The potential extent of Early Triassic Kockatea Shale equivalent source rocks in the Northern Carnarvon and Perth Basins (Western Australia)

Abbreviated title: Potential Early Triassic source rock extent

T. Taniwaki1, 2 *, C. Elders3, A. I. Holman1, K. Grice1

¹ Western Australian Organic & Isotope Geochemistry Centre, The Institute for Geoscience Research, School of Earth and Planetary Sciences, Curtin University, Perth, WA, Australia

² INPEX Corporation, Minato-ku, Tokyo, Japan

³ School of Earth and Planetary Sciences, Curtin University, Perth, Western Australia

ORCID ID: TT 0000-0003-2425-8690; CE 0000-0003-3317-6734; AH 0000-0001-5687-1268; KG 0000-0003-2136-3508

Present addresses: TT, School of Earth Planetary Sciences, Curtin University, Kent Street, Bentley, Western Australia, Australia 6102.

*Corresponding author (e-mail: takashi.taniwaki@inpex.co.jp)

Abstract

In the northern Perth Basin (Western Australia), the Early Triassic Kockatea Shale is the primary petroleum source rock. Possible source rocks in the Northern Carnarvon Basin are more varied and include the Upper Jurassic Dingo Claystone as well as the Early Triassic Locker Shale. Biomarker analyses were conducted on petroleum samples from these basins to understand the nature of the petroleum systems. Many of the analysed petroleum samples contain carotenoids (okenane, chlorobactane and isorenieratane) derived from photosynthetic sulfur bacteria, suggesting that their source rocks were deposited under conditions of photic zone euxinia (PZE) and/or derived from microbialites. In the northern Perth Basin, the major lithofacies contributing to the

source rock are dark coloured mudstones deposited under PZE conditions and/or derived from microbialites. In the southern Perth Basin, the potential source rock is either Permian, Jurassic or Cretaceous in age as indicated by the low concentrations or absence of carotenoids and the Triassic biomarker $n-C_{33}$ alkylcyclohexane. There is also a possibility that the Lower Triassic Locker Shale is the source rock of petroleum in the Tubridgi field on the Peedamullah Shelf of the Northern Carnarvon Basin, based on the similarity of biomarkers to Perth Basin petroleum sourced from the Kockatea Shale. However, the possibility of charge from the Upper Jurassic Dingo Claystone cannot be entirely excluded.

Introduction

The Perth and Northern Carnarvon basins are located on the western and northwestern coasts of Australia, respectively. In the northern Perth Basin, the Early Triassic Kockatea Shale is considered to be the primary source rock for petroleum based on Rock-Eval, biomarker and stable carbon isotope analyses (Thomas 1979; Scott 1994; Boreham et al. 2000; Thomas et al. 2004; Dawson et al. 2005; Grice et al. 2005c, a, b, 2007; McIldowie and Alexander 2005; Langhi et al. 2014; Grosjean et al. 2017). The basal section of the Kockatea Shale, which is assigned to the Hovea Member, has high total organic carbon (TOC, up to 5 %) and hydrogen indices (HI, up to 800 mg/gTOC) indicating good potential for petroleum generation (Thomas and Barber 2004; Taniwaki et al. 2021). In large parts of the southern Perth Basin, the source rock is assumed to be Permian in age because younger source rocks in Jurassic and Cretaceous sequences are too immature for hydrocarbon generation and expulsion, while the Lower Triassic is dominated by sandy lithofacies (Crostella and Backhouse 2000). However, in the central part of the basin such as the Vlaming Sub-basin, the Upper Jurassic Yarragadee Formation is buried deeply enough to reach maturity and is a source rock for oils containing relatively high abundances of conifer-derived organic materials (Crostella and Backhouse 2000). In the Northern Carnarvon Basin, there are several potential source rocks. The Upper Jurassic Dingo Claystone is recognised as a source rock in the Barrow and Exmouth sub-basins (Volkman et al. 1983; van Aarssen et al. 1996; Tindale et al. 1998), Lower to Middle Jurassic marine and deltaic sequences are untested potential source rocks (Edwards and Zumberge 2005) and the Middle to Upper Triassic fluvial-deltaic to marine Mungaroo Formation is also considered a source rock (Edwards and Zumberge 2005). The Lower Triassic Locker Shale, which is an equivalent of the Lower Triassic Kockatea Shale, also has source rock potential with high TOC and HI (Molyneux et al. 2016). Triassic or older strata have been cited as possible source rocks for the Tubridgi field on the Peedamullah Shelf (Yasin and Iasky 1998; Edwards and Zumberge 2005).

