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Comparison of palaeo oil charges with currently reservoired hydrocarbons using the geochemistry of oil-bearing fluid inclusions

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Abstract

This paper describes the use of oil-bearing fluid inclusions as time-specific markers of different oil migration events. Fluid inclusions are small samples of pore fluid trapped in framework minerals due to brittle deformation and fracturing during burial, or in diagenetic minerals during crystallisation. Recent advances in analytical techniques and instrumentation mean that it is now feasible to obtain detailed geochemical data on the trapped oils, which can be directly compared with either reservoired oils or with putative source rocks. Two techniques are currently being used, an off-line method which is suitable for comparing high molecular weight biomarker distributions and an on-line method which provides compositional data for the complete fluid which is trapped, including low molecular weight hydrocarbons and gases.

In this paper the results from two case studies involving the Jabiru and South Pepper oilfields are discussed. At Jabiru the oil trapped in fluid inclusions is genetically-related to, but is less mature than, the currently reservoired charge. This suggests continued expulsion of progressively more mature oil from the same or similar source rock facies. At South Pepper the fluid inclusion oil is both more mature and derived from a different, more calcareous source rock than the currently reservoired oil. The early oil is most likely derived from Triassic source rocks and was heavily biodegraded before re-charge of the South Pepper structure with Jurassic-sourced oil and gas.

Molecular composition of inclusion (MCI) studies such as these are powerful tools for elucidating the petroleum charge history to reservoirs. They provide molecular geochemical data on early oil charges which, when compared to presently reservoired oil, can be used to describe the changing nature of

reservoir fluids through time. They are successfully being applied to other reservoirs on the North-west Shelf of Australia, either in dry holes or where there is currently gas and where fluid inclusion oil represents the only sample of oil charge.

Introduction

Generated oil migrating to a reservoir rarely displays a uniform composition over time. Source rock horizons become more mature during burial, so will generate oil with progressively changing geochemistry. Deeper source rocks start generating oil, leading to variations in geochemical source parameters in the later oil charges. Earliest oil charge is likely to fill the largest pores and continued migration will fill progressively smaller pores and may mix with earlier charges. Reconstructing the oil charge history from the currently reservoired petroleum is complex, with considerable uncertainty as to the timing, source and phases of oil charge. One difficulty is the absence of end-member signatures due to the homogenisation process in the reservoir.

One approach is the use of oil-bearing fluid inclusions as time-specific markers of different oil migration events. Oil inclusions are small samples (usually <10 μm in diameter) of pore fluid encapsulated in framework minerals such as quartz, feldspar and carbonate as they crystallise. Oil inclusions form during the crystallisation of diagenetic minerals and through the brittle deformation and fracturing of framework minerals (detrital or diagenetic) during burial. They can be readily detected by fluorescence microscopy because of their distinctive fluorescence emission colours. The presence of high abundances of oil inclusions in the gas or water zones of reservoirs have previously been used to detect palaeo oil columns or residual zones¹⁻³. Recent advances in analytical techniques and instrumentation mean that it is now feasible to obtain detailed geochemical data on the trapped oils, which can be directly compared with either reservoired oils or with putative source rocks.

Several previous studies have examined the molecular composition of oil inclusions⁴⁻¹⁸. One important application of the analysis of these samples of palaeo-oil is to correlate and compare them with currently reservoired oils and deduce hydrocarbon charge histories. For example, an oil trapped in

calcite cements in the Fateh Field, Dubai was generated from an early mature source rock, prior to the pore system becoming dominated by oil⁶. A more complex oil charge history is recorded by oil inclusions in the Ula Field, North Sea^{11,12}. Early oil trapped in inclusions in K-feldspar overgrowths has a low maturity and different source characteristics to the current petroleum charge in the Ula Formation, which is derived from the Mandal Formation. Oil inclusions in authigenic albite and quartz have a composition intermediate between the K-feldspar inclusion oil and the current charge, suggesting that they record progressive dilution of the early reservoir oil with oil from the Mandal Formation^{11,12}. Alteration episodes can also be defined by comparison of fluid inclusion oil and current reservoir fluids¹⁰. Varying degrees of alteration by biodegradation and water washing were demonstrated for fluid inclusion oils in the Danish sector of the North Sea, suggesting large scale interaction of water with oil droplets while calcite fracture cements were forming.

This paper provides results of the molecular geochemical analysis of oil inclusions in two oil fields from the North-west Shelf of Australia, Jabiru in the Vulcan Sub-basin and South Pepper in the Barrow Sub-basin (Fig. 1). The early oil charges are correlated and compared with currently reservoir oils and the hydrocarbon charge histories are deduced. Two techniques have been used, an off-line method which is suitable for comparing high molecular weight biomarker distributions and an on-line method which provides compositional data for the complete fluid which is trapped, including low molecular weight hydrocarbons and gases. Details of these complementary techniques are provided in the Appendix.

Jabiru

Background. Jabiru was the first commercial oil field in the Timor Sea and was discovered in 1983¹⁹. Jabiru-1A penetrated a 57 m thick oil column and flowed oil from Middle and Upper Jurassic sandstones at 6,000 STBPD and 3,466 STBPD respectively. A residual oil column is present below the current oil-water contact (OWC) and is consistent with loss of oil from the trap as a result of Late Miocene to Early Pliocene fault reactivation^{20,21}. Oil-bearing fluid inclusions with predominantly blue and white fluorescence occur throughout the oil zone in the Middle Jurassic Plover Formation, and are trapped both in healed fractures in quartz grains and within quartz overgrowths¹. In this paper, oil-bearing fluid inclusions in a core sample from the oil zone at 1,637.1m in Jabiru-1A are compared geochemically with a production oil sample from the Jabiru field.

Results.

***n*-Alkanes.** Data for the oil released by the on-line crushing of fluid inclusions is compared using *m/z* 57 mass chromatograms in Fig. 2 to the distribution of hydrocarbons in the production oil, determined by split injection in the MSSV apparatus (see Appendix). The DST oil contains *n*-alkanes from *n*-C₆ to *n*-C₃₈ with a maxima at *n*-C₁₅, whereas the fluid

inclusion oil contains relatively more of the lower molecular weight homologues (< *n*-C₂₀), with a maxima at *n*-C₆. Small amounts of higher molecular weight *n*-alkanes up to *n*-C₂₈ were detected in the fluid inclusion oil by on-line crushing (Fig. 2). Off-line crushing of oil-bearing fluid inclusions showed *n*-alkanes from *n*-C₈ to *n*-C₃₆, with less discrimination against the higher molecular weight hydrocarbons than as determined by on-line crushing. There is a slight odd over even predominance at high molecular weights (CPI₂₂₋₃₂ = 1.08±0.003) for both the fluid inclusion oil and the production oil. The different distribution as determined by the two analytical approaches is due to: (1) the unavoidable evaporative effects associated with the work-up of the tiny amounts of hydrocarbons released from the fluid inclusions in the off-line method, and (2) an adsorption or matrix effect, which means that the MSSV technique is not so suitable for analysing the higher molecular weight hydrocarbons trapped in fluid inclusions. Any adsorption or matrix effects are probably due to adsorption of the more polar, higher molecular weight hydrocarbons onto the newly created quartz powder resulting from crushing of the quartz grains, which will have a large surface area and plenty of active sites. For these reasons, it is considered that the two analytical techniques are complementary, the off-line method being best for comparing high molecular weight biomarker distributions and the on-line method being best for low molecular weight hydrocarbons.

