apart from pit 1, where the kerogen was 2.4 ‰ lighter. This close equivalence matches previous observations of co-existing kerogen and S^0 (summarised by Anderson and Pratt, 1995) and has been attributed to a common sulfur source for the two species.

The $\delta^{34}\text{S}$ values of all kerogen samples, with the exception of pit 2, show a steady increase from +5 ‰ to +8 ‰ along the path of hydrothermal fluid flow (Figure 5.1). Such an increase is consistent with a genetic model in which base metal sulfides and organic sulfur are formed from sulfate carried by the mineralising fluid, likely sourced from evaporitic units that are present throughout the McArthur Basin (e.g. Cooke et al., 2000). Sulfate reduction (bacterial or thermochemical) produces sulfide with a significant depletion in ^{34}S , hence the residual sulfate is progressively enriched through Rayleigh distillation (e.g. Seal, 2006; Hartmann and Nielsen, 2012). The pit 2 kerogen value of +8.5 ‰ is an exception to this otherwise consistent trend. This sample also exhibits an anomalously low weight percentage of sulfur (8 wt. % of kerogen, compared to > 23 wt. % for the other samples), suggesting that it

may have been affected by localised processes that have removed a large fraction of organic sulfur, with the remainder being enriched in ^{34}S .

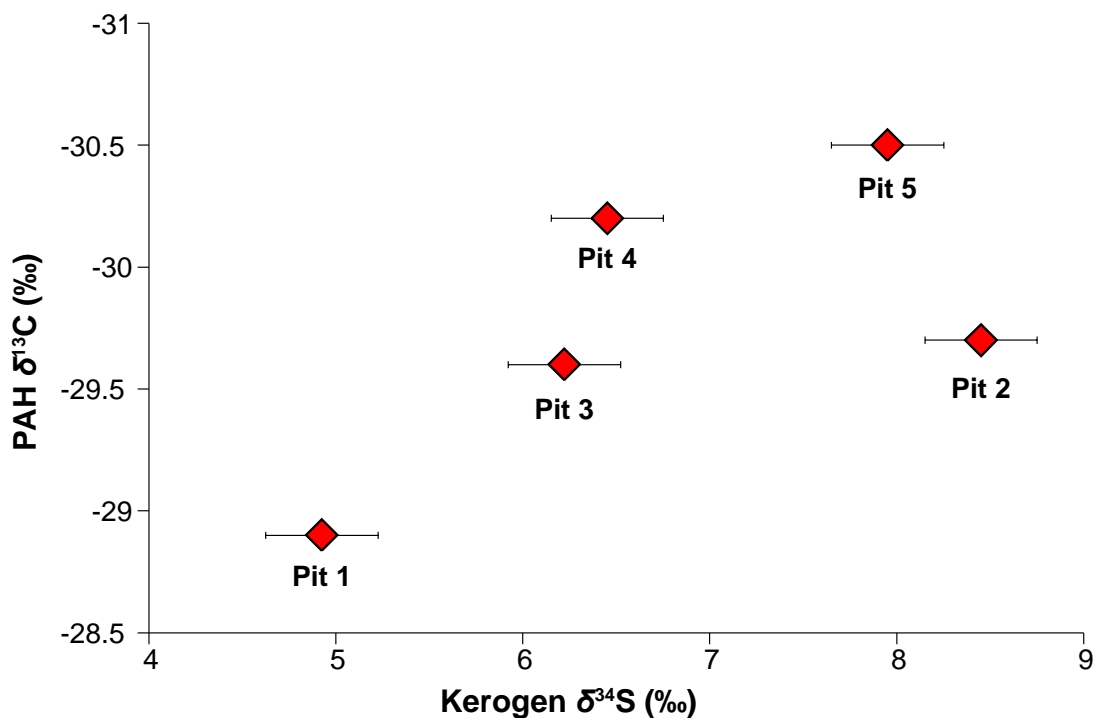


Figure 5.2: $\delta^{34}\text{S}$ of kerogen from the five HYC sample pits (error bars indicate uncertainty of 0.3 ‰), plotted against average $\delta^{13}\text{C}$ of PAHs (reported by Williford et al., 2011). The input of ^{13}C -enriched, non-indigenous PAHs decreases from pits 1 to 5 (page 129).

The large input of sulfate with the mineralising fluid also fits with the recent evidence for euxinic conditions during the formation of HYC whilst the wider McArthur Basin was predominantly ferruginous (**Chapter 3**). Such an influx of sulfate into the restricted HYC sub-basin could have caused the development of euxinic conditions via the increased production of sulfide by sulfate-reducing bacteria (Poulton et al., 2010). Temperature estimates for the mineralising fluids at HYC, which generally range between 150 and 200 °C (e.g. Large et al., 1998; Williford et al., 2011) are above the range at which microbes can survive. When the fluid reached the HYC sub-basin dissolved sulfate in the fluid would have been consumed by sulfate-reducing bacteria existing within the water column and sediments. The mixing of the hot mineralising fluid with the basin water would likely have lowered the temperature to within the viable range of sulfate reducing bacteria, which have been shown to be active at temperatures up to 85 °C (Canfield et al., 2000).

The increase in kerogen $\delta^{34}\text{S}$ along the path of fluid flow is further illustrated in Figure 5.2, in which $\delta^{34}\text{S}$ of kerogen is plotted against the average $\delta^{13}\text{C}$ of PAHs from the same sample pits reported by Williford et al. (2011). The $\delta^{13}\text{C}$ of PAHs decreases from pits 1 to 5 along the flow path of the mineralising fluid, due to the decreasing input of migrated PAHs that are relatively enriched in ^{13}C (Williford et al., 2011). The concurrent increase of kerogen $\delta^{34}\text{S}$ may be explained by a Rayleigh distillation process as discussed above. The $\delta^{34}\text{S}$ of elemental sulfur does not reflect a similar trend and shows no clear pattern along the flow path of the hydrothermal fluid. Elemental sulfur is a highly reactive species which can be consumed by oxidation and/or disproportionation reactions (see page 125) and can also be generated after deposition by the oxidation of sulfide minerals or aqueous sulfide (Steger and Desjardins, 1980; Zhang and Millero, 1993). Any trend in the $\delta^{34}\text{S}$ of elemental sulfur along the fluid flow path is likely to have been overprinted by such local effects.

A possible alternative explanation for the increase in kerogen $\delta^{34}\text{S}$ along the flow path of the mineralising fluid is a temperature control effect. The flow of the mineralising fluid is believed to have produced a gradient of decreasing temperature from pits 1 to 5 as the fluid cooled during deposition (Williford et al., 2011). The isotopic fractionation associated with BSR has been shown to be influenced by temperature, with increased temperatures generally producing higher rates of sulfate reduction and reduced fractionation (Kaplan and Rittenberg, 1964). If temperature was an important control, the highest temperature pit (pit 1) would have experienced the least fractionation during sulfate reduction and would thus be the most enriched in $\delta^{34}\text{S}$. This is the opposite of the observed trend, as seen in Figure 5.1, hence the temperature of the mineralising fluid does not appear to have significantly affected the $\delta^{34}\text{S}$ of organic sulfur at HYC. This finding fits with previous observations that the isotopic fractionation of BSR remains relatively constant at temperatures of 60 °C and above (Böttcher et al., 1999; Canfield et al., 2000).

Figure 5.3 shows a comparison of the measured $\delta^{34}\text{S}$ of kerogen and S^0 with previous sulfur isotopic studies of sulfide minerals from HYC and other McArthur Basin sediments. Detailed isotopic measurements have revealed two main phases of sulfide precipitation at HYC. Eldridge et al. (1993) proposed that first-generation pyrite (with $\delta^{34}\text{S}$ -13 to +15 ‰) was formed during early diagenesis from sulfide produced

by BSR, whilst a later second-generation pyrite (-5 to +45 ‰) was formed in a closed system from residual sulfide that was relatively more enriched in $\delta^{34}\text{S}$. A subsequent investigation by Ireland et al. (2004) identified two phases of sphalerite: an early sphalerite with $\delta^{34}\text{S}$ of 0 to +12 ‰ which precipitated prior to first-generation pyrite, and a later, heavier phase (+3 to +19 ‰). First-generation mineralisation comprises over 80 % of all pyrite and sphalerite at HYC (Ireland et al., 2004).

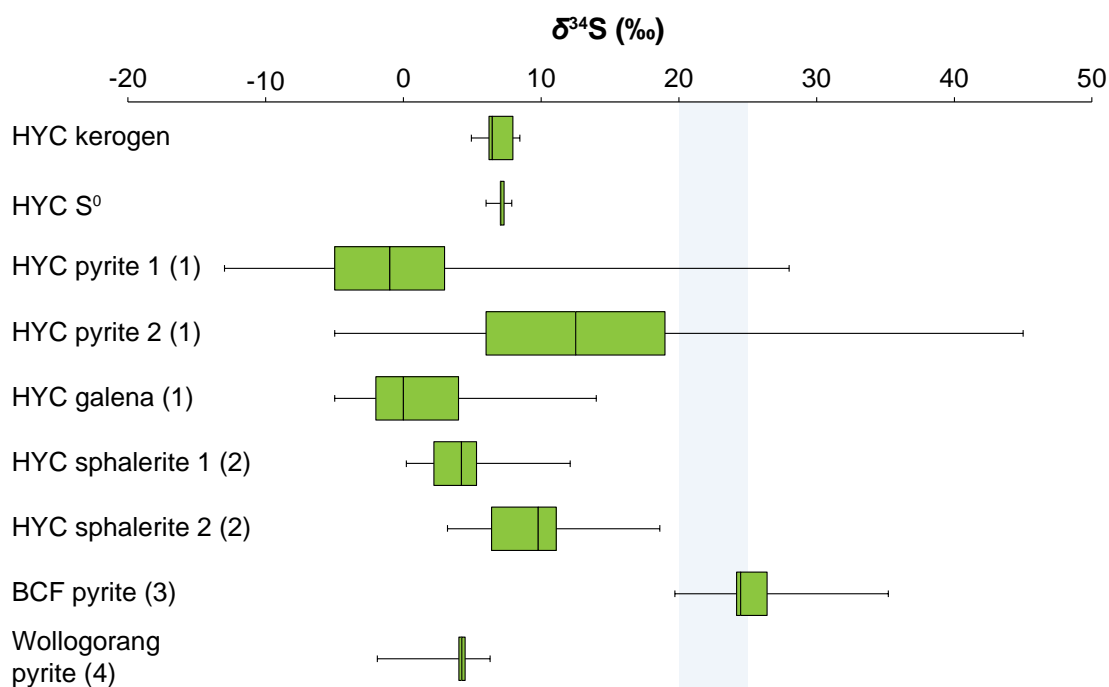


Figure 5.3: Box-and-whisker plots of $\delta^{34}\text{S}$ data for kerogen and S^0 from HYC (this study) and previously-reported $\delta^{34}\text{S}$ of sulfide minerals from HYC and the McArthur Basin. Whiskers show the full range of reported $\delta^{34}\text{S}$, boxes represent the middle 50 % of the data (first to third quartiles). Estimated isotopic composition of Paleoproterozoic seawater sulfate (+20 to +25 ‰; Strauss, 1993) is indicated by the lightly shaded area. 1 Eldridge et al. (1993), 2 Ireland et al. (2004), 3 Johnston et al. (2008), 4 Shen et al. (2002).

Kerogen and S^0 measured in this study are 3 to 7 ‰ heavier than the average $\delta^{34}\text{S}$ of first-generation HYC sulfides. This broadly fits with the findings of Anderson and Pratt (1995), who showed that kerogen and S^0 are ^{34}S -enriched from co-existing pyrite in marine sediments by an average of 10 ‰. S^0 and organic sulfur at HYC likely formed contemporaneously with the first-generation sulfides. The second generation of sulfides at HYC is relatively enriched in ^{34}S , which was attributed to the formation from ^{34}S -heavy pore-water sulfate in a closed system (Eldridge et al.,

1993). This limited supply of sulfur would have been efficiently scavenged by metal cations. The lower $\delta^{34}\text{S}$ of S^0 and organic sulfur indicates that these species were formed from the more freely available and relatively lighter sulfide responsible for the first-generation metal sulfides.

It is notable that the $\delta^{34}\text{S}$ of S^0 and kerogen show a greatly reduced range of values compared to base metal sulfides at HYC (Figure 5.3). S^0 and kerogen were analysed by bulk techniques using > 20 g of rock from each sample pit (page 124). Conversely, the ion probe and laser ablation measurements of Eldridge et al. (1993) and Ireland et al. (2004) measured $\delta^{34}\text{S}$ of base metal sulfides at high resolution, revealing extreme isotopic heterogeneity on a fine scale. Microscale *in situ* measurements of organic $\delta^{34}\text{S}$, such as those demonstrated by Bontognali et al. (2012), may reveal similar heterogeneity of organic sulfur isotopes.

Model of sulfur transformations at HYC

The measured $\delta^{34}\text{S}$ of S^0 and organic sulfur fit well with the simplified model of sulfur transformations during the deposition of HYC presented in Figure 5.4. The model is based on a middle Proterozoic seawater sulfate isotopic composition of +20 to +25 ‰ (Strauss, 1993). Sulfate reduction was assumed to be accompanied by an estimated ^{34}S -depletion of 20 ‰, which was proposed by Shen et al. (2002) as being typical for BSR in euxinic sections of the McArthur Basin with limited supply of sulfate. The HYC deposit was formed in a tectonically-controlled sub-basin in which local conditions were conducive to BSR and exchange with the main basin was partially restricted (McGoldrick et al., 2010).

This degree of fractionation is also within the range reported for thermochemical sulfate reduction (TSR; Machel et al., 1995). The respective contributions of BSR and TSR during the deposition of HYC have been difficult to resolve (Logan et al., 2001). Ireland et al. (2004) concluded that whilst both BSR and TSR likely contributed to the formation of the deposit, BSR was the dominant process. *n*-Alkane distributions indicative of sulfate-reducing bacteria have recently been detected in highly-mineralised regions of HYC (**Chapter 3**). The ^{34}S -enrichment of benzothiophenes compared to dibenzothiophenes has been proposed as a proxy for TSR (Amrani et al., 2012), however dibenzothiophenes have been detected only in trace amounts at HYC (page 126) whilst benzothiophenes have not been reported.

For the purposes of this simplified model it was considered that the sulfide was formed solely by BSR.

The assumed fractionation of 20 ‰ during BSR would produce sulfide with $\delta^{34}\text{S}$ of 0 to +5 ‰. Only minor fractionation occurs during the precipitation of sulfide minerals from dissolved sulfide (Price and Shieh, 1979; Böttcher et al., 1998; Butler et al., 2004), therefore the $\delta^{34}\text{S}$ of sulfide minerals is also expected to be close to 0 to +5 ‰. This is consistent with the sulfur isotopic composition of first-generation HYC sulfides measured by Eldridge et al. (1993) and Ireland et al. (2004), and also with the $\delta^{34}\text{S}$ of pyrite from the Wologorang Formation (-2 to +6 ‰), which underlies the BCF and through which the mineralising fluid is believed to have flowed (Donnelly and Jackson, 1988; Shen et al., 2002).

Dissolved sulfide that does not react to form sulfide minerals may be oxidised by a range of microorganisms and also by abiotic reactions (Canfield, 2001). The $\delta^{34}\text{S}$ of S^0 at HYC (+6 to +8 ‰) is slightly higher than the sulfide minerals (Figure 5.3), consistent with production by phototrophic sulfur bacteria. Biomarker evidence for the presence of phototrophic sulfur bacteria has been detected at HYC (**Chapter 3**), as well as non-mineralised sections of the BCF (Brocks et al., 2005). S^0 produced by phototrophic sulfur bacteria in bacterial culture experiments was reported to be 1 to 3 ‰ enriched in ^{34}S compared to the source sulfide (Zerkle et al., 2009). Conversely, a depletion of 4 to 5 ‰ is typical for the abiotic oxidation of sulfide to S^0 (Fry et al., 1988), which does not fit the available data. The $\delta^{34}\text{S}$ of S^0 at HYC must be interpreted with caution as a significant proportion has likely been consumed by oxidation and/or disproportionation reactions, and some may also have been generated by non-biological oxidation reactions after deposition (page 125). The isotopic composition of the remaining S^0 will have been modified by these post-depositional processes, so firm conclusions on its formation cannot be drawn based on this data. Nevertheless, the available isotopic and biomarker evidence supports the oxidation of sulfide by phototrophic sulfur bacteria.