During the Late Permian/Early Triassic, massive volcanic activity from the Siberian Traps caused both global warming and anoxia (Erwin 1994; Knoll *et al.* 1996; Wignall and Twitchett 1996; Twitchett *et al.* 2004; Nabbefeld *et al.* 2010; Song *et al.* 2014; Whiteside

and Grice 2016). Development of PZE in the ancient water-column has been recognized in Permian/Triassic sections around the globe, including the northern Perth Basin (Grice et al. 2005c). Under PZE conditions, anoxygenic photosynthetic sulfur bacteria can thrive at the chemocline (the transition between oxic and anoxic conditions) (Pfenning 1978). These bacteria include purple, green-green and green-brown coloured sulfur bacteria. These organisms make specific carotenoid pigments (purple sulfur bacteria: okenone, sulfur bacteria: chlorobactene: green-brown sulfur green-green bacteria: isorenieratene) which yield biomarkers following diagenesis in the water column/sediments (okenane, chlorobactane and isorenieratane, respectively). Such biomarkers have been identified in both sediments and petroleum, suggesting PZE depositional conditions (Grice et al. 1996, 2005c; Clifford et al. 1998; Pedentchouk et al. 2004; Maslen et al. 2009; Sousa Júnior et al. 2013; Tulipani 2013). In addition, similar bacterial communities can develop in microbialites (Brocks and Schaeffer 2008; Pagès et al. 2014; Fox et al. 2020; Schaefer et al. 2020). In this study, biomarker analyses were conducted on petroleum samples (crude oils and condensates) from both the Perth and Northern Carnarvon basins to evaluate the nature of their petroleum systems.

Geological setting

The Perth Basin developed during several rifting, subsidence and uplift events from the Devonian to the Early Cretaceous (Fig. 1-Fig. 2) (Jablonski and Saitta 2004; Norvick 2004). The Late Permian to Early Triassic Kockatea Shale was deposited in a transgressive deeper water setting as part of a post-rift sequence following Late Permian rifting. Facies distribution in the Kockatea Shale was controlled by remnant topography created by the rift event (Taniwaki *et al.* 2021). The Middle Triassic Woodada Formation and younger strata were deposited during subsequent phases of extension.

The tectono-stratigraphy in the Northern Carnarvon Basin is similar to the Perth Basin (Ferdinando *et al.* 2007; l'Anson *et al.* 2019). Late Permian rifting is also evident in the Northern Carnarvon Basin. The Early Triassic Locker Shale, the equivalent of the Kockatea Shale, was deposited during a transgression that forms part of the post rift sequence. The Middle Triassic Mungaroo Formation and younger strata were deposited during subsequent phases of subsidence and rifting. The Upper Jurassic Dingo Claystone was mainly deposited in an open marine anoxic deeper water setting (Hocking 1992). Parts of the basin experienced significant uplift and erosion in the Early Cretaceous, as expressed by the Valanginian Unconformity.



Fig. 1.





Data & Methodology

Samples

Twenty-one petroleum samples (crude oils and condensates) from both the Perth and Northern Carnarvon basins were used for this study (Fig. 1, Tab. 1). In the Northern Carnarvon Basin, one sample (Wanaea 1) comes from the Dampier Sub Basin and four other samples are derived from the Tubridgi field on the Peedamullah Shelf. The petroleum samples from the Northern Carnarvon Basin were recovered from the Cretaceous Birdrong Formation and Mardie Greensand Member (Tubridgi), and the Jurassic Angel Formation (Wanaea). In the Perth Basin, petroleum samples were derived from the Early Permian Carynginia Formation, Late Permian Dongara and Wagina Sandstones, Late Permian to Early Triassic Kockatea Shale, and Jurassic Cattamarra Coal Measures and Cockleshell Gully Formation. In the southern Perth Basin, the Early Permian Irwin River Coal Measures and Jurassic Yaraggadee Formation and Cattamarra Coal Measures are the reservoir formations for the samples.

Tab. 1.

Well	Туре	Basin	Formation	Age
Beharra Springs 1	Condensate	North Perth Basin	Carynginia Fm.	Permian
Beharra Springs North 1	Oil	North Perth Basin	Wagina Sandstone	Permian
Beharra Springs South 1	Oil	North Perth Basin	Kockatea Shale	Permian/Triassic
Dongara 04	Oil	North Perth Basin	Irwin River Coal Measures	Permian
Dongara 08	Oil	North Perth Basin	Dongara Sandstone	Permian
Dongara 12	Oil	North Perth Basin	Wagina Sandstone	Permian
Dongara 17	Oil	North Perth Basin	Dongara Sandstone	Permian
Hovea 1	Oil	North Perth Basin	Dongara Sandstone	Permian
Mt Horner 09	Oil	North Perth Basin	Cattamarra Coal Measures	Jurassic
North Yardanogo 1	Oil	North Perth Basin	Cockleshell Gully Fm.	Jurassic
Woodada 03	Oil	North Perth Basin	Carynginia Fm.	Permian
Woodada 05	Oil	North Perth Basin	Carynginia Fm.	Permian
Yardarino 1	Oil	North Perth Basin	Wagina Sandstone	Permian
Gage Roads 1	Oil	South Perth Basin	Yaraggadee Fm.	Jurassic
Walyering 2	Oil	South Perth Basin	Cattamarra Coal Measures	Jurassic