Gasoline Range Hydrocarbons. The distribution of low molecular weight compounds (< *n*-C₉) in the fluid inclusion oil is similar to that of the DST oil (Fig. 2). Methylcyclohexane is the most abundant hydrocarbon, with large amounts of cyclohexane, other alkylcyclohexanes and methylcyclopentane. The relative amounts of cyclic hydrocarbons, branched alkanes, *n*-alkanes and aromatic hydrocarbons has some variability between the inclusion oil and the production oil. For example, the peak due to *m*-+*p*-xylene is greater in the production oil (Fig. 2). Unlike other fluid inclusion oils, including the South Pepper inclusion oil discussed later, there is no anomalously large amount of water soluble compounds in the Jabiru inclusion oil.

Biomarkers. Biomarker distributions in the fluid inclusion oil are similar to those for the oil now reservoir in Jabiru (Table 1). For example, Pr/Ph ratios are 2.7±0.04 and there is a similar ratio of *n*-alkanes to isoprenoids (e.g. Pr/*n*-C₁₇ = 0.47±0.02). The C₃₅/C₃₅+C₃₄ homohopane ratio is similar, the relative amounts of C₂₉ and C₃₀ αβ hopanes are constant and there are only very small amounts of 28,30-bisnorhopane in both the fluid inclusion oil and the production oil. However, there are also some dissimilarities. The fluid inclusion oil contains relatively low amounts of 17α(H)-diahopanes (e.g. C₃₀*), Ts (18α(H),22,29,30-trisnorneohopane), C₂₉Ts (18α(H)-30-norneohopane), C₂₇ steranes and C₂₇ to C₂₉ diasteranes than the produced oil. For example, the C₃₀*/C₃₀ αβ hopane ratio is 0.16 for the fluid inclusion oil and 0.36 for the production oil.

The main hopane and sterane maturity-dependent ratios are at or close to equilibrium values and show little variation between the fluid inclusion oil and the production oil (Table 1).

Aromatic Hydrocarbons. Alkyl-naphthalenes, alkylphenanthrenes and alkyl-dibenzothiophenes were used to assess

thermal maturity variation between the fluid inclusion oil and the production oil. Partial mass chromatograms show the distribution of the isomers used (Fig. 3). The shaded peaks show the more thermally-stable, β -substituted isomers which become relatively more abundant at higher maturities (e.g. refs 22 and 23). 2-Methylnaphthalene, 2,6-+2,7-dimethylnaphthalene, 2,3,6-trimethylnaphthalene, 2,3,6,7-tetramethylnaphthalene, 3- and 2-methylphenanthrene, 4-methyl dibenzothiophene and 4,6-dimethyl dibenzothiophene all have a greater relative abundance in the production oil compared to the fluid inclusion oil (Fig. 3). This is expressed by several maturity-dependent ratios, which are plotted in a histogram in Fig. 4.

Discussion.

Source and Maturity Variations. The main maturity-dependent biomarker ratios show little variation between the fluid inclusion oil and the production oil from Jabiru (Fig. 4). These are at or close to equilibrium values, suggesting maturities at least in the peak oil-generating window. At high maturities, these biomarker ratios stop changing as the isomers reach an equilibrium mixture and therefore are less useful for determination of relative maturity levels of light oils or condensates^{24,25}. However the aromatic hydrocarbon data clearly shows that the production oil is derived from a more mature source rock than the fluid inclusion oil. Calculated reflectance, derived using the calibrated methylphenanthrene index²⁶, is 0.84% for the fluid inclusion oil, compared to 0.92% for the produced oil.

The distribution of *n*-alkanes, isoprenoids, hopanes and steranes is for the most part similar in the fluid inclusion oil and the production oil. The main differences are the relative proportions of the diahopanes, Ts, Tm, C₂₉Ts and the C₂₇:C₂₉ sterane and diasterane:sterane ratios (Table 1). These isomers can vary in abundance due either to source or to maturity variations. In this case, maturity level is the major controlling factor. This is deduced from the lack of source-parameter consistency, if the distribution of these isomers was primarily controlled by source. For example, the Pr/Ph of 2.7 for the fluid inclusion oil and the production oil suggest that they were both derived from a source rock(s) deposited under oxic-suboxic conditions. If the C₃₀*/C₂₉Ts ratio, which also varies with oxicity, was controlled mainly by source, then it should have similar values for both the oils. This is not the case, with considerably greater amounts of rearranged hopanes in the production oil (Table 1). Molecular mechanics calculations have indicated stabilities in the order 17 α (H)-diahopanes > 18 α (H)-neohopanes > 17 α (H)-hopanes²⁷. Therefore the higher C₃₀*/C₂₉Ts, C₂₉Ts/C₂₉ $\alpha\beta$ hopane and Ts/Tm ratios in the production oil compared to the fluid inclusion oil can be explained by a higher maturity for the former. Likewise, the higher C₂₇:C₂₉ sterane and diasterane:sterane ratios in the production oil can be explained by a maturity control rather than source facies variation, because C₂₇ steranes and the diasteranes are the more thermodynamically stable isomers (e.g. ref 28).

Oil Charge History, Jabiru. The geochemical data suggest that the oil trapped in fluid inclusions in Jabiru-1A is from the same source rock, or at least a similar source rock facies, but

was generated at a lower maturity than the average of the oil now in the reservoir. The oil is most likely derived from Middle or Upper Jurassic mudstones¹⁹, although these must be off-structure because sediments at this stratigraphic level in Jabiru-1A are immature for oil generation²¹. A high proportion of the fluid inclusion oil is in thin quartz overgrowths and was probably trapped soon after initial charge. The small overgrowths are consistent with a limited solute supply and inhibition of diagenetic cementation as a result of oil emplacement¹. Further charge to the Jabiru structure was of progressively higher maturity oil, which has altered the molecular composition of the oil now produced. The large residual oil zone at Jabiru indicates substantial loss of charge due to moderate fault reactivation²¹. Preferential loss of lower maturity oil from the top of the reservoir and its replacement with more recently generated, higher maturity oil is therefore consistent with the observed maturity data.

South Pepper

Background. The South Pepper oil field is located about 25 km SSW of Barrow Island in the Barrow Sub-basin and was discovered in 1982^{29,30}. South Pepper-1 encountered 14 m of gas underlain by a 9.0 m oil column at the top of the Lower Cretaceous Barrow Group and tested 10.9 MMCFD gas and 1,515 BOPD. Recent work, demonstrating a high abundance of blue fluorescing oil inclusions in carbonate-cemented sandstones within the present gas cap (1,220.8-1,225.3 m), has been used to suggest that a zone of high oil saturation once existed near the top of the Barrow Group¹⁸. In this paper, oil inclusions in a core sample from the gas cap at 1,220 m in South Pepper-1 are compared geochemically with three DST oils from the South Pepper field.

Results.

