A second type of highly asphaltic crude oil seepage stranded on the South Australian coastline

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HIGHLIGHTS (3-5 bullets, 85-character limit including spaces)
1) Report a new type of oil found on South Australian coastline termed asphaltic tar
2) Asphaltic tars share several source characteristics with well-studied asphaltites
3) Clear correlation to asphaltites is complicated by differences in thermal maturity
4) Asphaltic tars may have been altered by thermochemical sulphate reduction
ABSTRACT (296/300 words)

Strandings of semi-solid to solid asphalitic bitumen along the coastline of South Australia have been reported as far back as the late 1800s. Hitherto only a single variety, now referred to as asphaltite, has been attributed to seepage from the nearby Bight Basin. The geochemistry of the asphaltites suggest they were derived from a marine source rock deposited under anoxic or euxinic conditions, most likely a Cretaceous ocean anoxic event, and were generated within the early/main oil window. Here we identify a new type of semi-solid asphalitic bitumen collected following a severe storm event in 2016. Termed asphalitic tars, these viscous oils bear a strong geochemical resemblance to the asphaltites. Both oil types have high asphaltene contents, identical n-alkane carbon isotopic profiles and near identical source-specific sterane distributions. However, several notable geochemical variations can distinguish these new strandings from the asphaltites. The most notable of these differences include heavier bulk sulphur isotopic composition, extremely high abundances of Re and Os with distinct $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ values and thermal maturity parameters consistent with generation in the late oil window. The differences in sulphur isotopic composition and Re-Os systematics could be considered evidence that despite their other source-specific similarities, the asphal tic tars originated from a different source rock. However, alteration of these two parameters can occur due to thermochemical sulphate reduction. Conclusive identification of this alteration process typically relies on further diagnostic parameters which are unfortunately not available in the case of coastal oil strandings. This introduces uncertainty to the correlation of these two types of asphal tic oil. In either scenario, the similarities between these two types of oil suggest their source rock(s) contained highly comparable organic matter inputs. We therefore attribute the origin of these new asphal tic tar strandings to natural seepage from the offshore Bight Basin.

KEYWORDS (maximum of 8)

- Bight Basin; asphaltite; asphal tic tar; oil-oil correlation; CSIA;
sulphur isotopes; Re-Os; thermochemical sulphate reduction
1. INTRODUCTION

Ocean beaches along Australia’s southern margin are known to collect bitumen emitted from seafloor seeps associated with a variety of different petroleum systems (e.g. McKirdy et al., 1986, 1994; Padley, 1995; Edwards et al., 1998, 2016, 2018). Reports of asphaltene-rich coastal bitumen strandings (asphaltum, now referred to as asphaltite) in the region date back to the early 1800s and continue to the present (Trewartha, 1850; Tolmer, 1882; Sprigg and Woolley, 1963; Volkman et al., 1992; Edwards et al., 1998; Hall et al., 2014; Ross et al., 2017). Historical reports of these asphaltite strandings predate anthropogenic inputs of hydrocarbons to the region, suggesting that they are the product of natural offshore seepage. Although asphaltite is the least common variety of coastal bitumen recognised along the Australian coastline, it contributes the largest specimens, with individual pieces weighing up to 7 kg (Edwards et al., 1998, 2016).

Source and maturity-specific biomarkers indicate that these asphaltites are derived from a Mesozoic marine shale, deposited under sub-oxic to euxinic conditions, which expelled petroleum within the early oil window (Edwards et al., 1998; Hall et al., 2014; Scarlett et al., 2019). The source rock is presently thought to have been deposited during an oceanic anoxic event (OAE). However, interpretations vary from the Cenomanian-Turonian OAE2 (Totterdell et al., 2008; Boreham, 2009; Hall et al., 2014; Corrick et al., 2019), the Albian OAE1d (Boult et al., 2005; Hall et al., 2014), the Aptian OAE1a and Albian OAE1b events (Scarlett et al., 2019). Inspection of the GeoMark™ global petroleum database suggests that the asphaltites are not products of any documented petroleum system (Summons et al., 2001). Unlike the majority of the tar balls found along the South Australian coastline (viz. ‘waxy bitumens’) which have been geochemically linked to Cenozoic petroleum systems in southeast Asia (Padley, 1995; Edwards et al., 2016, 2018), the asphaltites are currently thought to originate from an undiscovered petroleum system in the offshore Bight Basin (Fig. 1A) located on Australia’s southern margin (Boreham et al., 2001; Totterdell et al., 2008; Hall et al., 2014). This interpretation is supported by analysis of organic-rich samples with similar geochemistry dredged from the basin (Totterdell et al., 2008; Boreham, 2009) and rhenium-osmium (Re-Os) geochronology of the asphaltites (Corrick et al., 2019), which
demonstrated their timing of generation is consistent with existing petroleum systems models for the basin (Struckmeyer et al., 2001; Totterdell et al., 2008). Previous studies have also proposed seepage from other nearby basins, such as the Otway Basin (Boult et al., 2005; Hall et al., 2014). However, recent modelling of the metocean conditions of the Great Australian Bight suggests that offshore seepage from the Otway Basin is unlikely to migrate west, a requirement given the observed spatial distribution of asphaltite strandings along the coastline (Ross et al., 2017). Seepage from the Ceduna or Duntroon sub-basins of the Bight Basin, however, is consistent with the documented regions of asphaltite stranding (Ross et al., 2017).

The Bight Basin comprises an approximately 15 km-thick succession of Late Jurassic to Cretaceous sediments (Fig. S1) deposited in response to the separation of Australia and Antarctica during the break-up of the supercontinent Gondwana (Fraser and Tilbury, 1979; Totterdell et al., 2000; Totterdell and Bradshaw, 2004). These Mesozoic deposits are unconformably overlain by Palaeogene sediments with no source potential (Totterdell et al., 2008). Proposed petroleum systems in the basin are primarily associated with thick mid- to late Cretaceous deltaic and marine sediments, namely the Blue Whale, White Pointer, Tiger and Hammerhead supersequences (Blevin et al., 2000; Struckmeyer et al., 2001; Totterdell et al., 2000, 2008). However, no working petroleum systems have yet been proven within the basin.

Aside from the asphaltite strandings, no other seeped hydrocarbons that have been found on the South Australian coastline are considered products of the Bight Basin. In this study we report a new variety of asphaltene-rich crude oil stranded on the southeastern coastline of South Australia in October 2016. Referred to herein as asphaltic tar, these new strandings display strong geochemical similarities to the asphaltites, suggesting that the two oil types may originate from lateral equivalents of the same source rock.
2. MATERIALS AND METHODS

2.1. Sample suite

The stranding locations of the specimens analysed in this study are shown in Figure 1A and their collection details are summarised in Table S1. Details of the four representative waxy bitumen samples also included in this study to illustrate their contrasting $n$-alkane $\delta^{13}$C profiles may be found in Ross et al. (2017). The asphaltites are visually distinctive, jet black, semi-solid to solid bitumens with a petroliferous odour and commonly exhibit deep shrinkage cracks (Fig. 1B). Fresh specimens with a soft and slightly pliable interior are rare, as most asphaltites collected on the coastline have become brittle, breaking apart with a diagnostic conchoidal fracture. The asphaltic tars are similarly jet black in colour but emit a stronger petroliferous odour and have remained viscous and sticky with a surficial sand coating (Fig. 1C).

The specimens compared in this study were recovered during three systematic annual surveys of 30 ocean beaches spanning the South Australian coastline in the period 2014 to 2016, as part of the Great Australian Bight Research Program (Ross et al., 2017). The sample suite was further supplemented with additional samples donated from private collections. Representative asphaltites were selected from each of the three surveys while ensuring a spatial distribution that encompassed the entire survey area (Fig. 1A). Asphaltic tar samples were only encountered in the final survey conducted in October of 2016, at the Number 1 and 2 Rocks beach in the Canunda National Park, located on the Bonney Coast approximately 40 km west of Mount Gambier. This survey occurred 24 days after a one-in-fifty-year storm event that affected much of the South Australian coastline (Bureau of Meteorology, 2016; Burns et al., 2017) and found the spatial distribution of coastal bitumen deviated significantly from the previous two surveys (Ross et al., 2017).
Figure 1: (A) Locations of analysed asphaltite and asphaltic tar samples and the Jurassic-Cretaceous sub-basins of the offshore Bight Basin. (B) Photograph of asphaltite sample W13/007507 collected from Waitpinga Beach in 2014, exhibiting characteristic shrinkage cracks. (C) Photograph of asphaltic tar sample 001059 collected from Number 1 and 2 Rocks in 2016.

