Title
Using Kerogen-Bound Polycyclic Aromatic Hydrocarbons to Better Assess Thermal Maturity of Ancient Source Rocks

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Using Kerogen-Bound Polycyclic Aromatic Hydrocarbons to Better Assess Thermal Maturity of Ancient Source Rocks

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Master of Science

in

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by

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ABSTRACT OF THE THESIS

Using Kerogen-Bound Polycyclic Aromatic Hydrocarbons to Better Assess Thermal Maturity of Ancient Source Rocks

by

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Master of Science, Graduate Program in Geological Sciences
University of California, Riverside, June 2016
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Thermal maturity parameters have traditionally focused around the peak-oil window while parameters for the late- to post-oil window are not well constrained. Previous studies have shown that 3-ring polycyclic aromatic hydrocarbons (PAHs) can be used to correctly predict the maturity order for sedimentary organic matter. PAHs are structurally stable molecules and, when bound within kerogen, the kinetics of thermal alteration are slowed. The utility and preservation systematics of kerogen-bound 5-ring PAH, as measured by the 252 Da fragment ion, have not been studied in depth. These molecules have the potential to extend the sensitivity of maturity parameters into the late-oil window and beyond.

Kerogen samples from five basins with a range of maturities and sedimentary environments were loaded with 5-wt% ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] and pyrolysed using catalytic hydropyrolysis (HyPy; 0°C to 250°C at 100°C min^{-1} then 250°C to 520°C at 8°C min^{-1}) to extract covalently-bound compounds. Extracted compounds were analyzed by gas chromatography-mass spectrometry (GC-MS).

The relative order of stability of kerogen-bound 5-ring PAH was shown to be perylene < benzo(a)pyrene < benzo(e)pyrene < benzofluoranthenes. The ratio of benzo(a)pyrene.benzo(e)pyrene (BaP/BeP) values range from 0.02 to 1.20. The ratio of perylene/benzo(e)pyrene (Per/BeP) values range from 0.01 to 0.65. Kerogen-bound benzo(a)pyrene was found to be most sensitive in the late-oil window. Kerogen-bound perylene was found to be most sensitive to change in the peak-oil window though still present at very low abundances in the most mature kerogen suite. The use of HyPy can release kerogen-bound 5-ring PAH to extend maturity parameters beyond the late-oil window, regardless of the sedimentary environment at the time of deposition.

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1. Introduction

1.1 Sedimentary organic matter

The possibility for preservation of sedimentary organic matter is determined by the amount of primary productivity and the burial rate of the organic carbon and the recalcitrance, or resistance to degradation, of the material (Durand 1980, Suess 1980). Preservation of organic-rich sediments (>0.5 wt% of organic carbon) is favored by anoxic depositional environments and warm, unvarying climates (Peters et al., 2005) but while there are cases of exceptional preservation of more labile compounds, over 99.9% of organic matter from dead organisms in lakes and oceans is typically recycled back into the water column (Hedges and Keil 1995). Despite the requirements and limitation for preserving rocks with significant amounts of total organic carbon (TOC), organic matter that makes it into the rock record provides information about the dominant primary producers and source biota as well as important paleoenvironmental conditions such as marine redox structure or sea surface temperature at the time of deposition (Killops and Killops 2005, Love et al., 2005, Peters et al., 2005).

Sedimentary organic matter undergoes significant chemical, biological, and thermal degradation beginning in the water column and persisting into the sedimentary sub-surface. The stages of organic matter transformation are referred to as diagenesis, catagenesis and metagenesis. Diagenesis is the earliest stage of organic matter alteration and is typically associated with low temperature and low pressure regimes (Killops and Killops 2005) under conditions in which microbes survive and mediate a large range of chemical transformations to the host organic matter. Typically, diagenetic alteration occurs below 50°C (McCarthy et al., 2011). Catagenesis is a thermally mediated stage where most of the petroleum and natural gas reserves are formed (Tissot and Welte 1984). Temperature ranges at which catagenesis generally occurs are between 50°C and 150°C.

The structural characterization of kerogen, operationally defined as the insoluble macromolecular organic matter which is formed from the earliest stages of water column and sedimentary diagenesis, is the main focus of this study. The other organic phase is bitumen, which is the mobile organic matter than can be extracted by organic solvents (Killops and Killops 2005) from sediments. In ancient sedimentary rocks, kerogen typically comprises >90 wt% of the total sedimentary organic matter, though most organic geochemical investigation focus exclusively on the characterization of organic molecules in the bitumen phase which is less complicated to deal with analytically.

Smaller molecular units are covalently cross-linked to form macromolecular geopolymers (Vandenbroucke and Largeau 2007) such as kerogen. Lipids covalently-linked in the macromolecular structure are more resistant to degradation and alteration compared to their unbound counterparts (Love et al., 1995). As a consequence, isomerization and degradation of kinetics of kerogen-bound molecules from the macromolecular structure are slightly retarded with respect to the same reactions in the bitumen phase.

Biomarkers, or biological markers, are the preserved molecular skeletons of precursor biologic compounds (Durand 1980, Brocks and Pearson 2005, Peters et al., 2005) found in sediments and oils. Biosynthesis often produces specific molecular isomers, with stereochemical configurations fixed at key chiral centers, to fit the biological function but they are often not the most thermodynamically stable form. Examples of these are sterols and hopanols that serve as cell membrane lipids in eukaryotes and bacteria, respectively. As these organic compounds are subjected to higher temperatures and pressures in sedimentary rocks, the molecules are rearranged to various abiotic stereoisomers to reduce the steric strain and become geologically stable (Peters et al., 2005). Hopanes, identified by the characteristic 191 Dalton (Da) fragment ion by mass spectrometry, are the stable hydrocarbon skeletal form of bacterially produced hopanoids. Biologically produced hopanoids have the (22R)-17β,21β(H) isomeric configuration and is shortened here to ββR. Intermediate isomers in stability are βαR and αβR. The most geologically stable form of the molecule is αβS. Steranes, identified by its characteristic 217 Da fragment, are derived from steroids produced primarily by eukaryotes. Biologically produced steroids have the (20R)-5α,14α,17α(H) isomeric configuration and is shortened here to αααR isomeric configuration. Intermediate isomers are αααS and αββR. The most geologically stable form of the molecule is αββS. With increasing thermal maturity, structural isomers of regular steranes called diasteranes will appear, but are most pronounced in siliciclastic lithofaces containing acidic clay minerals which appear to promote the transformation of diasteranes into regular steranes.

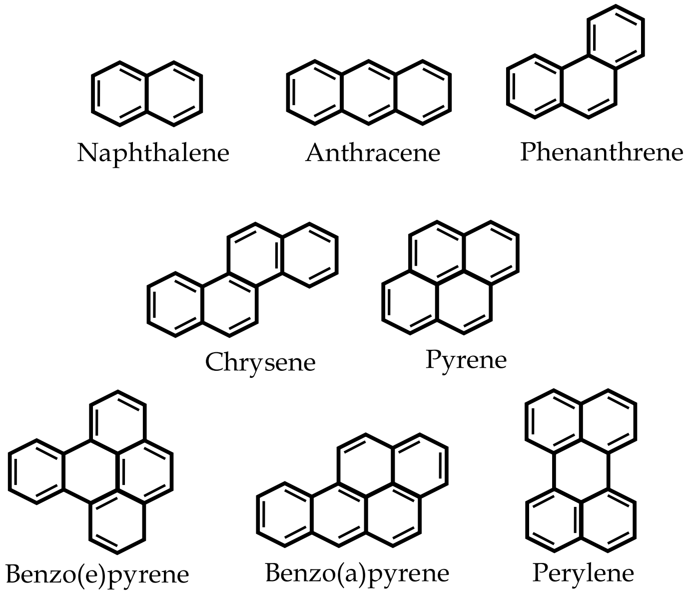


Figure 1 ***Select PAH Compounds.*** *A variety of polycyclic aromatic hydrocarbons (PAH) found in sediments and oils*

Polycyclic aromatic hydrocarbons (PAHs) are comprised of fused benzene molecules, six-carbon rings with delocalized π bonds. Three-ring PAHs anthracene, not discussed in this study, and phenanthrene are comprised of three fused benzene rings. Phenanthrene is identified on GC-MS by detection of a 178 Da molecular ion. Benzofluoranthene, benzo(a)pyrene, benzo(e)pyrene and perylene are usually the principal five-ring PAHs identified on gas chromatography-mass spectrometry (GC-MS) by using the 252 Da molecular ion.

Benzo(e)pyrene is the most stable five-ring PAH most resistant to degradation. Unbound perylene is highly volatile and cannot be detected in immature samples. Perylene can be detected in kerogen-bound samples.

1.2 Measures of thermal maturity

Thermal maturity of a source rock describes the extent to which the sedimentary organic matter has undergone heat-driven reactions (Peters et al., 2005) and the thermal stress experienced is a product of burial temperature and time of burial. The amount of thermal alteration undergone, as well as the petroleum-producting potential of a source rock can be categorized by its relationship to the oil window, the main zone of oil generation (Killops and Killops 2005). Immature source rocks have only gone through the earliest stage of organic matter alteration and have not generated any hydrocarbons. Source rocks in the early oil window have entered catagenesis and have begun to generate hydrocarbons. The peak oil window is the main stage of oil generation. The late oil window is the last stage of oil generation. The wet gas and condensate stage of the oil window has experienced high temperature regimes. At the wet gas and condensate stage of the oil window, only shorter hydrocarbons remain to generate gas. Beyond the wet gas and condensate, hydrocarbons are no longer generated and this is known as post-oil window.

Maturity parameters are based around useful analytical measurements which can help constrain where a source rock lies with respect to the oil window. Individually, each maturity parameter has its flaws. To get an accurate picture of any source rock, multiple maturity parameters must be used in tandem. The use of multiple maturity parameters provides the opportunity to narrow down the range of the oil window and provides self-consistency checks.