***n*-Alkanes.** Data for the oil released by the on-line crushing of fluid inclusions is compared in Fig. 5 to the distribution of hydrocarbons in a DST oil, determined by split injection in the MSSV. Unlike the DST oil, which contains *n*-alkanes from *n*-C₆ to *n*-C₃₂ with a maxima at *n*-C₁₁, the fluid inclusion oil mainly contains the lower molecular weight homologues (< *n*-C₁₅). Higher molecular weight *n*-alkanes up to *n*-C₃₅ were detected in the fluid inclusion oil using the off-line crushing method, albeit in low abundance¹⁸.

Gasoline Range Hydrocarbons. The distribution of low molecular weight compounds (< *n*-C₉) in the fluid inclusion oil is somewhat different to that in the DST oil (Fig. 5). Benzene and toluene are present in only trace amounts in the DST oil, whereas they are major components of the fluid inclusion oil, as are furan and methylfuran. Alkanes with methyl and dimethyl substituents (e.g. 3-methylpentane, 2- and 3-methylhexane, 2,2-dimethylpentane) are relatively

more abundant in the fluid inclusion oil. Cyclohexane is more abundant in the DST oil, but other cyclic compounds have similar distributions.

Biomarkers. Biomarker distributions in the fluid inclusion oil are markedly different to those for the oil now reservoired in South Pepper-1, as shown by the multiple reaction monitoring (MRM) chromatograms for the steranes and diasteranes (Fig. 6). At each carbon number (C_{27} to C_{30}) the diasteranes in the fluid inclusion oil are less abundant than the steranes, whereas the reverse is true for the DST oils. Sterane carbon number distributions are also different, with relatively less C_{28} steranes in the fluid inclusion oil. Although the ratio of total C_{27} / total C_{29} steranes is similar, the fluid inclusion oil contains slightly more C_{27} $\alpha\alpha\alpha$ 20R and less C_{29} $\alpha\alpha\alpha$ 20R than the DST oil. Both oils plot in the "marginal marine" field of the C_{27} : C_{28} : C_{29} ternary diagram (not shown) and contain significant amounts of 24-*n*-propyl cholestanes which are molecular markers indicative of marine algae³¹. The group of peaks eluting close to the retention time of 20R $\alpha\alpha\alpha$ 24-*n*-propyl cholestane in the m/z 414→231 MRM chromatogram (Fig. 6) are identified as dinosteranes and 4-methylstigmastanes^{32,33}.

Single ion monitoring (SIM) mass chromatograms show that hopane and methylhopane distributions for the fluid inclusion oil are also very different compared to the DST oil (Fig. 7). In the fluid inclusion oil, Ts/Tm and C_{29}/C_{30} $\alpha\beta$ hopane ~1 and the C_{35} homohopanes are a significant proportion of the extended homohopanes. C_{29} Ts and the diahopanes are in low abundance. Small amounts of gammacerane, 29,30- and 28,30-bisnorhopane and a series of peaks eluting after hopane and the homohopane doublets which were tentatively identified as C_{30} to C_{34} 17 α (H)-30-norhopanes were identified in the fluid inclusions oil by MRM¹⁸ (not shown). The m/z 205 mass chromatogram shows a complex series of Ring A methylhopanes in the fluid inclusion oil (Fig. 7), which are identified as predominantly the 2 α -methylhopanes^{18,34}. In contrast, the DST oil has higher Ts/Tm and C_{29}/C_{30} $\alpha\beta$ hopane ratios than the fluid inclusion oil and contains large amounts of C_{29} Ts and diahopanes. The extended homohopanes are in lower abundance and no gammacerane, 2 α -methyl-hopanes or 30-norhopanes could be detected. The DST oil does contain a large amount of the C_{29} 25-norhopane, whereas this demethylated hopane is of very low abundance in the fluid inclusion oil. One further difference is that the DST oil contains greater amounts of the moretananes, relative to the $\alpha\beta$ hopanes, than the fluid inclusion oil.

Discussion

Overall Oil Composition. The high amounts of benzene, toluene, furan and methylfuran in the fluid inclusion oil has two possible explanations. Firstly, these may suggest that the trapped oil is pristine and has not been affected by any water washing, as these compounds are among the most soluble of crude oil components in water³⁵. Secondly however, these water soluble compounds may be derived from aqueous fluid inclusions, which co-exist with oil-bearing fluid inclusions in this sample and were therefore crushed at the same time. Previous geochemical work on aqueous inclusions from Fateh Field in Dubai has demonstrated the presence of the same water soluble compounds, and it was suggested that this and

the co-existence of fresh oil and aqueous inclusions represents secondary migration "caught in the act"⁶. Further work is currently being undertaken on hand-picked populations of aqueous and oil-bearing fluid inclusions from South Pepper in order to unequivocally determine the origin of these water soluble compounds. However, the large amounts of low molecular weight (C_6 to C_{10}) *n*-alkanes in the fluid inclusion oil demonstrates that the oil was not biodegraded prior to entrapment.

The overall composition of the fluid inclusion oil is very biased towards the low molecular weight compounds ($<C_{15}$), although the off-line crushing technique shows that higher molecular weight hydrocarbons were trapped in the fluid inclusions as well, albeit in much lower abundance¹⁸. In this respect the fluid inclusion oil is very different to the currently reservoired oil, which contains abundant *n*-alkanes up to C_{25} (Fig. 5).

Source of Oil Trapped in Fluid Inclusions. The oil currently reservoired in the Barrow Group at the South Pepper structure is geochemically similar to other oils in the Carnarvon Basin and is likely to originate from the Upper Jurassic Dingo Claystone^{29,36}. The large amount of demethylated C_{29} 25-norhopane in this oil, together with abundant *n*-alkanes suggests overprinting of a pristine oil with the residue of a previously heavily biodegraded oil^{29,36}.

The biomarker data clearly shows that the oil trapped in the fluid inclusions is quite different to the currently reservoired oil. The major source parameters are plotted in a spider diagram (Fig. 8), which provides a good visualisation of this difference. The presence of 29,30-bisnorhopane and 30-norhopanes suggest that the fluid inclusion oil is derived from a source rock with a calcareous component^{37,38}. Further evidence for this is the near equal amounts of C_{29} and C_{30} $\alpha\beta$ hopanes, the low relative amount of C_{28} steranes and the significant amount of C_{35} homohopanes in the fluid inclusion oil. In addition, there are large amounts of 2 α -methylhopanes in the fluid inclusion oil, but not in the DST oils, which are biomarkers for prokaryotic source input and also carbonates in the source organic matter³⁴. The lower Pr/Ph ratio, trace of gammacerane, low abundance of diasteranes and lower amount of diahopanes all suggest a source rock which is quite different to the Dingo Claystone. It appears to have had a higher carbonate component and have been deposited in a more anoxic depositional environment than the Dingo Claystone. The presence of peaks attributed to 4 α -methylsteranes and C_{30} dinosteranes in the fluid inclusion oil is significant as these biomarkers are generally only found in marine oils from the Triassic onwards^{32,33}. Dinosteranes have not been reported in Palaeozoic oils, so unless these compounds were added during migration this probably excludes Devonian carbonates as the potential source for the fluid inclusion oil.