2.2. Bulk bitumen analyses

2.2.1. Whole-oil gas chromatography-mass spectrometry

A sub-sample (≤200 mg) was removed from each bitumen specimen and dissolved in 10 mL of dichloromethane/methanol (93:7, v:v). An aliquot of this solution was used for whole-oil GC-MS. Analyses of the samples collected in 2014 and 2015 were performed on an Agilent 6890 gas chromatograph interfaced with a 5973N MSD (electron energy 70 eV) and tuned using automatic setup parameters for each sequence. Chromatography was carried out on an Agilent HP-5MS fused silica column (30 m x 0.25 mm i.d. x 0.25 μm film thickness), using either a split (50 mL/min) or splitless injection mode, the latter employed if split injection
data showed low responses. The oven was programmed at an initial temperature of 50°C for 1 min, followed by heating at 8°C/min to 300°C. The carrier gas was helium at a flow rate of 1 mL/min. GC-MS analyses of the samples collected in 2016 were performed on an Agilent 7890B gas chromatograph interfaced with a 5977B MSD (electron energy 70 eV) and tuned using automatic setup parameters for each sequence. Chromatography was carried out on a J&W DB-5MS fused silica column (30 m x 0.25 mm i.d. x 0.25 µm film thickness), using the same operating conditions as employed for the 2014 and 2015 samples. In both cases, whole-oil GC-MS was conducted in scan mode (scan interval 45–500 AMU at approx. 3 scans/sec).

2.2.2. Elemental analysis (EA)

The sulphur content (weight %) of each sample was determined using a Perkin Elmer 2400 series II CHNS/O Elemental Analyzer in CHNS configuration. The combined combustion/reduction tube was packed with Perkin Elmer EA6000 and Perkin Elmer ‘Hi-Purity’ Copper (reaction temperature of 975°C). Results were calibrated against a Perkin Elmer Organic Analytical Standard (cystine, 3–4 mg) with a known abundance of sulphur (26.69 ± 0.3%). The maximum uncertainty in sulphur content values was ±0.5%.

2.2.3. Elemental analysis – isotope ratio mass spectrometry (EA-IRMS)

Sulphur isotope data ($\delta^{34}$S) were collected using a Eurovector EuroEA Elemental Analyzer modified with a Valco valve to allow separation of combustion $SO_2$ from $CO_2$ and $N_2$. Results from interior subsamples of each bitumen specimen were calibrated to two in-house standards (S2 and S3) of silver sulphide ($Ag_2S$) with $\delta^{34}$S values of +22.7‰ and -32.3‰, respectively. Due to the range in sulphur content between the asphaltites and asphaltic tars, results were calibrated against multiple weights of each standard (in the range 2–4 mg). The maximum uncertainty in $\delta^{34}$S values was ±0.38‰.

2.2.4. Re-Os isotopic composition

Re-Os analysis of three asphaltic tars was conducted using the same analytical approach as that taken for the asphaltites by Corrick et al. (2019), based on the methods of Selby et al.
The precision for all Re-Os data was determined using full error propagation of all sources of uncertainty.

2.3. **Analysis of saturated, aromatic and polar fractions**

2.3.1. **Oil fractionation**

The saturated, aromatic and polar fractions were separated from 20 mg aliquots of whole bitumen using the procedure of Bastow et al. (2007). The recovered saturated hydrocarbons and polar fractions were stored in 2 mL chromatography vials, while the aromatics fraction was stored in 2 mL amber glass vials to ensure minimal degradation by ultraviolet light.

2.3.2. **Separation of n-alkanes and branched/cyclic alkanes**

Saturates fractions were dissolved in cyclohexane and transferred on to 5Å molecular sieve (activated at 450°C) before heating in an oven at 80°C overnight to ensure complete n-alkane absorption. The resulting branched/cyclic alkane fraction was used for biomarker analyses (see Sections 2.3.3 and 2.3.4). For selected samples, the separated n-alkanes were then retrieved for compound-specific isotope analysis by digesting the molecular sieve in approximately 8 mL of 40% hydrofluoric acid in a polytetrafluoroethylene test tube and extracting the released n-alkanes using n-pentane. The resulting n-alkane fractions were concentrated under a stream of nitrogen prior to further analysis.

2.3.3. **Selected ion monitoring gas chromatography-mass spectrometry (SIM GC-MS)**

GC-MS analysis of the branched/cyclic alkanes was performed on an Agilent 7890A gas chromatograph interfaced with a 5975C MSD (electron energy 70 eV) tuned using automatic setup parameters on the day of the analysis. Chromatography was carried out on a J&W DB-5MS fused silica column (60 m x 0.25 mm i.d. x 0.25 µm film thickness). A 1 µL aliquot of the branched/cyclic saturate fraction dissolved in petroleum ether was injected into the split/splitless injector at 300°C operating in split mode (20 mL/min). After being held at an initial temperature of 40°C for 2 min., the oven was heated at 20°C/min to 200°C and then ramped to 310°C at 2°C/min. The carrier gas was helium at a flow rate of 1.5 mL/min.
2.3.4. **Gas chromatography tandem mass spectrometry (GC-MS-MS) with cold electron ionisation**

GC-MS-MS analysis of the branched/cyclic alkanes was performed on a Perkin Elmer 680 Clarus gas chromatograph interfaced with a Perkin Elmer iQT Quadrupole Time of Flight (QToF) mass spectrometer fitted with a Cold-EI source and tuned using automatic setup parameters for each sequence. Chromatography was carried out on a J&W DB-5MS fused silica column (60 m x 0.25 mm i.d. x 0.25 µm film thickness). A 1 µL aliquot of saturates fraction dissolved in cyclohexane was injected at 300°C into the injector operating in splitless mode. The oven was held at an initial temperature of 50°C for 1 min., followed by heating at 12°C/min to 180°C and then at 4°C/min to 310°C. Helium was the carrier gas at a flow rate of 2 mL/min.

2.3.5. **Carbon compound-specific isotope analysis (CSIA)**

The carbon isotopic composition (δ\(^{13}\)C) of individual \(n\)-alkanes from representative asphaltite, asphaltic tar and waxy bitumen samples was measured by gas chromatography-combustion-isotope ratio mass spectrometry using a 6890N GC connected to a GC-C/TC III combustion device coupled via open split to a Thermo MAT 253 mass spectrometer. The \(n\)-alkane fractions (1 µL) were injected into the inlet system in splitless mode (1 min). The injector was held at a temperature of 290°C. The \(n\)-alkanes were separated on a fused silica capillary column (SGE BP-5, 30 m x 0.25 mm ID, 0.25 mm film thickness). The GC oven was held at 50°C for 2 minutes, then heated at 25°C/min to 120°C, followed by a second heating ramp of 5°C/min to 310 °C, and finally held isothermal for 8 minutes. The analytes of the GC effluent stream were oxidised to CO\(_2\) in the combustion furnace at 950°C on a CuO/NiO/Pt catalyst. The produced CO\(_2\) was transferred on-line to the mass spectrometer to determine its δ\(^{13}\)C value. All results were calibrated to replicate measurements of individual \(n\)-alkanes from internal reference standards (IU A6 and B3). The maximum error in analytical precision was ±0.26‰.
2.3.6. **GC-MS analyses of aromatic and polar fractions**

Analyses of the aromatic and polar fractions were performed on a Perkin Elmer SQ8T/680 Clarus GC-MS fitted with a Perkin Elmer PE-5MS fused silica column (30 m x 0.25 mm i.d. x 0.25µm film thickness). A 1 µL aliquot was injected at 300°C into the injector operating in splitless mode. The oven was held at an initial temperature of 50°C for 1 min., followed by heating at 8°C/min to 300°C. Helium was the carrier gas at a flow rate of 1 ml/min. Data acquisition was conducted in scan mode (Scan 45–500AMU at approx. 3 scans/sec).