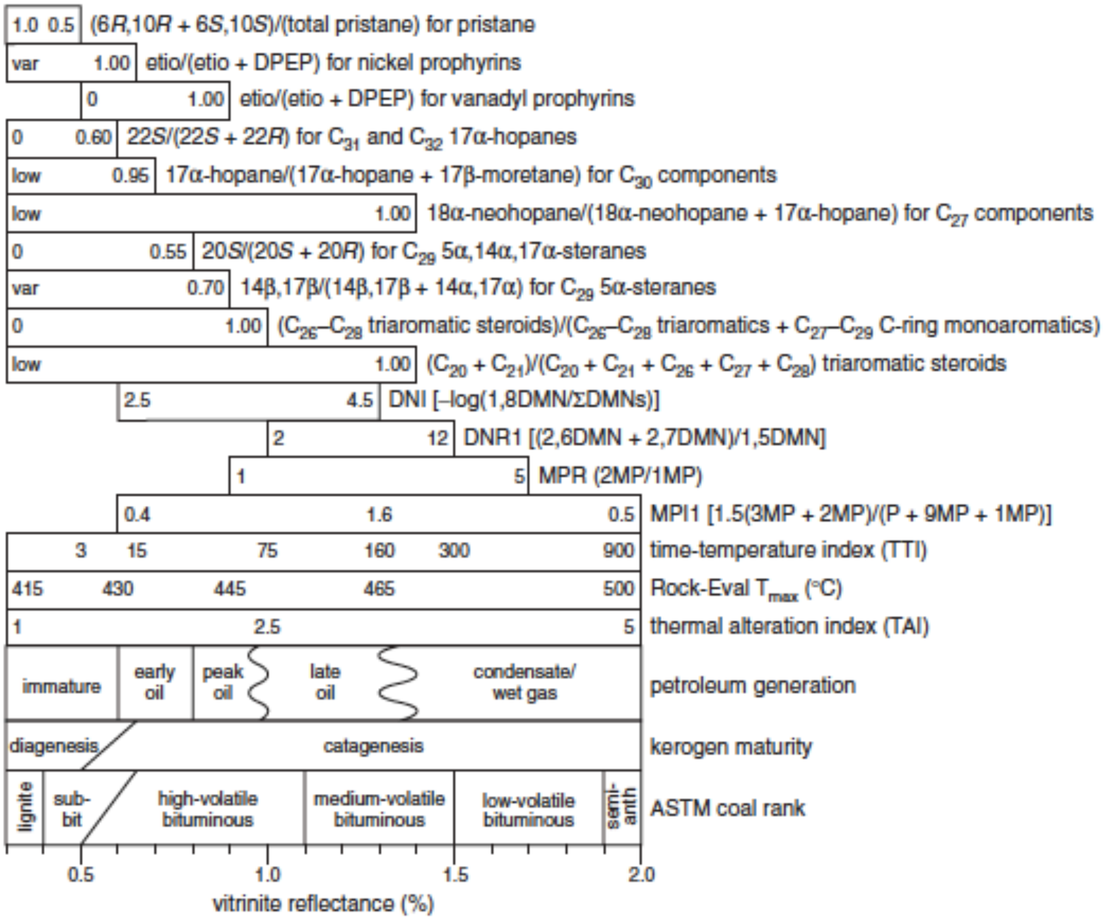


Figure 2 ***Correlation of Maturity Parameters.*** *Maturity parameters correlated with stages of sedimentary organic matter with maturation, coalification and petroleum generation (Killops and Killops 2005)*

1.2.1 Biomarker maturity parameters

A suite of saturated and aromatic hydrocarbon ratios has been devised over the course of at least four decades by petroleum geochemists as molecular maturity parameters. Used together, these ratios can span a wide range of thermal maturities, although most reach their equilibrium end-points during the early-to peak- oil window stages (see Figure 2).

The ratio between hopane and steranes to measure bacterial versus eukaryotic input to determine the dominant primary producer inputs in the water column at the time of sediment deposition. The average Phanerozoic values of hopane/sterane ratios for organic-rich rocks and oils lie in a reasonably narrow range of 0.5-2.0. The ratio between hopanes and steranes may provide a good check for contamination in ancient source rocks as eukaryotes were not prolific source biota until well into the Neoproterozoic (Love et al., 2009).

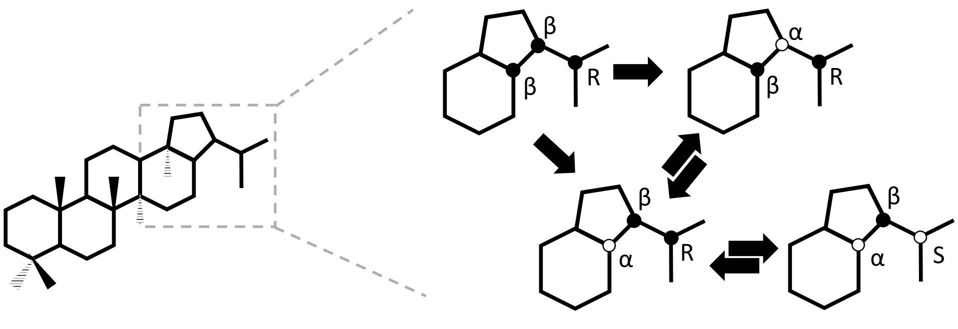
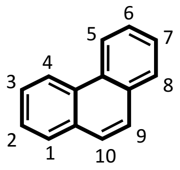
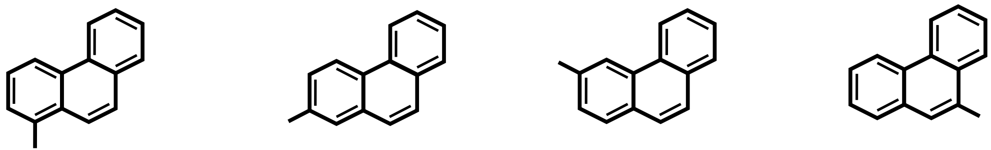


Figure 3 ***Isomeric configurations of hopanes.*** Top left: (22R)-17β,21β(H) (ββR)
Top right: (22R)-17β,21α(H) (βαR)
Bottom left: (22R)-17α,21β(H) (αβR)
Bottom right: (22S)-17α,21β(H) (αβS)

There is an equilibrium point for these maturity parameters as the biological isomer is not rearranged 100% into its stable form. The "R" configuration around the C_{10} and C_{11} carbon atoms are biologically produced for steranes and hopanes, respectively, and are rearranged to the "S" configuration. Hopanes reach thermal equilibrium in the early oil window when 22S/(22S+22R) equals 0.60 while steranes reach thermal equilibrium in the peak oil window when 20S/(20S+20R) equals 0.55 (Killops and Killops 2005). If a sample has reached hopane S/R equilibrium but not sterane S/R equilibrium, the thermal maturity is determined to be within the early to peak oil window. If both have reached equilibrium, thermal maturity is at or beyond the peak oil window and other maturity parameters are needed for better sensitivity.



Phenanthrene



1-Methylphenanthrene 2-Methylphenanthrene 3-Methylphenanthrene 9-Methylphenanthrene

Figure 4 ***Phenanthrene and methylphenanthrene compounds.*** *Phenanthrene with labeled carbon numbers and methylphenanthrene isomers*

The ratio of three-ring PAHs methylphenanthrene, identified by using 192 Da fragment ion, to phenanthrene, identified by using 178 Da fragment ion measures the thermal history of the sample as the methyl constituents of methylphenanthrene isomers are lost with increased temperature. Increased temperature results in decreased methylphenanthrene abundance with relation to phenanthrene (Marshall et al., 2007).

1.2.2 Other (non-biomarker) maturity parameters

Rock-Eval is a pyrolysis method of source rock characterization and evaluation that can provide information about the kerogen type and maturation stage of a sample. The pyrolysis of the samples as they are progressively heated to 550°C yield three peaks. The S_1 peak is a measure of free hydrocarbons already present in the rock; the S_2 peak is a measure of hydrocarbon and hydrocarbon-like compounds generated at higher temperatures, and the S_3 peak is a measure of carbon dioxide, water, and other oxygen-containing volatiles. The temperature at which S_2 reaches its peak is called T_{max} and corresponds to the temperature of maximum hydrocarbon generation from depolymerization of the kerogen (Tissot and Welte 1984). T_{max} is a lab generated value at which the molecules are cracking. It is not to be confused with max burial temperature.

Rock-Eval pyrolysis provides parameters to calculate the hydrogen index (HI) and oxygen index (OI). HI is the ratio of S_2 to TOC, measuring the amount of hydrogen in a source rock. S_2 corresponds to the breakdown of kerogen at higher temperatures, it represents the source rock potential with further maturation.

High HI values correspond to high hydrogen content remaining in the source rock and more potential to generate oil (McCarthy et al., 2011). OI is the ratio of S_3 to TOC, measuring the amount of oxygen in a source rock.

Vitrinite reflectance (R_O) is a petrographic, non-biomarker maturity parameter that uses reflected light microscopy on vitrinite, a maceral derived from vascular plants, to measure thermal maturity (Killops and Killops 2005). As it is subjected to increased temperatures, the carbon ring structures of vitrinite become aromatized and increase reflectivity (Peters et al., 2005). For non-coal material, reworked vitrinite and inertinite can interfere with the true vitrinite signal but can be identified with careful petrography. A limitation of R_O is that vascular plants were not prolific until the Devonian. Direct R_O calculations cannot be made in sedementary organic matter older than the Devonian. In these cases, T_{max} from Rock-Eval data can be used to calculate R_O.

1.3 Catalytic hydropyrolysis

The development of continuous-flow catalytic hydropyrolysis for rapid and reproducible recovery of biomarker compounds covalently-linked into geomacromolecules such as kerogen (insoluble sedimentary organic matter) has proven to be an important analytical breakthrough for ancient lipid biomarker research (Love et al., 1995-1997). Being covalently-bound, these biomarker structures are also immobile and therefore most assuredly genuine.

Sequestration by covalent binding is advanced from the earliest stages of sedimentary diagenesis (Farrimond et al., 2003), and this bound biomarker pool is better thermally preserved and much less susceptible to contamination effects than the conventionally-analyzed free hydrocarbons found in rock bitumen (solvent-extractable organic matter). The parallel analyses of free and bound biomarkers affords more confidence that we have correctly identified syngenetic compounds and this is a particularly important strategy when dealing with Precambrian and other ancient sedimentary rocks (Love et al., 2008, 2009). The combination of high pyrolysate yields and excellent retention of structural and stereochemical features in biomarker hydrocarbon products (Love et al., 1995-2009, Bishop et al., 1998, Murray et al., 1998) makes HyPy an ideal and proven technique for fragmenting kerogen and releasing this bound biomarker lipid pool.

Using the technique of catalytic hydropyrolysis (or HyPy, Love et al., 1995) to fragment kerogen we can release biomarkers from ancient kerogen with minimal change to structure and stereochemistry, thereby preserving their most diagnostic features. HyPy is a clean, rapid and reproducible technique that releases the bulk of analyzable products in simple hydrocarbon form which can be analysed in great detail by both conventional GC-MS and MRM-GC-MS techniques and compared directly with soluble biomarker distributions. The potency of the reaction medium in HyPy, using high pressure hydrogen gas and a molybdenum sulphide catalyst, allows us to generate genuine molecular constituents from even the most thermally mature and recalcitrant Precambrian kerogens (Brocks et al., 2003; Marshall et al., 2007).

Being covalently-linked, the bound biomarkers are immobile in rocks and therefore more assuredly genuine. Kerogen is formed rapidly in geologic time, with formation commencing in the water column and the macromolecular organic matter being largely in place over a timescale of hundreds to thousands of years of sub-surface burial after deposition (Farrimond et al., 2003). The ability to exhaustively remove soluble organic contaminants from sediments using solvent treatment while leaving no problematic residue has been demonstrated previously for ancient rock cores contaminated with oil-based drilling muds (e.g. Murray et al., 1998). Eliminating all traces of contamination from overmature samples may also require an initial low temperature HyPy treatment (terminating ~350^{o}C) to drive off strongly adsorbed molecules not accessible to solvent extraction (Brocks et al., 2003; Marshall et al., 2007).