Maturity of Oil Trapped in Fluid Inclusions. Hopane and sterane maturity parameters show that both oils are beyond the early oil generation window, as the homohopane isomerisation ratios (e.g. C_{31} $\alpha\beta$ S/S+R) and the C_{29} sterane S/S+R ratios have reached their end points. The maturity-dependent C_{29} $\alpha\beta/\alpha\beta+\beta\alpha$ hopane ratio is higher for the fluid inclusion oil (0.93) compared to the DST oils (0.83-0.85), and this maturity difference is corroborated by the C_{29} sterane $\alpha\beta\beta/\alpha\beta\beta+\alpha\alpha\alpha$ ratio (0.56, compared to 0.52-0.54). Furthermore, the overall

distribution of hydrocarbons in the fluid inclusion oil is biased towards lower molecular weights, compared to the DST oils. Therefore, it is suggested that the early charge, as represented by the fluid inclusion oil, was generated from a more mature source rock than the current charge.

Oil Charge History, South Pepper. This study suggests that a mature source rock, more calcareous and deposited under more anoxic and reducing conditions than the Dingo Claystone, was responsible for the first charge of oil to the South Pepper structure. The age constraint provided by the presence of dinosteranes in the fluid inclusion oil suggests a Triassic source rock. One possible source analogue is the basal Triassic Kockatea Shale in the Perth Basin^{39,40}.

The early oil charge was heavily biodegraded, probably during the mid-Miocene when meteoric waters penetrated to the Barrow Group⁴¹. Subsequently, a late heat flow pulse brought the middle to upper section of the Dingo Claystone into the oil generative window^{29,41}, and the second charge of Jurassic oil filled the South Pepper structure, mixing with the biodegraded residue of the first charge to give the current DST composition. The lack of geochemical evidence for Jurassic oil in the oil-bearing fluid inclusions at the top of the structure in the gas cap, and other petrographic data¹⁸, suggests that the later hydrocarbon charge involved synchronous oil and gas migration into the structure. The source of the gas is unconstrained but could reflect pre-Jurassic source rocks entering the gas window.

The importance of this new charge history is that many exploration wells to the east of Barrow Island contain biodegraded oils, notably Flinders Shoal-1, Georgette-1, Emma-1 and those of the Robe River area. These oils were previously considered to be products of progressively biodegraded, Jurassic-sourced oil^{36,41}. In contrast, these oils could also be analogues of the early charge identified in South Pepper, and charging with pre-Jurassic oils may have been a widespread occurrence on the eastern flank of the Barrow Sub-basin¹⁸. This study has demonstrated the ability to characterise palaeo oil charges which has created a new exploration play, as pre-Jurassic oils to the west may have escaped biodegradation and therefore remain an exploration target.

Conclusions

1. At Jabiru an early oil trapped in fluid inclusions has been identified which is less mature than the currently reservoired charge. This suggests continued expulsion of progressively more mature oil from the same or similar source rock facies.

2. At South Pepper fluid inclusion oil representing an early oil charge is both more mature and derived from a different, more calcareous source rock than the currently reservoired oil. The early oil is most likely derived from Triassic source rocks and was heavily biodegraded before re-charge of the South Pepper structure with Jurassic-sourced oil and gas.

3. Molecular composition of inclusion (MCI) studies such as these are powerful tools for elucidating the petroleum charge history to reservoirs. They are successfully being applied to other reservoirs on the North-west Shelf of Australia, where there is only fluid inclusion evidence of palaeo oil columns, either in dry holes or where there is currently gas.

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Appendix—Analytical Methods

Geochemical Analysis of Oil-bearing Fluid Inclusions. A pre-requisite for the successful analysis of the tiny amounts of oil trapped in fluid inclusions is the complete removal of oil from the outside of grains. In most molecular composition of inclusions (MCI) studies, including the Jabiru sandstone, this is achieved using strong oxidising agents (hydrogen peroxide, chromic acid), because quartz grains are the host mineral and are fully resistant to these chemicals. For South Pepper many of the oil-bearing fluid inclusions are in carbonate cements, so a different approach was followed so as to avoid removal of the carbonates. Vacuum solvent extraction (-80 KPa) was used to access any tightly bound oil remaining in pore space. Further soxhlet extraction and gas chromatographic analysis of the product showed no *n*-alkanes remaining and demonstrated that all oil had been removed from the outside of grains.

On-line Analysis Method. In order to assess the overall composition of the oil and gases trapped in the fluid inclusions, small amounts (~50 mg) of quartz grains were hand crushed in the metal insert of a Quantum MSSV-1 Thermal Analysis System (GC² Chromatography, Cheshire) using a metal plunger. The thermal analysis port was mounted on a

Hewlett Packard 5890 gas chromatograph interfaced to a VG AutoSpecQ. The port was held at 300°C and carrier gas (helium; 60 KPa head pressure) was passed through it in splitless mode during the crushing. Chromatography was carried out on a fused silica column (25 m x 0.25 mm i.d.) coated with GC5 (5% phenyl 95% methyl silicone, 0.3 µm film thickness). Oil and gases liberated during crushing were cryogenically trapped by passing a loop of the column through a liquid nitrogen bath. Any methane present in the fluid inclusions was not trapped during this procedure and was detected during the first 2 mins after crushing was initiated. After 2 mins the cryogenic trap was removed and the oven was programmed from an initial temperature of 10°C, followed by heating at 4°C min⁻¹ to 300°C. After 5 mins the thermal analysis port was switched into split mode (35 ml/min) to clean the port. The DST oils were analysed by split injection using a glass insert in the MSSV.

Off-line Analysis Method. Cleaned quartz grains (6-7 g) were crushed to a fine paste under a mixture of dichloromethane (DCM) and methanol (93:7) using a stainless steel crushing cylinder with a 55 ml capacity. Two stainless steel balls were placed in the container above the samples and 25 ml of the solvent mixture was added before closure of the container in air at atmospheric pressure. The container was vigorously shaken in a vertical motion with a throw of about 40 mm, using a modified rotary pump. This procedure crushed the quartz grains and carbonate cements and released the trapped oil, which partitioned into the solvent. The resultant suspension of finely crushed quartz in solvent was transferred to a beaker, ultrasonicated for 15 mins and allowed to settle for 5 mins. The solvent layer, containing some crushed quartz, was decanted to centrifuge tubes and the mixture centrifuged for 10 mins, enabling complete separation of the solvent from the crushed quartz. The solvent was decanted off to a round bottom flask. The crushed quartz was combined with the main quartz fraction in the beaker and then fresh solvent mixture (20 ml) was added. The mixture was stirred and the quartz was re-extracted by ultrasonication as described above. This procedure was repeated twice so as to remove all oil derived from the fluid inclusions which may have adsorbed on to the crushed quartz.

The DST and production oils were fractionated using standard column chromatography into aliphatic and aromatic hydrocarbon fractions. These and the fluid inclusion oils were analysed by GC-MS as described above, except that chromatography was carried out on a fused silica column (60 m x 0.25 mm i.d.) coated with DB5MS (modified 5% phenyl 95% methyl silicone, 0.25 µm film thickness), using a splitless injection technique.