2.4. **Asphaltene separation**

The asphaltene content of each specimen was determined by dissolving a bulk sub-sample (0.3–0.7 g) in a minimum volume of dichloromethane/methanol (93:7). The asphaltene fraction was then precipitated by adding an excess of n-pentane. After the asphaltene precipitate settled from suspension, the maltene supernatant was removed using a Pasteur pipette and further n-pentane added. This process was repeated several times, until the maltene fraction had been entirely removed. The remaining asphaltene fraction was then rinsed with a final wash of n-pentane, dried and weighed.

3. **RESULTS AND DISCUSSION**

3.1. **Comparison of source-specific saturated hydrocarbons**

Source-specific biomarker parameters of the asphaltites and asphaltic tars are listed in Table 1. The freshest asphaltite specimen (W13/007976) preserves n-alkanes as light as C₈ (note that lighter gasoline-range n-alkanes would lie outside the detection range), with a slightly bimodal front-end distribution displaying maxima at C₁₀ and C₁₃, thereafter decreasing in abundance towards C₃₅ (Fig. 2A). Relative to this specimen, other asphaltites in the sample suite have less low-molecular-weight n-alkanes. This mild weathering results in a unimodal n-alkane distribution in the range C₁₀–C₃₅, with a maximum between C₁₅ and C₁₇ (Fig. 2B). Although the majority of samples selected for comparison were not significantly weathered asphaltites, two mildly degraded specimens (W13/007493 and W13/007668) are also included in the sample suite for reference. These samples contain less n-alkanes,
demonstrated by elevated Pr/C$_{17}$ ratios compared to the other specimens. The asphaltic tar specimens preserve n-alkanes from C$_9$ to C$_{35}$ with a maximum at C$_{17}$ (Fig. 2C). Having been recovered from a single stranding location during one survey and being of highly uniform composition, the asphaltic tars are likely fragments of a single larger piece of tar separated by wave action during or shortly prior to stranding.

Figure 2: Whole-oil GC-MS total ion chromatograms for: (A) The freshest identified asphaltite specimen W13/007976; (B) A typical, lightly weathered asphaltite specimen W13/007507; and (C) An asphaltic tar specimen /001079; Np = norpristane, Pr = pristane, Ph = phytane, peak numbers correspond to n-alkane chain length.

The C$_{27}$ : C$_{28}$ : C$_{29}$ and C$_{27}$ Dia/(Dia+Reg) sterane ratios of both families are highly consistent (Fig. 3; Table 1). Some minor grouping of the two oils is based on the relative proportions of the C$_{27}$ and C$_{28}$ ααα 20R steranes. The asphaltic tars typically contain a slightly lower proportion of C$_{27}$ steranes and slightly elevated C$_{28}$ steranes. However, there remains some
overlap between the two oil types based on variability in these values in specific samples. The C$_{31}$ (22R)/C$_{30}$ αβ hopane ratios of the asphaltites and asphaltic tars are effectively identical, with respective values of 0.30–0.35 and 0.31–0.34, consistent with a marine source (Peters et al., 2005). This is supported in both oil families by the presence of diagnostic marine biomarkers such as dinosterane, a 4-methylsterane derived from marine dinoflagellates (Summons et al., 1987) and 24-n-propylcholestanes derived from marine chrysophyte algae (Moldowan et al., 1990). Furthermore, the complete lack of freshwater algal markers such as botryococcane (e.g. Moldowan and Seifert, 1980; McKirdy et al., 1986), and of angiosperm markers such as oleanane or bicadinanes (e.g. Edwards et al., 2018) together with a low abundance of tetracyclic polyprenoids (Holba et al., 2000) suggests negligible inputs from terrestrial or freshwater biota. Hence, the parent oils of both types of asphaltic bitumen originated from source rocks which contain only marine organic matter, consistent with the previously inferred source affinity of the asphaltites (Edwards et al., 1998; Hall et al., 2014).

Figure 3: Partial m/z 217 chromatograms of representative asphaltite and asphaltic tar specimens demonstrating the similarity of their sterane and diasterane distributions. For a full list of peak assignments see Supplementary Information.
Table 1: Asphaltene content and selected biomarker parameters of asphaltite and asphaltic tar specimens. See Supplementary Information for explanation of compound abbreviations.

| Samples | Asphaltene % | Sulphur % | $\delta^{34}$S (%o) | Pr / Ph | Pr/C\textsubscript{17} | 27 : 28 : 29 \textalpha\textalpha 20R steranes (m/z 217) | 27 : 28 : 29 \textalpha\textbeta 20R+S steranes (m/z 218) | C\textsubscript{37} Dia / (Dia+Reg) steranes (m/z 217) | C\textsubscript{35} homohopane index (%) | C\textsubscript{29} / C\textsubscript{30} \alpha\beta hopane (m/z 191) | C\textsubscript{31} (22R) / C\textsubscript{30} \alpha\beta hopane (m/z 191) | C\textsubscript{35} (22S) / C\textsubscript{34} (22S) hopane (m/z 191) | Ts / (Ts+Tm) |
|---------|--------------|-----------|---------------------|---------|-----------------|---------------------------------------------------|---------------------------------|---------------------------------------------|-----------------|------------------|------------------|------------------|------------------|------------------|
| Asphalmites | | | | | | | | | | | | | |
| W13/007472 | 59 | 4.0 | -5.79 | 1.3 | 0.5 | 40 : 23 : 36 | 37 : 25 : 37 | 0.41 | 9.3 | 0.64 | 0.34 | 0.95 | 0.40 |
| W13/007475 | 58 | 4.1 | -6.58 | 1.3 | 0.5 | 38 : 23 : 39 | 38 : 26 : 37 | 0.45 | 7.8 | 0.65 | 0.33 | 0.90 | 0.41 |
| W13/007476 | 53 | 4.3 | -5.34 | 1.3 | 0.5 | 43 : 20 : 38 | 38 : 25 : 37 | 0.42 | 7.6 | 0.60 | 0.35 | 0.90 | 0.41 |
| W13/007488 | 56 | 4.4 | -5.30 | 1.2 | 0.5 | 43 : 20 : 37 | 38 : 25 : 37 | 0.43 | 8.6 | 0.64 | 0.33 | 0.92 | 0.39 |
| W13/007493 | 52 | 4.1 | -5.97 | 1.4 | 0.7 | 44 : 19 : 36 | 37 : 25 : 38 | 0.34* | 8.3 | 0.69* | 0.31 | 0.91 | 0.35 |
| W13/007507 | 54 | 3.9 | -5.66 | 1.2 | 0.5 | 40 : 27 : 33 | 39 : 25 : 36 | 0.43 | 7.4 | 0.65 | 0.32 | 0.79 | 0.40 |
| W13/007516 | 55 | 4.0 | -6.15 | 1.3 | 0.5 | 44 : 19 : 37 | 38 : 25 : 37 | 0.42 | 8.0 | 0.66 | 0.33 | 0.91 | 0.38 |
| W13/007668 | 59 | 4.1 | -7.18 | 1.1 | 1.3 | 37 : 27 : 36 | 37 : 26 : 37 | 0.45 | 7.7 | 0.67 | 0.30 | 0.90 | 0.38 |
| W13/007671 | 54 | 3.8 | -7.59 | 1.1 | 0.5 | 37 : 23 : 39 | 37 : 25 : 38 | 0.42 | 7.9 | 0.65 | 0.32 | 0.90 | 0.41 |
| W13/007672 | 54 | 3.8 | -7.34 | 1.2 | 0.4 | 43 : 20 : 37 | 39 : 25 : 36 | 0.43 | 8.4 | 0.65 | 0.33 | 0.94 | 0.38 |
| W13/007845 | 51 | 3.7 | -8.82 | 1.2 | 0.5 | 39 : 27 : 34 | 39 : 26 : 35 | 0.46 | 7.2 | 0.64 | 0.30 | 0.82 | 0.37 |
| W13/007976 | 51 | 3.6 | -7.80 | 1.2 | 0.4 | 38 : 26 : 36 | 38 : 25 : 37 | 0.45 | 7.6 | 0.62 | 0.30 | 0.82 | 0.41 |
| Asphalitic Tar | | | | | | | | | | | | | |
| 001056 | 35 | 2.8 | +2.61 | 0.7 | 0.6 | 35 : 29 : 36 | 36 : 26 : 38 | 0.43 | 11.0 | 0.82 | 0.32 | 1.02 | 0.22 |
| 001063 | 32 | 3.2 | +2.88 | 0.7 | 0.5 | 35 : 29 : 36 | 36 : 26 : 38 | 0.43 | 10.4 | 0.80 | 0.32 | 1.00 | 0.22 |
| 001067 | 35 | 2.7 | +4.84 | 0.7 | 0.6 | 34 : 29 : 37 | 35 : 25 : 40 | 0.43 | 11.3 | 0.78 | 0.33 | 1.03 | 0.22 |
| 001068 | 25 | 3.2 | +4.50 | 0.8 | 0.6 | 35 : 29 : 36 | 36 : 25 : 39 | 0.44 | 10.6 | 0.75 | 0.31 | 1.01 | 0.22 |
| 001076 | 25 | 2.5 | +4.27 | 0.7 | 0.5 | 37 : 26 : 37 | 36 : 23 : 42 | 0.43 | 11.0 | 0.79 | 0.34 | 1.05 | 0.27 |
| 001079 | 27 | 3.0 | +4.30 | 0.7 | 0.6 | 33 : 29 : 38 | 35 : 25 : 41 | 0.43 | 11.8 | 0.73 | 0.33 | 1.02 | 0.19 |
| 001081 | 26 | 3.5 | +4.85 | 0.7 | 0.5 | 32 : 29 : 38 | 35 : 25 : 40 | 0.44 | 11.8 | 0.76 | 0.33 | 1.04 | 0.19 |