Two previous investigations on HyPy of overmature kerogens prepared from 2.5 Ga Mt. McRae shales and from 3.4-3.5 Ga Strelley Pool cherts from the Pilbara Craton (Western Australia) clearly demonstrated the proof-of-concept that genuine covalently-bound hydrocarbon constituents can be released by HyPy and easily detected by gas chromatography-mass spectrometry (GC-MS) (Brocks et al., 2003; Marshall et al., 2007). The main organic matter phase present in Archean rocks (>99 wt%) is overmature aromatic-rich kerogen. A complex distribution of soluble molecular products was generated, composed predominantly of aromatic hydrocarbons encompassing the full 1-ring to 7-ring PAH range. Importantly, a positive linear correlation was observed between the degree of alkylation a 3-ring polyaromatic hydrocarbon compound, phenanthrene, with bulk structural and molecular parameters derived from elemental analysis and Raman spectroscopy.

More recently, HyPy was used to fragment Archean kerogens from a suite of samples from AIDP-2 and AIDP-3 cores from Pilbara Craton, comprising black shales from 2.65 Ga Jeerinah Formation and carbonates from 2.63 Ga Carawine Formation, which constitute the cleanest sedimentary cores drilled to date for organic geochemistry (French et al., 2015). Overall product yields from HyPy of kerogens from Jeerinah Formation black shales were significantly lower than for kerogens prepared from Carawine dolomites and their PAH profiles displayed a significantly lower degree of alkylation indicating poorer preservation (French et al., 2015), likely reflecting a higher degree of thermal alteration for black shale organics promoted by organic matter-acidic clay mineral interactions during burial maturation. Absolute yields of PAH compounds released by HyPy of kerogens were typically an order of magnitude higher than for the extractable PAH released by solvent extraction for the same rocks (French et al., 2015). Furthermore, the $\delta^{13}C$ of individual bound PAH compounds released by HyPy

(-42.6 to -45.9‰) were a close match with the distinctive ^{13}C-depleted bulk total organic carbon (TOC) values of $\delta^{13}C_{org}$ measured for the host bulk sedimentary organic matter (from -43 to -48‰). The PAH and n-alkanes generated by HyPy in this study constitute the most ^{13}C-depleted individual molecular signatures reported for Archean sedimentary organic matter (French et al., 2015), strongly indicating that these are primary Archean organic molecules. Hopanes, steranes and tricyclic terpane biomarkers were below detection limits in all HyPy products of AIDP core samples using multiple reaction monitoring (MRM)-GC-MS, consistent with a lack of polycyclic biomarker alkanes reported previously from HyPy of Archean kerogens from Pilbara Craton (e.g. Brocks et al., 2003).

2. Aims of this study

Samples of ancient sedimentary core taken during recent appraisal and development activities by Shell were used as the main sample set for this study. A representative set of samples from a range of maturities and different sedimentary environments have been employed. In addition to the Shell sedimentary rocks, pre-extracted rocks from the Ediacaran (541-635 Ma) Douhantuo Formation (South China) and from the Walcott Member of the Kwagunt Formation, Chuar Group, from the Grand Canyon (USA) of Tonian age (740- 780 Ma) were used to augment the dataset.

A fundamental motivation of this study is to better constrain the maturity order of sedimentary rocks at high levels of thermal maturity where existing methods are unreliable. Current maturity parameters are limited in their sensitivity to source rocks beyond the peak oil window.

A key focus of this study is investigating the preservation systematics of five-ring PAH compounds covalently-linked with kerogen, especially as a function of increasing thermal stress associated with late stage thermal maturity (late- and post- oil window maturity). Established biomarker and non-biomarker maturity parameters will be used as self-consistency checks to ensure the data produced in this investigation present reasonable and reliable conclusions.

3. Material and Methods

3.1 Kerogen sources

The samples analyzed in this study were acquired from five localities: the Gulf Coast Basin, the Alberta Basin, the Northumberland Basin, the Chuar Group, and the Nanhua Basin. Sand fired at 850ºC overnight is used as an experimental blank. Rock-eval data were collected externally.

Samples from the Gulf Coast Basin are upper Cretaceous marl of the Boquillas Formation. Five samples from the Duke and Queen wells were collected at depths of ~900m to ~2500m, respectively.

Samples from the Alberta Basin are lower Triassic phosphatic shale collected from the Skylark and Heron wells. Each well has a sample from the Doig Formation and a sample from the Montney Formation. Two lower Triassic samples were collected from the Phoenix Well in the Alberta Basin but the lithology and formation for this well is unassigned.

The Northumberland Basin samples are Carboniferous calcareous shale collected from the Boulmer Outcrop in the Millstone Grit Group. These samples experienced two thermal heating events: formation of a sill above the samples and an intrusive feeder dyke into the sill. The samples were taken with relation to distance from the dyke. In Table 1, values under "Depth" marked with an asterisk (*) show distances from the intrusive dyke. In this study, samples closer to the dyke, 7.94m to 10.3m, are referred to as “proximal” while samples further from the dyke, 29.8m to 48.8m, are referred to as “distal.”

Samples from the Chuar Group, Neoproterozoic in age, roughly 742 Ma +/- 6 Ma, come from the Walcott Member of the Kwagunt Formation. There are two samples from the Nankoweap Butte and two samples from Sixtymile Canyon.

Samples from the Nanhua Basin, Ediacaran (635-551 Ma) in age, come from the Doushantuo Formation in South China.

Age	Lithology	Basin	Sample	Depth	R_O	TOC	HI
Upper Cretaceous	Marl	GC Basin Duke Well	FPC 933695	911.40	0.75	1.5	513
Upper Cretaceous	Marl	GC Basin Duke Well	FPC 933686	917.46	0.75	2.3	513
Upper Cretaceous	Marl	GC Basin Duke Well	FPC 933687	956.61	0.75	5.2	471
Upper Cretaceous	Marl	GC Basin Duke Well	FPC 933688	964.52	0.75	5.4	437
Upper Cretaceous	Marl	GC Basin Duke Well	FPC 933689	969.92	0.75	5.4	478
Neoproterozoic		Chuar Sixtymile Canyon	SW4			3.57	80
Neoproterozoic		Chuar Sixtymile Canyon	SWE2			5.61	255
Neoproterozoic		Chuar Nankoweap Butte	36	595		4.70	88
Neoproterozoic		Chuar Nankoweap Butte	50	749		3.54	64
Lower Triassic	P. Shale	Alberta Basin Heron Well	FPC 905757	2199.9	1.2	5.43	
Lower Triassic	P. Shale	Alberta Basin Heron Well	FPC 905758	2056	1.2	2.79	
Upper Cretaceous	Marl	GC Basin Queen Well	FPC 933690	2534.49	1.19	1.8	83
Upper Cretaceous	Marl	GC Basin Queen Well	FPC 933691	2557.96	1.19	1.7	88
Upper Cretaceous	Marl	GC Basin Queen Well	FPC 933692	2564.54	1.19	2.8	79
Upper Cretaceous	Marl	GC Basin Queen Well	FPC 933693	2578.61	1.19	1.7	
Upper Cretaceous	Marl	GC Basin Queen Well	FPC 933694	2593.47	1.19	4.4	57
Lower Triassic	P. Shale	Alberta Basin Skylark Well	FPC 905755	2754.5	1.3	3.77	17
Lower Triassic	P. Shale	Alberta Basin Skylark Well	FPC 905756	2951.98	1.3		
Lower Triassic	Unassigned	Alberta Basin Phoenix Well	FPC 905753	3061.8	1.4		27
Lower Triassic	Unassigned	Alberta Basin Phoenix Well	FPC 905754	3161.75	1.5		24
Ediacaran		Nanhua Basin Doushantuo	CapB				
Ediacaran		Nanhua Basin Doushantuo	HJ01 (Cap)	0.7			
Ediacaran		Nanhua Basin Doushantuo	HN10	140.9			
Ediacaran		Nanhua Basin Doushantuo	HN21	152			
Carboniferous	C. Shale	Northumberland Distal	FPL 910060A	29.8*		4.7	6
Carboniferous	C. Shale	Northumberland Distal	FPL 910060B	29.8*		4.7	6
Carboniferous	C. Shale	Northumberland Distal	FPL 910062A	48.8*		0.54	65
Carboniferous	C. Shale	Northumberland Proximal	FPL 910058A	7.94*		5.22	7
Carboniferous	C. Shale	Northumberland Proximal	FPL 910058B	7.94*		5.22	7
Carboniferous	C. Shale	Northumberland Proximal	FPL 910059	10.3*		4.62	9

Table 1 Kerogen sample list

**Distance to intrusive feeder dyke*

3.2 Rock preparation

Whole rock samples collected from the Chuar Group were prepared by cutting the outer portion off using a rock saw. The inner portion of the rock was cut down into cubes and sonicated in methanol, dichloromethane (DCM), n-hexane, and DCM for 5 minutes each. Enough solvent was used to cover the entire cut portion; the volume of solvent used to sonicate varied by sample. The cleaned, cut rocks were dried in the fume hood overnight.

The cut rocks were powdered in a Shatterbox using a ceramic puck-mill. Sand fired at 850ºC overnight was used to clean the inside of the puck-mill and remove residual rock powder from previous samples. The dish and puck were solvent rinsed using methanol, DCM and n-hexane. The puck-mill was loaded with 20g to 40g of cut rock and pulsed for 30 seconds.

3.3 Solvent extraction

Teflon vessels were wiped down using KimWipes wet with methanol, DCM and n-hexane. The vessels were filled with 25mL DCM-methanol (9:1 v/v) and cleaned using Microwave Accelerated Reaction Systems (MARS) at 100°C for 15 minutes. 5-6g of rock powder was loaded into a clean Teflon vessel with 30 mL DCM-methanol (9:1 v/v). The bitumen was extracted in the MARS at 100°C for 15 minutes. Elemental sulfur was removed from the total lipid extract (TLE) using copper pellets activated with hydrochloric acid and rinsed with deionized water, methanol, and dichloromethane to remove the residual acid.

3.3 Catalytic hydropyrolysis (HyPy)

The kerogen was loaded with 5 wt% ammonium dioxydithiomolybdate [$(NH_4)_2MoO_2S_2$] dissolved in an aqueous-methanol solution. The catalyst loaded sample was placed into a steel reactor tube kept in the heating region by a clean steel wool ball. Steel wool was cleaned by soxhlet extracting it for 48 hours and flash firing at 550ºC for one hour. The HyPy trap was filled with 35-70 mesh silica gel also kept in place by clean steel wool.

The reactor tube was heated from ambient temperature to 250ºC at 100ºC min^{-1} then to 520ºC at 8ºC min^{-1}. Dry ice was placed around the trap to reduce the amount of volatile loss. A constant flow of hydrogen at $6dm^3$ min^{-1} measured at ambient temperature and pressure through the reactor tube allowed the extracted hydrocarbons to adsorb onto the silica gel in the trap.

3.4 Extract separation

The TLE was separated via silica gel adsorption chromatography. Columns were prepared by plugging the bottom with silica wool and a small amount of 35-70 mesh silica gel. The rest of the column was dry packed with 230-400 mesh silica gel. The TLE was loaded over the top. For HyPy extracted samples, the TLE is trapped on 35-70 mesh silica so columns were dry packed with less 230-400 mesh silica gel. Hexane, DCM-hexane (1:1 v/v) and DCM-methanol (3:1 v/v) to elute saturated hydrocarbons, aromatic hydrocarbons, and polar compounds, respectively. Weights for each of the fractions were taken after the solvent evaporated off.