Blank runs were run before and after each of the fluid inclusion preparations, using exactly the same experimental conditions. These showed very low levels of background hydrocarbons, which quantitation showed did not interfere with the integrity of the fluid inclusion oil results.

TABLE 1—BIOMARKER DATA FOR JABIRU FLUID INCLUSION OIL AND PRODUCTION OIL

	Fluid inclusion oil	Production oil
Pr/Ph	2.66	2.75
Pr/n-C ₁₇	0.49	0.46
Ph/n-C ₁₈	0.19	0.18
CPI ₂₂₋₃₂	1.09	1.08
n-C ₃₁ /n-C ₁₉	0.09	0.04
Wax index (n-C ₂₁ +n-C ₂₂ /n-C ₂₈ +n-C ₂₉)	3.07	5.05
Ts/Tm	2.24	3.08
C ₂₉ Ts/C ₂₉ αβ hopane	0.54	0.96
C ₃₀ [*] /C ₂₉ Ts	0.66	1.00
C ₃₀ [*] /C ₃₀ αβ hopane	0.16	0.36
C ₂₉ hopane αβ/αβ+βα	0.85	0.84
C ₃₀ hopane αβ/αβ+βα	0.90	0.89
C ₃₁ αβ 22S/22S+22R	0.57	0.58
C ₃₂ αβ 22S/22S+22R	0.58	0.57
C ₃₅ /C ₃₅ +C ₃₄ homohopanes	0.26	0.29
28,30-bisnorhopane/C ₃₀ αβ hopane	0.02	0.01
C ₂₉ αβ hopane/C ₃₀ αβ hopane	0.43	0.37
C ₂₉ ααα+αββ steranes / C ₂₉ αβ hopanes	0.59	0.78
% C ₂₇ ααα 20R	40.2	47.1
% C ₂₈ ααα 20R	21.6	21.8
% C ₂₉ ααα 20R	38.2	31.1
C ₃₀ /C ₂₉ ααα 20R	0.18	0.13
C ₂₇ + C ₂₉ βα diasteranes / ααα+αββ steranes	1.45	2.20
C ₂₉ ααα S/S+R	0.54	0.50
C ₂₇ ααα S/S+R	0.42	0.46
C ₂₉ αββ/αββ+ααα	0.54	0.57
C ₂₇ αββ/αββ+ααα	0.48	0.52
C ₂₉ βα diasterane S/S+R	0.61	0.60

$$CPI_{22-32} = \frac{1}{2} \left[\frac{C_{23} + C_{25} + C_{27} + C_{29} + C_{31}}{C_{22} + C_{24} + C_{26} + C_{28} + C_{30}} + \frac{C_{23} + C_{25} + C_{27} + C_{29} + C_{31}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} \right]$$

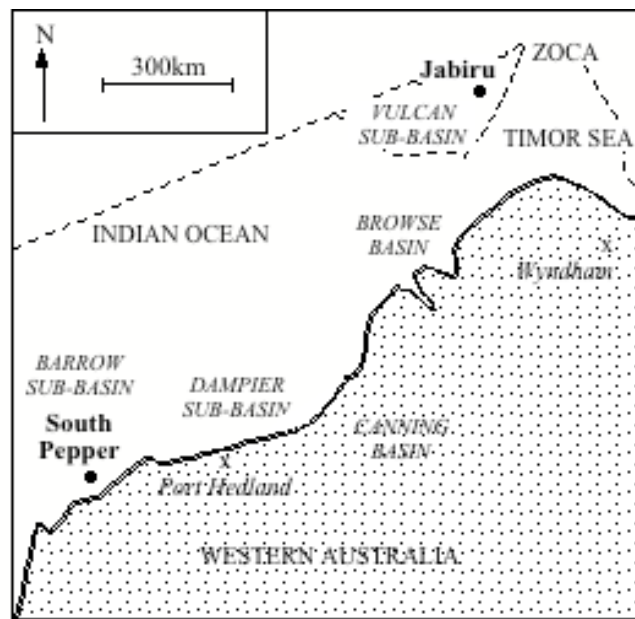


Fig. 1.—Location map showing the position of the South Pepper and Jabiru fields, North-west Shelf of Australia.