* = Ratio variation attributed to significant weathering of the specimen

\[ C_{27} \text{ Dia} / (\text{Dia+Reg}) \text{ steranes} = \left( \frac{C_{27} \text{ \betaa} 20S + 20R}{C_{27} \text{ \betaa} 20S + 20R + C_{27} \text{ \alphaalpha} 20S + 20R} \right) \]

\[ C_{35} \text{ homohopane index} = \left( \frac{C_{35} 17\alpha(H),21\beta(H)-\text{homohopanes} (22S + 22R)}{\Sigma C_{35} 17\alpha(H),21\beta(H)-\text{homohopanes} (22S + 22R)} \right) \times 10 \]
The pristane/phytane ratio (Pr/Ph), a commonly used indicator of source redox conditions (Powell and McKirdy, 1973), varies between 1.1 and 1.4 in the asphaltite sample suite, suggesting that their source rock was deposited under sub-oxic conditions. However, their high C\textsubscript{35} homohopane index values (7–9) and high sulphur content (≈ 4 wt. %) are consistent with more reducing conditions. The Pr/Ph ratios of the asphaltic tars are consistently lower, suggesting anoxia (<1; Table 1). This evidence of anoxia is further supported by a higher abundance of C\textsubscript{35} homohopanes, expressed by high values of the C\textsubscript{35} homohopane index (10–12) and C\textsubscript{35}/C\textsubscript{34} hopane ratio (1.00–1.05). Despite the evidence of a more oxygen-depleted (anoxic) setting (cf. the conflicting sub-oxic to anoxic parameters of the asphaltites), the sulphur content of the asphaltic tars varies between 2.5 and 3.5%, which is generally lower than that of the asphaltites (viz. 3.6–4.4% in the analysed suite).

The lithofacies of the asphaltite’s source rock has previously been interpreted as a shale containing little to no carbonate, based on their C\textsubscript{29}/C\textsubscript{30} \(\alpha\beta\) hopane ratio being < 1 (Fig. 4, Table 1), their high relative abundance of diasteranes and the complete absence of 2\(\alpha\)-methylhopanes (Edwards et al., 1998). Abundant 2\(\alpha\)-methylhopanes are observed in oils derived from carbonate source rocks (Summons et al., 1999), while lower abundances are reported in deeper water facies, a trend attributed to the distribution of their precursor cyanobacteria which predominantly reside in shallow-water ecosystems (Eigenbrode et al., 2008). The unusual absence of 2\(\alpha\)-methylhopanes in the asphaltites could therefore support the interpretation that the source rock was deposited in a deepwater setting, consistent with their complete lack of molecular markers indicating terrestrial or freshwater organic matter inputs.

Unlike the asphaltites, the asphaltic tars contain 2\(\alpha\)-methylhopanes in low abundance. However, the significance of their presence is uncertain, as 2\(\alpha\)-methylhopanes appear to require cracking from kerogen and are hence strongly affected by burial temperature (Peters et al. 2005). Additionally, the 17\(\alpha\)-22,29,30-trisnorhopane (Tm) occurs in much higher abundance relative to the 18\(\alpha\)-22,29,30-trisnorneohopane (Ts). These compounds are usually compared in the Ts/(Ts+Tm) ratio, which is commonly employed as a thermal
maturity parameter (Seifert and Moldowan, 1978). However, the low values of this ratio obtained from the asphaltic tars (0.19–0.27) are inconsistent with other thermal maturity parameters which indicate that these samples originated from the late oil window (discussed in Section 3.3). In addition to thermal maturity, the relative influence of lithology and redox conditions of the source rock on the Ts/(Ts+Tm) ratio is not fully understood, with several studies reporting systematically lower values in oils derived from carbonate source rocks deposited under anoxic conditions (McKirdy et al., 1983, 1984; Rullkötter et al., 1985; Price et al., 1987). Aside from this anomalous parameter, the composition of the asphaltic tars appears consistent with their derivation from an anoxic shale. To explain their abnormal Ts/(Ts+Tm) values, we tentatively propose that the source rock composition has a relatively high carbonate content, lying between the endmembers of shale and carbonate (i.e. a calcareous shale). In an anoxic setting, this may have been sufficient to account for their unusually low Ts/(Ts+Tm) values, despite the high thermal maturity of the parent oil.

Figure 4: Partial m/z 191 chromatograms of (A) asphaltite sample W13/007976; and (B) asphaltic tar sample /001068. See Supplementary Information for full list of compound abbreviations.
3.2. Comparison of stable isotopic composition

The overall similarity of the asphaltic tars and asphaltites indicated by their near-identical source-specific sterane compositions is further reinforced by their internally consistent n-alkane δ\(^{13}\)C profiles, a valuable tool in the geochemical correlation of crude oils (e.g. Murray et al., 1994; Dowling et al., 1995; Blevin et al., 1998). The carbon isotopic composition of individual hydrocarbons in a crude oil is controlled principally by the primary organic matter inputs to its source rock. Hence oils derived from similar sources share comparable compound-specific δ\(^{13}\)C values (Hayes et al., 1990; Murray et al., 1994). The n-alkane δ\(^{13}\)C profiles of representative asphaltites and asphaltic tars, and of selected examples of Indonesian-derived waxy bitumens which also strand on the South Australian coastline (Ross et al., 2017) are shown in Figure 5. The isotopic values for each individual n-alkane in these specimens are listed in Table S2. The waxy bitumens, products of distal petroleum systems with source characteristics notably different to those of the asphaltites (cf. Edwards et al., 2018), contain C\(_{15+}\) n-alkanes with δ\(^{13}\)C values ranging between approximately –25.5 and –32‰. These results align with those of a previous assessment of the waxy bitumens' n-alkane isotopic composition, which demonstrated their similarity to the Minas and Duri oils from the Central Sumatra Basin (Dowling et al., 1995). In contrast, the n-alkane δ\(^{13}\)C values of the asphaltites and asphaltic tars are more uniform, with values between –30 and –34‰. Similarly, flat n-alkane δ\(^{13}\)C profiles are observed in other oils derived from marine source rocks (Murray et al., 1994).
Figure 5: CSIA data on n-alkanes from interior subsamples of different coastal bitumen oil families collected from the South Australian coastline. The carbon isotopic profile of the asphaltic tar specimen plots in the same region as those of numerous asphaltites but differs markedly from those of waxy coastal bitumens derived from petroleum systems in Southeast Asia. Each of the waxy bitumen varieties shown are derived from different oil families identified using the presence/absence and abundance of key biomarker alkanes identifiable using whole-oil GC-MS (Corrick et al., 2016; Ross et al., 2017).