3.5 Gas Chromatography-Mass Spectrometry (GC-MS)

The saturate and aromatic fractions were transferred using DCM into 250 µL inserts in 2 mL vials. The fractions were analyzed on an Agilent 7890A GC interfaced to an Agilent 5975C MSD. The GC was equipped with a 60m DB-1MS capillary column and run with He carrier gas.

4. Results

4.1 Aliphatic hydrocarbons distribution from Duke and Queen kerogens

The aliphatic compounds in the Duke Well and Queen Well samples were analyzed in detail using full scan analysis on a benchtop Agilent MSD GC-MS and utilizing a Waters Autospec Premier GC-MS for multiple reaction monitoring (MRM) GC-MS. MRM GC-MS is a more sensitive and selective analytical technique than the full scan or selected ion monitoring analyses on the benchtop Agilent GC-MS and can detect molecules at lower abundance.

The 191 Da fragment ion chromatogram for Duke Well sample FPC 933695 (Figure 5) shows a classic "bound hopane" profile for oil window mature kerogens with a high C_{27} Tm value with respect to C_{27} Ts. $C_{29}H$ $\alpha\beta$ and $C_{30}H$ $\alpha\beta$ are present and a high S to R ratio for $C_{31}H$ – $C_{35}H$ $\alpha\beta$. For the Queen Well sample FPC 922894 (Figure 6), C_{27} Tm is high relative to C_{27} Ts. $C_{29}H$ $\alpha\beta$ and $C_{30}H$ $\alpha\beta$ are present. The S to R ratio varies from $C_{31}H$ – $C_{35}H$ $\alpha\beta$. The $\beta\beta$ isomeric configuration is present in $C_{29}H$ and even prominent in $C_{31}H$ – $C_{35}H$.

The 217 Da fragment ion chromatogram for FPC 933695 (Figure 7, top) shows C_{28} – C_{30} $\alpha\alpha\alpha$S and $\alpha\alpha\alpha$R as well as C_{27} – C_{29} $\alpha\beta\beta$S and $\alpha\beta\beta$R The chromatogram shows that the relative abundances of $\alpha\beta\beta$S and $\alpha\beta\beta$R are greater than the abundances of $\alpha\alpha\alpha$S and $\alpha\alpha\alpha$R. The chromatogram for Queen Well sample FPC 933695 (Figure 7, bottom) shows $\alpha\alpha\alpha$R dominating the C_{27} – C_{29} sterane signal. C_{28} and C_{29} $\alpha\alpha\alpha$S are seen in small abundances. The signal for aliphatics in the saturated fraction in the Queen Well samples was dominated by *n*-alkanes.

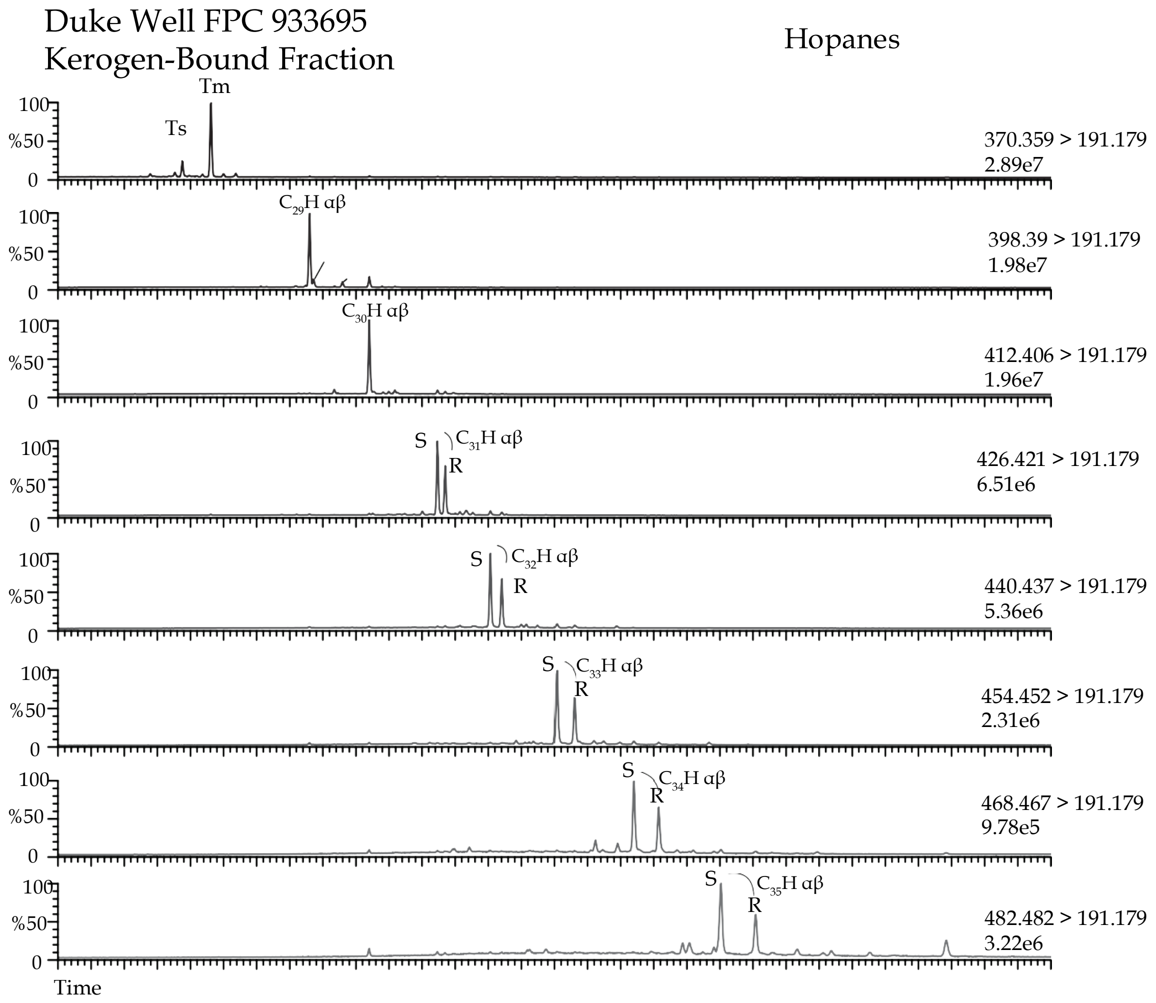


Figure 5 ***Duke Well Hopane Chromatograms.*** *Partial 191 Da ion chromatograms measured on MRM GC-MS of major hopanes generated from catalytic hydropyrolysis (HyPy) of kerogen from Duke Well FPC 933695*

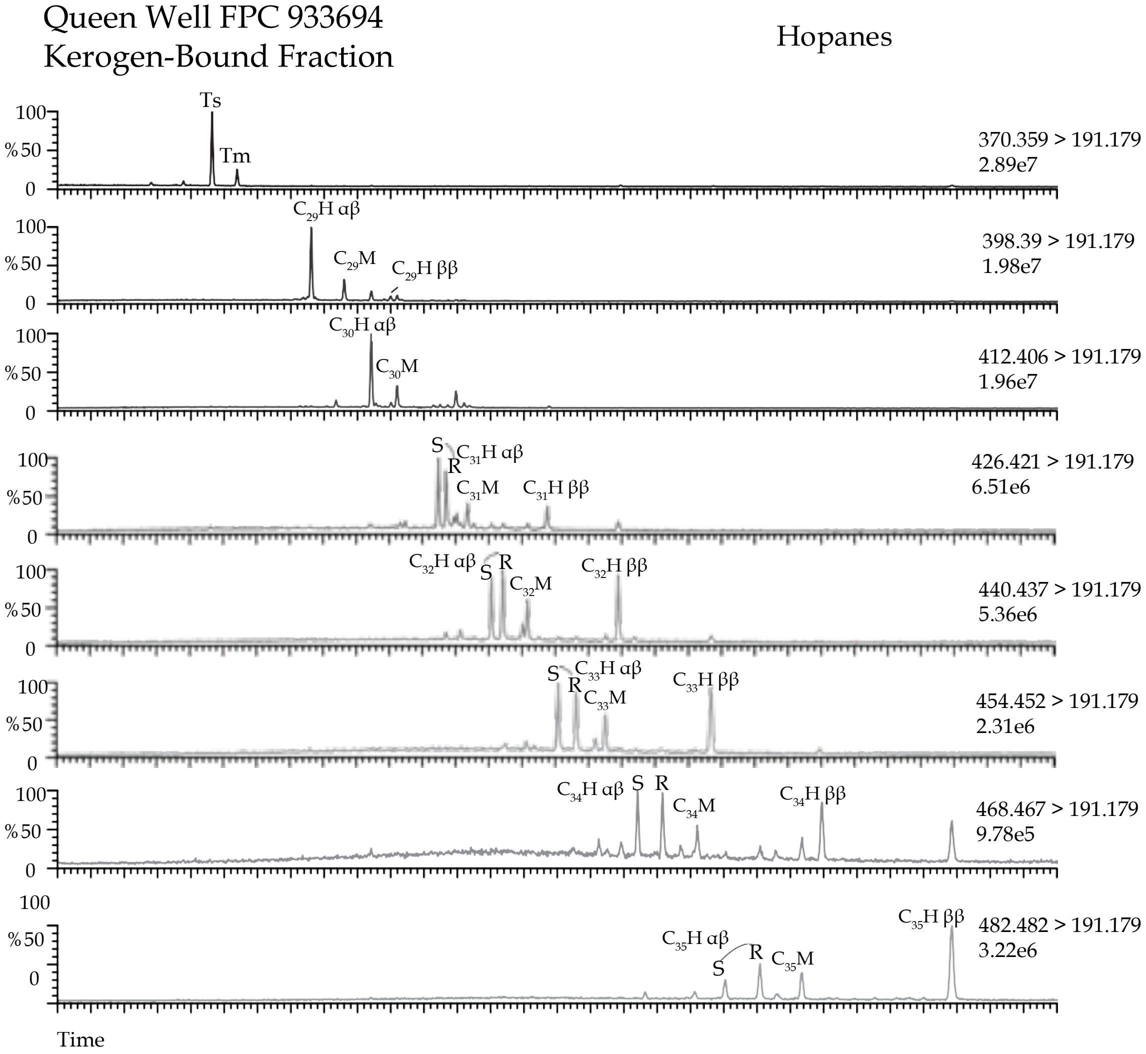


Figure 6 ***Queen Well Hopane Chromatorgrams.*** *Partial 191 Da ion chromatograms measured on MRM GC-MS of major hopanes generated from catalytic hydropyrolysis (HyPy) of kerogen from Queen Well FPC 933694*