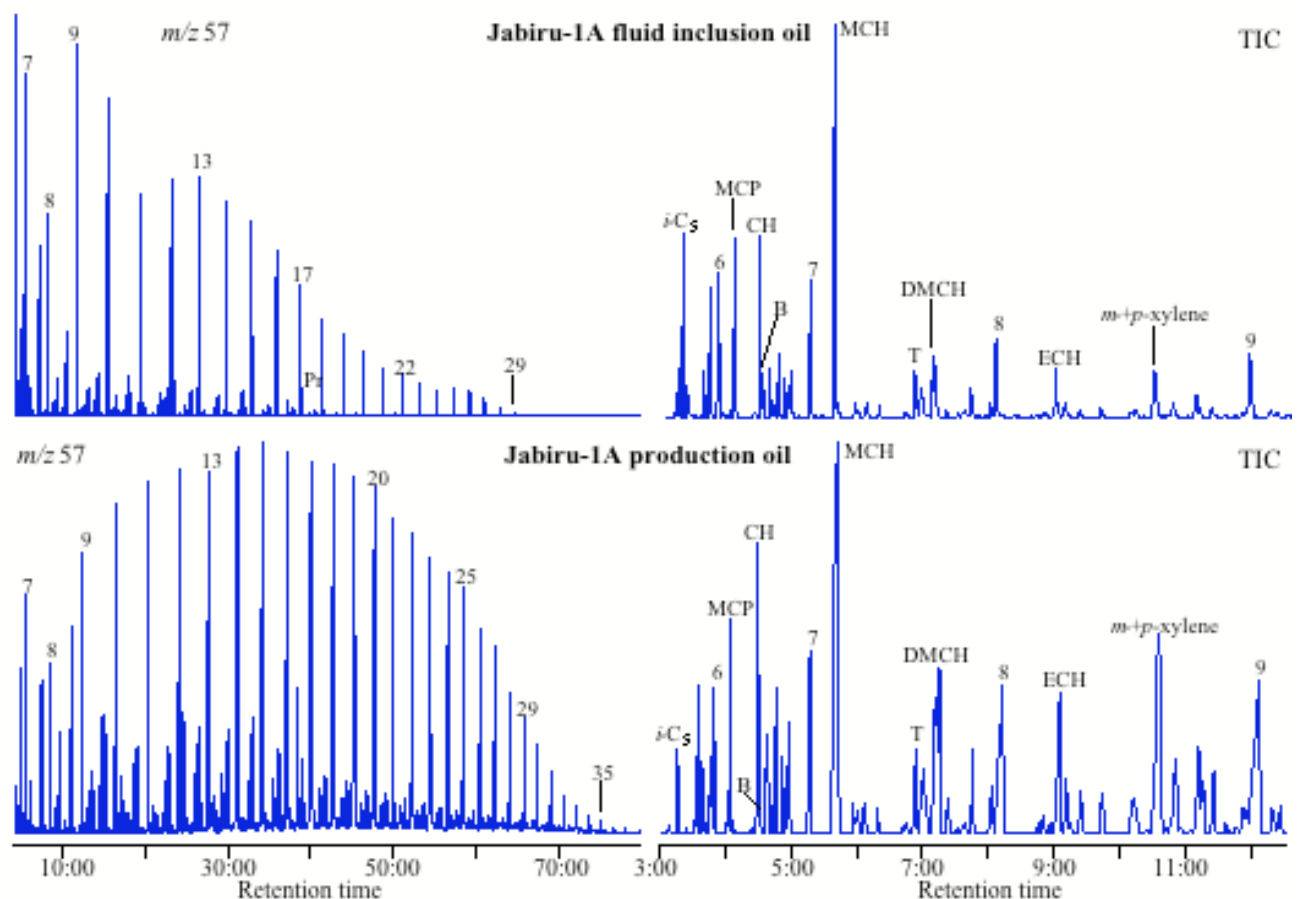


Fig. 2.—Total ion chromatograms over the gasoline range and m/z 57 mass chromatograms obtained by on-line analysis for the fluid inclusion oil from Jabiru-1A, and by whole oil split injection for the production oil from the same well. Numbers refer to n -alkane chain length, i -C₅ = iso-pentane, MCP = methylcyclopentane, CH = cyclohexane, B = benzene, MCH = methylcyclohexane, T = toluene, DMCH = dimethylcyclohexane and ECH = ethylcyclohexane.

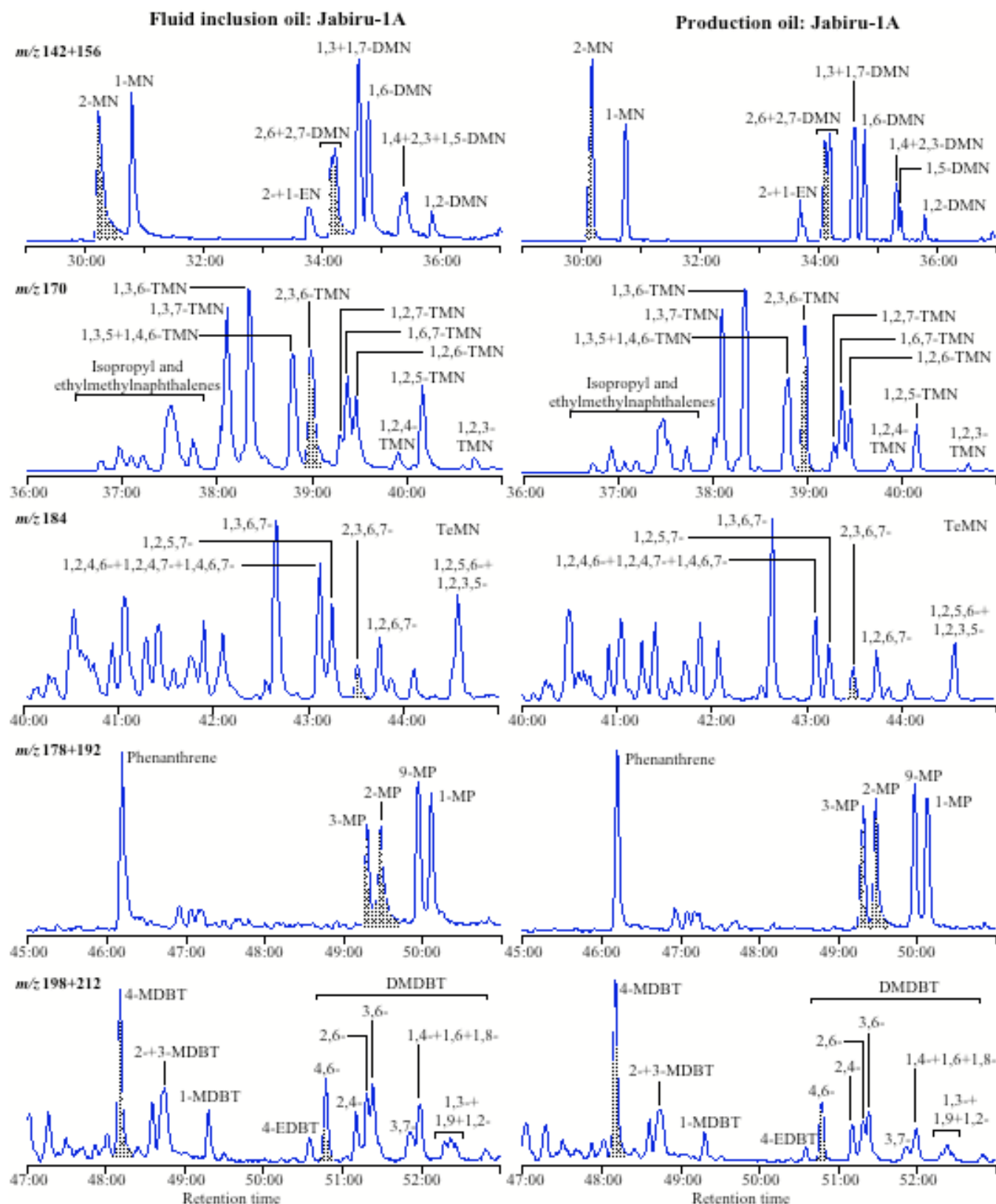


Fig. 3.—Partial *m/z* 142+156, 170, 184, 178+192 and 198+212 mass chromatograms for the fluid inclusion oil and the production oil from Jabiru-1A, showing the distribution of aromatic hydrocarbons. Isomer abbreviations are methyl-naphthalenes (MN), ethyl-naphthalenes (EN), dimethyl-naphthalenes (DMN), trimethyl-naphthalenes (TMN), tetramethyl-naphthalenes (TeMN), methylphenanthrenes (MP), methyl-dibenzothiophenes (MDBT), ethyl-dibenzothiophenes (EDBT) and dimethyl-dibenzothiophenes (DMDBT). Shaded peaks are the more thermally stable isomers.