Although the carbon isotopic values of the two oil families are highly consistent, their bulk sulphur isotopic compositions ($\delta^{34}$S) differ considerably. The $\delta^{34}$S signature of an oil may be used to aid oil-oil and oil-source correlations, as the unaltered value typically reflects that of the source kerogen (Thode et al., 1961; Thode and Monster, 1970; Orr, 1986). Although the primary source of the sulphur in marine organic matter is seawater sulphate, the process of bacterial sulphate reduction in the sediment prior to deeper burial results in organically-bound sulphur becoming depleted in $^{34}$S (Jones and Starkey, 1957; Harrison and Thode, 1958; Thode et al., 1960). Hence, the $\delta^{34}$S values of petroleum generated from this organic matter are typically ca. 15‰ lighter than contemporaneous inorganically precipitated sulphur minerals such as gypsum, which may either accurately preserve the composition of seawater or be enriched in $^{34}$S (Thode and Monster, 1965). In asphaltites, bulk $\delta^{34}$S values range between -3.6 and -4.6‰, while the values for the asphaltic tars are between +2.61 and +4.85‰, reflecting a much greater enrichment in the heavier isotope (Table 1). Given
the variability in the $\delta^{34}$S composition of seawater sulphate during the Cretaceous, these heavier values remain geologically reasonable (cf. Paytan et al., 2004). However, the sulphur isotopic composition of crude oil may also be altered to heavier values under certain conditions (discussed in Section 4.2).

3.3. Comparison of thermal maturity parameters

The maturity parameters of the asphaltite and asphaltic tar samples are summarised in Table 2. As discussed previously, although the $T_s/(T_s+T_m)$ ratio may often constrain thermal maturity, it is unreliable in this case due to likely source interference. The methylphenanthrene index (MPI-1), arguably the most robust molecular measure of thermal maturity (Radke, 1987), varies between 0.49 and 0.62 across the asphaltite samples. Using the relationship between MPI-1 and vitrinite reflectance defined by Radke and Welte (1983), the calculated vitrinite reflectance ($R_v$) of the asphaltites' source rock falls between 0.7 and 0.8%, indicating a thermal maturity in the early/main oil window, consistent with previous studies (Volkman et al., 1992; Edwards et al., 1998; Hall et al., 2014; Scarlett et al., 2019). Other aromatic maturity indices, namely the methylnaphthalene ratio (MNR) and dimethylnaphthalene ratio (DNR-1), yield slightly higher maturities in the range 0.9–1.0% $R_v$. This may be the result of mixing with a more mature oil charge, which will influence the methylnaphthalenes of the oil more than the higher-molecular-weight methylphenanthrenes.

The asphaltites used for comparison in this study were collected from widely separated stranding locations along the coastline (Fig. 1A) and, with few exceptions, preserve phenanthrene, comparable to those in previous studies (cf. Volkman et al., 1992; Edwards et al., 1998; Hall et al., 2014). Therefore, most asphaltites within the sample suite have undergone minimal alteration due to water-washing, supporting the interpretation that they are the product of a local seafloor seep (Hall et al., 2014). However, degraded asphaltites do occur (e.g. samples W13/007493 and W13/007668). Such mild to moderately degraded examples exhibit significant alteration to the methyl- and dimethylnaphthalenes, while the MPI-1 ratio appears relatively unaffected (Corrick et al., 2019).
Table 2: Thermal maturity parameters and calculated vitrinite reflectance (Rc) values of asphaltites and asphaltic tars. MPI-1 ratio after Cassani et al. (1988). Relationship between MPI-1 and Rc after Radke and Welte (1983). MNR, DNR-1 ratios and their respective relationships to Rc after Radke et al. (1984). See Supplementary Information for all compound abbreviations.

<table>
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<tr>
<th>Sample</th>
<th>Tricyclics / 17α-hopanes</th>
<th>MPI-1</th>
<th>Rc (%) from MPI-1</th>
<th>MNR</th>
<th>Rc (%) from MNR</th>
<th>DNR-1</th>
<th>Rc (%) from DNR-1</th>
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* Ratio altered due to significant water washing and removal of key aromatic compounds.

The aromatic hydrocarbon fraction of the asphaltic tars differs notably from that of the asphaltites (Fig. S2, Table 2). Their MPI-1 values of 1.23–1.34 are equivalent to Rc values of 1.1–1.2%, indicating a thermal maturity within the late oil window. MNR and DNR-1 likewise yield Rc values of 1.1 and 1.2% respectively. This consistency between aromatic maturity indicators suggests the asphaltic tars are unlikely to represent a mix of earlier and later expulsion products (c.f. the higher Rc values from MNR and DNR-1 vs. MPI-1 in the asphaltites). Like the asphaltites, the preservation of somewhat water-soluble naphthalenes, despite exposure to the marine environment, supports the interpretation that the asphaltic tars also originated from a nearby petroleum system.
The abundance of tricyclic terpanes relative to 17α-hopanes has been shown to increase at higher thermal maturities due to the preferential release of tricyclic terpanes from kerogen (Aquino Neto et al., 1983; van Graas, 1990; Farrimond et al., 1999). The tricyclic terpanes/17α-hopanes ratios of the asphaltites are low (0.07–0.15), consistent with their other maturity parameters which suggest generation and expulsion from a source rock in the early oil window. The markedly higher thermal maturity of the asphaltic tars indicated by their aromatic maturity parameters is further supported by their higher tricyclic terpanes/17α-hopanes ratio of 0.24–0.34 (Table 2). However, the abundance and composition of tricyclic and tetracyclic terpanes can also reflect source input (Peters et al., 2005). This makes distinguishing the influence of source and thermal maturity difficult when comparing two oils of markedly different maturities.

3.4. Comparison of Re-Os systematics

The Re-Os geochronology of crude oils has been demonstrated to constrain the timing of oil generation and expulsion from the source rock (Selby et al., 2005; Selby and Creaser, 2005; Finlay et al., 2011; Lillis and Selby, 2013; Liu et al., 2018). Application of the Re-Os geochronometer to asphaltites recently collected from the South Australian coastline provided a generation age of 74 ± 26 Ma (n = 16; Corrick et al., 2019), while analysis of a smaller suite of archival specimens collected in the 1990’s yielded a set of data points with lower analytical uncertainty which define an age of 103 ± 22 Ma (n = 5; Scarlett et al., 2019). These generation ages show 19 Myr of potential overlap when considering their respective uncertainties. However, the remaining variation between these two determined ages is unlikely to be solely attributable to the differences in analytical uncertainty between these two studies, as the results obtained from numerous asphaltites analysed by Corrick et al. (2019), despite their higher analytical uncertainty, do not overlap with, or plot along the isochron defined by Scarlett et al. (2019). This suggests that a geologic component to the variation is also likely. The overall high uncertainty present in both of the determined ages may be associated with the mixing of increasingly mature oil, given the variation observed between the aromatic maturity parameters used herein (Table 2).
The asphaltic tars contain 30.1–31.4 parts per billion (ppb) Re and 599.9–627.6 parts per trillion (ppt)Os, concentrations significantly greater than in the asphaltites, which contain between 2.6–4.2 ppb Re and 24.6–45.0 ppt Os (Corrick et al., 2019; Scarlett et al., 2019).