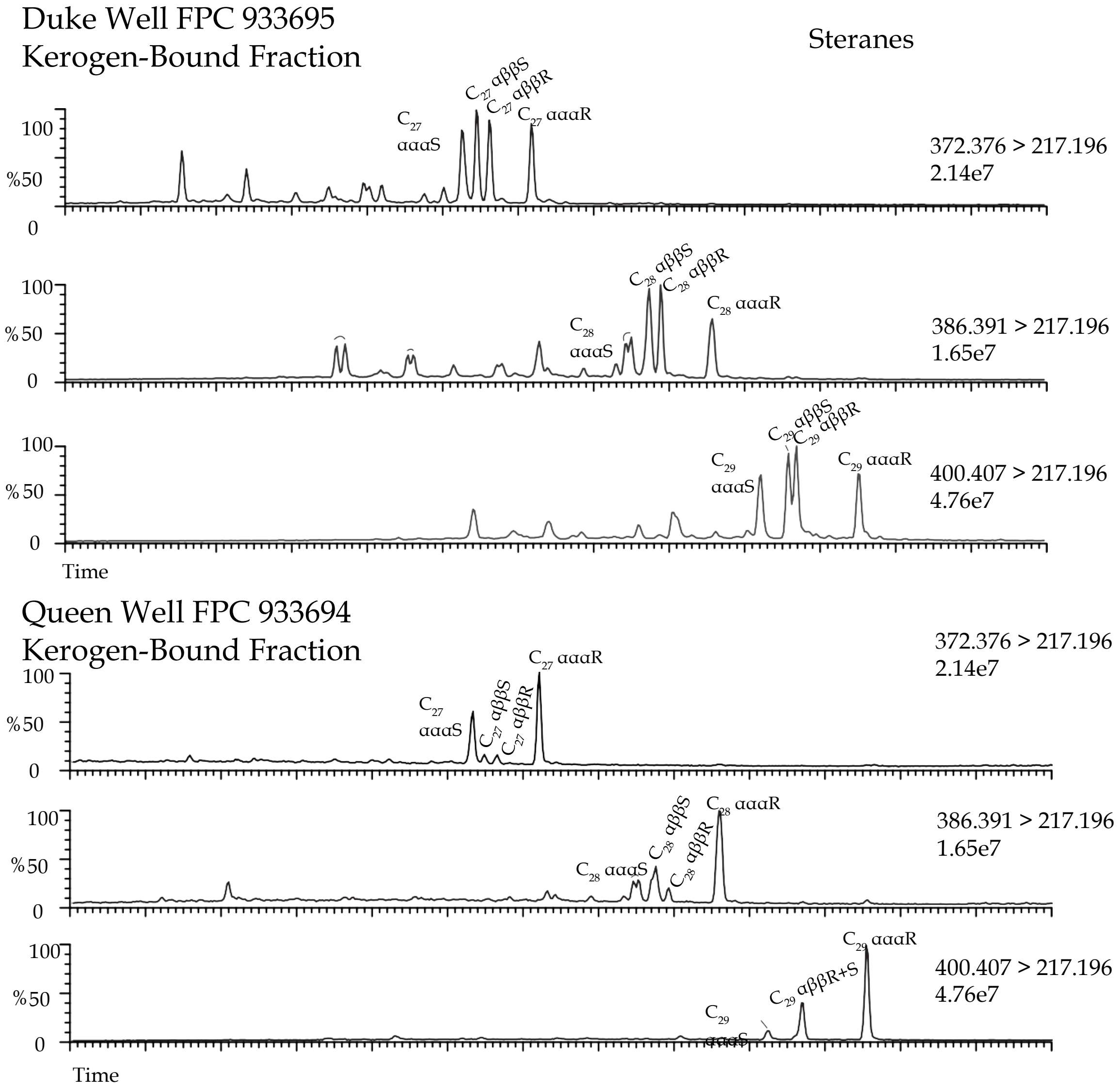


Figure 7 ***Duke Well and Queen Well Sterane Chromatograms.*** *Partial 217 Da ion chromatograms measured on MRM GC-MS of steranes generated from catalytic hydropyrolysis (HyPy) of kerogen from Duke Well FPC 933695 (top) and Queen Well FPC 933694 (bottom)*

4.2 Aromatic hydrocarbon distribution

The aromatic hydrocarbons were analyzed on an Agilent GC-MSD. For this study, we focused on three-ring PAHs and five-ring PAHs.

4.2.1 Three-ring PAHs

The ratio of summed methylphenanthrenes to phenanthrene (MeP/P) was compared for the HyPy products from kerogen from sedimentary rocks from five basins encompassing thermal maturity series (See Table 1). The value of methylphenanthrene in this ratio is the sum of the four main methylphenanthrene isomers (2-, 3-, 9-, and 1-methylphenanthrene in order of elution by gas chromatography). Values range as low as 0.23 (Northumberland Basin Proximal) to as high as 3.51 (Nankoweap Butte). (See Table 2)

4.2.2 Five-ring PAHs

The five-ring PAH analyses were performed on the aromatic hydrocarbon fraction of the total soluble products generated from pre-extracted rocks or kerogens from the Gulf Coast Basin, Alberta Basin, Northumberland Basin, Nanhua Basin and Chuar Group. This provides a useful maturity series and also covers a wide range of geological ages of sedimentary rocks, from Neoproterozoic to Cretaceous. At least four different 5-ring PAH compounds can be seen in the 252 Da ion chromatograms in all samples.

The percents of benzo(e)pyrene, benzo(a)pyrene and perylene show the relative abundances of each compound in HyPy products. The percent of perylene ranges from 1.13% to 25.22% and is typically higher in the lower maturity samples, the percent of benzo(a)pyrene ranges from 2.39% to 48.80% and the percent of benzo(e)pyrene ranges from 38.67% to 96.48%. The highest percentages of benzo(e)pyrene came from Northumberland Basin Proximal samples, which comprises the most mature rocks used in this investigation. The lowest percentages of benzo(e)pyrene came from the Duke Well samples of the Gulf Coast Basin, which comprise the lease mature substrates used.

The ratios of benzo(a)pyrene to benzo(e)pyrene (BaP/BeP) range from 0.02 (Northumberland Basin) to 1.20 (Alberta Basin). Samples from the same well generally cluster together (Figure 10). With the exceptions of the Heron Well and one sample within the Nanhua Basin, the difference in BaP/BeP values comparing samples within each well is not greater than 0.19. In the Nanhua Basin, the highest BaP/BeP value is 0.67, and the closest value within the basin is 0.43. The BaP/BeP ratio in the Heron Well ranges from 0.79 to 1.20, which is a difference of 0.41. Due to the large discrepancy in BaP/BeP values and the high amounts of C_{35} ββ seen in the aliphatic fraction, sample FPC 905758 is omitted from the graphs. The sample data can be found in Table 3.

The ratio of perylene to benzo(e)pyrene (Per/BeP) ranges from 0.01 in the Northumberland Basin to 0.65 in the Gulf Coast Basin. (See Figure 11) There is tight clustering of samples by well and location with the exception of the Duke Well in the Gulf Coast Basin and the Heron Well in the Alberta Basin. For the other locations, the maximum range for the Per/BeP ratio is 0.07. Within the Duke Well, the Per/BeP ratio ranges from 0.19 to 0.65, a difference of 0.46. In the Heron Well, there is a difference of 0.14.

Basin	Sample	HI	MeP/P
GC Basin Duke Well	FPC 933695	513	0.78
GC Basin Duke Well	FPC 933686	513	1.10
GC Basin Duke Well	FPC 933687	471	1.37
GC Basin Duke Well	FPC 933688	437	0.82
GC Basin Duke Well	FPC 933689	478	0.92
Chuar Sixtymile Canyon	SWE2	255	3.01
Chuar Sixtymile Canyon	SW4	80	2.32
Chuar Nankoweap Butte	36	88	3.51
Chuar Nankoweap Butte	50	64	1.90
Alberta Basin Heron Well	FPC 905757		1.48
Alberta Basin Heron Well	FPC 905758		2.42
GC Basin Queen Well	FPC 933690	83	0.85
GC Basin Queen Well	FPC 933691	88	1.01
GC Basin Queen Well	FPC 933692	79	1.04
GC Basin Queen Well	FPC 933693		0.91
GC Basin Queen Well	FPC 933694	57	0.85
Alberta Basin Skylark Well	FPC 905755	17	1.87
Alberta Basin Skylark Well	FPC 905756		1.04
Alberta Basin Phoenix Well	FPC 905753	27	1.50
Alberta Basin Phoenix Well	FPC 905754	24	1.21
Nanhua Basin Doushantuo	CapB		0.24
Nanhua Basin Doushantuo	HJ01 (Cap)		0.36
Nanhua Basin Doushantuo	HN10		0.75
Nanhua Basin Doushantuo	HN21		0.60
Northumberland Distal	FPL 910060A	6	0.64
Northumberland Distal	FPL 910060B	6	0.89
Northumberland Distal	FPL 910062A	65	0.43
Northumberland Proximal	FPL 910058A	7	0.23
Northumberland Proximal	FPL 910058B	7	0.44
Northumberland Proximal	FPL 910059	9	1.09

Table 2 Sample data for three-ring PAHs

Basin	Sample	HI	BeP %	BaP/BeP	Per/BeP
GC Basin Duke Well	FPC 933695	513	48.01%	0.90	0.19
GC Basin Duke Well	FPC 933686	513	40.99%	1.10	0.34
GC Basin Duke Well	FPC 933687	471	38.67%	1.00	0.58
GC Basin Duke Well	FPC 933688	437	38.83%	0.93	0.65
GC Basin Duke Well	FPC 933689	478	42.20%	0.92	0.45
Chuar Sixtymile Canyon	SWE2	255	47.44%	0.98	0.13
Chuar Sixtymile Canyon	SW4	80	48.78%	0.85	0.20
Chuar Nankoweap Butte	36	88	54.56%	0.65	0.19
Chuar Nankoweap Butte	50	64	58.83%	0.55	0.15
Alberta Basin Heron Well	FPC 905757		52.47%	0.79	0.12
Alberta Basin Heron Well	FPC 905758		40.70%	1.20	0.26
GC Basin Queen Well	FPC 933690	83	58.82%	0.63	0.07
GC Basin Queen Well	FPC 933691	88	59.39%	0.63	0.05
GC Basin Queen Well	FPC 933692	79	55.88%	0.73	0.06
GC Basin Queen Well	FPC 933693		59.16%	0.65	0.04
GC Basin Queen Well	FPC 933694	57	53.79%	0.78	0.08
Alberta Basin Skylark Well	FPC 905755	17	53.11%	0.80	0.08
Alberta Basin Skylark Well	FPC 905756		59.10%	0.64	0.06
Alberta Basin Phoenix Well	FPC 905753	27	62.90%	0.54	0.05
Alberta Basin Phoenix Well	FPC 905754	24	71.43%	0.35	0.05
Nanhua Basin Doushantuo	CapB		70.09%	0.40	0.03
Nanhua Basin Doushantuo	HJ01 (Cap)		68.98%	0.42	0.03
Nanhua Basin Doushantuo	HN10		68.64%	0.43	0.02
Nanhua Basin Doushantuo	HN21		57.78%	0.67	0.06
Northumberland Distal	FPL 910060A	6	77.56%	0.26	0.03
Northumberland Distal	FPL 910060B	6	78.34%	0.23	0.04
Northumberland Distal	FPL 910062A	65	80.60%	0.22	0.02
Northumberland Proximal	FPL 910058A	7	94.88%	0.03	0.02
Northumberland Proximal	FPL 910058B	7	96.48%	0.02	0.01
Northumberland Proximal	FPL 910059	9	95.40%	0.03	0.01