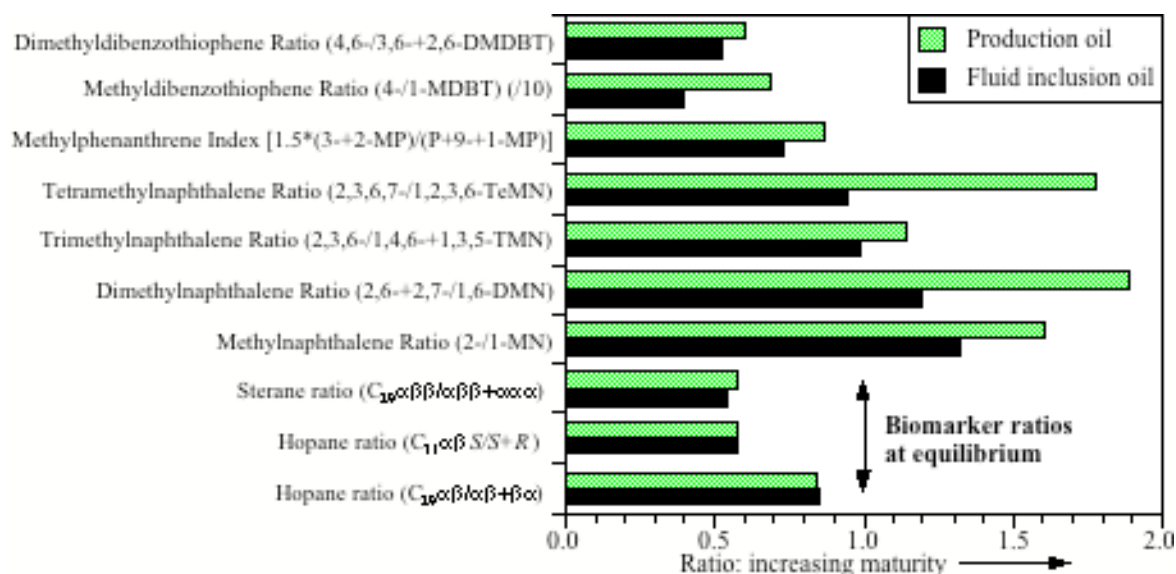


Fig. 4.—Histogram of maturity ratios for the Jabiru-1A production and fluid inclusion oils. The biomarker ratios are at equilibrium, suggesting maturities at least in the peak oil generation window. The aromatic maturity parameters show a consistently greater maturity for the production oil. Calculated reflectance from the Methylphenanthrene Index is 0.84% for the fluid inclusion oil, 0.92% for the production oil. For isomer abbreviations and identifications see Fig. 3.

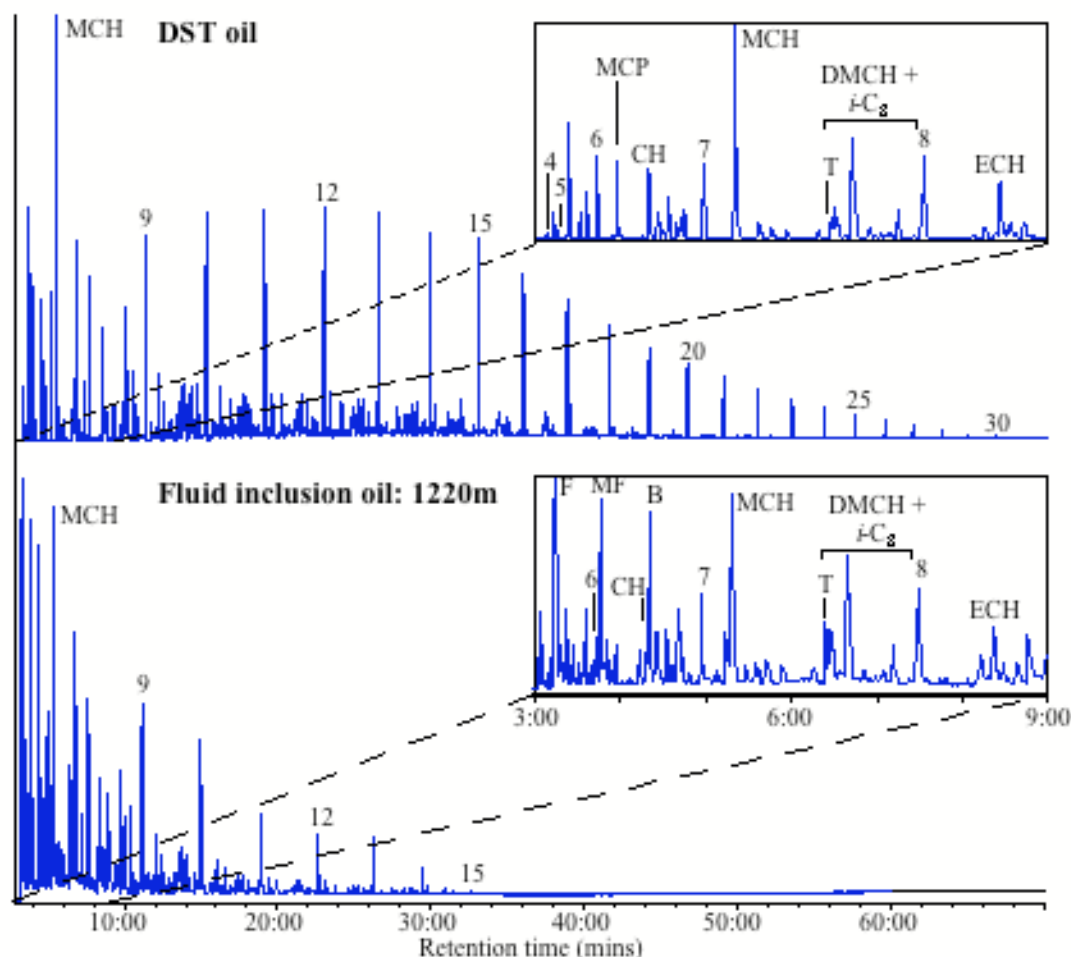


Fig. 5.—Total ion chromatograms of a DST oil from South Pepper analysed by split injection and the fluid inclusion oil from 1220m, analysed by the Quantum MSSV apparatus. Numbers refer to *n*-alkane chain length, CH = cyclohexane, MCH = methylcyclohexane, DMCH = dimethylcyclohexane, ECH = ethylcyclohexane, MCP = methylcyclopentane, B = benzene, T = toluene, *i*-C_n = methylphenanes, F = furan, MF = methylfuran.