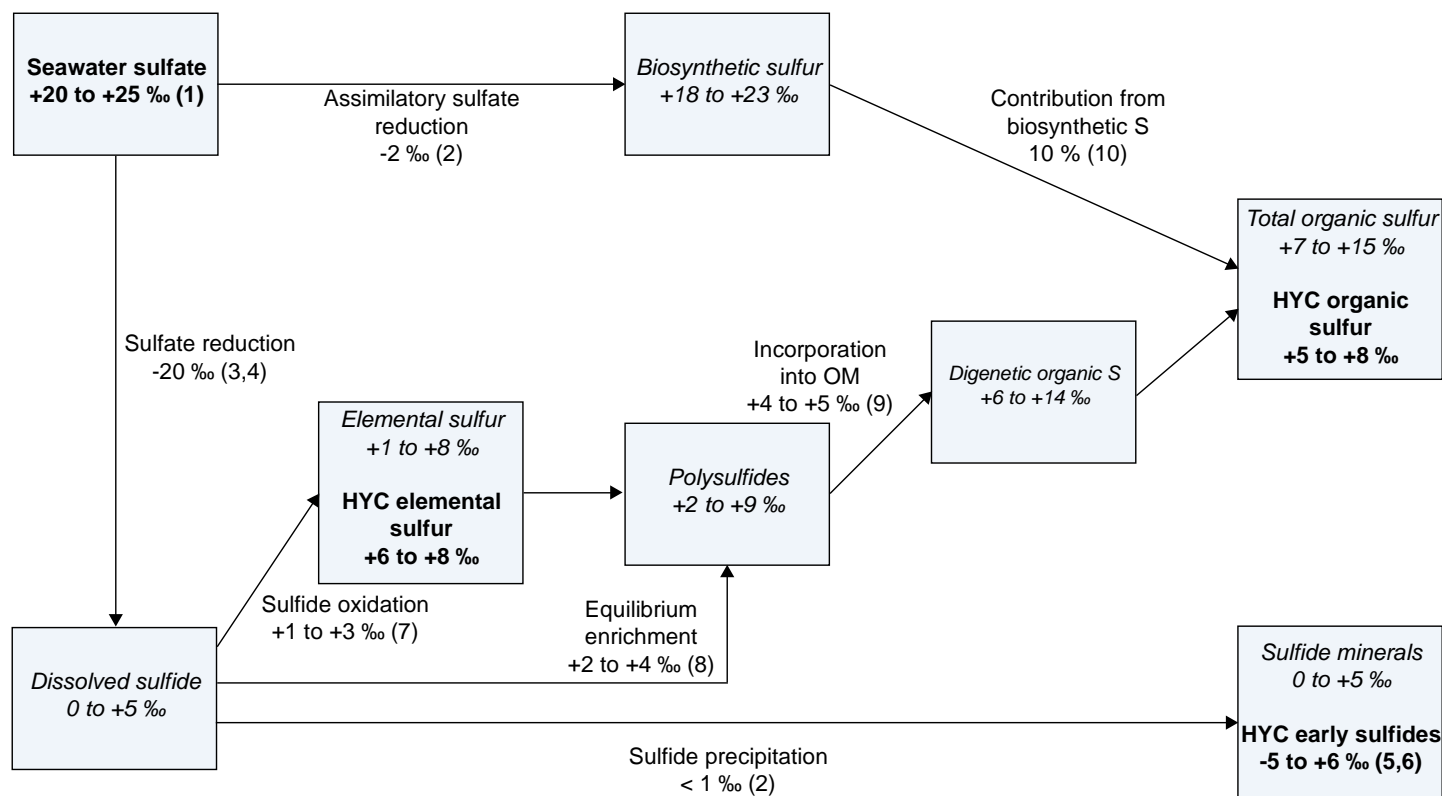


Figure 5.4: Proposed scheme for the formation of organic sulfur, S^0 and sulfide minerals at HYC. Details of the scheme are discussed on pages 131-134. Boxes represent the $\delta^{34}\text{S}$ of the various sulfur species (vertical axis is not to scale), and arrows represent predicted fractionations during transformation processes. $\delta^{34}\text{S}$ values in bold were measured either in this study (S^0 and organic sulfur) or by previous researchers. $\delta^{34}\text{S}$ values in italics are predictions calculated from the measured values and fractionations reported in previous studies. 1 Strauss (1993), 2 Canfield (2001), 3 Shen et al. (2002), 4 Machel et al. (1995), 5 Eldridge et al. (1993), 6 Ireland et al. (2004), 7 Zerkle et al. (2009), 8 Amrani et al. (2006), 9 Amrani and Aizenshtat (2004), 10 Anderson and Pratt (1995).

Polysulfide ions exist in equilibrium with S^0 and dissolved sulfide, and have been shown in laboratory experiments to be 2 to 4 ‰ enriched in ^{34}S compared to sulfide (Amrani et al., 2006). The incorporation of polysulfides into OM may result in further enrichment. This process has not been widely studied, but Amrani and Aizenshtat (2004) reported that the reaction of model polysulfide solutions with pure carbonyl compounds produced organic sulfur compounds (primarily alkyl chains connected by polysulfide bridges) that were ^{34}S -enriched by 4 to 5 ‰.

Sedimentary organic sulfur is thought to derive from a combination of diagenetic and biosynthetic pathways, with biosynthetic sulfur being relatively enriched in ^{34}S as it is formed with similar $\delta^{34}S$ to the seawater sulfate source (Kaplan and Rittenberg, 1964; Brüchert and Pratt, 1996). Biosynthetic sulfur has been estimated to contribute up to 25 % of organic sulfur in marine sediments (Anderson and Pratt, 1995; Brüchert and Pratt, 1996; Passier et al., 1999), although this proportion may be reduced with thermal maturation as the highly labile biosynthetic sulfur compounds are expected to be rapidly remineralised (Werne et al., 2003). Assuming a contribution from biosynthetic sulfur of 10 %, the model predicts organic sulfur with $\delta^{34}S$ between +7 and +15 ‰. The measured $\delta^{34}S$ of HYC kerogen (+5 to +8 ‰) is at the lower end of this range. This may suggest a lower degree of ^{34}S -enrichment during incorporation of sulfur into OM than was reported from the laboratory experiments of Amrani and Aizenshtat (2004). Recently reported compound-specific $\delta^{34}S$ measurements of diagenetic organic sulfur compounds from the Cariaco Basin showed that some compounds were significantly ^{34}S -depleted compared to co-existing sulfide (Raven et al., 2013), suggesting that diagenetic sulfurisation may result in a wider range of fractionations than previously reported. Alternatively the contribution from biosynthetic sulfur at HYC may have been lower than the assumed 10 %.

The model shown in Figure 5.4 presents only a simplified view of the chemical transformations of sulfur during the deposition of HYC, but matches well with the measured $\delta^{34}S$ of S^0 and kerogen. It should be noted that the simplified model presented here is based on a system that is open for all relevant processes. A natural environment with closed or semi-closed precipitation conditions, and the potential for changes in conditions during the evolution of the system, may alter the predicted

trends and further complicate interpretations of the genetic relationships of the different sulfur-bearing phases.

Conclusions

The sulfur isotopic composition of S^0 and organic sulfur at HYC reveals information on sulfur cycling during the formation of the base metal sulfide deposit. These species are 3 to 7 ‰ enriched in ^{34}S compared to first-generation sulfide minerals. The measured $\delta^{34}S$ values strongly support a genetic model in which S^0 and organic sulfur were formed simultaneously with base metal sulfides from dissolved sulfide that was produced by BSR. Organic sulfur is believed to have been formed through the incorporation of polysulfide ions into OM. Whilst the five pit samples represent a modest sample set, the organic sulfur displayed a trend of increasing $\delta^{34}S$ along the path of the mineralising fluid which may result from Rayleigh distillation, suggesting that $\delta^{34}S$ of organic sulfur may be useful for the targeted exploration of minerals. The enrichment in ^{34}S of S^0 compared to HYC sulfide minerals suggests that phototrophic sulfur oxidation may have been an important process, but the likely alteration of the isotopic signal by post-depositional processes renders this conclusion uncertain.

Although organic sulfur and S^0 are quantitatively minor components of the total sulfur inventory at HYC, this study has shown that they reveal important aspects of the sulfur cycle during the formation of the deposit, complementing and extending the more traditional studies of mineral sulfides. These species should not be neglected in isotopic investigations of base metal deposits, or of any sedimentary system in which the sulfur cycle plays an important role.

Acknowledgements

This study was conducted as part of the CSIRO Flagship Collaboration Fund Cluster for Organic Geochemistry of Mineral Systems, led by Curtin University. AH thanks Curtin University for an Australia Postgraduate Award scholarship and CSIRO for a top-up scholarship. Robert Herman is thanked for technical support with HPLC. MEB wishes to thank Iris Schmiedinger for mass spectrometry support. The authors thank Editor-in-Chief David Hilton and two anonymous reviewers for their helpful reviews.

References

- Aizenshtat Z., Krein E.B., Vairavamurthy M.A., Goldstein T.P., 1995. Role of sulfur in the transformations of sedimentary organic matter: a mechanistic overview. In *Geochemical Transformations of Sedimentary Sulfur* (eds. Vairavamurthy M.A., Schoonen M.A.A.). American Chemical Society, Washington, D.C. pp 16-37.
- Amrani A., Aizenshtat Z., 2004. Mechanisms of sulfur introduction chemically controlled: $\delta^{34}\text{S}$ imprint. *Organic Geochemistry* **35**, 1319-1336.
- Amrani A., Deev A., Sessions A.L., Tang Y., Adkins J.F., Hill R.J., Moldowan J.M., Wei Z., 2012. The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction. *Geochimica et Cosmochimica Acta* **84**, 152-164.
- Amrani A., Kamyshny A., Lev O., Aizenshtat Z., 2006. Sulfur stable isotope distribution of polysulfide anions in an $(\text{NH}_4)_2\text{S}_n$ aqueous solution. *Inorganic Chemistry* **45**, 1427-1429.
- Anderson T.F., Pratt L.M., 1995. Isotopic evidence for the origin of organic sulfur and elemental sulfur in marine sediments. In *Geochemical Transformations of Sedimentary Sulfur* (eds. Vairavamurthy M.A., Schoonen M.A.A.). American Chemical Society, Washington, D.C. pp 378-396.
- Asif M., Alexander R., Fazeelat T., Pierce K., 2009. Geosynthesis of dibenzothiophene and alkyl dibenzothiophenes in crude oils and sediments by carbon catalysis. *Organic Geochemistry* **40**, 895-901.
- Bontognali T.R.R., Sessions A.L., Allwood A.C., Fischer W.W., Grotzinger J.P., Summons R.E., Eiler J.M., 2012. Sulfur isotopes of organic matter preserved in 3.45-billion-year-old stromatolites reveal microbial metabolism. *Proceedings of the National Academy of Sciences* **109**, 15146-15151.
- Böttcher M.E., 2011. Sulfur cycle. In *Encyclopedia of Geobiology* (eds. Reitner J., Thiel V.). Springer, Dordrecht, The Netherlands. pp 859-864.
- Böttcher M.E., Sievert S.M., Kuever J., 1999. Fractionation of sulfur isotopes during dissimilatory reduction of sulfate by a thermophilic gram-negative bacterium at 60 °C. *Archives of Microbiology* **172**, 125-128.

- Böttcher M.E., Smock A.M., Cypionka H., 1998. Sulfur isotope fractionation during experimental precipitation of iron(II) and manganese(II) sulfide at room temperature. *Chemical Geology* **146**, 127-134.
- Böttcher M.E., Thamdrup B., Vennemann T.W., 2001. Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta* **65**, 1601-1609.
- Broadbent G.C., Myers R.E., Wright J.V., 1998. Geology and origin of shale-hosted Zn-Pb-Ag mineralization at the Century Deposit, Northwest Queensland, Australia. *Economic Geology* **93**, 1264-1294.
- Brocks J.J., Love G.D., Summons R.E., Knoll A.H., Logan G.A., Bowden S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866-870.
- Brüchert V., Pratt L.M., 1996. Contemporaneous early diagenetic formation of organic and inorganic sulfur in estuarine sediments from St. Andrew Bay, Florida, USA. *Geochimica et Cosmochimica Acta* **60**, 2325-2332.
- Brunner B., Bernasconi S.M., 2005. A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. *Geochimica et Cosmochimica Acta* **69**, 4759-4771.
- Butler I.B., Böttcher M.E., Rickard D., Oldroyd A., 2004. Sulfur isotope partitioning during experimental formation of pyrite via the polysulfide and hydrogen sulfide pathways: implications for the interpretation of sedimentary and hydrothermal pyrite isotope records. *Earth and Planetary Science Letters* **228**, 495-509.
- Canfield D.E., 1989. Reactive iron in marine sediments. *Geochimica et Cosmochimica Acta* **53**, 619-632.
- Canfield D.E., 2001. Biogeochemistry of sulfur isotopes. *Reviews in Mineralogy and Geochemistry* **43**, 607-636.
- Canfield D.E., Habicht K.S., Thamdrup B., 2000. The Archean sulfur cycle and the early history of atmospheric oxygen. *Science* **288**, 658-661.

- Canfield D.E., Teske A., 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature* **382**, 127-132.
- Canfield D.E., Thamdrup B., 1994. The production of ^{34}S -depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* **266**, 1973-1975.
- Chandra A.P., Gerson A.R., 2011. Pyrite (FeS_2) oxidation: A sub-micron synchrotron investigation of the initial steps. *Geochimica et Cosmochimica Acta* **75**, 6239-6254.
- Chen J., Walter M.R., Logan G.A., Hinman M.C., Summons R.E., 2003. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: organic geochemistry and ore genesis. *Earth and Planetary Science Letters* **210**, 467-479.
- Chen K.Y., Morris J.C., 1972. Kinetics of oxidation of aqueous sulfide by oxygen. *Environmental Science & Technology* **6**, 529-537.
- Cooke D.R., Bull S.W., Donovan S., Rogers J.R., 1998. K-metasomatism and base metal depletion in volcanic rocks from the McArthur Basin, Northern Territory; implications for base metal mineralization. *Economic Geology* **93**, 1237-1263.
- Cooke D.R., Bull S.W., Large R.R., McGoldrick P.J., 2000. The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb-Zn (sedex) deposits. *Economic Geology* **95**, 1-18.
- Dartiguelongue C., Behar F., Budzinski H., Scacchi G., Marquaire P.M., 2006. Thermal stability of dibenzothiophene in closed system pyrolysis: experimental study and kinetic modelling. *Organic Geochemistry* **37**, 98-116.
- Donnelly T.H., Jackson M.J., 1988. Sedimentology and geochemistry of a mid-Proterozoic lacustrine unit from northern Australia. *Sedimentary Geology* **58**, 145-169.
- Druschel G.K., Labrenz M., Thomsen-Ebert T., Fowle D.A., Banfield J.F., 2002. Geochemical modeling of ZnS in biofilms: an example of ore depositional processes. *Economic Geology* **97**, 1319-1329.

- Eldridge C.S., Williams N., Walshe J.L., 1993. Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe SHRIMP: II. A study of the H.Y.C. deposit at McArthur River, Northern Territory, Australia. *Economic Geology* **88**, 1-26.
- Farquhar J., Wu N., Canfield D.E., Oduro H., 2010. Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits. *Economic Geology* **105**, 509-533.
- Fenton S., Grice K., Twitchett R.J., Böttcher M.E., Looy C.V., Nabbefeld B., 2007. Changes in biomarker abundances and sulfur isotopes of pyrite across the Permian–Triassic (P/Tr) Schuchert Dal section (East Greenland). *Earth and Planetary Science Letters* **262**, 230-239.
- Fossing H., Gallardo V.A., Jorgensen B.B., Huttel M., Nielsen L.P., Schulz H., Canfield D.E., Forster S., Glud R.N., Gundersen J.K., Kuver J., Ramsing N.B., Teske A., Thamdrup B., Ulloa O., 1995. Concentration and transport of nitrate by the mat-forming sulphur bacterium *Thioploca*. *Nature* **374**, 713-715.
- Fry B., Ruf W., Gest H., Hayes J.M., 1988. Sulfur isotope effects associated with oxidation of sulfide by O₂ in aqueous solution. *Chemical Geology: Isotope Geoscience section* **73**, 205-210.
- Habicht K.S., Gade M., Thamdrup B., Berg P., Canfield D.E., 2002. Calibration of sulfate levels in the Archean ocean. *Science* **298**, 2372-2374.
- Hartmann M., Nielsen H., 2012. $\delta^{34}\text{S}$ values in recent sea sediments and their significance using several sediment profiles from the western Baltic Sea. *Isotopes in Environmental and Health Studies* **48**, 7-32.
- Hebting Y., Schaeffer P., Behrens A., Adam P., Schmitt G., Schneckenburger P., Bernasconi S.M., Albrecht P., 2006. Biomarker evidence for a major preservation pathway of sedimentary organic carbon. *Science* **312**, 1627-1631.
- Henneke E., Luther G.W., de Lange G.J., Hoefs J., 1997. Sulphur speciation in anoxic hypersaline sediments from the eastern Mediterranean Sea. *Geochimica et Cosmochimica Acta* **61**, 307-321.