Table 3 Sample data for five-ring PAHs

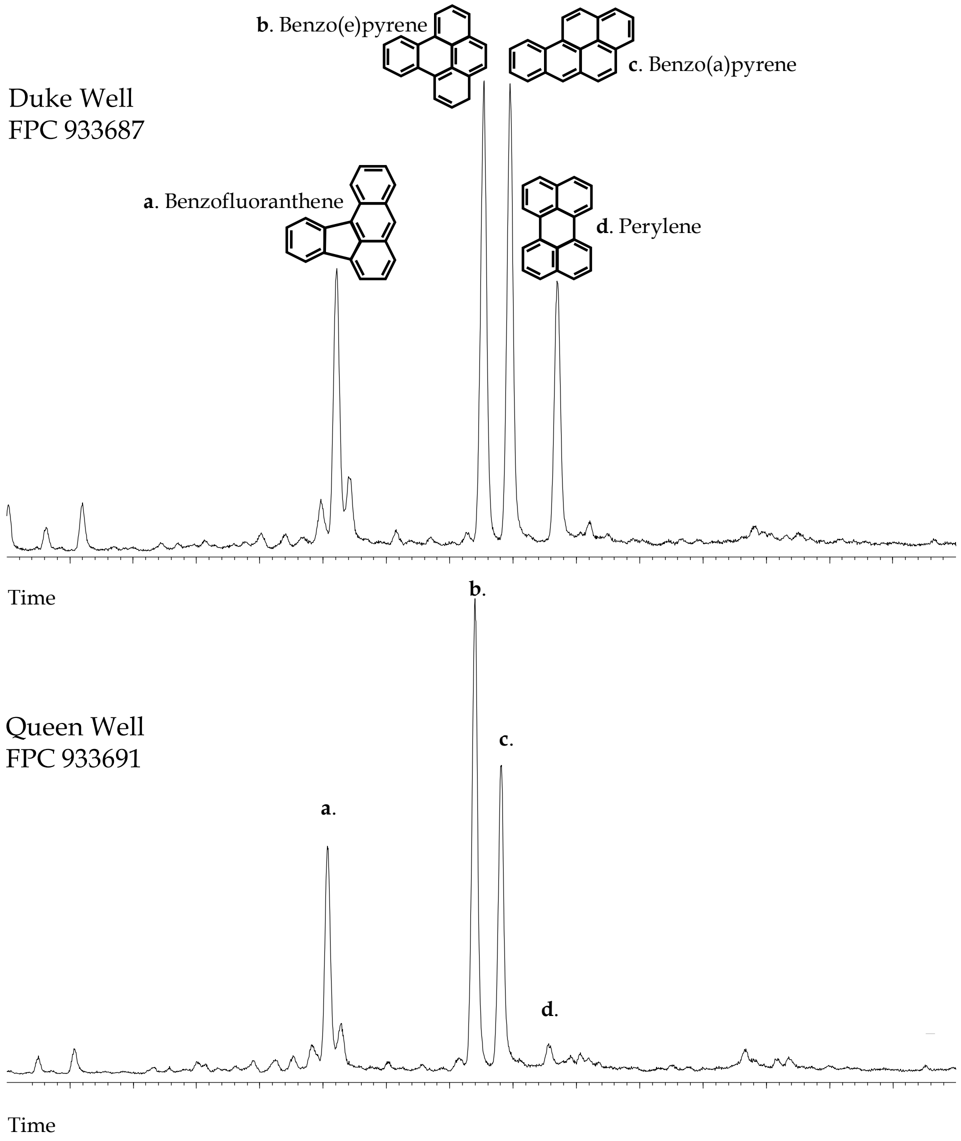
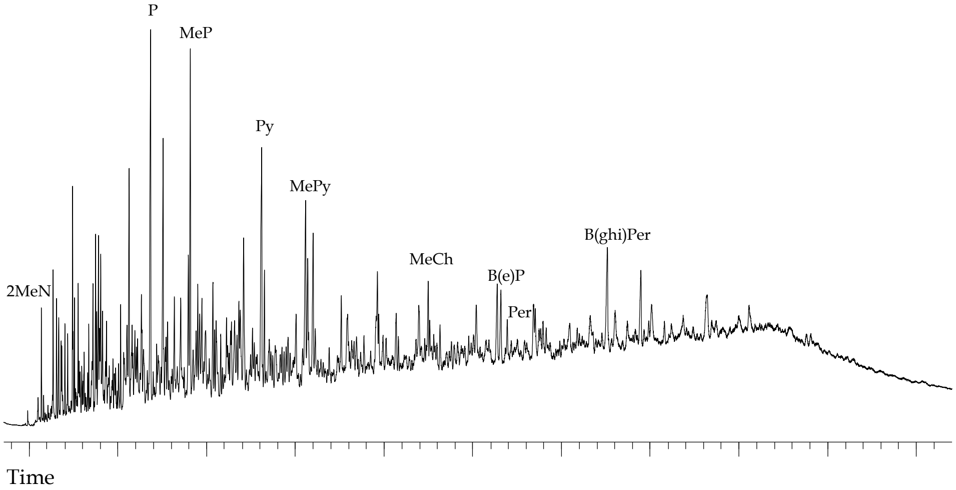


Figure 8 ***Duke Well and Queen Well 252 Da ion chromatograms.*** *Partial 252 Da ion chromatograms of the major 5-ring PAH compounds generated from catalytic hydropyrolysis (HyPy) of kerogen from Duke Well FPC 933687 (top) and Queen Well FPC 933691 (bottom)*

Duke Well
FPC 933689



Queen Well
FPC 933691

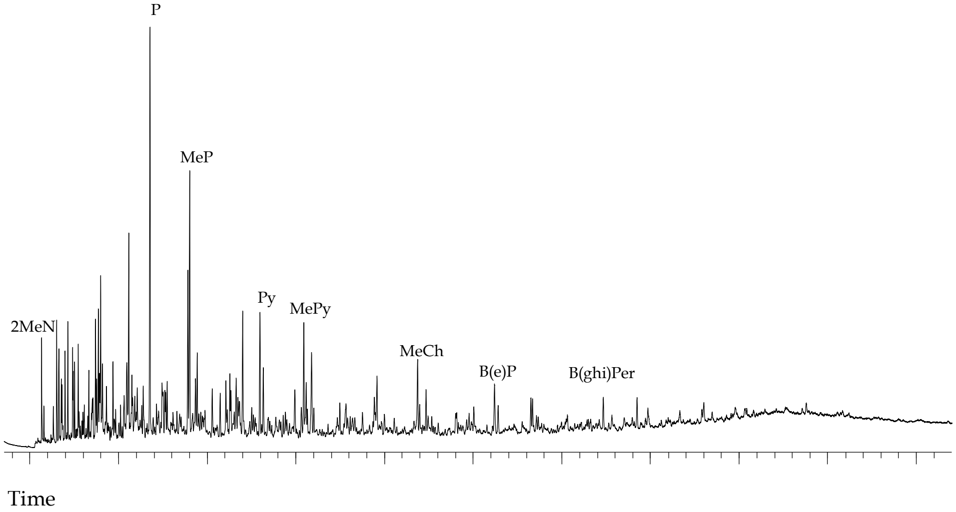


Figure 9 ***Duke Well and Queen Well aromatic hydrocarbon TICs.*** *Total ion current (TIC) chromatorgrams of aromatic hydrocarbons generated from catalytic hydropyrolysis (HyPy) of kerogen from Duke Well sample FPC 933689 (top) and Queen Well sample FPC 933691 (bottom)*

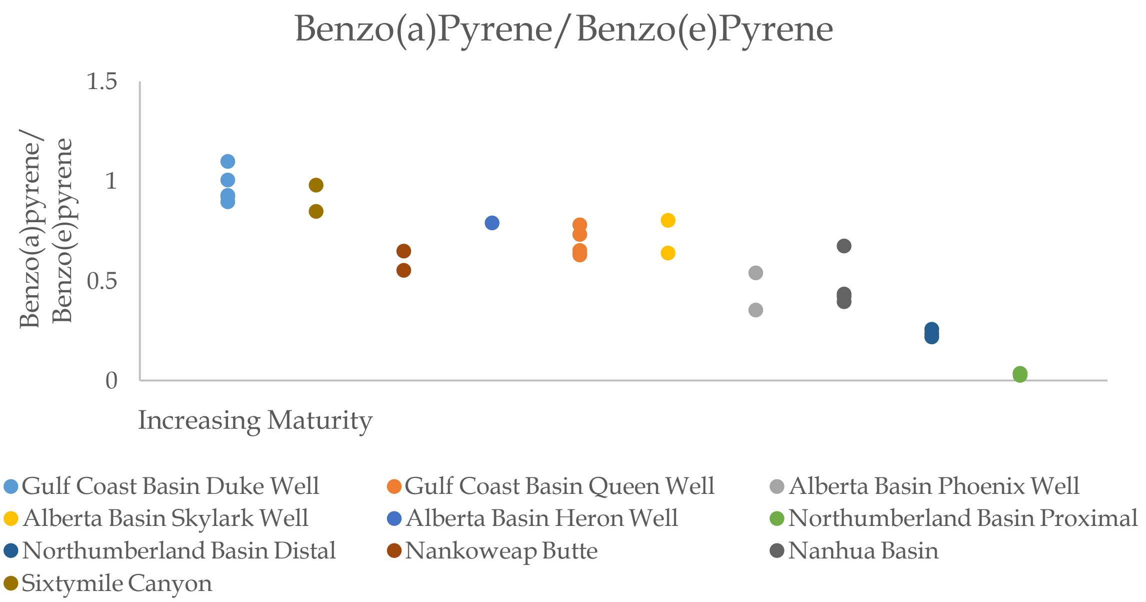


Figure 10 ***BaP/BeP Ratio.*** *Ratio of benzo(a)pyrene to benzo(e)pyrene from HyPy of kerogen-bound samples with respect to increasing maturity*

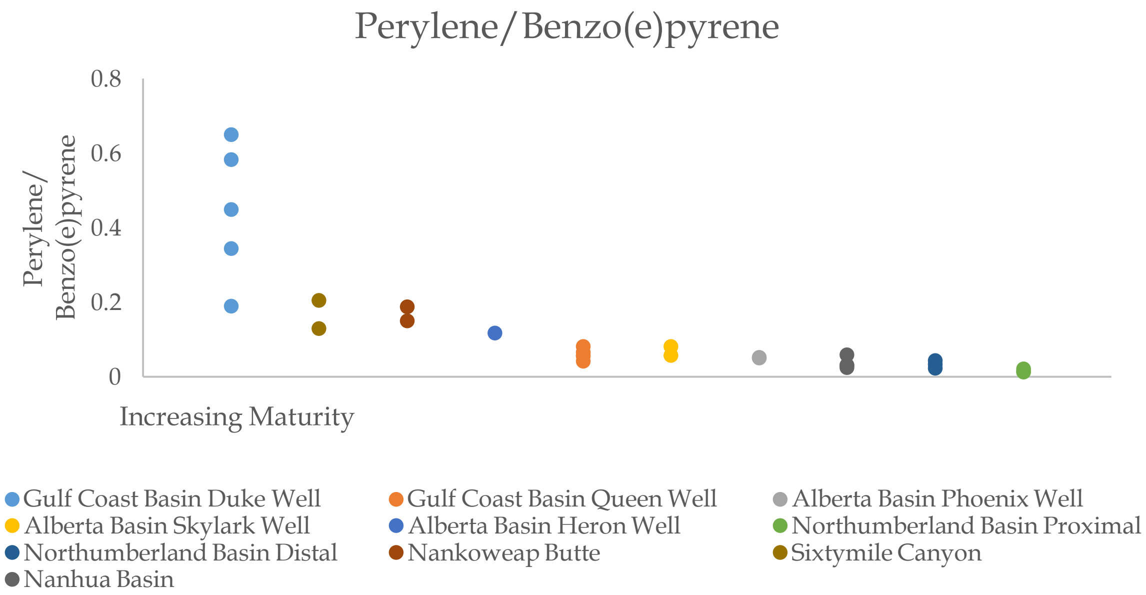


Figure 11 ***Per/BeP Ratio.*** *Ratio of perylene to benzo(e)pyrene from HyPy of kerogen-bound samples with respect to increasing maturity*