Whicher Range 1	Oil	South Perth Basin	Irwin River Coal Measures	Permian	
Tubridgi 02	Oil	North Carnarvon Basin	Birdong Sandstone	Cretaceous	
Tubridgi 04	Oil	North Carnarvon Basin	Mardie Greensand Mbr. &	Cretaceous	
	On North Carnaryon Basin		Birdong Sandstone		
Tubridgi 05	Oil	North Carnarvon Basin	Mardie Greensand Mbr.	Cretaceous	
Tubridgi 07	Oil	North Carnarvon Basin	Mardie Greendand Mbr.,	Cretaceous	
U			Birdong Sandstone & Nanutarra Fm.		
Wanaea 1	Oil	North Carnarvon Basin	Angel Fm.	Jurassic	

Fractionation of samples

The petroleum samples were fractionated into saturated, aromatic, and polar fractions using small scale silica gel column chromatography. Samples (~10 mg) were weighed and put onto a 5.5 cm column packed with activated silica gel (160 °C overnight). The saturated hydrocarbons were eluted with 4 mL of *n*-hexane. The aromatic hydrocarbons were separated using a mixture of 1.2 mL dichloromethane and 2.8 mL of *n*-hexane. The polar fraction was eluted with a 1:1 mixture of methanol (2 mL) and dichloromethane (2 mL). Each fraction was evaporated to dryness with a nitrogen purge and then weighed.

Analysis

Gas chromatography-mass spectrometry (GC-MS) analyses were conducted on both saturated and aromatic hydrocarbon fractions. Gas chromatography-metastable reaction monitoring-mass spectrometry (GC-MRM-MS) was also conducted on all samples.

Gas Chromatography-Mass Spectrometry (GC-MS)

For the saturated fractions, an Agilent 5973B MSD interfaced to an Agilent 7890B gas chromatograph was used for GC-MS analysis. A J&W Scientific DB-1MS column of 60 m length, 250 μ m inner diameter and 0.25 μ m film thickness was installed. The GC oven was programmed from 40 °C to 325 °C at a heating rate of 3 °C/min. The holding time at initial and final temperature was 1 and 30 minutes, respectively. The MS was set with an ionisation energy of 70 eV and measured a mass range from 50 to 550 Daltons.

For the aromatic fractions, an Agilent 5975B MSD interfaced to an Agilent 6890N gas chromatograph was used for GC-MS analysis. A J&W DB-5MS column of 60 m length, 250 μ m inner diameter and 0.25 μ m film thickness was used. The oven program and scanned range of the MS was the same as that used for the saturated fractions.

GC-MS, metastable reaction monitoring- (GC-MRM-MS)

Saturated and aromatic fractions were combined in equal amounts for GC-MRM-MS analysis. An Agilent 7890B GC interfaced to an Agilent 7010B Triple Quadruple MS operated in metastable reaction monitoring (MRM) mode was used for the analysis. A DB-5MS UI capillary column of 60 m length, 250 μ m inner diameter, and 0.25 μ m film thickness was installed. The temperature of the GC oven was set from 40 °C to 325 °C with a heating rate of 4 °C/min. The final holding time was 20.75 minutes. The MS was programmed at 50 eV ionisation energy. The QQQ temperature was set at 150 °C. D4-C₂₇ $\alpha\alpha\alpha$ cholestane was added as an internal standard to the combined sample. Compounds were identified by comparing with reference standards, matching retention times and elution order.

Rock samples

Rock samples from the earliest Triassic part of the Kockatea Shale from the northern Perth Basin were used for comparison with petroleum samples. The rock samples were analyzed and described in detail by Taniwaki *et al.* (2022).