- Huston D.L., Stevens B., Southgate P.N., Muhling P., Wyborn L., 2006. Australian Zn-Pb-Ag ore-forming systems: a review and analysis. *Economic Geology* **101**, 1117-1157.
- Ireland T., Large R.R., McGoldrick P., Blake M., 2004. Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore textures in the McArthur River (HYC) Zn-Pb-Ag deposit, Northern Territory, Australia. *Economic Geology* **99**, 1687-1709.
- Johnston D.T., Farquhar J., Summons R.E., Shen Y., Kaufman A.J., Masterson A.L., Canfield D.E., 2008. Sulfur isotope biogeochemistry of the Proterozoic McArthur Basin. *Geochimica et Cosmochimica Acta* **72**, 4278-4290.
- Jørgensen B.B., 1982. Mineralization of organic matter in the sea bed - the role of sulphate reduction. *Nature* **296**, 643-645.
- Jørgensen B.B., Nelson D.C., 2004. Sulfide oxidation in marine sediments: geochemistry meets microbiology. In *Sulfur Biogeochemistry - Past and Present* (eds. Amend J.P., Edwards K.J., Lyons T.W.). Geological Society of America Special Paper 379, Boulder, Colorado. pp 63-81.
- Kamysny A., Ferdelman T.G., 2010. Dynamics of zero-valent sulfur species including polysulfides at seep sites on intertidal sand flats (Wadden Sea, North Sea). *Marine Chemistry* **121**, 17-26.
- Kaplan I.R., Rittenberg S.C., 1964. Microbiological fractionation of sulphur isotopes. *Journal of General Microbiology* **34**, 195-212.
- Lambert I.B., Scott K.M., 1973. Implications of geochemical investigations of sedimentary rocks within and around the McArthur zinc-lead-silver deposit, Northern Territory. *Journal of Geochemical Exploration* **2**, 307-330.
- Large R.R., Bull S.W., Cooke D.R., McGoldrick P.J., 1998. A genetic model for the HYC deposit, Australia: based on regional sedimentology, geochemistry, and sulfide-sediment relationships. *Economic Geology* **93**, 1345-1368.
- Logan G.A., Hinman M.C., Walter M.R., Summons R.E., 2001. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. *Geochimica et Cosmochimica Acta* **65**, 2317-2336.

- Machel H.G., Krouse H.R., Sassen R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry* **10**, 373-389.
- Mann J.L., Vocke R.D., Kelly W.R., 2009. Revised $\delta^{34}\text{S}$ reference values for IAEA sulfur isotope reference materials S-2 and S-3. *Rapid Communications in Mass Spectrometry* **23**, 1116-1124.
- McGoldrick P., Winefield P., Bull S., Selley D., Scott R., 2010. Sequences, synsedimentary structures, and sub-basins: the where and when of SEDEX zinc systems in the southern McArthur Basin, Australia. In *The Challenge of Finding New Mineral Resources: Global Metallogeny, Innovative Exploration, and New Discoveries. Volume II: Zinc-Lead, Nickel-Copper-PGE, and Uranium* (eds. Goldfarb R.J., Marsh E.E., Monecke T.). Society of Economic Geologists Special Publication Number 15, Littleton, Colorado. pp 367-389.
- Melendez I., Grice K., Trinajstić K., Ladjavardi M., Greenwood P., Thompson K., 2013. Biomarkers reveal the role of photic zone euxinia in exceptional fossil preservation: an organic geochemical perspective. *Geology* **41**, 123-126.
- Nabbefeld B., Grice K., Schimmelmann A., Sauer P.E., Böttcher M.E., Twitchett R.J., 2010a. Significance of δD (kerogen), $\delta^{13}\text{C}$ (kerogen) and $\delta^{34}\text{S}$ (pyrite) from several Permian/Triassic (P/Tr) sections. *Earth and Planetary Science Letters* **295**, 21-29.
- Nabbefeld B., Grice K., Schimmelmann A., Summons R.E., Troitzsch U., Twitchett R.J., 2010b. A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks. *Organic Geochemistry* **41**, 78-87.
- Nabbefeld B., Grice K., Twitchett R.J., Summons R.E., Hays L., Böttcher M.E., Asif M., 2010c. An integrated biomarker, isotopic and palaeoenvironmental study through the Late Permian event at Lusitaniadalen, Spitsbergen. *Earth and Planetary Science Letters* **291**, 84-96.
- Page R.W., Sweet I.P., 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences* **45**, 219-232.

- Passier H.F., Böttcher M.E., De Lange G.J., 1999. Sulphur enrichment in organic matter of eastern Mediterranean sapropels: a study of sulphur isotope partitioning. *Aquatic Geochemistry* **5**, 99-118.
- Planavsky N.J., McGoldrick P., Scott C.T., Li C., Reinhard C.T., Kelly A.E., Chu X., Bekker A., Love G.D., Lyons T.W., 2011. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448-451.
- Poulton S.W., Fralick P.W., Canfield D.E., 2010. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geoscience* **3**, 486-490.
- Powell T.G., Jackson M.J., Sweet I.P., Crick I.H., Boreham C.J., Summons R.E., 1987. Petroleum geology and geochemistry, Middle Proterozoic McArthur Basin. Australia Bureau of Mineral Resources, Geology and Geophysics, record 1987/48.
- Price F.T., Shieh Y.N., 1979. Fractionation of sulfur isotopes during laboratory synthesis of pyrite at low temperatures. *Chemical Geology* **27**, 245-253.
- Raven M.R., Sessions A., Adkins J., 2013. The sulfur isotopic compositions of individual organic compounds in Cariaco Basin, In: González-Pérez J.A., González-Vila F.J., Jiménez-Morillo N.T., Almendros G. (Eds.), 26th International Meeting on Organic Geochemistry, Tenerife.
- Seal R.R., 2006. Sulfur isotope geochemistry of sulfide minerals. *Reviews in Mineralogy and Geochemistry* **61**, 633-677.
- Shen Y., Canfield D.E., Knoll A.H., 2002. Middle Proterozoic ocean chemistry: evidence from the McArthur Basin, northern Australia. *American Journal of Science* **302**, 81-109.
- Sim M.S., Bosak T., Ono S., 2011. Large sulfur isotope fractionation does not require disproportionation. *Science* **333**, 74-77.
- Sinninghe Damsté J.S., de Leeuw J.W., 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: state of the art and future research. *Organic Geochemistry* **16**, 1077-1101.
- Steger H.F., Desjardins L.E., 1980. Oxidation of sulfide minerals. V. Galena, sphalerite and chalcocite. *The Canadian Mineralogist* **18**, 365-372.

- Strauss H., 1993. The sulfur isotopic record of Precambrian sulfates: new data and a critical evaluation of the existing record. *Precambrian Research* **63**, 225-246.
- Werne J.P., Lyons T.W., Hollander D.J., Formolo M.J., Sinninghe Damsté J.S., 2003. Reduced sulfur in euxinic sediments of the Cariaco Basin: sulfur isotope constraints on organic sulfur formation. *Chemical Geology* **195**, 159-179.
- Werne J.P., Lyons T.W., Hollander D.J., Schouten S., Hopmans E.C., Sinninghe Damsté J.S., 2008. Investigating pathways of diagenetic organic matter sulfurization using compound-specific sulfur isotope analysis. *Geochimica et Cosmochimica Acta* **72**, 3489-3502.
- Williford K.H., Grice K., Logan G.A., Chen J., Huston D., 2011. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters* **301**, 382-392.
- Wortmann U.G., Bernasconi S.M., Böttcher M.E., 2001. Hypersulfidic deep biosphere indicates extreme sulfur isotope fractionation during single-step microbial sulfate reduction. *Geology* **29**, 647-650.
- Yücel M., Konovalov S.K., Moore T.S., Janzen C.P., Luther G.W., 2010. Sulfur speciation in the upper Black Sea sediments. *Chemical Geology* **269**, 364-375.
- Zerle A.L., Farquhar J., Johnston D.T., Cox R.P., Canfield D.E., 2009. Fractionation of multiple sulfur isotopes during phototrophic oxidation of sulfide and elemental sulfur by a green sulfur bacterium. *Geochimica et Cosmochimica Acta* **73**, 291-306.
- Zhang J.-Z., Millero F.J., 1993. The products from the oxidation of H₂S in seawater. *Geochimica et Cosmochimica Acta* **57**, 1705-1718.
- Zopfi J., Böttcher M.E., Jørgensen B.B., 2008. Biogeochemistry of sulfur and iron in Thioploca-colonized surface sediments in the upwelling area off central Chile. *Geochimica et Cosmochimica Acta* **72**, 827-843.
- Zopfi J., Ferdelman T.G., Fossing H., 2004. Distribution and fate of sulfur intermediates - sulfite, tetrathionate, thiosulfate, and elemental sulfur - in marine sediments. In *Sulfur Biogeochemistry - Past and Present* (eds. Amend

J.P., Edwards K.J., Lyons T.W.). Geological Society of America Special Paper 379, Boulder, Colorado. pp 97-116.

Chapter 6

Conclusions

This PhD project has explored novel aspects of the organic geochemistry of the 1.64 Ga Here's Your Chance (HYC) Pb/Zn/Ag deposit. The HYC deposit is the largest of the Paleoproterozoic sediment-hosted Pb/Zn/Ag deposits in northern Australia. OM from the deposit has experienced extensive hydrothermal alteration through the action of the mineralising fluid. The aims of this project were to detect organic evidence of the depositional environment of HYC, to relate this evidence to the processes of mineral deposition, and to further investigate the effects of hydrothermal alteration on OM at the deposit.

The HYC samples used in this project were taken along the estimated flow path of the mineralising fluid. A fraction of extractable OM occluded within the kerogen / mineral matrix (Bitumen II) from these samples was isolated and analysed by GC-MS and stable carbon compound-specific isotope analysis (CSIA), and compared with the freely-extractable OM (Bitumen I) and isolated kerogen. Pyrolysis experiments were performed on an immature, unmineralised sample from the host Barney Creek Formation (BCF) to assess the ability of laboratory simulations to replicate the effects of hydrothermal alteration on sedimentary OM, and to investigate the effect of base metal sulfides on the maturation of OM. Reduced

sulfur species are sensitive indicators of redox and other environmental conditions and are highly abundant in the deposit, so the $\delta^{34}\text{S}$ of elemental sulfur (S^0) and organic sulfur (kerogen) from the deposit were measured. The application of these novel organic geochemical techniques can reveal important information on the formation of mineral deposits that cannot be obtained by traditional techniques.

Depositional environment and sulfur biogeochemistry of HYC

Sediment-hosted Pb/Zn/Ag deposits such as HYC are believed to form in euxinic basins. In **Chapters 2 and 3** Bitumen II was isolated from five highly-mineralised samples. In several samples a distinctive distribution of long chain *n*-alkanes (C_{22} to C_{38}) was detected with an even-numbered predominance and $\delta^{13}\text{C}$ of -32 to -34 ‰. These features were attributed to the presence of sulfate-reducing bacteria (SRB) and phototrophic sulfur bacteria (PSB). Their presence in Bitumen II strongly suggests they are indigenous to HYC, and this was further supported by the close correlation of $\delta^{13}\text{C}$ with that of kerogen isolated from the deposit. The $\delta^{34}\text{S}$ of kerogen and S^0 (**Chapter 5**) was consistent with their formation from sulfide produced by bacterial sulfate reduction. S^0 and organic sulfur were enriched in ^{34}S compared to base metal sulfides, which may be the result of phototrophic sulfide oxidation. The above evidence for the presence of SRB and PSB suggests that the HYC deposit was formed under euxinic conditions which may have extended into the photic zone. Micro-Scale Sealed Vessel pyrolysis (MSSVpy) of an unmineralised sample from the BCF (**Chapter 4**) produced all of the general characteristics observed at HYC, such as the destruction of aliphatic biomarkers and the formation of PAHs, implying that sedimentary OM at the deposit was impacted by hydrothermal alteration.

There is evidence that the influx of mineralising fluid that carried base metals to HYC may also have resulted in significant changes to environmental conditions. The $\delta^{34}\text{S}$ values of kerogen and S^0 (**Chapter 5**) range from +5 to +8 ‰. These values are significantly depleted compared to pyrite from the unmineralised BCF, but close to the $\delta^{34}\text{S}$ of base metal sulfides from mineralised zones in the deposit. The $\delta^{34}\text{S}$ of organic sulfur increased from +5 to +8 ‰ along the flow path of the mineralising fluid. This increase is consistent with Rayleigh distillation, with continuous sulfate reduction causing the sulfate carried with the fluid to become progressively more

enriched in ^{34}S . The sulfur isotopic evidence is consistent with the transport of sulfate by the mineralising fluid, which was reduced to sulfide by sulfate-reducing bacteria. This sulfide rapidly reacted with abundant metal ions carried by the fluid to precipitate base metal sulfides, with the remaining sulfide being oxidised to generate S^0 and organic sulfur.

Effects of hydrothermal alteration on HYC OM

Bitumen I at HYC was strongly affected by hydrothermal alteration, and may also have been overprinted by non-indigenous hydrocarbons carried by the mineralising fluid. Bitumen II is closely associated with the kerogen / mineral matrix and is hence believed to be protected against alteration and overprinting. *n*-Alkane distributions that showed evidence for the presence of SRB and PSB (**Chapter 3**) were detected in Bitumen II, but not in Bitumen I. PAH maturity parameters gave conflicting information as to the relative maturities of Bitumens I and II. The MPI-1 parameter was much lower in Bitumen II than Bitumen I, but this appears to be primarily due to the reduced proportions of methylated phenanthrene isomers in Bitumen II compared to unmethylated phenanthrene. The MPR parameter is approximately equal in Bitumens I and II (within 0.1 for four samples), which suggests that they may have experienced similar levels of thermal maturity. The differences in *n*-alkane distribution between the two fractions may primarily be a result of migration, rather than thermal maturity. There is strong evidence that Bitumen II *n*-alkanes are indigenous to HYC, based on the close correlation of $\delta^{13}\text{C}$ with isolated kerogen. Conversely Bitumen I *n*-alkanes are 4 to 6 ‰ enriched in ^{13}C , suggesting they are not indigenous, and may have been transported to HYC with the mineralising fluid.

Laboratory simulation of hydrothermal alteration was achieved with the application of MSSVpy to an immature, unmineralised sample from the BCF (**Chapter 4**). The pyrolysis experiments approximately replicated the characteristic PAH distributions and maturity profiles of the HYC deposit. However, methylated phenanthrenes were detected in much lower abundances than seen at HYC, possibly due to demethylation reactions during pyrolysis. MSSVpy in the presence of abundant metal sulfides (PbS or ZnS) showed that these minerals can have a significant effect on PAH maturity ratios, likely due to surface catalytic effects on methylation and demethylation

reactions. These effects are complex and more research will be required to understand their influence on the maturity of natural systems such as HYC.

Application of novel organic geochemical techniques to ore deposit studies

This PhD project used contemporary organic geochemical techniques that have not previously been applied to the characterisation of ore deposits. The isolation and analysis of Bitumen II is a recent development and has been demonstrated for only a limited number of samples. Here, Bitumen II was extracted from HYC sediments, and subsequent analyses showed that it was not contaminated with residual Bitumen I (**Chapter 2**). This implies that it is composed entirely of OM that was occluded within the kerogen / mineral matrix. Analysis of Bitumen II revealed evidence of SRB and PSB present during the formation of the deposit (**Chapter 3**). The diagnostic molecular features of these bacteria were not observed in Bitumen I, highlighting the value of analysing Bitumen II from ancient, heavily altered environments. It was also found that high-MW PAHs are less efficiently Soxhlet extracted than alkanes and low-MW PAHs (**Chapter 2**). High-MW PAHs are important products of hydrothermal alteration and often present in OM of ore deposits; hence this result has important implications for organic studies of these systems. Extraction times greater than 72 hours may be required if high-MW PAHs are to be accurately quantified.

MSSVpy, a method previously used to study the kinetics of oil formation, was able to successfully simulate the effects of hydrothermal alteration on sedimentary OM (**Chapter 4**). Pyrolysis of an unmineralised BCF sample spiked with PbS or ZnS showed that sulfide minerals can affect the behaviour of PAHs during thermal maturation. The effects of base metal sulfides on organic maturation had not previously been explored in detail. MSSVpy is a relatively simple analytical method requiring only mg quantities of sample. The present study suggests it would be a potentially useful screening tool for ore deposit exploration.

Reduced sulfur species are abundant in sedimentary Pb/Zn ore deposits, but organic sulfur and S^0 have traditionally been neglected in sulfur isotopic studies of these systems. It was shown in **Chapter 5** that while these species are not quantitatively

abundant, their $\delta^{34}\text{S}$ values can reveal valuable information about the transformation processes of sulfur during ore formation, and hence about the depositional environment. Therefore, isotopic measurements of organic sulfur and S^0 can provide additional information that is not captured by the traditional analysis of sulfide minerals, and these species should be considered in future sulfur isotopic studies.

Limitations and future work

Given the novel nature of the main analytical techniques used in this PhD project, more work will be required to fully realise their potential and to give a greater understanding of the results obtained. The analysis of Bitumen II (**Chapters 2 and 3**) will be greatly valuable in systems that have experienced extensive alteration or migration, but the use of high volumes of hydrofluoric acid renders the preparation dangerous and difficult to implement in most laboratories. The technique is currently limited to small volumes (less than 5 g) of sample; hence the amount of Bitumen II obtained is small. Stable carbon CSIA of Bitumen II PAHs would have been invaluable to demonstrate their syngeneity, but was not possible due to the low amounts of PAHs obtained. Likewise it was not possible to measure the hydrogen isotopic composition of Bitumen II, as hydrogen CSIA is less sensitive than carbon CSIA. An isolation process that allows for greater sample sizes should be developed, although dedicated laboratories may be required for the handling of hydrofluoric acid in high volumes. A wider investigation of Bitumen II from a range of sample sites is also necessary to more robustly determine the behaviour of aromatic hydrocarbons. Bitumen II from HYC contained a far reduced proportion of methylated phenanthrenes compared to Bitumen I (**Chapter 3**), but the reasons for this reduction are unclear. It was hypothesised that OM in Bitumen II experiences restricted access to the ‘methyl pool’ from which methyl groups are donated, but further studies are necessary to confirm this.