5. Discussion

5.1 Aliphatic hydrocarbons

The hopane and sterane traces, as shown by using the 191 Da and 217 Da fragment ions respectively, for the samples from the Duke Well are consistent with traces of a kerogen-bound sample with R_O of 0.75 approaching the end of the early oil window. C_{27} Ts to C_{27} Tm ratios are expected to be high with increasing maturity in unbound samples, Ts is formed diagenetically over time so it is expected that C_{27} Tm relative to C_{27} Ts is high. Ts should not be seen bound within the kerogen in the early stages of diagenesis. The presence of αβ and the absence of ββ and βα hopanes in the Duke Well shows the rearrangement of the molecules from the biologically produced compound to the geologically-stable isomer. The ratio of S/S+R hopanes has reached thermal equilibrium showing that the Duke Well samples have gotten to the early oil window.

The Queen Well has R_O values of 1.19, placing samples in the late oil window stage. Given the thermal maturity of the Queen Well as provided by the vitrinite reflectance, the presence of ββ hopanes is suspicious. The detection of βα and ββ hopanes using MRM GC-MS suggests that the hopanes in the sample have not reached thermal equilibrium. This is inconsistent with the rock-eval data as hopanes should reach thermal equilibrium at the beginning of the early oil window. These likely represents contaminants introduced as drilling additives. Lignites are one of the very few problematic organic solids occasionally added during drilling of wells. Although lignite contributions relatively easy to identify in product distributions, the lignite contribution account for the apparent immature features of bound steranes and hopanes seen particularly prominent in the Queen series. As will be seen in subsequent sections, the lignite did not significantly interfere with the 5-ring PAH distributions since lignites contain predominantly 1-3 ring PAH compounds linked within the kerogen.

5.2 Aromatic hydrocarbons

Aromatic hydrocarbons are structurally stable molecules and the kinetics of thermal alteration are slowed within kerogen as the covalent bonds linking the molecules need to be cleaved. Overall, we can gauge that the thermal stability of 5-ring PAH compound bound into kerogen increases in the order:

perylene < benzo(a)pyrene < benzo(e)pyrene < benzofluoranthene

The range of sample ages from Proterozoic to Phanerozoic show that the parameters gathered can span geologic time. Unlike maturity parameters such as vitrinite reflectance where the samples must be younger than Devonian age for a direct measurement, it is shown here that benzo(e)pyrene, benzo(a)pyrene and perylene can be found bound in the kerogen of samples as old as the

Mesoproterozoic. These parameters are controlled by maturity as opposed to organic matter input.

5.2.1 Benzo(e)pyrene and non-biomarker maturity parameters

There is an inverse correlation of hydrogen index (HI) with percent of benzo(e)pyrene (Figure 12). With increasing maturity, HI, as measured from rock-eval data by taking the ratio of S_2 to TOC, decreases. The inverse correlation shows that the percent of benzo(e)pyrene increases with increasing maturity. It follows then that the relative amounts of benzo(a)pyrene and perylene are decreasing with increasing maturity. This is consistent with benzo(a)pyrene and perylene being more volatile and susceptible to degradation with increasing temperatures. This correlation with a separate maturity parameter provides a self-consistency check that shows that the observed relationships are genuine signals.

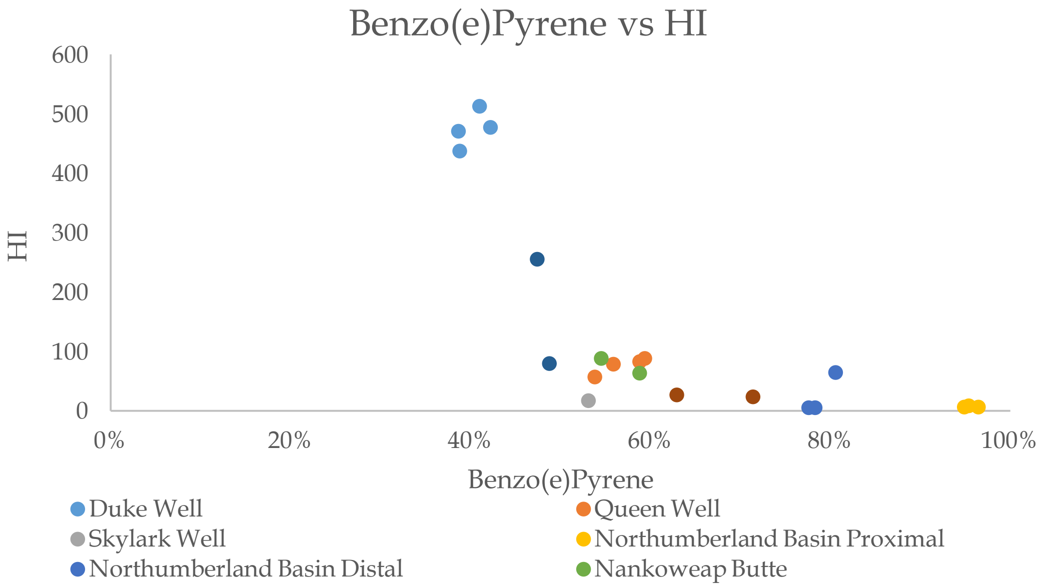


Figure 12 ***BeP vs HI Cross-plot.*** *Cross-plot of benzo(e)pyrene from HyPy of kerogen-bound samples vs hydrogen index (HI)*

5.2.2 Presence of perylene

The presence of perylene in the HyPy products, generated from even the most thermally mature kerogens in the sample set, and its progressive loss in the kerogen bound phase relative to the other 5-ring PAH compounds with increasing maturity is noteworthy. Perylene has been detected in overmature kerogen products from Strelly Pool cherts previously (Marshall et al., 2007) but the detailed systematics of the preservation of perylene relative to other 5-ring PAH has not been investigated until now. Perylene is not detectable as a free hydrocarbon in the bitumen phase for rocks of early-oil window and higher maturity.

Perylene values as measured by Per/BeP drop across the peak to late oil window transition. Figure 11 shows that the least mature kerogens produce the highest ratio values and largest spread of values for the Duke kerogen series. The Duke Well samples have R_O values of 0.75, placing them at the end of the early oil window. At higher stages of thermal maturity with values of 1.19 to 1.5, the remaining samples with measured R_O fall in the late oil window. The relative thermodynamic stability of the kerogen-bound perylene vs the other PAH compounds controls the values of the ratio which gradually falls in magnitude.

The presence of perylene in HyPy products could prove to be an important and novel molecular signature for identifying macromolecular organic matter formed during early diagenesis under low temperature conditions

(<50°C) and will be useful for distinguishing kerogen and other primary macromolecular organic fractions from pyrobitumens (residues formed from thermal cracking of oil). Despite undergoing protracted burial and being subjected to increasing temperatures and pressures, detectable amounts of kerogen-bound perylene can be readily detected in the aromatic fraction of HyPy products even for overmature ancient kerogens.

5.2.3 Benzo(a)pyrene

The wide spread of benzo(a)pyrene values as measured by BaP/BeP introduces the potential to use this ratio for samples in the late oil window and beyond. Unlike the ratio of Per/BeP where the values drop off close to zero for samples in the late oil window, BaP/BeP can be measured for samples in and beyond the late oil window.

There is a positive correlation between the ratio of Per/BeP and the ratio of BaP/BeP (Figure 13). As perylene values increase, the amount of benzo(a)pyrene increases. Unsurprisingly, the large disparity in Per/BeP values for the Duke Well distorts the trend. The values of perylene increase more rapidly than the values of benzo(e)pyrene.

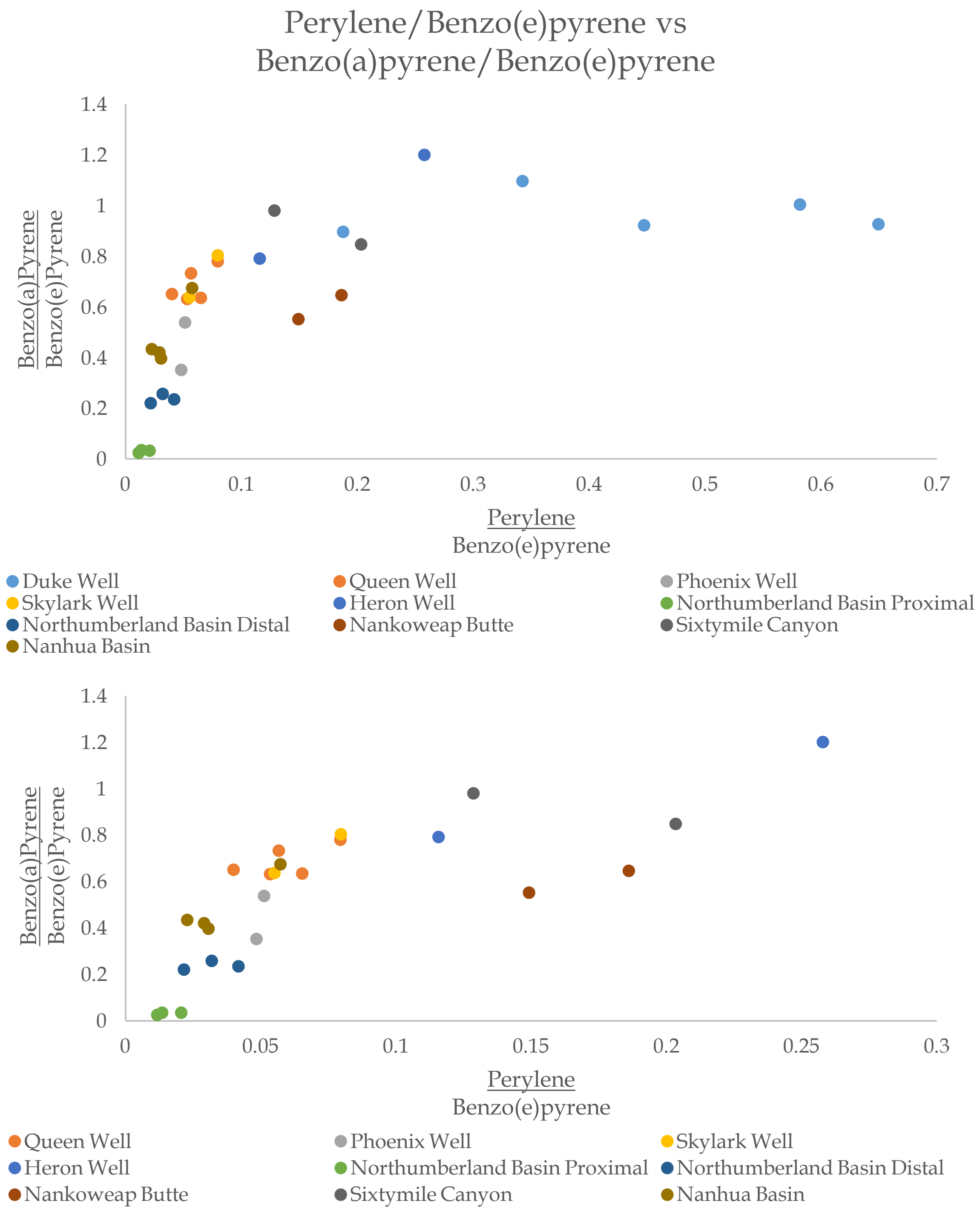


Figure 13 ***Per/BeP vs BaP/BeP Cross-plot.*** *Cross-plot of perylene/benzo(e)pyrene vs benzo(a)pyrene/benzo(e)pyrene from HyPy of kerogen-bound samples Bottom: Duke Well kerogen suite excluded*