Results and discussion

Thermal maturity assessment

The thermal maturity of each sample was determined based on C_{32} 22S/(22S+22R) $\alpha\beta$ homohopane, 17β , 21α C₃₀ hopane/ 17α , 21β C₃₀ hopane (moretane/hopane), C₂₉ 20S/(20S+20R) ($\alpha\alpha\alpha+\alpha\beta\beta$) sterane ratio, $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ C₂₉ sterane, $18\alpha22,29,30$ trisnorhopane (Ts) to 17a22,29,30-trisnorhopane (Tm) ratio (Ts/(Ts+Tm)) and diasteranes/(diasteranes+regular steranes): ΣC₂₇₋₂₉ diasteranes/(ΣC_{27-29} diasteranes+ ΣC_{27-29} steranes) (abbreviated to Dia/(Dia+Reg)) (Tab. 3). C_{32} 22S/(22S+22R) $\alpha\beta$ -homohopane, moretane/hopane and C₂₉ 20S/(20S+20R) ($\alpha\alpha\alpha+\alpha\beta\beta$) sterane ratios reached their thermal equilibrium values, indicating that the thermal maturity is equivalent to at least 0.8 % vitrinite reflectance (Ro) (Peters *et al.* 2004). $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ C_{29} sterane, Ts/(Ts+Tm) and Dia/(Dia+Reg) are still lower than their thermal equilibrium values indicating that the thermal maturity for all samples is less than 0.9 % Ro equivalent. Therefore, the thermal maturity level of samples ranges between 0.8 and 0.9 % Ro equivalent (Peters et al. 2004).

Characteristics of major biomarkers (Pr/Ph, C_{35} homohopane index, gammacerane index, and C_{27-29} regular sterane ratio)

Tubridgi petroleum appears to have experienced biodegradation (biodegradation rank: 3-4, (Trolio et al, 1999; Grice et al. 2000; Wenger *et al.* 2002; Peters *et al.* 2004)) based on the elevated unresolved complex mixture and the depletion of *n*-alkanes in total ion chromatograms, most significantly in Tubridgi 7. Samples from other fields do not show significant biodegradation.

Pr/Ph ratios show a significant difference between the basins: 1.7-4.1 for most of the Northern Carnarvon Basin petroleum, 0.4-1.3 for the northern Perth Basin and 1.4-1.8 for the southern Perth Basin. However, Pr/Ph in the Tubridgi petroleum appears to be influenced by biodegradation (Tab. 2 and S1). C_{35} homohopane and gammacerane indices (hopane index: C_{35} (22*S*+22*R*) $\alpha\beta$ -homohopane/ C_{34} (22*S*+22*R*) $\alpha\beta$ -homohopane, gammacerane index: gammacerane/(gammacerane+ $C_{30}\alpha\beta$ -homohopane)) overlap between basins (Tab. 2 and S1). C_{27} to C_{29} regular sterane ratios also show similar

characteristics between basins, except petroleum from Gage Roads 1. C_{27} and C_{29} regular steranes generally range between 30-50%, and C_{28} regular steranes generally range between 20-30%. However, the sterane ratio in Gage Roads 1 shows a higher abundance of C_{29} regular sterane reaching 81% (Tab. 2 and S1).

Relative abundance of carotenoid biomarkers (okenane, chlorobactane and isorenieratane) in petroleum samples

Most of the petroleum samples contain biomarkers derived from anoxygenic photosynthetic sulfur bacteria (okenane: purple sulfur bacteria, chlorobactane: green-green sulfur bacteria, isorenieratane: green-brown sulfur bacteria) (Fig. 3). Beharra Springs North 1 does not contain either chlorobactane or okenane but does contain isorenieratane. Beharra Springs South 1, Whicher Range 1 and Tubridgi 7 contain both chlorobactane and isorenieratane but no okenane. Wanaea 1 and Walyering 2 do not contain chlorobactane, isorenieratane nor okenane (Fig. 4).

Tab. 2.

	Pr/Ph	C ₃₅ homohopane index	Gammacerane index	C ₂₇₋₂₉ regular sterane ratio	<i>n-</i> C ₃₃ ACH ratio	Okenane ratio	Carotenoids (ug/gTOC)
Northern	1.7-	0.4-1.0	0.01-0.06	C ₂₇ : 30-50%	0-0.01	1.00-1.05	Ok: 0.00-0.32
Carnarvon Basin	4.1			C ₂₈ : 30-50%			Ch: 0.00-6.19
				C ₂₉ : 20-30%			ls: 0.00-22.46
Northern	0.4-	0.4-0.7	0.02-0.08	C ₂₇ : 30-50%	0.02-0.57	1.00-1.15	Ok: 0.00-1.26
Perth Basin	1.3			C ₂₈ : 30-50%			Ch: 0.00-4.18
				C ₂₉ : 20-30%			ls: 0.06-159.86
Southern	1.4-	0.1-0.7	0.01-0.05	C ₂₇ : 30-50%	0-0.02	1.00-1.06	Ok: 0.00-0.04
Perth Basin	1.8			C ₂₈ : 30-50%			Ch: 0.00-0.21
				C ₂₉ : 20-30%			ls: 0.00-0.37
				*Gage Roads 1			
				C ₂₇ : 8%			
				C ₂₈ : 11%			
				C ₂₉ : 81%			

Tab. 3.