MSSVpy was shown to simulate the hydrothermal alteration of sedimentary OM and to reveal the influence of metal sulfides on organic maturation (**Chapter 4**). The present study was however limited to one sample, three pyrolysis temperatures (300, 330 and 360 °C) and two mineral additives (PbS and ZnS). A wider range of temperatures, both above and below the range applied here, would expand the

analysis and confirm observed trends. Preliminary attempts to heat samples at 400 °C caused frequent rupturing of the pyrolysis tubes, so it may be necessary to manufacture tubes from a more heat-resistant material or to place the tubes in pressurised autoclaves to balance the high internal pressure. The MSSVpy study showed that metal sulfides influenced the behaviour of PAH maturity parameters during maturation, but a thorough understanding of the associated reaction mechanism will require more detailed study.

The integration of these analyses with several other recently-developed analytical techniques would provide a natural extension of the present study. MSSVpy is an online pyrolysis technique; therefore the pyrolysate cannot be fractionated before GC-MS analysis. The resulting pyrograms are ‘busy’ and analytes often co-elute (**Chapter 4**). Coupling of MSSVpy to a GC×GC-TOFMS instrument would vastly increase the separation of analytes and allow for accurate quantification of low-abundance components.

The $\delta^{34}\text{S}$ measurements of S^0 and organic sulfur presented in **Chapter 5** were average values of sulfur isolated from 20 g or more of rock. They do not reflect the high degree of isotopic heterogeneity observed from previous measurements of sulfide minerals, which were obtained through ion-probe and laser-ablation techniques at resolutions of 100 μm or less. High-resolution $\delta^{34}\text{S}$ measurements of organic sulfur have recently been reported, and would give greater understanding of the formation of organic sulfur at HYC. The kerogen analyses provided only a bulk $\delta^{34}\text{S}$ measurement of organic sulfur. Attempts were made to measure the $\delta^{34}\text{S}$ of DBTs using the newly-developed gas chromatography – inductively-coupled plasma mass spectrometry (GC-ICPMS) facility at the University of Western Australia, but the abundance of DBTs was too low for accurate measurement. Improving the sensitivity of this technology may allow for compound-specific sulfur isotope measurements to be made, opening another powerful avenue of research into the sulfur cycle at HYC.

Bibliography

Every reasonable effort has been made to acknowledge the owners of copyright material. I would be pleased to hear from any copyright owner who has been omitted or incorrectly acknowledged.

A

Aizenshtat Z., Krein E.B., Vairavamurthy M.A., Goldstein T.P., 1995. Role of sulfur in the transformations of sedimentary organic matter: a mechanistic overview. In *Geochemical Transformations of Sedimentary Sulfur* (eds. Vairavamurthy M.A., Schoonen M.A.A.). American Chemical Society, Washington, D.C. pp 16-37.

Alexander R., Bastow T.P., Fisher S.J., Kagi R.I., 1995. Geosynthesis of organic compounds: II. Methylation of phenanthrene and alkylphenanthrenes. *Geochimica et Cosmochimica Acta* **59**, 4259-4266.

Alexander R., Kagi R.I., Rowland S.J., Sheppard P.N., Chirila T.V., 1985. The effects of thermal maturity on distributions of dimethylnaphthalenes and trimethylnaphthalenes in some Ancient sediments and petroleums. *Geochimica et Cosmochimica Acta* **49**, 385-395.

Amrani A., Aizenshtat Z., 2004. Mechanisms of sulfur introduction chemically controlled: $\delta^{34}\text{S}$ imprint. *Organic Geochemistry* **35**, 1319-1336.

Amrani A., Deev A., Sessions A.L., Tang Y., Adkins J.F., Hill R.J., Moldowan J.M., Wei Z., 2012. The sulfur-isotopic compositions of benzothiophenes and dibenzothiophenes as a proxy for thermochemical sulfate reduction. *Geochimica et Cosmochimica Acta* **84**, 152-164.

Amrani A., Kamyshny A., Lev O., Aizenshtat Z., 2006. Sulfur stable isotope distribution of polysulfide anions in an $(\text{NH}_4)_2\text{S}_n$ aqueous solution. *Inorganic Chemistry* **45**, 1427-1429.

Amrani A., Sessions A.L., Adkins J.F., 2009. Compound-specific $\delta^{34}\text{S}$ analysis of volatile organics by coupled GC/multicollector-ICPMS. *Analytical Chemistry* **81**, 9027-9034.

Anderson T.F., Pratt L.M., 1995. Isotopic evidence for the origin of organic sulfur and elemental sulfur in marine sediments. In *Geochemical Transformations of Sedimentary Sulfur* (eds. Vairavamurthy M.A., Schoonen M.A.A.). American Chemical Society, Washington, D.C. pp 378-396.

Arnold G.L., Anbar A.D., Barling J., Lyons T.W., 2004. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304**, 87-90.

Asif M., Alexander R., Fazeelat T., Pierce K., 2009. Geosynthesis of dibenzothiophene and alkyl dibenzothiophenes in crude oils and sediments by carbon catalysis. *Organic Geochemistry* **40**, 895-901.

B

Berglund M., Wieser M.E., 2011. Isotopic compositions of the elements 2009 (IUPAC Technical Report). *Pure and Applied Chemistry* **83**, 397-410.

Berwick L.J., Greenwood P.F., Smernik R.J., 2010. The use of MSSV pyrolysis to assist the molecular characterisation of aquatic natural organic matter. *Water Research* **44**, 3039-3054.

Blumer M., 1975. Curtisite, idrialite and pendletonite, polycyclic aromatic hydrocarbon minerals: their composition and origin. *Chemical Geology* **16**, 245-256.

Bontognali T.R.R., Sessions A.L., Allwood A.C., Fischer W.W., Grotzinger J.P., Summons R.E., Eiler J.M., 2012. Sulfur isotopes of organic matter preserved in 3.45-billion-year-old stromatolites reveal microbial metabolism. *Proceedings of the National Academy of Sciences* **109**, 15146-15151.

Boreham C.J., Crick I.H., Powell T.G., 1988. Alternative calibration of the Methylphenanthrene Index against vitrinite reflectance: application to maturity measurements on oils and sediments. *Organic Geochemistry* **12**, 289-294.

Böttcher M.E., 2011. Sulfur cycle. In *Encyclopedia of Geobiology* (eds. Reitner J., Thiel V.). Springer, Dordrecht, The Netherlands. pp 859-864.

- Böttcher M.E., Sievert S.M., Kuever J., 1999. Fractionation of sulfur isotopes during dissimilatory reduction of sulfate by a thermophilic gram-negative bacterium at 60 °C. *Archives of Microbiology* **172**, 125-128.
- Böttcher M.E., Smock A.M., Cypionka H., 1998. Sulfur isotope fractionation during experimental precipitation of iron(II) and manganese(II) sulfide at room temperature. *Chemical Geology* **146**, 127-134.
- Böttcher M.E., Thamdrup B., Vennemann T.W., 2001. Oxygen and sulfur isotope fractionation during anaerobic bacterial disproportionation of elemental sulfur. *Geochimica et Cosmochimica Acta* **65**, 1601-1609.
- Bowell R.J., Gize A.P., Foster R.P., 1993. The role of fulvic acid in the supergene migration of gold in tropical rain forest soils. *Geochimica et Cosmochimica Acta* **57**, 4179-4190.
- Brasier M.D., Lindsay J.F., 1998. A billion years of environmental stability and the emergence of eukaryotes: new data from northern Australia. *Geology* **26**, 555-558.
- Bray E.E., Evans E.D., 1961. Distribution of n-paraffins as a clue to recognition of source beds. *Geochimica et Cosmochimica Acta* **22**, 2-15.
- Broadbent G.C., Myers R.E., Wright J.V., 1998. Geology and origin of shale-hosted Zn-Pb-Ag mineralization at the Century Deposit, Northwest Queensland, Australia. *Economic Geology* **93**, 1264-1294.
- Brocks J.J., 2011. Millimeter-scale concentration gradients of hydrocarbons in Archean shales: live-oil escape or fingerprint of contamination? *Geochimica et Cosmochimica Acta* **75**, 3196-3213.
- Brocks J.J., Buick R., Logan G.A., Summons R.E., 2003. Composition and syngeneity of molecular fossils from the 2.78 to 2.45 billion-year-old Mount Bruce Supergroup, Pilbara Craton, Western Australia. *Geochimica et Cosmochimica Acta* **67**, 4289-4319.
- Brocks J.J., Grice K., 2011. Biomarkers (molecular fossils). In *Encyclopedia of Geobiology* (eds. Reitner J., Thiel V.). Springer, Dordrecht, The Netherlands. pp 147-167.

- Brocks J.J., Grosjean E., Logan G.A., 2008. Assessing biomarker syngeneity using branched alkanes with quaternary carbon (BAQCs) and other plastic contaminants. *Geochimica et Cosmochimica Acta* **72**, 871-888.
- Brocks J.J., Love G.D., Summons R.E., Knoll A.H., Logan G.A., Bowden S.A., 2005. Biomarker evidence for green and purple sulphur bacteria in a stratified Palaeoproterozoic sea. *Nature* **437**, 866-870.
- Brocks J.J., Schaeffer P., 2008. Okenane, a biomarker for purple sulfur bacteria (Chromatiaceae), and other new carotenoid derivatives from the 1640 Ma Barney Creek Formation. *Geochimica et Cosmochimica Acta* **72**, 1396-1414.
- Brocks J.J., Summons R.E., 2003. Sedimentary hydrocarbons, biomarkers for early life. In *Treatise on Geochemistry Volume 8 - Biogeochemistry* (ed. Schlesinger W.H.). Elsevier-Pergamon, Oxford. pp 63-115.
- Brothers L., Engel M.H., Krooss B.M., 1991. The effects of fluid flow through porous media on the distribution of organic compounds in a synthetic crude oil. *Organic Geochemistry* **17**, 11-24.
- Brüchert V., Pratt L.M., 1996. Contemporaneous early diagenetic formation of organic and inorganic sulfur in estuarine sediments from St. Andrew Bay, Florida, USA. *Geochimica et Cosmochimica Acta* **60**, 2325-2332.
- Brunner B., Bernasconi S.M., 2005. A revised isotope fractionation model for dissimilatory sulfate reduction in sulfate reducing bacteria. *Geochimica et Cosmochimica Acta* **69**, 4759-4771.
- Bull S.W., 1998. Sedimentology of the Palaeoproterozoic Barney Creek formation in DDH BMR McArthur 2, southern McArthur basin, Northern Territory. *Australian Journal of Earth Sciences* **45**, 21-31.
- Butler I.B., Böttcher M.E., Rickard D., Oldroyd A., 2004. Sulfur isotope partitioning during experimental formation of pyrite via the polysulfide and hydrogen sulfide pathways: implications for the interpretation of sedimentary and hydrothermal pyrite isotope records. *Earth and Planetary Science Letters* **228**, 495-509.

C

- Canfield D.E., 1989. Reactive iron in marine sediments. *Geochimica et Cosmochimica Acta* **53**, 619-632.
- Canfield D.E., 1998. A new model for Proterozoic ocean chemistry. *Nature* **396**, 450-453.
- Canfield D.E., 2001. Biogeochemistry of sulfur isotopes. *Reviews in Mineralogy and Geochemistry* **43**, 607-636.
- Canfield D.E., Habicht K.S., Thamdrup B., 2000. The Archean sulfur cycle and the early history of atmospheric oxygen. *Science* **288**, 658-661.
- Canfield D.E., Teske A., 1996. Late Proterozoic rise in atmospheric oxygen concentration inferred from phylogenetic and sulphur-isotope studies. *Nature* **382**, 127-132.
- Canfield D.E., Thamdrup B., 1994. The production of ^{34}S -depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* **266**, 1973-1975.
- Carlson R.M.K., Chamberlain D.E., 1986. Steroid biomarker-clay mineral adsorption free energies: implications to petroleum migration indices. *Organic Geochemistry* **10**, 163-180.
- Chandra A.P., Gerson A.R., 2011. Pyrite (FeS_2) oxidation: A sub-micron synchrotron investigation of the initial steps. *Geochimica et Cosmochimica Acta* **75**, 6239-6254.
- Chen J., Walter M.R., Logan G.A., Hinman M.C., Summons R.E., 2003. The Paleoproterozoic McArthur River (HYC) Pb/Zn/Ag deposit of northern Australia: organic geochemistry and ore genesis. *Earth and Planetary Science Letters* **210**, 467-479.
- Chen K.Y., Morris J.C., 1972. Kinetics of oxidation of aqueous sulfide by oxygen. *Environmental Science & Technology* **6**, 529-537.
- Chikaraishi Y., Naraoka H., Poulson S.R., 2004. Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. *Phytochemistry* **65**, 1369-1381.

- Clayton C.J., 1991. Effect of maturity on carbon isotope ratios of oils and condensates. *Organic Geochemistry* **17**, 887-899.
- Cleaves H.J., Michalkova Scott A., Hill F.C., Leszczynski J., Sahai N., Hazen R., 2012. Mineral-organic interfacial processes: potential roles in the origins of life. *Chemical Society Reviews* **41**, 5502-5525.
- Cody G.D., Boctor N.Z., Brandes J.A., Filley T.R., Hazen R.M., Yoder Jr H.S., 2004. Assaying the catalytic potential of transition metal sulfides for abiotic carbon fixation. *Geochimica et Cosmochimica Acta* **68**, 2185-2196.
- Cooke D.R., Bull S.W., Donovan S., Rogers J.R., 1998. K-metasomatism and base metal depletion in volcanic rocks from the McArthur Basin, Northern Territory; implications for base metal mineralization. *Economic Geology* **93**, 1237-1263.
- Cooke D.R., Bull S.W., Large R.R., McGoldrick P.J., 2000. The importance of oxidized brines for the formation of Australian Proterozoic stratiform sediment-hosted Pb-Zn (sedex) deposits. *Economic Geology* **95**, 1-18.
- Crick I.H., 1992. Petrological and maturation characteristics of organic matter from the Middle Proterozoic McArthur Basin, Australia. *Australian Journal of Earth Sciences* **39**, 501-519.
- Crick I.H., Boreham C.J., Cook A.C., Powell T.G., 1988. Petroleum geology and geochemistry of middle Proterozoic McArthur Basin, Northern Australia II: assessment of source rock potential. *AAPG Bulletin* **72**, 1495-1514.
- Croxford N.J.W., 1968. A mineralogical examination of the McArthur lead-zinc-silver deposit. *Proceedings: Australasian Institute of Mining and Metallurgy* **226**, 97-108.
- Croxford N.J.W., Jephcott S., 1972. The McArthur lead-zinc-silver deposit, N.T. *Proceedings: Australasian Institute of Mining and Metallurgy* **243**, 1-26.

D

- Dartiguelongue C., Behar F., Budzinski H., Scacchi G., Marquaire P.M., 2006. Thermal stability of dibenzothiophene in closed system pyrolysis: experimental study and kinetic modelling. *Organic Geochemistry* **37**, 98-116.
- Davidson G.J., Dashlooty S.A., 1993. The Glyde Sub-basin: a volcanoclastic-bearing pull-apart basin coeval with the McArthur River base-metal deposit, Northern Territory. *Australian Journal of Earth Sciences* **40**, 527-543.
- Dawson D., Grice K., Alexander R., 2005. Effect of maturation on the indigenous δD signatures of individual hydrocarbons in sediments and crude oils from the Perth Basin (Western Australia). *Organic Geochemistry* **36**, 95-104.
- Dawson D., Grice K., Wang S.X., Alexander R., Radke J., 2004. Stable hydrogen isotopic composition of hydrocarbons in torbanites (Late Carboniferous to Late Permian) deposited under various climatic conditions. *Organic Geochemistry* **35**, 189-197.
- Dembicki Jr H., Meinschein W.G., Hattin D.E., 1976. Possible ecological and environmental significance of the predominance of even-carbon number C₂₀-C₃₀ n-alkanes. *Geochimica et Cosmochimica Acta* **40**, 203-208.
- Des Marais D.J., 1997. Long-term evolution of the biogeochemical carbon cycle. *Reviews in Mineralogy and Geochemistry* **35**, 429-448.
- Dick J.M., Evans K.A., Holman A.I., Jaraula C.M.B., Grice K., 2013. Estimation and application of the thermodynamic properties of aqueous phenanthrene and isomers of methylphenanthrene at high temperature. *Geochimica et Cosmochimica Acta* **122**, 247-266.
- Disnar J.R., Sureau J.F., 1990. Organic matter in ore genesis: progress and perspectives. *Organic Geochemistry* **16**, 577-599.
- Donnelly T.H., Jackson M.J., 1988. Sedimentology and geochemistry of a mid-Proterozoic lacustrine unit from northern Australia. *Sedimentary Geology* **58**, 145-169.
- Dow W.G., 1977. Kerogen studies and geological interpretations. *Journal of Geochemical Exploration* **7**, 79-99.