Such high abundances of Re and Os are unusual, particularly as these elements predominantly reside within the asphaltene fraction of crude oil (Selby et al., 2007; Georgiev et al., 2016; Liu and Selby, 2018; Liu et al., 2019) and the asphaltic tars contain less asphaltenes (22–35% versus 51–59% in the asphaltites; Table 1). The $^{187}$Re/$^{188}$Os and $^{187}$Os/$^{188}$Os ratios of the analysed asphaltic tars are highly uniform at 332.2–333.9 and 3.057–3.063, respectively (Table S3). These values overlap when considering the range of analytical uncertainty. Thus, insufficient variation exists to apply a linear regression to these data points to determine a meaningful generation age for the asphaltic tars. Their homogenous Re and Os composition is likely due to both the small number of samples analysed ($n = 3$), and the high probability that the specimens analysed represent individual fragments of a single larger piece of tar, as discussed previously. Whilst internally consistent, these values differ from those obtained from the asphaltites (Fig. 6), which yield $^{187}$Re/$^{188}$Os values between 400.5–547.8 and $^{187}$Os/$^{188}$Os values of 1.122–1.334 (Corrick et al., 2019; Scarlett et al., 2019).
Figure 6: Comparison of Re-Os ratios of asphaltic tars with those of asphaltites analysed by Corrick et al. (2019) and Scarlett et al. (2019). Results for individual samples are listed in Table S3. MSWD = mean square of weighted deviates.

4. DO BOTH OILS ORIGINATE FROM THE SAME SOURCE ROCK?

The geochemistries of these two varieties of asphaltic crude oil exhibit several source-related similarities, such as their highly comparable sterane distributions and \( n \)-alkane \( \delta^{13}C \) values. However, clear and systematic differences are also evident between these two oil types, most notably in their respective \( Ts/(Ts+Tm) \) ratios, bulk \( \delta^{34}S \) values and Re-Os systematics. Oil-oil and oil-source correlations can become particularly complex when taking into account possible lateral variations in both the organic facies and thermal maturity of the source rock. Therefore, the relationship between these two oil types must be considered in terms of two competing interpretations: (1) The asphaltic tars and asphaltites were derived from separate source rocks which contained similar organic facies; or (2) both oil types originated from lateral equivalents of the same source rock unit. In the latter interpretation, the observed geochemical variations reflect minor lateral variability in the source rock composition, combined with increased thermal maturity and possible alteration by thermochemical sulphate reduction (TSR; discussed below).
In both scenarios, correlation of the two oil types based on multiple source-specific parameters supports their derivation from organic-rich rocks which contained highly comparable organic matter inputs. Thus, these two asphaltic oils are likely to have originated from within the same basin, presently considered to be the offshore Bight Basin. However, the implications of the two potential interpretations for the quality and location of the asphaltic tars’ parent petroleum system may differ considerably.

4.1. The case for two separate source rocks

Multiple marine intervals with high source potential are proposed to occur throughout the Blue Whale, White Pointer, Tiger and Hammerhead supersequences of the Bight Basin (Blevin et al., 2000; Totterdell et al., 2000; Struckmeyer et al., 2001; Totterdell et al., 2008); and many of these now lie within different stages of the hydrocarbon generation window, depending on their location. For example, in the depocentre of the Ceduna Sub-basin, the proposed source rocks in the Blue Whale and White Pointer supersequences reside in the gas window or overmature zones, while laterally these intervals pass through both the main and late oil window in both the marginal and basinward areas (Fig. 7). It is reasonable to consider that organic matter inputs to a marine sedimentary basin would be similar, though not necessarily identical through time. An interpretation of two discrete marine source rock intervals with similar organic matter inputs would permit the near-identical compound-specific δ¹³C values and sterane distributions of the asphaltites and asphaltic tars. However, the observed differences in δ³⁴S values and Re-Os systematics may be attributed to variations of seawater chemistry through time (e.g. Paytan et al., 2004; Du Vivier et al., 2014). Although this may account for different ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os values between the two oils, it does not explain the unusually high abundance of Re and Os present in the asphaltic tars. Whilst the possibility of two separate sources cannot be discounted, this interpretation relies predominantly on attributing all observed variations between these two asphaltic oil strandings to differences in source rock composition, with little to no acknowledgement of the role that lateral facies variation and differing thermal maturity may also have had on the composition of the oil generated throughout the basin.
Figure 7: Cross-section of the Ceduna Sub-basin of the Bight Basin with supersequence boundaries, proposed source intervals (> 4% TOC) and modelled present-day maturity (% $R_o$) zones. Figure modified after Totterdell et al. (2008).

4.2. The case for a single source rock

The geochemical differences between the asphalitic tars and asphaltites may also be attributed to a combination of minor lateral variation in source rock facies, differences in thermal maturity and alteration of the asphalitic tars by TSR. This latter process occurs when oil comes into contact with a source of dissolved sulphate at temperatures at or above 100–140°C (Goldhaber and Orr, 1995; Machel, 2001). Potential sources of dissolved sulphate include buried seawater, basin brines (groundwater) or dissolved evaporite deposits of gypsum or anhydrite (Machel, 2001). During TSR, low-molecular-weight hydrocarbons are oxidised in order to reduce the dissolved sulphate. Branched and $n$-alkanes are the most reactive, followed by cyclic and monoaromatic compounds (Krouse et al., 1988; Manzano et al., 1997; Machel, 2001). Products of this reaction include hydrogen sulphide ($H_2S$), carbonate, metal sulphides and pyrobitumen (Machel, 2001). The release of $H_2S$ in particular can also have important technical implications for oil production, as the oxidation reduces the overall hydrocarbon potential and production costs are increased due to the toxicity of $H_2S$ and its associated corrosion of drilling equipment.

Both the sulphur isotopic composition and Re-Os systematics of a crude oil, two parameters typically inherited from seawater at the time of source rock deposition, are severely altered...
during TSR. Alteration of primary $\delta^{34}$S values occurs due to the back reaction of the resulting 
$\text{H}_2\text{S}$ with the oil. This incorporates sulphur derived from the dissolved sulphate, driving the 
$\delta^{34}$S composition towards heavier values (e.g. Orr, 1974; Lillis and Selby, 2013). This is 
consistent with the observed difference in $\delta^{34}$S composition between the asphaltic tars and 
asphaltites (Table 1). TSR has also been observed to reset the Re-Os systematics of crude 
oils, with the resulting age representing the cessation of this alteration process (Lillis and 
Selby, 2013). Oils affected by TSR are enriched in both Re and Os relative to the parent oil 
and possess different $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios (Lillis and Selby, 2013). This suggests 
that during TSR both Re and Os are also transferred from the dissolved sulphate phase to 
the oil, though the exact nature of this process remains unclear. The resulting $^{187}\text{Re}/^{188}\text{Os}$ 
and $^{187}\text{Os}/^{188}\text{Os}$ values of the oil will therefore represent mixed signatures of the original oil 
and the dissolved sulphate. The nature of this alteration is unlikely to be systematic in all 
cases (i.e. $^{187}\text{Os}/^{188}\text{Os}$ will not always increase), as the composition of the dissolved sulphate 
will vary in different settings according to the sources of Re and Os (e.g. balance of Re and 
Os derived from mantle inputs vs. continental weathering). Disruption of the Re-Os 
systematics due to TSR is consistent with the differences observed between the asphaltites 
and asphaltic tars. In particular, the significant enrichment of both Re and Os in the latter, 
despite their lower asphaltene content. Although the asphaltic tars lacked the necessary 
variation to produce a meaningful isochron, it is likely that their Re-Os systematics actually 
constrain the cessation of TSR. Hence, their marked departure from those of the asphaltites, 
which are considered to record a generation age (Corrick et al., 2019; Scarlett et al., 2019).