Well	Basin		C ₃₂ αβ-hα	22S/(22S+22R) omohopane	Moretane/ Hopane	C ₂₉ 20S/(20S+20R) sterane ratio	αββ/(αββ+ααα) C ₂₉ Sterane	Ts/(Ts +Tm)	Dia/(Dia +Reg)
Beharra Springs 1	North Basin	Perth	0.61		0.06	0.42	0.63	0.61	0.49
Beharra Springs North 1	North Basin	Perth	0.61		N/I	0.29	0.72	N/I	0.35
Beharra Springs South 1	North Basin	Perth	0.58		0.07	0.43	0.64	0.69	0.55
Dongara 04	North Basin	Perth	0.61		0.06	0.47	0.59	0.49	0.35
Dongara 08	North Basin	Perth	0.58		0.06	0.44	0.61	0.65	0.49
Dongara 12	North Basin	Perth	0.58		0.07	0.44	0.54	0.56	0.54
Dongara 17	North Basin	Perth	0.60		0.07	0.46	0.50	0.70	0.32
Hovea 1	North Basin	Perth	0.60		0.07	0.46	0.46	0.54	0.27

Mt Horner 09	North Perth Basin	0.55	0.05	0.47	0.58	0.76	0.42
North Yardanogo 1	North Perth Basin	0.59	0.05	0.46	0.58	0.71	0.34
Woodada 03	North Perth Basin	0.57	0.06	0.46	0.57	0.78	0.41
Woodada 05	North Perth Basin	0.55	0.06	0.47	0.60	0.84	0.60
Yardarino 1	North Perth Basin	0.58	0.04	0.45	0.64	0.77	0.57
Gage Roads 1	South Perth Basin	0.60	0.09	0.45	0.50	0.31	0.64
Walyering 2	South Perth Basin	0.56	0.04	0.41	0.59	0.74	0.54
Whicher Range 1	South Perth Basin	0.60	0.04	0.47	0.66	0.65	0.56
Tubridgi 02	North Carnarvon Basin	0.63	0.05	0.48	0.59	0.56	0.23
Tubridgi 04	North Carnarvon Basin	0.61	0.05	0.45	0.57	0.56	0.40

Tubridgi 05	North Carnarvon Basin	0.59	0.05	0.48	0.58	0.61	0.42
Tubridgi 07	North Carnarvon Basin	0.58	0.09	0.34	0.45	0.64	0.38
Wanaea 1	North Carnarvon Basin	0.58	0.06	0.48	0.65	0.80	0.70

The effect of thermal maturity on the concentrations of okenane, chlorobactane and isorenieratane is evaluated by comparing these biomarkers with $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ C₂₉ sterane (Fig. 5). The concentrations of okenane, chlorobactane and isorenieratane generally decrease with increasing thermal maturity, suggesting that the compounds are likely affected by thermal maturity. The most significant change in concentrations occurs when $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ C₂₉ sterane ratio reaches 0.6. The rate of decrease of each carotenoid concentration is similar. The okenane ratio, which is the relative abundance of okenane to chlorobactane and isorenieratane, distinguishes PZE dominated conditions (lower okenane ratio) and microbialite facies (higher okenane ratio) in less mature rock samples (Brocks and Schaeffer 2008; Pagès *et al.* 2014; Schaefer *et al.* 2020) but this ratio could be influenced by thermal maturity in the more mature petroleum samples and caution is therefore required if using it for comparison between samples from different wells.

The absence of some of these carotenoid biomarkers in Beharra Springs North 1, Beharra Springs South 1, Whicher Range 1 and Wanaea 1 could be the result of relatively higher thermal maturity, as $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ C₂₉ sterane of these samples is higher than 0.64, which is nearly the thermal equilibrium value. However, $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ C₂₉ sterane of Tubridgi 7 and Walyering 2 is lower (0.45 and 0.59, respectively), although Tubridgi 7 does not have okenane and Walyering 2 lacks all three carotenoid biomarkers. The absence of okenane in Tubridgi 7 may be the result of biodegradation. The absence of these biomarkers from Walyering 2 could indicate a difference in paleoenvironmental conditions during deposition of their source rocks. Gage Roads 1 and Whicher Range 1 in the southern Perth Basin contain carotenoids, but their concentrations are low compared to oils from the northern Perth and Northern Carnarvon basins.