Druschel G.K., Labrenz M., Thomsen-Ebert T., Fowle D.A., Banfield J.F., 2002. Geochemical modeling of ZnS in biofilms: an example of ore depositional processes. *Economic Geology* **97**, 1319-1329.

E

Eglinton G., Hamilton R.J., 1967. Leaf epicuticular waxes. *Science* **156**, 1322-1335.

Eldridge C.S., Williams N., Walshe J.L., 1993. Sulfur isotope variability in sediment-hosted massive sulfide deposits as determined using the ion microprobe SHRIMP: II. A study of the H.Y.C. deposit at McArthur River, Northern Territory, Australia. *Economic Geology* **88**, 1-26.

F

Falkowski P.G., 2012. The global carbon cycle: biological processes. In *Fundamentals of Geobiology* (eds. Knoll A.H., Canfield D.E., Konhauser K.O.). Blackwell Publishing Ltd., Chichester. pp 5-19.

Farquhar J., Wu N., Canfield D.E., Oduro H., 2010. Connections between sulfur cycle evolution, sulfur isotopes, sediments, and base metal sulfide deposits. *Economic Geology* **105**, 509-533.

Fenton S., Grice K., Twitchett R.J., Böttcher M.E., Looy C.V., Nabbefeld B., 2007. Changes in biomarker abundances and sulfur isotopes of pyrite across the Permian–Triassic (P/Tr) Schuchert Dal section (East Greenland). *Earth and Planetary Science Letters* **262**, 230-239.

Fetzer J.C., Simoneit B.R.T., Budzinski H., Garrigues P., 1996. Identification of large PAHs in bitumens from deep-sea hydrothermal vents. *Polycyclic Aromatic Compounds* **9**, 109-120.

Fossing H., Gallardo V.A., Jorgensen B.B., Huttel M., Nielsen L.P., Schulz H., Canfield D.E., Forster S., Glud R.N., Gundersen J.K., Kuver J., Ramsing N.B., Teske A., Thamdrup B., Ulloa O., 1995. Concentration and transport of nitrate by the mat-forming sulphur bacterium *Thioploca*. *Nature* **374**, 713-715.

Freeman K.H., 2001. Isotopic biogeochemistry of marine organic carbon. *Reviews in Mineralogy and Geochemistry* **43**, 579-605.

Fry B., Ruf W., Gest H., Hayes J.M., 1988. Sulfur isotope effects associated with oxidation of sulfide by O₂ in aqueous solution. *Chemical Geology: Isotope Geoscience section* **73**, 205-210.

G

Garrigues P., De Sury R., Angelin M.L., Bellocq J., Oudin J.L., Ewald M., 1988. Relation of the methylated aromatic hydrocarbon distribution pattern to the maturity of organic matter in ancient sediments from the Mahakam delta. *Geochimica et Cosmochimica Acta* **52**, 375-384.

Garrigues P., Oudin J.L., Parlanti E., Monin J.C., Robcis S., Bellocq J., 1990. Alkylated phenanthrene distribution in artificially matured kerogens from Kimmeridge clay and the Brent Formation (North Sea). *Organic Geochemistry* **16**, 167-173.

Garven G., Bull S.W., Large R.R., 2001. Hydrothermal fluid flow models of stratiform ore genesis in the McArthur Basin, Northern Territory, Australia. *Geofluids* **1**, 289-311.

Gatellier J.-P., Disnar J.-R., 1989. Organic matter and gold-ore association in a hydrothermal deposit, France. *Applied Geochemistry* **4**, 143-149.

Gehre M., Strauch G., 2003. High-temperature elemental analysis and pyrolysis techniques for stable isotope analysis. *Rapid Communications in Mass Spectrometry* **17**, 1497-1503.

George S.C., Ahmed M., 2002. Use of aromatic compound distributions to evaluate organic maturity of the Proterozoic middle Velkerri Formation, McArthur Basin, Australia. In *The Sedimentary Basins of Western Australia 3: Proceedings of the Petroleum Exploration Society of Australia Symposium 2002* (eds. Keep M., Moss S.J.). Petroleum Exploration Society of Australia, Perth. pp 253-270.

- George S.C., Llorca S.M., Hamilton P.J., 1994. An integrated analytical approach for determining the origin of solid bitumens in the McArthur Basin, northern Australia. *Organic Geochemistry* **21**, 235-248.
- Giordano T.H., 2002. Transport of Pb and Zn by carboxylate complexes in basinal ore fluids and related petroleum-field brines at 100 °C: the influence of pH and oxygen fugacity. *Geochemical Transactions* **3**, 56-72.
- Gizè A.P., 1999. Organic alteration in hydrothermal sulfide ore deposits. *Economic Geology* **94**, 967-979.
- Gizè A.P., 1999. A special issue on organic matter and ore deposits; interactions, applications, and case studies: introduction. *Economic Geology* **94**, 963-965.
- Gizè A.P., Barnes H.L., 1987. The organic geochemistry of two Mississippi Valley-type lead-zinc deposits. *Economic Geology* **82**, 457-470.
- Gizè A.P., Barnes H.L., 1994. Organic contributions to Mississippi Valley-type lead-zinc genesis - a critical assessment. In *Sediment-hosted Zn-Pb ores - Special publication no. 10 of the Society for Geology Applied to Mineral Deposits* (eds. Fontboté L., Boni M.). Springer-Verlag, Berlin. pp 13-26.
- Greenwood P.F., Brocks J.J., Grice K., Schwark L., Jaraula C.M.B., Dick J.M., Evans K.A., 2013. Organic geochemistry and mineralogy. I. Characterisation of organic matter associated with metal deposits. *Ore Geology Reviews* **50**, 1-27.
- Greenwood P.F., Leenheer J.A., McIntyre C., Berwick L.J., Franzmann P.D., 2006. Bacterial biomarkers thermally released from dissolved organic matter. *Organic Geochemistry* **37**, 597-609.
- Greenwood P.F., Lengkeek N.A., Piggott M.J., Pierce K., 2009. Structural identification and mass spectral interpretation of C_{3n} highly branched alkanes in sediment and aquatic extracts and evidence for their anthropogenic origin. *Organic Geochemistry* **40**, 1055-1062.
- Grice K., Backhouse J., Alexander R., Marshall N., Logan G.A., 2005a. Correlating terrestrial signatures from biomarker distributions, $\delta^{13}\text{C}$, and palynology in fluvio-deltaic deposits from NW Australia (Triassic–Jurassic). *Organic Geochemistry* **36**, 1347-1358.

- Grice K., Brocks J.J., 2011. Biomarkers (organic, compound-specific isotopes). In *Encyclopedia of Geobiology* (eds. Reitner J., Thiel V.). Springer, Dordrecht, The Netherlands. pp 167-182.
- Grice K., Cao C., Love G.D., Böttcher M.E., Twitchett R.J., Grosjean E., Summons R.E., Turgeon S.C., Dunning W., Jin Y., 2005. Photic zone euxinia during the Permian-Triassic superanoxic event. *Science* **307**, 706-709.
- Grice K., Lu H., Atahan P., Asif M., Hallmann C., Greenwood P.F., Maslen E., Tulipani S., Williford K., Dodson J., 2009. New insights into the origin of perylene in geological samples. *Geochimica et Cosmochimica Acta* **73**, 6531-6543.
- Grice K., Nabbefeld B., Maslen E., 2007. Source and significance of selected polycyclic aromatic hydrocarbons in sediments (Hovea-3 well, Perth Basin, Western Australia) spanning the Permian-Triassic boundary. *Organic Geochemistry* **38**, 1795-1803.
- Grice K., Schaeffer P., Schwark L., Maxwell J.R., 1996. Molecular indicators of palaeoenvironmental conditions in an immature Permian shale (Kupferschiefer, Lower Rhine Basin, north-west Germany) from free and S-bound lipids. *Organic Geochemistry* **25**, 131-147.
- Grice K., Schaeffer P., Schwark L., Maxwell J.R., 1997. Changes in palaeoenvironmental conditions during deposition of the Permian Kupferschiefer (Lower Rhine Basin, northwest Germany) inferred from molecular and isotopic compositions of biomarker components. *Organic Geochemistry* **26**, 677-690.
- Grosjean E., Logan G.A., 2007. Incorporation of organic contaminants into geochemical samples and an assessment of potential sources: examples from Geoscience Australia marine survey S282. *Organic Geochemistry* **38**, 853-869.

H

- Habicht K.S., Gade M., Thamdrup B., Berg P., Canfield D.E., 2002. Calibration of sulfate levels in the Archean ocean. *Science* **298**, 2372-2374.

- Han J., Calvin M., 1969. Hydrocarbon distribution of algae and bacteria, and microbiological activity in sediments. *Proceedings of the National Academy of Sciences of the United States of America* **64**, 436-443.
- Hartgers W.A., Sinninghe Damsté J.S., Requejo A.G., Allan J., Hayes J.M., Ling Y., Xie T.-M., Primack J., de Leeuw J.W., 1994. A molecular and carbon isotopic study towards the origin and diagenetic fate of diaromatic carotenoids. *Organic Geochemistry* **22**, 703-725.
- Hartmann M., Nielsen H., 2012. $\delta^{34}\text{S}$ values in recent sea sediments and their significance using several sediment profiles from the western Baltic Sea. *Isotopes in Environmental and Health Studies* **48**, 7-32.
- Hayes J.M., 2001. Fractionation of carbon and hydrogen isotopes in biosynthetic processes. *Reviews in Mineralogy and Geochemistry* **43**, 225-277.
- Hayes J.M., Freeman K.H., Popp B.N., Hoham C.H., 1990. Compound-specific isotopic analyses: a novel tool for reconstruction of ancient biogeochemical processes. *Organic Geochemistry* **16**, 1115-1128.
- Hebting Y., Schaeffer P., Behrens A., Adam P., Schmitt G., Schneckenburger P., Bernasconi S.M., Albrecht P., 2006. Biomarker evidence for a major preservation pathway of sedimentary organic carbon. *Science* **312**, 1627-1631.
- Henneke E., Luther G.W., de Lange G.J., Hoefs J., 1997. Sulphur speciation in anoxic hypersaline sediments from the eastern Mediterranean Sea. *Geochimica et Cosmochimica Acta* **61**, 307-321.
- Hinman M.C., 1996. Constraints, timing and processes of stratiform base metal mineralisation at the HYC Ag-Pb-Zn deposit, McArthur River. In *MIC '96 extended conference abstracts: New developments in metallogenic research: The McArthur, Mount Isa, Cloncurry Minerals Province* (eds. Baker T., Rotherham J.F., Richmond J.M., Mark G., Williams P.J.). James Cook University of North Queensland Economic Geology Research Unit, Townsville. pp 56-59.

- Ho E.S., Meyers P.A., Mauk J.L., 1990. Organic geochemical study of mineralization in the Keweenaw Nonesuch Formation at White Pine, Michigan. *Organic Geochemistry* **16**, 229-234.
- Hoefs J., 2009. *Stable Isotope Geochemistry*. Springer, Berlin.
- Horsfield B., Disko U., Leistner F., 1989. The micro-scale simulation of maturation: outline of a new technique and its potential applications. *Geologische Rundschau* **78**, 361-373.
- Horsfield B., Leistner F., Hall K., 2015. Microscale sealed vessel pyrolysis. In *Principles and Practice of Analytical Techniques in Geosciences* (ed. Grice K.). Royal Society of Chemistry, Oxford. pp 209-250.
- Huston D.L., Stevens B., Southgate P.N., Muhling P., Wyborn L., 2006. Australian Zn-Pb-Ag ore-forming systems: a review and analysis. *Economic Geology* **101**, 1117-1157.

I

- Imhoff J.F., 2006. The Chromatiaceae. In *The Prokaryotes Volume 6: Proteobacteria: Gamma Subclass* (eds. Dworkin M., Falkow S., Rosenberg E., Schleifer K.-H., Stackebrandt E.). Springer, New York. pp 846-873.
- Ireland T., Bull S.W., Large R.R., 2004. Mass flow sedimentology within the HYC Zn-Pb-Ag deposit, Northern Territory, Australia: evidence for syn-sedimentary ore genesis. *Mineralium Deposita* **39**, 143-158.
- Ireland T., Large R.R., McGoldrick P., Blake M., 2004. Spatial distribution patterns of sulfur isotopes, nodular carbonate, and ore textures in the McArthur River (HYC) Zn-Pb-Ag deposit, Northern Territory, Australia. *Economic Geology* **99**, 1687-1709.

J

- Jackson M.J., Southgate P.N., Winefield P.R., Barnett K., Zeilinger I., 2000. Revised sub-division and regional correlation of the McArthur Basin succession based

on NABRE's 1995-8 sequence stratigraphic studies. Australian Geological Survey Organization Record 2000/03, Canberra.

Jackson M.J., Sweet I.P., Powell T.G., 1988. Studies on petroleum geology and geochemistry, middle Proterozoic, McArthur Basin northern Australia I: petroleum potential. *The APEA Journal* **28**, 283-302.

Johnston D.T., Farquhar J., Summons R.E., Shen Y., Kaufman A.J., Masterson A.L., Canfield D.E., 2008. Sulfur isotope biogeochemistry of the Proterozoic McArthur Basin. *Geochimica et Cosmochimica Acta* **72**, 4278-4290.

Jørgensen B.B., 1982. Mineralization of organic matter in the sea bed - the role of sulphate reduction. *Nature* **296**, 643-645.

Jørgensen B.B., Nelson D.C., 2004. Sulfide oxidation in marine sediments: geochemistry meets microbiology. In *Sulfur Biogeochemistry - Past and Present* (eds. Amend J.P., Edwards K.J., Lyons T.W.). Geological Society of America Special Paper 379, Boulder, Colorado. pp 63-81.

K

Kamyshny A., Ferdelman T.G., 2010. Dynamics of zero-valent sulfur species including polysulfides at seep sites on intertidal sand flats (Wadden Sea, North Sea). *Marine Chemistry* **121**, 17-26.

Kannenbergh E.L., Poralla K., 1999. Hopanoid biosynthesis and function in bacteria. *Naturwissenschaften* **86**, 168-176.

Kaplan I.R., Rittenberg S.C., 1964. Microbiological fractionation of sulphur isotopes. *Journal of General Microbiology* **34**, 195-212.

Kawka O.E., Simoneit B.R.T., 1990. Polycyclic aromatic hydrocarbons in hydrothermal petroleum from the Guaymas Basin spreading center. *Applied Geochemistry* **5**, 17-27.

Kawka O.E., Simoneit B.R.T., 1994. Hydrothermal pyrolysis of organic matter in Guaymas Basin: I. Comparison of hydrocarbon distributions in subsurface sediments and seabed petroleum. *Organic Geochemistry* **22**, 947-978.

- Kendall B., Creaser R.A., Gordon G.W., Anbar A.D., 2009. Re–Os and Mo isotope systematics of black shales from the Middle Proterozoic Velkerri and Wollongorang Formations, McArthur Basin, northern Australia. *Geochimica et Cosmochimica Acta* **73**, 2534-2558.
- Killops S., Killops V., 2005. *Introduction to Organic Geochemistry*. Blackwell Publishing, Oxford.
- Killops S.D., Massoud M.S., 1992. Polycyclic aromatic hydrocarbons of pyrolytic origin in ancient sediments: evidence for Jurassic vegetation fires. *Organic Geochemistry* **18**, 1-7.
- Koopmans M.P., Köster J., van Kaam-Peters H.M.E., Kenig F., Schouten S., Hartgers W.A., de Leeuw J.W., Sinninghe Damsté J.S., 1996. Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia. *Geochimica et Cosmochimica Acta* **60**, 4467-4496.
- Kristjansson J.K., Schönheit P., Thauer R.K., 1982. Different K_s values for hydrogen of methanogenic bacteria and sulfate reducing bacteria: an explanation for the apparent inhibition of methanogenesis by sulfate. *Archives of Microbiology* **131**, 278-282.
- Krouse H.R., Coplen T.B., 1997. Reporting of relative sulfur isotope-ratio data (Technical Report). *Pure and Applied Chemistry* **69**, 293-295.
- Kvalheim O.M., Christy A.A., Telnæs N., Bjørseth A., 1987. Maturity determination of organic matter in coals using the methylphenanthrene distribution. *Geochimica et Cosmochimica Acta* **51**, 1883-1888.

L

- Ladjavardi M., Berwick L.J., Grice K., Boreham C.J., Horsfield B., 2013. Rapid offline isotopic characterisation of hydrocarbon gases generated by micro-scale sealed vessel pyrolysis. *Organic Geochemistry* **58**, 121-124.
- Ladygina N., Dedyukhina E.G., Vainshtein M.B., 2006. A review on microbial synthesis of hydrocarbons. *Process Biochemistry* **41**, 1001-1014.