5.2.3 Methylphenanthrene/Phenanthrene

Marshall et al., (2007) previously showed a good correlation between MeP/P ratio and atomic H/C from elemental analysis, as well as with maturity parameters derived from Raman spectroscopy for a suite of overmature Archean kerogens from the Strelly Pool chert. Although many of the more thermally mature samples in our dataset do generate the lowest bound MeP/P ratios, this maturity parameter is more prone to artifacts from evaporative losses of phenanthrene (relative to methylphenanthrenes) in comparison to five-ring PAH ratios for HyPy products. Care must be taken to assess which products have been prone to a high degree of product evaporative losses from analysis of the total aliphatic and aromatic hydrocarbon profiles from full scan GC-MS.

A cross-plot of MeP/P and Per/BeP (Figure 14) shows an overall positive linear correlation across the whole sample set. The positive correlation becomes more obvious when the Duke Well samples are removed from the plot. Samples with MeP/P values over 3 are likely artifacts from evaporative losses as described above. As expected, samples with low values of perylene have relatively low values of MeP/P. Previous studies have determined that the ratio of MeP/P decreases with increasing maturity. A positive linear correlation is also observed when comparing BaP/BeP vs MeP/P on cross-plot (Figure 15).

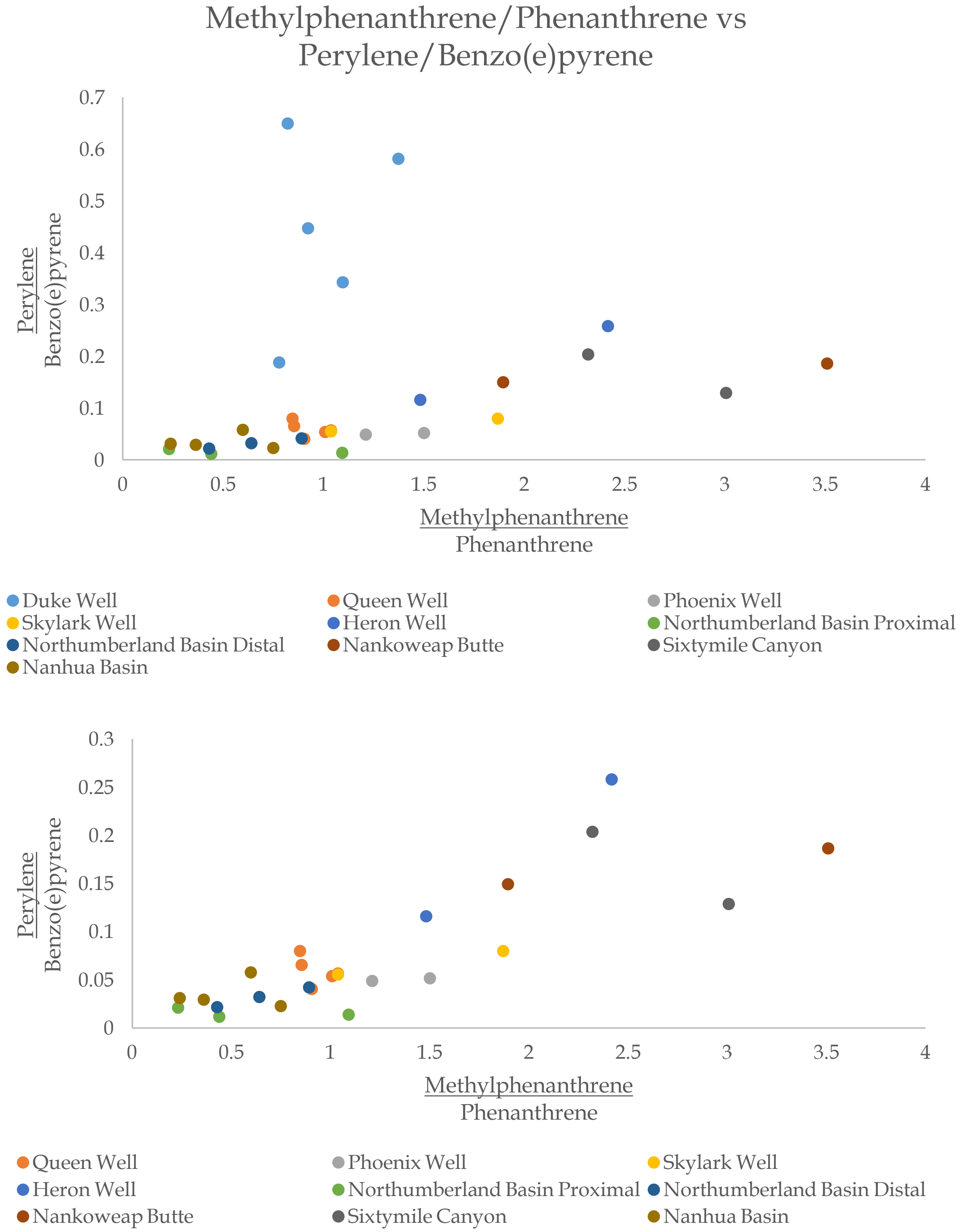


Figure 14 ***MeP/P vs Per/BeP cross-plot.*** *Cross plot of methylphenanthrene/phenanthrene vs perylene/benzo(e)pyrene from HyPy of kerogen-bound samples*
Bottom: Duke Well kerogen suite excluded

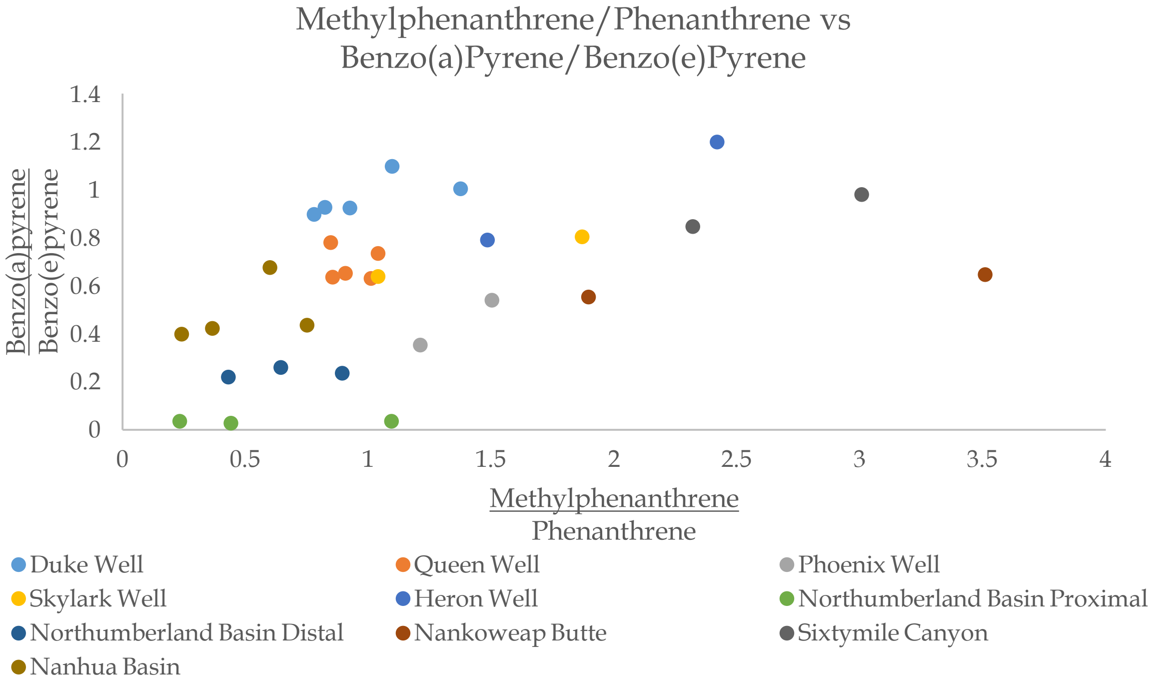


Figure 15 ***MeP/P vs BaP/BeP Cross-plot.*** *Cross-plot of methylphenanthrene/phenanthrene vs benzo(a)pyrene/benzo(e)pyrene from HyPy of kerogen-bound samples*

6. Conclusions

In this study, detailed catalytic hydropyrolysis (HyPy) was performed on ancient sedimentary kerogen to investigate the utility and systematics of polycyclic aromatic hydrocarbons (PAHs). A number of clear trends were identified:

- 5-ring kerogen-bound PAH distributions generated by HyPy show systematic behavior as a function of thermal maturity from early- to post- oil window maturity and thus are informative for petroleum geochemistry.

- At high stages of thermal maturity (peak- oil window and beyond), the relative stability of the 5-ring PAH controls the molecular maturity ratios regardless of the age of the rock or the composition of the source organic matter (e.g. realtive contribution of eukaryotes versus prokaryotes).

- Perylene is the most reactive 5-ring PAH relative to the other 5-ring PAH compounds but bound perylene could still be detected in even the most thermally mature kerogen analyzed in this study. Bound perylene has the potential to serve as an indicator of macromolecular organic matter formed under low temperature diagenesis (<50^{O}C) and surviving protracted burial over hundreds of millions to billions of years in the sedimentary rock record. For petroleum geochemistry, it may distinguish kerogen and asphaltenes from pyrobitumens (residues formed from thermal cracking of oil).

- The relative order of stability of kerogen-bound PAH was shown to be: perylene < benzo(a)pyrene < benzo(e)pyrene < benzofluoranthenes

- The ratio of bound perylene to benzo(e)pyrene is most sensitive to change within the peak oil window. The values are relatively high towards the end of the early oil window, as represented by the Duke Well kerogen suite, and drop significantly by the late oil window. Even at very low values from samples in the late oil window, the actual maturity series is predicted.

- The ratio of benzo(a)pyrene/benzo(e)pyrene is most sensitive to change in the late oil window, potentially further. Samples within the late oil window still show robust signal. The most thermally mature sample suite is where the benzo(a)pyrene/benzo(e)pyrene signal becomes very low.

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