Fig. 6 shows peaks for okenane, chlorobactane and isorenieratane from Tubridgi 2, 4, 5 and 7. These samples show a similar distribution of carotenoid biomarkers to rock (PZE and microbialite facies) and petroleum samples from the northern Perth Basin (Fig. 3).The similarity implies that the source of the Tubridgi petroleum samples shares similar paleoenvironmental conditions to the Kockatea Shale in the northern Perth Basin.



Fig. 3.



Fig. 4.

Implications for source rocks

Perth Basin

In the northern Perth Basin, the Kockatea Shale is considered to be a primary source rock based on source-oil correlation, especially using the C₃₃ *n*-alkylcyclohexane ratio (*n*-C₃₃ ACH ratio, *n*-C₃₃ACH/*n*-C₃₄) (Dawson *et al.* 2005; Grice *et al.* 2005a; McIldowie and Alexander 2005; Jones *et al.* 2011; Owens *et al.* 2018). The samples analysed in this study also show variable abundances of *n*-C₃₃ ACH (Fig. 7). In addition to *n*-C₃₃ ACH, the presence of carotenoid biomarkers (okenane, chlorobactane and isorenieratane) provides further evidence that the Lower Triassic Kockatea Shale is the primary source rock for oils in the basin. In the Kockatea Shale rock samples, these carotenoid biomarkers and *n*-C₃₃ ACH were only identified in the dark-coloured shale deposited under PZE conditions, and in microbialite samples (Taniwaki *et al.* 2022). Rock-Eval analysis shows that these lithofacies have higher source rock potential than other lithofacies that comprise the Kockatea Shale (TOC: up to 3.4 % and HI: up to 579 mg/gTOC), suggesting they are the main contributors to the petroleum systems (Taniwaki *et al.* 2021).

In the southern Perth Basin, oils from Gage Roads 1 and Whicher Range 1 contain some carotenoids, but their concentrations are low compared with the concentration in the northern Perth Basin. Walyering 2 does not contain these carotenoids. In addition, $n-C_{33}$ ACH is absent from these petroleum samples. The low concentration of carotenoids in Whicher Range 1 and their absence from Walyering 2 could be because these samples have a higher level of thermal maturity (Figure 5). In addition, the high relative abundance of C₂₉ steranes in Gage Roads 1 indicates significant input of terrigenous organic material. It is possible therefore that the low concentration of carotenoid biomarkers in this sample may result from dilution by terrestrial organic material. However, the low concentrations and/or absence of carotenoids and the lack of $n-C_{33}$ ACH in these petroleum samples suggest that the Lower Triassic Kockatea Shale is not a source of oils in the southern Perth Basin. This is consistent with the observation that the Lower Triassic is dominated by sandy lithofacies in this part of the basin and favours the assumption that they are derived from potential Permian shaly coals (Summons et al. 1995; Crostella and Backhouse 2000 and references herein), and where sufficiently deeply buried, Jurassic (Summons et al. 1995; Crostella and Backhouse 2000 and references herein) or Cretaceous (Summons et al. 1995; Crostella and Backhouse 2000 and references herein) source rocks.







Fig. 6.



Northern Carnarvon Basin

Multiple source rocks from the Triassic to Cretaceous are recognised in the Northern Carnarvon Basin (and more generally on the entire the North West Shelf). The identification of source rocks is sometimes made difficult because of the mixing of liquids from different sources during migration and within reservoirs (Longley *et al.* 2002). However, the Upper Jurassic Dingo Claystone is traditionally considered to be one of the main petroleum source rocks (e.g. Volkman *et al.* 1983; lasky *et al.* 2002; Longley *et al.* 2002; Edwards and Zumberge 2005; Boreham *et al.* 2008). This is based on source-oil correlation using steranes, hopanes and plant-derived aromatic biomarker evidence in the Barrow sub-basin (Volkman *et al.* 1983; van Aarssen *et al.* 1996). Basin modeling shows that the Dingo Claystone reached the oil window after the Late Cretaceous in the Exmouth sub-basin and generated large volumes of hydrocarbons (Tindale *et al.* 1998), confirming its potential importance in this basin. A range of other source rocks have been proposed from Cretaceous and Jurassic intervals (e.g. Longley *et al.* 2002; Edwards and Zumberge 2005). The source rock potential of the Triassic has also been identified (Molyneux *et al.* 2016).