- Lahav N., Chang S., 1976. The possible role of solid surface area in condensation reactions during chemical evolution: reevaluation. *Journal of Molecular Evolution* **8**, 357-380.
- Lambert I.B., Scott K.M., 1973. Implications of geochemical investigations of sedimentary rocks within and around the McArthur zinc-lead-silver deposit, Northern Territory. *Journal of Geochemical Exploration* **2**, 307-330.
- Landais P., 1996. Organic geochemistry of sedimentary uranium ore deposits. *Ore Geology Reviews* **11**, 33-51.
- Landais P., Michels R., Elie M., 1994. Are time and temperature the only constraints to the simulation of organic matter maturation? *Organic Geochemistry* **22**, 617-630.
- Large D.J., Gizé A.P., 1996. Pristane/phytane ratios in the mineralized Kupferschiefer of the Fore-Sudetic Monocline, southwest Poland. *Ore Geology Reviews* **11**, 89-103.
- Large R.R., Bull S.W., Cooke D.R., McGoldrick P.J., 1998. A genetic model for the HYC deposit, Australia: based on regional sedimentology, geochemistry, and sulfide-sediment relationships. *Economic Geology* **93**, 1345-1368.
- Large R.R., Bull S.W., McGoldrick P.J., Walters S., Derrick G.M., Carr G.R., 2005. Stratiform and strata-bound Zn-Pb-Ag deposits in Proterozoic sedimentary basins, Northern Australia. In *Economic Geology 100th Anniversary Volume* (eds. Hedenquist J.W., Thompson J.F.H., Goldfarb R.J., Richards J.P.). Society of Economic Geologists, Littleton, Colorado. pp 931-963.
- Le Métayer P., Grice K., Chow C.N., Caccetta L., Maslen E., Dawson D., Fusetti L., 2014. The effect of origin and genetic processes of low molecular weight aromatic hydrocarbons in petroleum on their stable carbon isotopic compositions. *Organic Geochemistry* **72**, 23-33.
- Leach D.L., Bradley D.C., Huston D., Pisarevsky S.A., Taylor R.D., Gardoll S.J., 2010. Sediment-hosted lead-zinc deposits in Earth history. *Economic Geology* **105**, 593-625.
- Leach D.L., Sangster D.F., Kelly K.D., Large R.R., Garven G., Allen C.R., Gutzmer J., Walters S., 2005. Sediment-hosted lead-zinc deposits: a global perspective.

- In *Economic Geology 100th Anniversary Volume* (eds. Hedenquist J.W., Thompson J.F.H., Goldfarb R.J., Richards J.P.). Society of Economic Geologists, Littleton, Colorado. pp 561-607.
- Lewan M.D., 1997. Experiments on the role of water in petroleum formation. *Geochimica et Cosmochimica Acta* **61**, 3691-3723.
- Lewan M.D., Winters J.C., McDonald J.H., 1979. Generation of oil-like pyrolyzates from organic-rich shales. *Science* **203**, 897-899.
- Lindsay J.F., Brasier M.D., 2000. A carbon isotope reference curve for ca. 1700-1575 Ma, McArthur and Mount Isa Basins, Northern Australia. *Precambrian Research* **99**, 271-308.
- Lockhart R.S., Berwick L.J., Greenwood P., Grice K., Kraal P., Bush R., 2013. Analytical pyrolysis for determining the molecular composition of contemporary monosulfidic black ooze. *Journal of Analytical and Applied Pyrolysis* **104**, 640-652.
- Logan G.A., Calver C.R., Gorjan P., Summons R.E., Hayes J.M., Walter M.R., 1999. Terminal Proterozoic mid-shelf benthic microbial mats in the Centralian Superbasin and their environmental significance. *Geochimica et Cosmochimica Acta* **63**, 1345-1358.
- Logan G.A., Hayes J.M., Hieshima G.B., Summons R.E., 1995. Terminal Proterozoic reorganization of biogeochemical cycles. *Nature* **376**, 53-56.
- Logan G.A., Hinman M.C., Walter M.R., Summons R.E., 2001. Biogeochemistry of the 1640 Ma McArthur River (HYC) lead-zinc ore and host sediments, Northern Territory, Australia. *Geochimica et Cosmochimica Acta* **65**, 2317-2336.
- Londry K.L., Jahnke L.L., Des Marais D.J., 2004. Stable carbon isotope ratios of lipid biomarkers of sulfate-reducing bacteria. *Applied and Environmental Microbiology* **70**, 745-751.
- Lyons T.W., Gellatly A.M., McGoldrick P.J., Kah L.C., 2006. Proterozoic sedimentary exhalative (SEDEX) deposits and links to evolving global ocean chemistry. *Geological Society of America Memoirs* **198**, 169-184.

M

- Machel H.G., Krouse H.R., Sassen R., 1995. Products and distinguishing criteria of bacterial and thermochemical sulfate reduction. *Applied Geochemistry* **10**, 373-389.
- Mackenzie K.L., Marshall C.P., Walter M.R., 2008. Regional organic geochemistry of host sediments of Palaeoproterozoic McArthur River Ore deposit, Australia. *Theoretical Chemistry Accounts* **119**, 143-153.
- Madigan M.T., Takigiku R., Lee R.G., Gest H., Hayes J.M., 1989. Carbon isotope fractionation by thermophilic phototrophic sulfur bacteria: evidence for autotrophic growth in natural populations. *Applied and Environmental Microbiology* **55**, 639-644.
- Mann J.L., Vocke R.D., Kelly W.R., 2009. Revised $\delta^{34}\text{S}$ reference values for IAEA sulfur isotope reference materials S-2 and S-3. *Rapid Communications in Mass Spectrometry* **23**, 1116-1124.
- Marshall C.P., Love G.D., Snape C.E., Hill A.C., Allwood A.C., Walter M.R., Van Kranendonk M.J., Bowden S.A., Sylva S.P., Summons R.E., 2007. Structural characterization of kerogen in 3.4 Ga Archaean cherts from the Pilbara Craton, Western Australia. *Precambrian Research* **155**, 1-23.
- Marzi R., Torkelson B.E., Olson R.K., 1993. A revised carbon preference index. *Organic Geochemistry* **20**, 1303-1306.
- Maslen E., Grice K., Dawson D., Wang S., Horsfield B., 2013. Stable hydrogen isotopes of isoprenoids and *n*-alkanes as a proxy for estimating the thermal history of sediments through geological time. In *Analyzing the Thermal History of Sedimentary Basins: Methods and Case Studies* (eds. Harris N.B., Peters K.E.). Society for Sedimentary Geology Special Publication No. 103, Tulsa, Oklahoma.
- Maslen E., Grice K., Gale J.D., Hallmann C., Horsfield B., 2009. Crocetane: a potential marker of photic zone euxinia in thermally mature sediments and crude oils of Devonian age. *Organic Geochemistry* **40**, 1-11.
- Matthews D.E., Hayes J.M., 1978. Isotope-ratio-monitoring gas chromatography-mass spectrometry. *Analytical Chemistry* **50**, 1465-1473.

- McCollom T.M., Simoneit B.R.T., Shock E.L., 1999. Hydrous pyrolysis of polycyclic aromatic hydrocarbons and implications for the origin of PAH in hydrothermal petroleum. *Energy & Fuels* **13**, 401-410.
- McGoldrick P., Winefield P., Bull S., Selley D., Scott R., 2010. Sequences, synsedimentary structures, and sub-basins: the where and when of SEDEX zinc systems in the southern McArthur Basin, Australia. In *The Challenge of Finding New Mineral Resources: Global Metallogeny, Innovative Exploration, and New Discoveries. Volume II: Zinc-Lead, Nickel-Copper-PGE, and Uranium* (eds. Goldfarb R.J., Marsh E.E., Monecke T.). Society of Economic Geologists Special Publication Number 15, Littleton, Colorado. pp 367-389.
- Melendez I., Grice K., Trinajstić K., Ladjavardi M., Greenwood P., Thompson K., 2013. Biomarkers reveal the role of photic zone euxinia in exceptional fossil preservation: an organic geochemical perspective. *Geology* **41**, 123-126.
- Melzer E., Schmidt H.L., 1987. Carbon isotope effects on the pyruvate dehydrogenase reaction and their importance for relative carbon-13 depletion in lipids. *Journal of Biological Chemistry* **262**, 8159-8164.
- Moldowan J.M., Sundararaman P., Schoell M., 1986. Sensitivity of biomarker properties to depositional environment and/or source input in the Lower Toarcian of SW-Germany. *Organic Geochemistry* **10**, 915-926.
- Moodley L., Middelburg J.J., Herman P.M.J., Soetaert K., de Lange G.J., 2005. Oxygenation and organic-matter preservation in marine sediments: direct experimental evidence from ancient organic carbon-rich deposits. *Geology* **33**, 889-892.
- Mueller E., Philp R.P., 1998. Extraction of high molecular weight hydrocarbons from source rocks: an example from the Green River Formation, Uinta Basin, Utah. *Organic Geochemistry* **28**, 625-631.
- Mukhopadhyay P.K., 1994. Vitrinite reflectance as maturity parameter. In *Vitrinite Reflectance as a Maturity Parameter* (eds. Mukhopadhyay P.K., Dow W.G.). American Chemical Society, Washington, D.C. pp 1-24.

Munier-Lamy C., Adrian P., Berthelin J., Rouiller J., 1986. Comparison of binding abilities of fulvic and humic acids extracted from recent marine sediments with UO_2^{2+} . *Organic Geochemistry* **9**, 285-292.

N

Nabbefeld B., Grice K., Schimmelmann A., Sauer P.E., Böttcher M.E., Twitchett R.J., 2010. Significance of δD (kerogen), $\delta^{13}\text{C}$ (kerogen) and $\delta^{34}\text{S}$ (pyrite) from several Permian/Triassic (P/Tr) sections. *Earth and Planetary Science Letters* **295**, 21-29.

Nabbefeld B., Grice K., Schimmelmann A., Summons R.E., Troitzsch U., Twitchett R.J., 2010. A comparison of thermal maturity parameters between freely extracted hydrocarbons (Bitumen I) and a second extract (Bitumen II) from within the kerogen matrix of Permian and Triassic sedimentary rocks. *Organic Geochemistry* **41**, 78-87.

Nabbefeld B., Grice K., Summons R.E., Hays L.E., Cao C., 2010. Significance of polycyclic aromatic hydrocarbons (PAHs) in Permian/Triassic boundary sections. *Applied Geochemistry* **25**, 1374-1382.

Nabbefeld B., Grice K., Twitchett R.J., Summons R.E., Hays L., Böttcher M.E., Asif M., 2010. An integrated biomarker, isotopic and palaeoenvironmental study through the Late Permian event at Lusitaniadalen, Spitsbergen. *Earth and Planetary Science Letters* **291**, 84-96.

O

Orr W.L., 1986. Kerogen/asphaltene/sulfur relationships in sulfur-rich Monterey oils. *Organic Geochemistry* **10**, 499-516.

Overmann J., 2006. The family Chlorobiaceae. In *The Prokaryotes Volume 7: Proteobacteria: Delta, Epsilon Subclass* (eds. Dworkin M., Falkow S., Rosenberg E., Schleifer K.-H., Stackebrandt E.). Springer, New York. pp 359-378.

P

- Page R.W., Jackson M.J., Krassay A.A., 2000. Constraining sequence stratigraphy in north Australian basins: SHRIMP U–Pb zircon geochronology between Mt Isa and McArthur River. *Australian Journal of Earth Sciences* **47**, 431-459.
- Page R.W., Sweet I.P., 1998. Geochronology of basin phases in the western Mt Isa Inlier, and correlation with the McArthur Basin. *Australian Journal of Earth Sciences* **45**, 219-232.
- Passier H.F., Böttcher M.E., De Lange G.J., 1999. Sulphur enrichment in organic matter of eastern Mediterranean sapropels: a study of sulphur isotope partitioning. *Aquatic Geochemistry* **5**, 99-118.
- Pawlowska M.M., Butterfield N.J., Brocks J.J., 2013. Lipid taphonomy in the Proterozoic and the effect of microbial mats on biomarker preservation. *Geology* **41**, 103-106.
- Peters K.E., Walters C.C., Moldowan J.M., 2005. *The Biomarker Guide Volume 1 - Biomarkers and Isotopes in the Environment and Human History*. Cambridge University Press, Cambridge.
- Peters K.E., Walters C.C., Moldowan J.M., 2005. *The Biomarker Guide Volume 2 - Biomarkers and Isotopes in Petroleum Exploration and Earth History*. Cambridge University Press, Cambridge.
- Planavsky N.J., McGoldrick P., Scott C.T., Li C., Reinhard C.T., Kelly A.E., Chu X., Bekker A., Love G.D., Lyons T.W., 2011. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448-451.
- Plumb K.A., 1979. Structure and tectonic style of the Precambrian shields and platforms of northern Australia. *Tectonophysics* **58**, 291-325.
- Poulton S.W., Fralick P.W., Canfield D.E., 2010. Spatial variability in oceanic redox structure 1.8 billion years ago. *Nature Geoscience* **3**, 486-490.
- Powell T.G., Jackson M.J., Sweet I.P., Crick I.H., Boreham C.J., Summons R.E., 1987. Petroleum geology and geochemistry, Middle Proterozoic McArthur Basin. Australia Bureau of Mineral Resources, Geology and Geophysics, record 1987/48.

- Poynter J., Eglinton G., 1990. Molecular composition of three sediments from hole 717C: The Bengal Fan. In *Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 116* (eds. Cochran J.R., Stow D.A.V.). Ocean Drilling Program, College Station, Texas. pp 155-161.
- Price F.T., Shieh Y.N., 1979. Fractionation of sulfur isotopes during laboratory synthesis of pyrite at low temperatures. *Chemical Geology* **27**, 245-253.
- Price L.C., 1993. Thermal stability of hydrocarbons in nature: limits, evidence, characteristics, and possible controls. *Geochimica et Cosmochimica Acta* **57**, 3261-3280.
- Price L.C., Clayton J.L., 1992. Extraction of whole versus ground source rocks: fundamental petroleum geochemical implications including oil-source rock correlation. *Geochimica et Cosmochimica Acta* **56**, 1213-1222.
- Püttmann W., Fermont W.J.J., Speczik S., 1991. The possible role of organic matter in transport and accumulation of metals exemplified at the Permian Kupferschiefer formation. *Ore Geology Reviews* **6**, 563-579.
- Püttmann W., Merz C., Speczik S., 1989. The secondary oxidation of organic material and its influence on Kupferschiefer mineralization of southwest Poland. *Applied Geochemistry* **4**, 151-161.

Q

R

- Radke M., 1988. Application of aromatic compounds as maturity indicators in source rocks and crude oils. *Marine and Petroleum Geology* **5**, 224-236.
- Radke M., Welte D.H., Willsch H., 1982. Geochemical study on a well in the Western Canada Basin: relation of the aromatic distribution pattern to maturity of organic matter. *Geochimica et Cosmochimica Acta* **46**, 1-10.
- Radke M., Welte D.H., Willsch H., 1986. Maturity parameters based on aromatic hydrocarbons: influence of the organic matter type. *Organic Geochemistry* **10**, 51-63.

- Radke M., Willsch H., Leythaeuser D., Teichmüller M., 1982. Aromatic components of coal: relation of distribution pattern to rank. *Geochimica et Cosmochimica Acta* **46**, 1831-1848.
- Raven M.R., Sessions A., Adkins J., 2013. The sulfur isotopic compositions of individual organic compounds in Cariaco Basin, In: González-Pérez J.A., González-Vila F.J., Jiménez-Morillo N.T., Almendros G. (Eds.), 26th International Meeting on Organic Geochemistry, Tenerife.
- Rawlings D.J., Korsch R.J., Goleby B.R., Gibson G.M., Johnstone D.W., Barlow M., 2004. The 2002 Southern McArthur Basin Seismic Reflection Survey, Geoscience Australia record 2004/17, Canberra.
- Řezanka T., Sokolov M.Y., Viden I., 1990. Unusual and very-long-chain fatty acids in *Desulfotomaculum*, a sulfate-reducing bacterium. *FEMS Microbiology Letters* **73**, 231-237.
- Rieger A., Schwark L., Cisternas M.-E., Miller H., 2008. Genesis and evolution of bitumen in Lower Cretaceous lavas and implications for strata-bound copper deposits, North Chile. *Economic Geology* **103**, 387-404.
- Robl T.L., Davis B.H., 1993. Comparison of the HF-HCl and HF-BF₃ maceration techniques and the chemistry of resultant organic concentrates. *Organic Geochemistry* **20**, 249-255.
- Rospondek M.J., Marynowski L., Chachaj A., Góra M., 2009. Novel aryl polycyclic aromatic hydrocarbons: phenylphenanthrene and phenylanthracene identification, occurrence and distribution in sedimentary rocks. *Organic Geochemistry* **40**, 986-1004.
- Rospondek M.J., Marynowski L., Góra M., 2007. Novel arylated polyaromatic thiophenes: Phenyl-naphtho[b]thiophenes and naphthylbenzo[b]thiophenes as markers of organic matter diagenesis buffered by oxidising solutions. *Organic Geochemistry* **38**, 1729-1756.