A second potential explanation for resetting Re-Os systematics is oil-water interaction 
without TSR. Laboratory experiments have also shown Re and Os may be rapidly transferred 
to liquid oil when in contact with a solution enriched in Re and Os (Mahdaoui et al., 2015; 
Hurtig et al., 2019). Though these studies cannot fully mimic natural oil-water interactions in 
a geologic setting, their results suggest that interaction of oil with formation waters, which 
contain much lower abundances of Re and Os, may be capable of altering and resetting the 
Re-Os composition of an oil, given sufficiently high water/oil ratios (ca. 250). In this case, 
such formation waters would require highly radiogenic Os in order to alter the $^{187}\text{Os}/^{188}\text{Os}$ 
ratios of the asphaltic tars to their observed values (3.057–3.063), which are much higher
than those reported for the asphaltites (1.122–1.334: Corrick et al., 2019; Scarlett et al., 2019). However, the influence of basinal water on the Re-Os systematics of crude oils and their application to constraining the timing of generation has been demonstrated to be limited or negligible in the Duvernay petroleum system of the West Canada Sedimentary Basin (Liu et al., 2018) wherein certain oils contain very low concentrations of both Re (0.04–3.78 ppb) and Os (0.6–41.2 ppt). Such examples should be extremely sensitive to any Re-Os contamination, but such alteration is not observed. Therefore, overprinting from typical interaction with formation waters is unlikely, given the evidence supportive of their alteration by TSR.

Definitive identification that a crude oil has been altered by TSR typically requires identification of thiaadamantanes (Wei et al., 2012), or a combination of evidence from obtained from complementary analyses, notably assessment of the resulting gases (H₂S and CO₂), low-molecular-weight hydrocarbons and precipitated phases including carbonates, pyrobitumens and metal sulphides (e.g. Machel et al., 1995; Machel, 2001; Li et al., 2005; Hao et al., 2008; Liu et al., 2016). Unfortunately, the asphaltic tars do not appear to contain any compounds with mass spectra consistent with thiaadamantane or its various methylated homologues. However, if thiaadamantanes were originally present, they would likely have been lost along with the other low-molecular-weight hydrocarbons due to weathering in the marine environment. Therefore, without fresh examples for comparison, the absence of thiaadamantanes does not definitively preclude TSR in this case. Furthermore, as these oils were collected from the coastline, complementary analyses of the other products of TSR discussed above are not available for comparison as the location of the reservoir is not known. Given this ambiguity, we cannot conclusively determine that TSR has altered the asphaltic tars, although we note it would be consistent with their bulk δ³⁴S values and Re-Os systematics. Analysis of these oils in a more concentrated form using GC-MS-MS targeting the 2-thiaadamantane and the methylated thiaadamantanes may be able to assess this interpretation further. Alternatively, comparison of the compound-specific sulphur isotopic composition of the benzothiophenes and dibenzothiophenes may also be diagnostic (Amrani et al., 2012).
The other noted differences between the asphaltites and asphaltic tars are consistent with minor lateral variation in organic facies and the expulsion of the latter from the source rock later in the oil generation window. The carbonate content and redox conditions of a source rock formation may vary laterally across a basin due to its proximity to shallow water carbonate systems and variations in seafloor topography beneath a stratified water column, respectively. Such variability would be consistent with the minor variations in redox parameters (e.g. Pr/Ph, C_{35} homohopane index) between the two oil types and a calcareous shale source for the asphaltic tars, as indicated by their unusually low Ts/(Ts+Tm) values for an oil generated in the late oil window. The higher thermal maturity of the asphaltic tars is also consistent with their greater abundance of tricyclic terpanes relative to hopanes when compared to the asphaltites. Finally, both increasing thermal maturity and TSR are known to affect the $\delta^{13}C$ composition of the oil. Mature oils contain individual low-molecular-weight hydrocarbons which are 1–3‰ more enriched in $^{13}C$ relative to their less mature equivalents, while alteration by TSR results in even greater enrichment (> +15‰: Rooney, 1995). The light hydrocarbons affected by these processes are not preserved in the asphaltic tars, and therefore neither of these diagnostic changes can be assessed based on the isotopic composition of their C_{13}–C_{35} n-alkanes (Fig. 5).

In summary, whilst the differences between the asphaltites and asphaltic tars could be attributed to their derivation from separate source rocks, the specific points of variation are also consistent with the latter’s higher thermal maturity, alteration by TSR and minor lateral variation in source facies (Table 3).
Table 3: Summary of processes capable of creating the observed geochemical differences between the asphaltic tars and asphaltites under the single source rock interpretation.

<table>
<thead>
<tr>
<th>Deviation from asphaltite geochemistry</th>
<th>Potential mechanisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Higher abundance of tricyclic terpanes relative to hopanes</td>
<td>• Preferential expulsion of terpanes from kerogen at higher thermal maturities (Aquino Neto et al., 1983; van Graas, 1990; Farrimond et al., 1999)</td>
</tr>
<tr>
<td>(2) Lower sulphur content</td>
<td>• Lateral variability in euxinic conditions across basin • Thermal decomposition of organosulphur compounds in oil to gases (Orr, 1974; Tissot and Welte, 1984)</td>
</tr>
<tr>
<td>(3) Heavier $\delta^{34}$S values</td>
<td>• Uptake of sulphur from dissolved sulphates and/or back reaction of $\text{H}_2\text{S}$ during TSR (Orr, 1974; Lillis and Selby, 2013)</td>
</tr>
<tr>
<td>(4) Enriched Re and Os abundance and highly different Re-Os ratios</td>
<td>• Alteration due to TSR (Lillis and Selby, 2013)</td>
</tr>
<tr>
<td>(5) Pr/Ph &lt; 1</td>
<td>• Lateral variability of source rock redox conditions</td>
</tr>
<tr>
<td>(6) Minor variation in $\text{C}<em>{29}/\text{C}</em>{30}$ $\alpha\beta$ hopane ratio</td>
<td>• Minor lateral variability in source rock carbonate content • Preferential thermal degradation of $\text{C}_{30}$ $\alpha\beta$ hopane (Peters et al., 2005)</td>
</tr>
<tr>
<td>(7) Presence of 2$\alpha$-methylhopanes</td>
<td>• Minor increase in carbonate content • Increased thermal maturity</td>
</tr>
<tr>
<td>(8) Lower $\text{Ts} / (\text{Ts}+\text{Tm})$</td>
<td>• Greater relative abundance of Tm attributed to higher carbonate content and anoxic conditions rather than thermal maturity (e.g. McKirdy et al., 1983, 1984; Rullkötter et al., 1985; Price et al., 1987)</td>
</tr>
</tbody>
</table>

4.3. Potential mechanisms of heavy petroleum formation

Naturally occurring viscous tars/bitumen may form in response to a variety of different processes. These include: (1) extensive biodegradation of crude oil in a shallow subsurface reservoir; (2) weathering and amalgamation of a sea-surface oil slick, leaving a viscous residue which may be subsequently separated by wave action (Logan et al., 2010; Warnock et al., 2015); (3) *in situ* thermal maturation of a crude oil resulting in the formation of pyrobitumen (Machel, 2001); (4) separation of heavy petroleum to form subsurface tar mats, which may occur in several different ways (Dahl and Speers, 1986; Wilhelms and Larter, 1994a, 1994b); and (5) direct seepage of heavy petroleum onto the seafloor (e.g. Brüning et al., 2010), where it then becomes immobile.

Many of these potential mechanisms are inconsistent with the composition of the asphal tic tars and may therefore be discounted. Firstly, although they have a slightly lower $n$-alkane
content than the freshest examples of asphaltite, the asphaltic tars do not appear to be heavily biodegraded, as they still contain C₁₀₊ n-alkanes. The preservation of the somewhat water-soluble naphthalenes in the least altered asphaltites and the entire suite of asphaltic tars also suggests that, despite their interaction with seawater, water washing has not been extensive. This likely precludes their formation from the weathering and amalgamation of an oil slick, whether from a spilled oil or natural seepage. Liquid oil in seawater will disperse into a thin surface slick with an extremely high surface area to volume ratio, making the oil extremely vulnerable to water washing, oxidation and microbial action. Generally, such oil in the marine environment will lose the majority of its low-molecular-weight components in a matter of hours (Head et al., 2006). Additionally, other known examples of marine tars amalgamating from sea surface oil slicks notably required calm oceanic conditions to form (e.g. Lorenson et al., 2009). The high energy environment of the Great Australian Bight, including the intense storm which occurred prior to the collection of the asphaltic tars, is unlikely to be supportive of this process.