The absence of carotenoid biomarkers and $n-C_{33}$ ACH in the Wanaea petroleum sample favours derivation from a source rock deposited under more oxic conditions without PZE or the development of microbialites. However, the absence of these biomarkers may be due to thermal maturity effects because the sample shows higher thermal maturity than that of the Tubridgi petroleum samples, although the hopane index does show more oxic conditions than the Tubridgi samples. Although it is not possible to define precise sources, it is possible that Wanaea petroleum has migrated from source rocks deposited under more oxic conditions and is unlikely to be derived from any source rocks with characteristics similar to the Lower Triassic Kockatea Shale in the Perth Basin. This is consistent with the currently held view that Wanaea oil migrated from an Upper Jurassic source rock in the Lewis and Kendrew troughs (Longley et al. 2002). A characteristic of this source rock is that it contains terrigenous organic matter deposited under deltaic conditions. This distinguishes it from the Lower Triassic Kockatea Shale deposited under anoxic conditions under marine conditions, and explains the more oxic signature of oils derived from the Upper Jurassic source rock compared to those derived from a Lower Triassic Kockatea Shale-type source rock.

By contrast, the presence of carotenoid biomarkers derived from sulfur bacteria in the Tubridgi petroleum samples suggests that their source rock was developed under PZE conditions and/or was formed by microbialites. The biomarker characteristics of the Tubridgi petroleum samples are similar to the petroleum from the northern Perth Basin (Tab. 2 and S1), as well as to the mudstones deposited under PZE conditions and the microbialites from the Lower Triassic Kockatea Shale. Triassic and older strata subcrop the Valanginian unconformity on the Peedamullah Shelf and are present beneath the Tubridgi Field (lasky *et al.* 2002). These have been suggested as potential sources for

Tubridgi oils based on the presence of aromatic dinosteranes and the absence of coniferderived biomarkers such as retene, which are generally considered as proxies of Late Triassic-Middle Jurassic sources (Yasin and Iasky 1998; Iasky *et al.* 2002; Edwards and Zumberge 2005). The biomarker characteristics support the possibility that Tubridgi petroleum comes from the Lower Triassic Locker Shale which is an equivalent of the Lower Triassic Kockatea Shale. Further evidence that the Triassic acts as a source of oil in the Northern Carnarvon Basin comes from oil inclusions reported from the Upper Triassic Mungaroo Formation in the Pinhoe 1/ST1 well on the Exmouth Plateau, which indicate the presence of a paleo oil column (Bourdet 2016). It is difficult to envisage migration of petroleum from the Upper Jurassic Dingo Claystone because there is no large fault displacing the stratigraphically younger Dingo Claystone into a downdip position against the Middle Triassic Mungaroo Formation (Bernecker *et al.* 2018). The stratigraphic relationships suggest that the source of the oil is from within the Triassic – either local oil-prone sources within the Mungaroo Formation, or from the Lower Triassic Locker Shale.

The relative abundance of n-C₃₃ ACH is a key biomarker used for correlation to the Lower Triassic Kockatea Shale in the northern Perth Basin, but it is absent from the Northern Carnarvon Basin samples including the Tubridgi wells. This absence could result either from thermal maturation, because this compound reduces in concentration as thermal maturity increases (Thomas and Barber 2004) (Fig. 7) or biodegaradation because alkylcyclohexanes are generally affected at biodegradation rank 3-4 (Wenger et al. 2002; Abdula 2019). Although the Tubridgi Field petroleum comes from a source rock deposited under PZE conditions, there are no published analyses to indicate whether or not the Dingo Claystone or other potential Jurasic source rocks were also deposited under these conditions. Furthermore, it cannot be determined if the petroleum in the Barrow and Exmouth sub-basins migrated from a source rock developed under PZE conditions and/or a microbialite source rock because published analyses are focused on steranes, hopanes and parameters related to terrestrial organic matter (Volkman et al. 1983; van Aarssen et al. 1996). This different analytical approach, and the limited nature of published analyses, precludes a direct comparison of the Tubdrigi petroleum samples analysed in this study with both the Dingo Claystone and the oils from the Barrow subbasin. Therefore, despite the evidence to support a Lower Triassic source rock, a contribution from a Jurassic source rock to Tubridgi petroleum in the Peedamullah Shelf cannot be completely excluded. Further analysis of the Northern Carnarvon Basin petroleum and source rocks is clearly required. If the contribution from the Lower Triassic Locker Shale is substantiated, this opens up the potential for new plays on the southern margin of the Northern Carnarvon Basin and potentially more broadly in the basin.