S

- Safarik I., Strausz O.P., 1997. The thermal decomposition of hydrocarbons. Part 2. Alkylaromatic hydrocarbons: alkylbenzenes. *Research on Chemical Intermediates* **23**, 63-99.
- Sauer P.E., Schimmelmann A., Sessions A.L., Topalov K., 2009. Simplified batch equilibration for D/H determination of non-exchangeable hydrogen in solid organic material. *Rapid Communications in Mass Spectrometry* **23**, 949-956.
- Saxby J.D., 1970. Isolation of kerogen in sediments by chemical methods. *Chemical Geology* **6**, 173-184.
- Schenk H.J., Horsfield B., 1993. Kinetics of petroleum generation by programmed-temperature closed-versus open-system pyrolysis. *Geochimica et Cosmochimica Acta* **57**, 623-630.
- Schidlowski M., 1988. A 3,800-million-year isotopic record of life from carbon in sedimentary rocks. *Nature* **333**, 313-318.
- Schimmelmann A., Sessions A.L., Mastalerz M., 2006. Hydrogen isotopic (D/H) composition of organic matter during diagenesis and thermal maturation. *Annual Review of Earth and Planetary Sciences* **34**, 501-533.
- Schwark L., Püttmann W., 1990. Aromatic hydrocarbon composition of the Permian Kupferschiefer in the Lower Rhine Basin, NW Germany. *Organic Geochemistry* **16**, 749-761.
- Schwark L., Stoddart D., Keuser C., Spitthoff B., Leythaeuser D., 1997. A novel sequential extraction system for whole core plug extraction in a solvent flow-through cell — application to extraction of residual petroleum from an intact pore-system in secondary migration studies. *Organic Geochemistry* **26**, 19-31.
- Seal R.R., 2006. Sulfur isotope geochemistry of sulfide minerals. *Reviews in Mineralogy and Geochemistry* **61**, 633-677.
- Seewald J.S., 2001. Aqueous geochemistry of low molecular weight hydrocarbons at elevated temperatures and pressures: constraints from mineral buffered laboratory experiments. *Geochimica et Cosmochimica Acta* **65**, 1641-1664.

- Seifert W.K., Moldowan J.M., 1978. Applications of steranes, terpanes and monoaromatics to the maturation, migration and source of crude oils. *Geochimica et Cosmochimica Acta* **42**, 77-95.
- Sessions A.L., 2006. Isotope-ratio detection for gas chromatography. *Journal of Separation Science* **29**, 1946-1961.
- Sessions A.L., Burgoyne T.W., Schimmelmann A., Hayes J.M., 1999. Fractionation of hydrogen isotopes in lipid biosynthesis. *Organic Geochemistry* **30**, 1193-1200.
- Shen Y., Canfield D.E., Knoll A.H., 2002. Middle Proterozoic ocean chemistry: evidence from the McArthur Basin, northern Australia. *American Journal of Science* **302**, 81-109.
- Sherman L.S., Waldbauer J.R., Summons R.E., 2007. Improved methods for isolating and validating indigenous biomarkers in Precambrian rocks. *Organic Geochemistry* **38**, 1987-2000.
- Sicree A.A., Barnes H.L., 1996. Upper Mississippi Valley district ore fluid model: the role of organic complexes. *Ore Geology Reviews* **11**, 105-131.
- Sim M.S., Bosak T., Ono S., 2011. Large sulfur isotope fractionation does not require disproportionation. *Science* **333**, 74-77.
- Simoneit B.R.T., 1994. Lipid/bitumen maturation by hydrothermal activity in sediments of Middle Valley, Leg 139. In *Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 139* (eds. Mottl M.J., Davis E.E., Fisher A.T., Slack J.F.). Ocean Drilling Program, College Station, Texas. pp 447-465.
- Simoneit B.R.T., Lein A.Y., Peresykin V.I., Osipov G.A., 2004. Composition and origin of hydrothermal petroleum and associated lipids in the sulfide deposits of the Rainbow Field (Mid-Atlantic Ridge at 36°N). *Geochimica et Cosmochimica Acta* **68**, 2275-2294.
- Sinninghe Damsté J.S., de Leeuw J.W., 1990. Analysis, structure and geochemical significance of organically-bound sulphur in the geosphere: state of the art and future research. *Organic Geochemistry* **16**, 1077-1101.

- Sinninghe Damsté J.S., Kohnen M.E.L., Horsfield B., 1998. Origin of low-molecular-weight alkylthiophenes in pyrolysates of sulphur-rich kerogens as revealed by micro-scale sealed vessel pyrolysis. *Organic Geochemistry* **29**, 1891-1903.
- Skrzypek G., Paul D., 2006. $\delta^{13}\text{C}$ analyses of calcium carbonate: comparison between the GasBench and elemental analyzer techniques. *Rapid Communications in Mass Spectrometry* **20**, 2915-2920.
- Smith J.W., George S.C., Batts B.D., 1995. The geosynthesis of alkylaromatics. *Organic Geochemistry* **23**, 71-80.
- Spangenberg J.E., Macko S.A., 1998. Organic geochemistry of the San Vicente zinc-lead district, eastern Pucará Basin, Peru. *Chemical Geology* **146**, 1-23.
- Spirakis C.S., 1996. The roles of organic matter in the formation of uranium deposits in sedimentary rocks. *Ore Geology Reviews* **11**, 53-69.
- Steenbergen C.L.M., Korthals H.J., 1982. Distribution of phototrophic microorganisms in the anaerobic and microaerophilic strata of Lake Vechten (The Netherlands). Pigment analysis and role in primary production. *Limnology and Oceanography* **27**, 883-895.
- Steger H.F., Desjardins L.E., 1980. Oxidation of sulfide minerals. V. Galena, sphalerite and chalcocite. *The Canadian Mineralogist* **18**, 365-372.
- Stein S.E., 1978. On the high temperature chemical equilibria of polycyclic aromatic hydrocarbons. *The Journal of Physical Chemistry* **82**, 566-571.
- Strauss H., 1993. The sulfur isotopic record of Precambrian sulfates: new data and a critical evaluation of the existing record. *Precambrian Research* **63**, 225-246.
- Summons R.E., Powell T.G., 1987. Identification of aryl isoprenoids in source rocks and crude oils: biological markers for the green sulphur bacteria. *Geochimica et Cosmochimica Acta* **51**, 557-566.
- Summons R.E., Powell T.G., Boreham C.J., 1988. Petroleum geology and geochemistry of the Middle Proterozoic McArthur Basin, Northern Australia: III. Composition of extractable hydrocarbons. *Geochimica et Cosmochimica Acta* **52**, 1747-1763.

Summons R.E., Taylor D., Boreham C.J., 1994. Geochemical tools for evaluating petroleum generation in Middle Proterozoic sediments of the McArthur Basin, Northern Territory, Australia. *The APEA Journal* **34**, 692-706.

Sun Y.-Z., 1998. Influences of secondary oxidation and sulfide formation on several maturity parameters in Kupferschiefer. *Organic Geochemistry* **29**, 1419-1429.

Szczerba M., Rospondek M.J., 2010. Controls on distributions of methylphenanthrenes in sedimentary rock extracts: critical evaluation of existing geochemical data from molecular modelling. *Organic Geochemistry* **41**, 1297-1311.

T

Theng B.K.G., Aislabie J., Fraser R., 2001. Bioavailability of phenanthrene intercalated into an alkylammonium–montmorillonite clay. *Soil Biology and Biochemistry* **33**, 845-848.

U

V

Vahrman M., Watts R.H., 1972. The smaller molecules obtainable from coal and their significance: Part 6. Hydrocarbons from coal heated in thin layers. *Fuel* **51**, 235-241.

van Aarssen B.G.K., Bastow T.P., Alexander R., Kagi R.I., 1999. Distributions of methylated naphthalenes in crude oils: indicators of maturity, biodegradation and mixing. *Organic Geochemistry* **30**, 1213-1227.

van Graas G.W., 1990. Biomarker maturity parameters for high maturities: calibration of the working range up to the oil/condensate threshold. *Organic Geochemistry* **16**, 1025-1032.

Vandenbroucke M., Largeau C., 2007. Kerogen origin, evolution and structure. *Organic Geochemistry* **38**, 719-833.

- Venkatesan M.I., Dahl J., 1989. Organic geochemical evidence for global fires at the Cretaceous/Tertiary boundary. *Nature* **338**, 57-60.
- Vogl K., Glaeser J., Pfannes K., Wanner G., Overmann J., 2006. *Chlorobium chlorochromatii* sp. nov., a symbiotic green sulfur bacterium isolated from the phototrophic consortium "Chlorochromatium aggregatum". *Archives of Microbiology* **185**, 363-372.
- Voigtmann M.F., Yang K., Batts B.D., Smith J.W., 1994. Evidence for synthetic generation of methylphenanthrenes in sediments. *Fuel* **73**, 1899-1903.
- Volkman J.K., 2003. Sterols in microorganisms. *Applied Microbiology and Biotechnology* **60**, 495-506.

W

- Wächtershäuser G., 1988. Before enzymes and templates: theory of surface metabolism. *Microbiological Reviews* **52**, 452-484.
- Wakeham S.G., Schaffner C., Giger W., 1980. Polycyclic aromatic hydrocarbons in Recent lake sediments—I. Compounds having anthropogenic origins. *Geochimica et Cosmochimica Acta* **44**, 403-413.
- Wakeham S.G., Schaffner C., Giger W., 1980. Polycyclic aromatic hydrocarbons in Recent lake sediments—II. Compounds derived from biogenic precursors during early diagenesis. *Geochimica et Cosmochimica Acta* **44**, 415-429.
- Waldbauer J.R., Sherman L.S., Sumner D.Y., Summons R.E., 2009. Late Archean molecular fossils from the Transvaal Supergroup record the antiquity of microbial diversity and aerobiosis. *Precambrian Research* **169**, 28-47.
- Walker R.N., Logan R.G., Binnekamp J.G., 1977. Recent geological advances concerning the H.Y.C. and associated deposits, McArthur River, N.T. *Journal of the Geological Society of Australia* **24**, 365-380.
- Werne J.P., Lyons T.W., Hollander D.J., Formolo M.J., Sinninghe Damsté J.S., 2003. Reduced sulfur in euxinic sediments of the Cariaco Basin: sulfur isotope constraints on organic sulfur formation. *Chemical Geology* **195**, 159-179.

- Werne J.P., Lyons T.W., Hollander D.J., Schouten S., Hopmans E.C., Sinninghe Damsté J.S., 2008. Investigating pathways of diagenetic organic matter sulfurization using compound-specific sulfur isotope analysis. *Geochimica et Cosmochimica Acta* **72**, 3489-3502.
- Werner R.A., Brand W.A., 2001. Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Communications in Mass Spectrometry* **15**, 501-519.
- Wilhelms A., Horstad I., Karlsen D., 1996. Sequential extraction—a useful tool for reservoir geochemistry? *Organic Geochemistry* **24**, 1157-1172.
- Williams N., 1978. Studies of the base metal sulfide deposits at McArthur River, Northern Territory, Australia: I. The Cooley and Ridge deposits. *Economic Geology* **73**, 1005-1035.
- Williford K.H., Grice K., Logan G.A., Chen J., Huston D., 2011. The molecular and isotopic effects of hydrothermal alteration of organic matter in the Paleoproterozoic McArthur River Pb/Zn/Ag ore deposit. *Earth and Planetary Science Letters* **301**, 382-392.
- Wise S.A., Campbell R.M., West W.R., Lee M.L., Bartle K.D., 1986. Characterization of polycyclic aromatic hydrocarbon minerals curtisite, idrialite and pendletonite using high-performance liquid chromatography, gas chromatography, mass spectrometry and nuclear magnetic resonance spectroscopy. *Chemical Geology* **54**, 339-357.
- Wortmann U.G., Bernasconi S.M., Böttcher M.E., 2001. Hypersulfidic deep biosphere indicates extreme sulfur isotope fractionation during single-step microbial sulfate reduction. *Geology* **29**, 647-650.

X**Y**

Yücel M., Konovalov S.K., Moore T.S., Janzen C.P., Luther G.W., 2010. Sulfur speciation in the upper Black Sea sediments. *Chemical Geology* **269**, 364-375.

Z

Zerkle A.L., Farquhar J., Johnston D.T., Cox R.P., Canfield D.E., 2009. Fractionation of multiple sulfur isotopes during phototrophic oxidation of sulfide and elemental sulfur by a green sulfur bacterium. *Geochimica et Cosmochimica Acta* **73**, 291-306.

Zhang J.-Z., Millero F.J., 1993. The products from the oxidation of H₂S in seawater. *Geochimica et Cosmochimica Acta* **57**, 1705-1718.

Zopfi J., Böttcher M.E., Jørgensen B.B., 2008. Biogeochemistry of sulfur and iron in Thioploca-colonized surface sediments in the upwelling area off central Chile. *Geochimica et Cosmochimica Acta* **72**, 827-843.

Zopfi J., Ferdelman T.G., Fossing H., 2004. Distribution and fate of sulfur intermediates - sulfite, tetrathionate, thiosulfate, and elemental sulfur - in marine sediments. In *Sulfur Biogeochemistry - Past and Present* (eds. Amend J.P., Edwards K.J., Lyons T.W.). Geological Society of America Special Paper 379, Boulder, Colorado. pp 97-116.

Appendix

The following pages detail the rights granted by Elsevier, to the first author of the publications that form **Chapter 2**, **Chapter 3**, **Chapter 4** and **Chapter 5** of this thesis, to reproduce the full article in a thesis or dissertation.

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Jan 16, 2014

This is a License Agreement between Alex Holman ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Alex Holman
Customer address	6 Omaha Court Gosnells, WA 6110
License number	3311030049163
License date	Jan 16, 2014
Licensed content publisher	Elsevier
Licensed content publication	Organic Geochemistry
Licensed content title	Efficiency of extraction of polycyclic aromatic hydrocarbons from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag ore deposit and implications for a study of Bitumen II
Licensed content author	Alex I. Holman, Kliti Grice, Caroline M.B. Jaraula, Arndt Schimmelmann, Jochen J. Brocks
Licensed content date	November 2012
Licensed content volume number	52
Licensed content issue number	
Number of pages	7
Start Page	81
End Page	87
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your	Organic Geochemistry of the Paleoproterozoic Here's

thesis/dissertation	Your Chance Pb/Zn/Ag Deposit
Expected completion date	Jan 2014
Estimated size (number of pages)	175
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.

3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:

"Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit - "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."

4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.

5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)

6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.

7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. Warranties: Publisher makes no representations or warranties with respect to the licensed material.

10. Indemnity: You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. No Transfer of License: This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. No Amendment Except in Writing: This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. Objection to Contrary Terms: Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. Revocation: Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. **Website:** The following terms and conditions apply to electronic reserve and author websites:

Electronic reserve: If licensed material is to be posted to website, the web site is to be password-protected and made available only to bona fide students registered on a relevant course if:

This license was made in connection with a course,

This permission is granted for 1 year only. You may obtain a license for future website posting,

All content posted to the web site must maintain the copyright information line on the bottom of each image,

A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com> , and

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

17. **Author website** for journals with the following additional clauses:

All content posted to the web site must maintain the copyright information line on the bottom of each image, and the permission granted is limited to the personal version of your paper. You are not allowed to download and post the published electronic version of your article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> . As part of our normal production

process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

18. Author website for books with the following additional clauses:

Authors are permitted to place a brief summary of their work online only.

A hyper-text must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version.

Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

19. Website (regular and for author): A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx>. or for books to the Elsevier homepage at <http://www.elsevier.com>

20. Thesis/Dissertation: If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

21. Other Conditions:

v1.6

If you would like to pay for this license now, please remit this license along with your payment made payable to "COPYRIGHT CLEARANCE CENTER" otherwise you will be invoiced within 48 hours of the license date. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501203908.

Once you receive your invoice for this order, you may pay your invoice by credit card. Please follow instructions provided at that time.

Make Payment To:
Copyright Clearance Center
Dept 001
P.O. Box 843006
Boston, MA 02284-3006

For suggestions or comments regarding this order, contact RightsLink Customer Support: customercare@copyright.com or +1-877-622-5543 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Sep 11, 2014

This is a License Agreement between Alex Holman ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Alex Holman
Customer address	6 Omaha Court Gosnells, WA 6110
License number	3465731270195
License date	Sep 11, 2014
Licensed content publisher	Elsevier
Licensed content publication	Geochimica et Cosmochimica Acta
Licensed content title	Bitumen II from the Paleoproterozoic Here's Your Chance Pb/Zn/Ag deposit: Implications for the analysis of depositional environment and thermal maturity of hydrothermally-altered sediments
Licensed content author	Alex I. Holman, Kliti Grice, Caroline M.B. Jaraula, Arndt Schimmelmann
Licensed content date	15 August 2014
Licensed content volume number	139
Licensed content issue number	n/a
Number of pages	12
Start Page	98
End Page	109
Type of Use	reuse in a thesis/dissertation
Portion	full article
Format	both print and electronic

Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Organic Geochemistry of the Paleoproterozoic Here's Your Chance Pb/Zn/Ag Deposit
Expected completion date	Sep 2014
Estimated size (number of pages)	170
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD

Terms and Conditions

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
 "Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit -
 "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may

attract a fee.

7. **Reservation of Rights:** Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or

invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting. **For journal authors:** the following clauses are applicable in addition to the above: Permission granted is limited to the author accepted manuscript version* of your paper.

***Accepted Author Manuscript (AAM) Definition:** An accepted author manuscript (AAM) is the author's version of the manuscript of an article that has been accepted for publication and which may include any author-incorporated changes suggested through the processes of submission processing, peer review, and editor-author communications. AAMs do not include other publisher value-added contributions such as copy-editing, formatting, technical enhancements and (if relevant) pagination.