In-situ thermal maturation of reservoired crude oil or alteration by TSR are known to form pyrobitumen. These solid residues are only weakly soluble in organic solvents (Wilhelms and Larter, 1994b) and are unlikely to seep. Previous assessment of their origin by Hall et al. (2014) demonstrated that the asphaltites are not pyrobitumen as they readily dissolve in dichloromethane. Although the asphaltic tars were generated and expelled during the late oil window, they are similarly soluble in dichloromethane and therefore they, too, cannot be considered residues of thermal maturation.

Hall et al. (2014) proposed that the asphaltites are transported remnants of subsurface tar mats, also known as viscous oil zones, polar-enriched zones (Larter et al., 1990) or heavy oil tar zones (Haldorsen et al., 1985). These deposits of heavy petroleum are reported in both clastic and carbonate settings and may range in thickness from <1 m to as much as 6 m (Larter et al., 1990; Wilhelms and Larter, 1994a, 1994b). Well characterised examples demonstrate these emplacements of heavy petroleum share comparable biomarker geochemistry with their parent oils but are more enriched in asphaltenes (20–60 wt %; cf.
1–5 wt % in the oil leg: Wilhelms and Larter, 1994a, 1994b). Tar mats are readily soluble in organic solvents, clearly distinguishing them from weakly soluble pyrobitumen formed during reservoir maturation (Milner et al., 1977; Wilhelms and Larter, 1994a). These deposits may separate from the main oil charge in response to several different processes, including gravity segregation, introduction of gas to the reservoir and decreasing reservoir pressures, or are due to permeability barriers (Milner et al., 1977; Dahl and Speers, 1986; Wilhelms and Larter, 1994a, 1994b). In particular, deasphalting of the oil in response to gas generation from a maturing reservoir oil could account for the formation of the asphalitic tars, given that their thermal maturity ($R_c = 1.1–1.2\%$) lies at the boundary of the wet gas window ($R_c = 1.3\%$). Migration of gas into the reservoir is also possible, given the faulting which may connect to regions of the basin in the gas window (Fig. 7). However, ultimately none of the processes listed above can be discounted, as the resulting heavy petroleum in each case displays no diagnostic changes to its geochemistry. A more detailed knowledge of the geologic context of their parent petroleum system is therefore required to assess these mechanisms further.

Considering the asphalitic tars and asphaltite strandings as pieces of previously emplaced tar mats is also problematic, as it also requires facilitating their migration to the seafloor, despite their tendency to remain in place in the subsurface. Hall et al. (2014) suggested that following their formation as tar mats, the asphaltites escaped the subsurface by way of submarine canyon incision. However, it is more likely that seepage of both the asphaltites and the asphalitic tars is analogous to the asphalt flows observed on the seafloor in the Gulf of Mexico (Brüning et al., 2010). In this case, heavy petroleum that has not yet become immobile reaches the seafloor in a viscous state and flows away from the seepage site. The loss of volatile components, oxidation and other processes progressively increases the viscosity of the oil to the point where it becomes immobile and ultimately solidifies. The deposit forms deep fissures and cracks due to the loss of its low-molecular-weight hydrocarbons. The bitumen eventually fragments, releasing material into the overlying water column where it can become entrained in ocean currents. This process is certainly consistent with the shrinkage cracks seen in the larger asphaltites (Fig. 1B). The asphalitic tars, which have not solidified, may be more analogous to the seafloor tar mounds/whips.
observed off the southern coast of Santa Barbara (Lorenson et al., 2009). In this case, however, the oil has not been extensively biodegraded like that encountered in the Santa Barbara seeps.

4.4. Constraining the location of the asphaltic tar petroleum system

The prior coastal surveys conducted in November 2014 and September 2015 found no examples of this new variety of asphaltic crude oil across the 30 systematically surveyed beaches (Ross et al., 2017). There are similarly no reports of any oil matching their geochemical signature in previous studies of Australian coastal bitumen (McKirdy, 1984a, 1984b; Currie et al., 1992; Volkman et al., 1992; Summons et al., 1993; Alexander et al., 1994; Padley, 1995; Edwards et al., 1998, Hall et al., 2014; Edwards 2016, 2018). The beach where the asphaltic tars were found, Number 1 and 2 Rocks, is also the most prominent collection point for coastal bitumen identified on the South Australian coastline (Padley, 1995; Edwards et al., 2016; Ross et al., 2017). Despite the abundance of coastal bitumen recovered from this site, no asphaltites were found there during the three annual surveys conducted in 2014–2016 (Ross et al., 2017), nor during the systematic bi-monthly surveys conducted in 1990 and 1991 (Padley, 1995; Edwards et al., 2016). However, it is important to acknowledge that the asphaltic tar strandings were collected just 24 days after a one-in-fifty-year storm event which affected much of the South Australian coastline (Bureau of Meteorology, 2016; Burns et al., 2017). The resulting abnormal wind and wave behaviour likely caused a significant departure from their traditional oceanic transport pathway and ultimate stranding location. Therefore, the single stranding location of the asphaltic tars presently provides little constraint on their point of origin.

If the asphaltic tars were derived from an oil affected by TSR then the parent oil must reside within a region of the subsurface which meets the required minimum onset temperature of 100–140° (Goldhaber and Orr, 1995; Machel, 2001). This may permit assessment of potential reservoirs based on the general increase in temperature with depth (e.g. Fig. 7). However, locally increased temperatures will also occur in proximity to volcanism and circulating hydrothermal fluids. The Bight Basin hosts an approximately 50,000 km² complex
of volcanic intrusions in the Ceduna Sub-basin and the overlying Eucla Basin, with isolated igneous bodies also reported in the adjacent Duntroon Sub-basin (Schofield and Totterdell, 2008). Thus, circulating hydrothermal fluids could also provide the necessary temperatures and dissolved sulphate for TSR to occur within shallower regions of the basin. This is further supported by the recent identification of hydrocarbon-containing fluid inclusion assemblages in the Duntroon Sub-basin which appear to have been altered by hydrothermal fluids [Bourdet et al., submitted]. However, no hydrocarbons extracted from fluid inclusions in the Bight Basin have a composition consistent with the asphaltites or asphaltic tars (Kempton et al., submitted; Gong et al., submitted).

Oils altered by TSR are primarily encountered in reservoirs with limited clay content such as clean sandstones or carbonates, as the presence of iron within clay minerals will react with available H$_2$S to form pyrite, rather than permitting it to accumulate to high concentrations (Worden and Smalley, 2011; Machel, 2001). In order for TSR to occur in clastic sediments containing clays, a larger source of dissolved sulphate is required (e.g. dissolved evaporite deposits) to exhaust all of the available iron before H$_2$S can accumulate. Presently there are no proposed carbonate reservoirs or evaporite deposits within the Bight Basin. Therefore, if the asphaltic tars have been altered by TSR, the reservoir would likely reside within clean sandstones deposited as part of the Ceduna delta, using sulphate sourced from groundwaters or circulating hydrothermal fluids. However, as the evidence for alteration by TSR is not conclusive, proposing an exact location for the parent petroleum system within this frontier basin remains speculative.

5. CONCLUSIONS

A new type of stranded crude oil termed ‘asphaltic tar’ was encountered during coastal surveys of South Australia in October 2016. These strandings share source-specific features with the well-studied asphaltites, also found on the South Australian coastline. Thermal maturity parameters constrain the asphaltic tar to the late oil window, unlike the asphaltites which were generated within the early oil window. The contrasting thermal maturity of the two oil types renders their correlation uncertain. Despite their source-specific similarities,
differences in several geochemical parameters of the two oil types suggest that each may have originated from separate source rocks with comparable marine organic matter inputs. However, the most prominent differences accord with the higher thermal maturity of the asphaltic tar and its alteration by thermochemical sulphate reduction. Both interpretations are consistent with these two oil types originating from within the same basin. As the asphaltites are presently attributed to an undiscovered petroleum system in the nearby Bight Basin, we consider these newly discovered asphaltic tars to have a similar origin.

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