Conclusions

Petroleum samples from the Perth Basin and the Tubridgi Field on the Peedamullah Shelf of the Northern Carnarvon Basin contain carotenoid biomarkers derived from photosynthetic sulfur bacteria, suggesting that the source rocks developed under PZE conditions and/or were formed by microbialites. In the northern Perth Basin, biomarkers proved that the microbialites and/or dark coloured mudstone deposited under PZE conditions in the Kockatea Shale are a major contributing lithofacies to the petroleum system. On the other hand, in the southern Perth Basin, it is possible that the source rock is Permian, Jurassic or Cretaceous in age based on the low concentrations or absence of carotenoids, the lack of $n-C_{33}$ ACH and the overall geological setting. The presence of carotenoid biomarkers in the Tubridgi petroleum on the Peedamullah Shelf shows that petroleum also migrated from a source rock developed under PZE conditions and/or formed by microbialites. The similarity of biomarker characteristics to the Perth Basin petroleum suggests that this source rock could have been the Lower Triassic Locker Shale. However, the possibility of a contributuion from the Dingo Claystone or other Jurassic source rocks to the Tubridgi petroleum cannot be excluded due to the absence of $n-C_{33}$ ACH and the lack of previous analyses targeting the carotenoids in the Dingo Claystone and oils derived from it. Further analysis of Northern Carnarvon Basin petroleum and source rocks has the potential to resolve this issue and to open up new plays on the southern margin of the Northern Carnarvon Basin and possibly more broadly in the basin.

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Author contributions

Takashi Taniwaki, Kliti Grice and Chris Elders designed the experiments. Petroleum samples used in this chapter were from those already available in the laboratory by Kliti Grice. Kliti Grice and Chris Elders supplied the technical advice for the interpretation of the results. The fractionation of petroleum samples and GC-MS analysis were performed by Takashi Taniwaki with help from Alex Holman and Peter Hopper. The manuscript was prepared during the PhD project by Takashi Taniwaki with detailed comments and discussion from Kliti Grice, Chris Elders and Alex I. Holman.

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Figure caption

Fig. 1. Location of both Perth and Northern Carnarvon basins and petroleum samples. A represents the location of both basins and samples with gravity anomaly map as background showing basin geometry. The public domain data used for the gravity map is published by the Scripps Institution of Oceanography (Sandwell and Smith 2009; Sandwell *et al.* 2013, 2014). B shows the detailed sample location around the Tubridgi Field in the Northern Carnarvon Basin. C indicates the detailed sample location around the northern Perth Basin. Yellow points represent the location of wells where rock sample analysis was conducted (Taniwaki *et al.* 2021).

Fig. 2. Stratigraphy in both (A) northern Perth and (B) Northern Carnarvon basins (Ferdinando *et al.* 2007; l'Anson *et al.* 2019). Light and dark grey: deeper water mudstone, yellow: shallow marine sandstone: brown: fluvial to deltaic/marine sediments, blue- green: open marine glacial sediments.

Fig. 3. GC-MRM-MS peaks of okenane, isorenieratane and chlorobactane from petroleum samples (A: Hovea 1, B: Tubridgi 5). Hovea 1 is located on the northern Perth Basin and Tubridgi 5 is located on the Peedamullah Shelf in the Northern Carnarvon Basin.

Fig. 4. Distribution of carotenoid biomarkers (okenane, chlorobactane and isorenieratane). A shows the entire region covering samples from the Northern Carnarvon Basin to the southern Perth Basin. B represents the detailed distribution around the Tubridgi Field in the Northern Carnarvon Basin. C indicates the distribution around the northern Perth Basin.

Fig. 5. The influence of thermal maturity on carotenoid biomarkers (A: okenane, B: chlorobactane, C: isorenieratane).

Fig. 6. GC-MRM-MS peaks of okenane, isorenieratane and chlorobactane from petroleum samples of Tubridgi 2, 4, 5 and 7.

Fig. 7. The thermal maturity influence on $n-C_{33}$ ACH ratio. $n-C_{33}$ ACH ratio = $n-C_{33}$ ACH $/C_{34}$ n-alkane.

Table caption

Tab. 1. Type of fluids, basin location, reservoir age and Formation and for each petroleum sample.

Tab. 2. Characteristics of biomarkers (Pr/Ph, C_{35} homohopane index, gammacerane index, and C_{27-29} regular sterane ratio, $n-C_{33}$ ACH ratio, okenane ratio and carotenoids). Ok = okenane. Ch = chlorobactane. Is = Isorenieratane.

Tab. 3. C_{32} 22*S*/(22*S*+22*R*) $\alpha\beta$ -homohopane, Moretane/Hopane, C_{29} 20*S*/(20*S*+20*R*) sterane ratio, $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)C_{29}$ Sterane, Ts/(Ts+Tm) and Dia/(Dia+Reg) of each sample for thermal maturity evaluation. N/I indicates not identified.