You are not allowed to download and post the published journal article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at

<http://www.sciencedirect.com/science/journal/xxxxx>. As part of our normal production process, you will receive an e-mail notice when your article appears on

Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Posting to a repository: Authors may post their AAM immediately to their employer's institutional repository for internal use only and may make their manuscript publically available after the journal-specific embargo period has ended. Please also refer to [Elsevier's Article Posting Policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only.. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

20. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Elsevier Open Access Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals.

Authors publishing in an Open Access journal or who choose to make their article Open Access in an Elsevier subscription journal select one of the following Creative Commons user licenses, which define how a reader may reuse their work: Creative Commons Attribution License (CC BY), Creative Commons Attribution – Non Commercial - ShareAlike (CC BY NC SA) and Creative Commons Attribution – Non Commercial – No Derivatives (CC BY NC ND)

Terms & Conditions applicable to all Elsevier Open Access articles:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation.

The author(s) must be appropriately credited.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: You may distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text or data mine the article, including for commercial purposes without permission from Elsevier

CC BY NC SA: For non-commercial purposes you may distribute and copy the article, create extracts, abstracts and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text and data mine the article and license new adaptations or creations under identical terms without permission from Elsevier

CC BY NC ND: For non-commercial purposes you may distribute and copy the article and include it in a collective work (such as an anthology), provided you do not alter or modify the article, without permission from Elsevier

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Promotional purposes (advertising or marketing)
- Commercial exploitation (e.g. a product for sale or loan)
- Systematic distribution (for a fee or free of charge)

Please refer to [Elsevier's Open Access Policy](#) for further information.

21. Other Conditions:

v1.6

You will be invoiced within 48 hours of this transaction date. You may pay your invoice by credit card upon receipt of the invoice for this transaction. Please follow instructions provided at that time.

To pay for this transaction now; please remit a copy of this document along with your payment. Payment should be in the form of a check or money order referencing your account number and this invoice number RLNK501399912.

Make payments to "COPYRIGHT CLEARANCE CENTER" and send to:

Copyright Clearance Center

Dept 001

P.O. Box 843006

Boston, MA 02284-3006

Please disregard electronic and mailed copies if you remit payment in advance.

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

**ELSEVIER LICENSE
TERMS AND CONDITIONS**

Sep 18, 2014

This is a License Agreement between Alex Holman ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Alex Holman
Customer address	6 Omaha Court Gosnells, WA 6110
License number	3471730972933
License date	Sep 18, 2014
Licensed content publisher	Elsevier
Licensed content publication	Organic Geochemistry
Licensed content title	Effects of sulfide minerals on aromatic maturity parameters: Laboratory investigation using micro-scale sealed vessel pyrolysis
Licensed content author	Alex I. Holman, Paul F. Greenwood, Jochen J. Brocks, Kliti Grice
Licensed content date	Available online 16 September 2014
Licensed content volume number	n/a
Licensed content issue number	n/a
Number of pages	1
Start Page	None
End Page	None
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	full article
Format	both print and electronic
Are you the author of this Elsevier article?	Yes
Will you be translating?	No

Title of your thesis/dissertation	Organic Geochemistry of the Paleoproterozoic Here's Your Chance Pb/Zn/Ag Deposit
Expected completion date	Sep 2014
Estimated size (number of pages)	
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
 "Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit -
 "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may attract a fee.
7. Reservation of Rights: Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.
8. License Contingent Upon Payment: While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received

from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. **Translation:** This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. **Posting licensed content on any Website:** The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which

you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting.

For journal authors: the following clauses are applicable in addition to the above: Permission granted is limited to the author accepted manuscript version* of your paper.

***Accepted Author Manuscript (AAM) Definition:** An accepted author manuscript (AAM) is the author's version of the manuscript of an article that has been accepted for publication and which may include any author-incorporated changes suggested through the processes of submission processing, peer review, and editor-author communications. AAMs do not include other publisher value-added contributions such as copy-editing, formatting, technical enhancements and (if relevant) pagination.

You are not allowed to download and post the published journal article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing at

<http://www.sciencedirect.com/science/journal/xxxxx>. As part of our normal production process, you will receive an e-mail notice when your article appears on Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Posting to a repository: Authors may post their AAM immediately to their employer's institutional repository for internal use only and may make their manuscript publically available after the journal-specific embargo period has ended. Please also refer to [Elsevier's Article Posting Policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only.. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

20. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Elsevier Open Access Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals.

Authors publishing in an Open Access journal or who choose to make their article Open Access in an Elsevier subscription journal select one of the following Creative Commons user licenses, which define how a reader may reuse their work: Creative Commons Attribution License (CC BY), Creative Commons Attribution – Non Commercial - ShareAlike (CC BY NC SA) and Creative Commons Attribution – Non Commercial – No Derivatives (CC BY NC ND)

Terms & Conditions applicable to all Elsevier Open Access articles:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation.

The author(s) must be appropriately credited.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: You may distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text or data mine the article, including for commercial purposes without permission from Elsevier

CC BY NC SA: For non-commercial purposes you may distribute and copy the article, create extracts, abstracts and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text and data mine the article and license new adaptations or creations under identical terms without permission from Elsevier

CC BY NC ND: For non-commercial purposes you may distribute and copy the article and include it in a collective work (such as an anthology), provided you do not alter or modify the article, without permission from Elsevier

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Promotional purposes (advertising or marketing)
- Commercial exploitation (e.g. a product for sale or loan)
- Systematic distribution (for a fee or free of charge)

Please refer to [Elsevier's Open Access Policy](#) for further information.

21. Other Conditions: Permission is granted to submit your article in electronic format. This license permits you to post this Elsevier article online if it is embedded within your thesis. You are also permitted to post your Author Accepted Manuscript online however, posting of the final published article is prohibited. Please refer to Elsevier's Posting Policy for further information:

<http://www.elsevier.com/wps/find/authors.authors/postingpolicy>

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.

ELSEVIER LICENSE
TERMS AND CONDITIONS

Sep 17, 2014

This is a License Agreement between Alex Holman ("You") and Elsevier ("Elsevier") provided by Copyright Clearance Center ("CCC"). The license consists of your order details, the terms and conditions provided by Elsevier, and the payment terms and conditions.

All payments must be made in full to CCC. For payment instructions, please see information listed at the bottom of this form.

Supplier	Elsevier Limited The Boulevard, Langford Lane Kidlington, Oxford, OX5 1GB, UK
Registered Company Number	1982084
Customer name	Alex Holman
Customer address	6 Omaha Court Gosnells, WA 6110
License number	3471160792157
License date	Sep 17, 2014
Licensed content publisher	Elsevier
Licensed content publication	Chemical Geology
Licensed content title	New aspects of sulfur biogeochemistry during ore deposition from $\delta^{34}\text{S}$ of elemental sulfur and organic sulfur from the Here's Your Chance Pb/Zn/Ag deposit
Licensed content author	Alex I. Holman, Kliti Grice, Paul F. Greenwood, Michael E. Böttcher, John L. Walshe, Katy A. Evans
Licensed content date	10 November 2014
Licensed content volume number	387
Licensed content issue number	n/a
Number of pages	7
Start Page	126
End Page	132
Type of Use	reuse in a thesis/dissertation
Intended publisher of new work	other
Portion	full article
Format	both print and electronic

Are you the author of this Elsevier article?	Yes
Will you be translating?	No
Title of your thesis/dissertation	Organic Geochemistry of the Paleoproterozoic Here's Your Chance Pb/Zn/Ag Deposit
Expected completion date	Sep 2014
Estimated size (number of pages)	170
Elsevier VAT number	GB 494 6272 12
Permissions price	0.00 USD
VAT/Local Sales Tax	0.00 USD / 0.00 GBP
Total	0.00 USD
Terms and Conditions	

INTRODUCTION

1. The publisher for this copyrighted material is Elsevier. By clicking "accept" in connection with completing this licensing transaction, you agree that the following terms and conditions apply to this transaction (along with the Billing and Payment terms and conditions established by Copyright Clearance Center, Inc. ("CCC"), at the time that you opened your Rightslink account and that are available at any time at <http://myaccount.copyright.com>).

GENERAL TERMS

2. Elsevier hereby grants you permission to reproduce the aforementioned material subject to the terms and conditions indicated.
3. Acknowledgement: If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source, permission must also be sought from that source. If such permission is not obtained then that material may not be included in your publication/copies. Suitable acknowledgement to the source must be made, either as a footnote or in a reference list at the end of your publication, as follows:
 "Reprinted from Publication title, Vol /edition number, Author(s), Title of article / title of chapter, Pages No., Copyright (Year), with permission from Elsevier [OR APPLICABLE SOCIETY COPYRIGHT OWNER]." Also Lancet special credit -
 "Reprinted from The Lancet, Vol. number, Author(s), Title of article, Pages No., Copyright (Year), with permission from Elsevier."
4. Reproduction of this material is confined to the purpose and/or media for which permission is hereby given.
5. Altering/Modifying Material: Not Permitted. However figures and illustrations may be altered/adapted minimally to serve your work. Any other abbreviations, additions, deletions and/or any other alterations shall be made only with prior written authorization of Elsevier Ltd. (Please contact Elsevier at permissions@elsevier.com)
6. If the permission fee for the requested use of our material is waived in this instance, please be advised that your future requests for Elsevier materials may

attract a fee.

7. **Reservation of Rights:** Publisher reserves all rights not specifically granted in the combination of (i) the license details provided by you and accepted in the course of this licensing transaction, (ii) these terms and conditions and (iii) CCC's Billing and Payment terms and conditions.

8. **License Contingent Upon Payment:** While you may exercise the rights licensed immediately upon issuance of the license at the end of the licensing process for the transaction, provided that you have disclosed complete and accurate details of your proposed use, no license is finally effective unless and until full payment is received from you (either by publisher or by CCC) as provided in CCC's Billing and Payment terms and conditions. If full payment is not received on a timely basis, then any license preliminarily granted shall be deemed automatically revoked and shall be void as if never granted. Further, in the event that you breach any of these terms and conditions or any of CCC's Billing and Payment terms and conditions, the license is automatically revoked and shall be void as if never granted. Use of materials as described in a revoked license, as well as any use of the materials beyond the scope of an unrevoked license, may constitute copyright infringement and publisher reserves the right to take any and all action to protect its copyright in the materials.

9. **Warranties:** Publisher makes no representations or warranties with respect to the licensed material.

10. **Indemnity:** You hereby indemnify and agree to hold harmless publisher and CCC, and their respective officers, directors, employees and agents, from and against any and all claims arising out of your use of the licensed material other than as specifically authorized pursuant to this license.

11. **No Transfer of License:** This license is personal to you and may not be sublicensed, assigned, or transferred by you to any other person without publisher's written permission.

12. **No Amendment Except in Writing:** This license may not be amended except in a writing signed by both parties (or, in the case of publisher, by CCC on publisher's behalf).

13. **Objection to Contrary Terms:** Publisher hereby objects to any terms contained in any purchase order, acknowledgment, check endorsement or other writing prepared by you, which terms are inconsistent with these terms and conditions or CCC's Billing and Payment terms and conditions. These terms and conditions, together with CCC's Billing and Payment terms and conditions (which are incorporated herein), comprise the entire agreement between you and publisher (and CCC) concerning this licensing transaction. In the event of any conflict between your obligations established by these terms and conditions and those established by CCC's Billing and Payment terms and conditions, these terms and conditions shall control.

14. **Revocation:** Elsevier or Copyright Clearance Center may deny the permissions described in this License at their sole discretion, for any reason or no reason, with a full refund payable to you. Notice of such denial will be made using the contact information provided by you. Failure to receive such notice will not alter or

invalidate the denial. In no event will Elsevier or Copyright Clearance Center be responsible or liable for any costs, expenses or damage incurred by you as a result of a denial of your permission request, other than a refund of the amount(s) paid by you to Elsevier and/or Copyright Clearance Center for denied permissions.

LIMITED LICENSE

The following terms and conditions apply only to specific license types:

15. Translation: This permission is granted for non-exclusive world **English** rights only unless your license was granted for translation rights. If you licensed translation rights you may only translate this content into the languages you requested. A professional translator must perform all translations and reproduce the content word for word preserving the integrity of the article. If this license is to re-use 1 or 2 figures then permission is granted for non-exclusive world rights in all languages.

16. Posting licensed content on any Website: The following terms and conditions apply as follows: Licensing material from an Elsevier journal: All content posted to the web site must maintain the copyright information line on the bottom of each image; A hyper-text must be included to the Homepage of the journal from which you are licensing at <http://www.sciencedirect.com/science/journal/xxxxx> or the Elsevier homepage for books at <http://www.elsevier.com>; Central Storage: This license does not include permission for a scanned version of the material to be stored in a central repository such as that provided by Heron/XanEdu.

Licensing material from an Elsevier book: A hyper-text link must be included to the Elsevier homepage at <http://www.elsevier.com>. All content posted to the web site must maintain the copyright information line on the bottom of each image.

Posting licensed content on Electronic reserve: In addition to the above the following clauses are applicable: The web site must be password-protected and made available only to bona fide students registered on a relevant course. This permission is granted for 1 year only. You may obtain a new license for future website posting. **For journal authors:** the following clauses are applicable in addition to the above: Permission granted is limited to the author accepted manuscript version* of your paper.

***Accepted Author Manuscript (AAM) Definition:** An accepted author manuscript (AAM) is the author's version of the manuscript of an article that has been accepted for publication and which may include any author-incorporated changes suggested through the processes of submission processing, peer review, and editor-author communications. AAMs do not include other publisher value-added contributions such as copy-editing, formatting, technical enhancements and (if relevant) pagination.

You are not allowed to download and post the published journal article (whether PDF or HTML, proof or final version), nor may you scan the printed edition to create an electronic version. A hyper-text must be included to the Homepage of the journal from which you are licensing

at <http://www.sciencedirect.com/science/journal/xxxxx>. As part of our normal production process, you will receive an e-mail notice when your article appears on

Elsevier's online service ScienceDirect (www.sciencedirect.com). That e-mail will include the article's Digital Object Identifier (DOI). This number provides the electronic link to the published article and should be included in the posting of your personal version. We ask that you wait until you receive this e-mail and have the DOI to do any posting.

Posting to a repository: Authors may post their AAM immediately to their employer's institutional repository for internal use only and may make their manuscript publically available after the journal-specific embargo period has ended. Please also refer to [Elsevier's Article Posting Policy](#) for further information.

18. **For book authors** the following clauses are applicable in addition to the above: Authors are permitted to place a brief summary of their work online only.. You are not allowed to download and post the published electronic version of your chapter, nor may you scan the printed edition to create an electronic version. **Posting to a repository:** Authors are permitted to post a summary of their chapter only in their institution's repository.

20. **Thesis/Dissertation:** If your license is for use in a thesis/dissertation your thesis may be submitted to your institution in either print or electronic form. Should your thesis be published commercially, please reapply for permission. These requirements include permission for the Library and Archives of Canada to supply single copies, on demand, of the complete thesis and include permission for UMI to supply single copies, on demand, of the complete thesis. Should your thesis be published commercially, please reapply for permission.

Elsevier Open Access Terms and Conditions

Elsevier publishes Open Access articles in both its Open Access journals and via its Open Access articles option in subscription journals.

Authors publishing in an Open Access journal or who choose to make their article Open Access in an Elsevier subscription journal select one of the following Creative Commons user licenses, which define how a reader may reuse their work: Creative Commons Attribution License (CC BY), Creative Commons Attribution – Non Commercial -ShareAlike (CC BY NC SA) and Creative Commons Attribution – Non Commercial – No Derivatives (CC BY NC ND)

Terms & Conditions applicable to all Elsevier Open Access articles:

Any reuse of the article must not represent the author as endorsing the adaptation of the article nor should the article be modified in such a way as to damage the author's honour or reputation.

The author(s) must be appropriately credited.

If any part of the material to be used (for example, figures) has appeared in our publication with credit or acknowledgement to another source it is the responsibility of the user to ensure their reuse complies with the terms and conditions determined by the rights holder.

Additional Terms & Conditions applicable to each Creative Commons user license:

CC BY: You may distribute and copy the article, create extracts, abstracts, and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text or data mine the article, including for commercial purposes without permission from Elsevier

CC BY NC SA: For non-commercial purposes you may distribute and copy the article, create extracts, abstracts and other revised versions, adaptations or derivative works of or from an article (such as a translation), to include in a collective work (such as an anthology), to text and data mine the article and license new adaptations or creations under identical terms without permission from Elsevier

CC BY NC ND: For non-commercial purposes you may distribute and copy the article and include it in a collective work (such as an anthology), provided you do not alter or modify the article, without permission from Elsevier

Any commercial reuse of Open Access articles published with a CC BY NC SA or CC BY NC ND license requires permission from Elsevier and will be subject to a fee.

Commercial reuse includes:

- Promotional purposes (advertising or marketing)
- Commercial exploitation (e.g. a product for sale or loan)
- Systematic distribution (for a fee or free of charge)

Please refer to [Elsevier's Open Access Policy](#) for further information.

21. Other Conditions:

v1.6

Questions? customercare@copyright.com or +1-855-239-3415 (toll free in the US) or +1-978-646-2777.

Gratis licenses (referencing \$0 in the Total field) are free. Please retain this printable license for your reference. No payment is required.