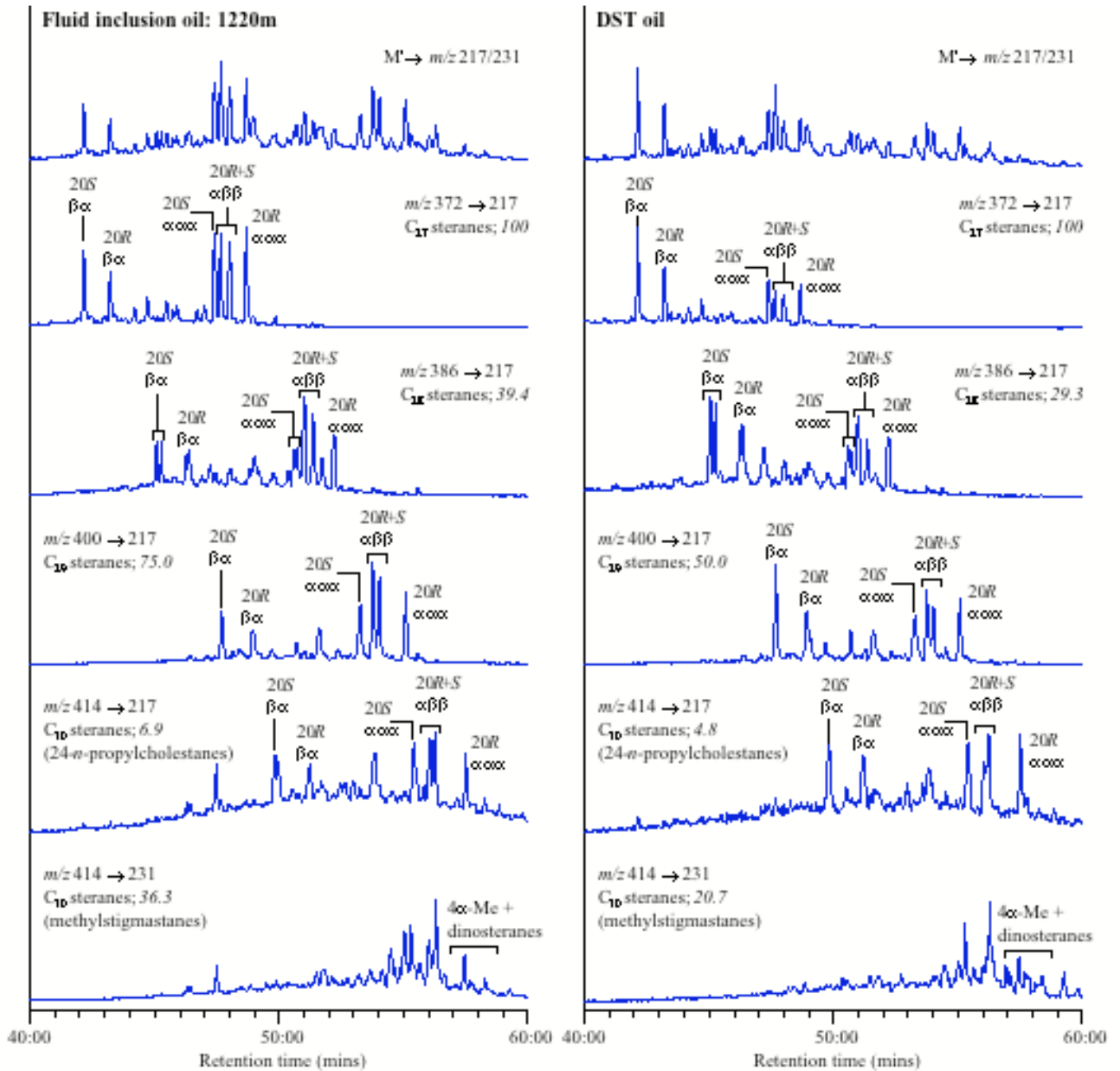


Fig. 6.—Partial MRM chromatograms for the fluid inclusion oil (1220m) and a DST oil, South Pepper-1, showing the distribution of C_{27} , C_{28} , C_{29} and C_{30} steranes and diasteranes. Chromatograms are identified by reaction transition, carbon number and relative abundance. Peak assignments define the stereochemistry at C-20 (R and S); $\alpha\alpha\alpha\alpha$ and $\alpha\beta\beta$ denote 13[R(H), 17 α (H)] diasteranes, 5 α (H), 14 α (H), 17 α (H)-steranes and 5 α (H), 14[R(H), 17[R(H)]-steranes respectively.

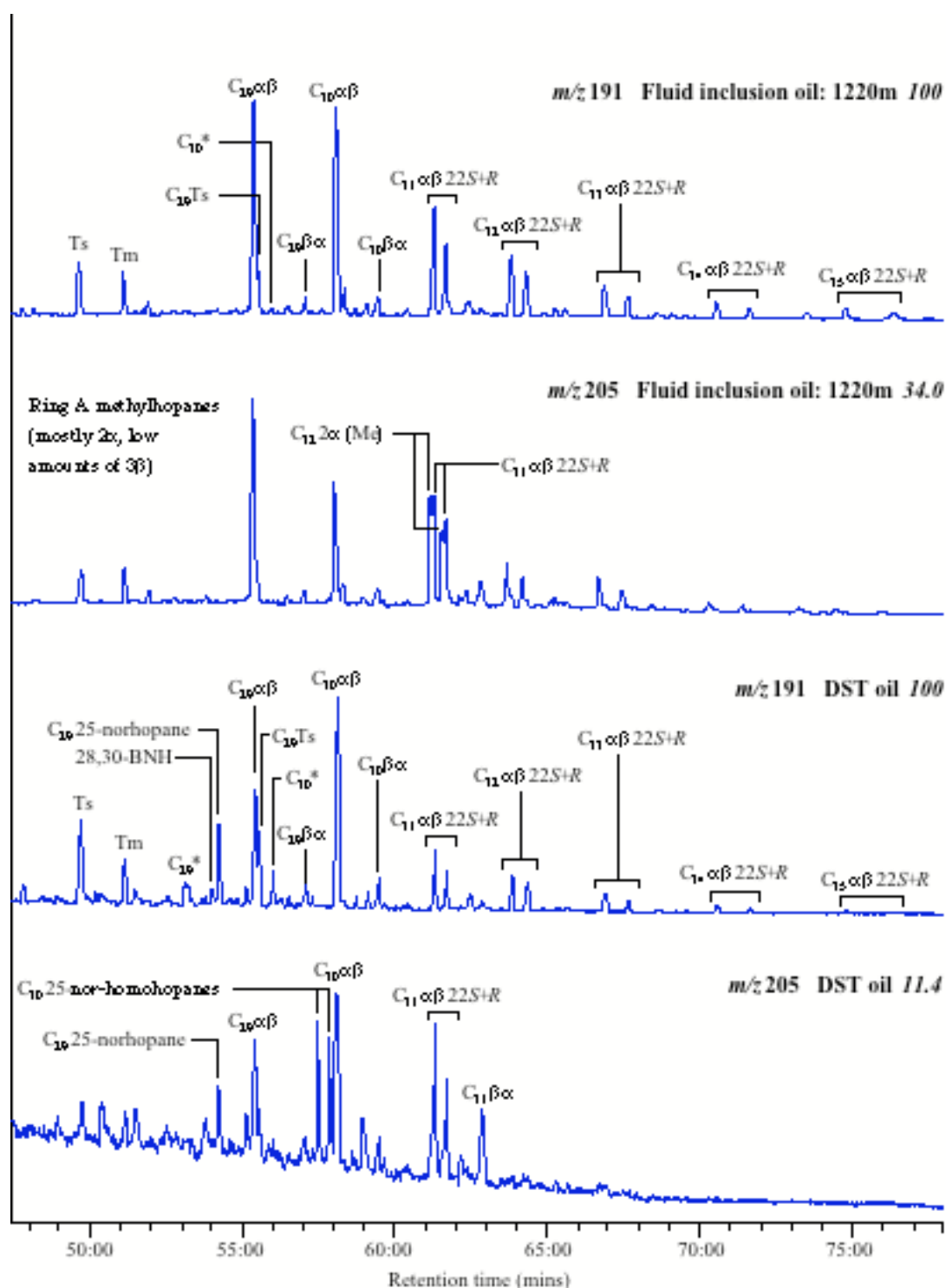


Fig. 7.—Partial m/z 191 and 205 mass chromatograms for the fluid inclusion oil (1220m) and a DST oil, South Pepper-1, showing the distribution of hopanes and methylhopanes. Peak assignments define the stereochemistry at C-22 (R and S); $\alpha\beta$ and $\beta\alpha$ denote 17 α (H),21 β (H) and 17 β (H),21 α (H)-hopanes respectively. $T_s = C_{27}$ 18 α (H),22,29,30-trisnorhopane, $T_{1m} = C_{27}$ 17 α (H),22,29,30-trisnorhopane, * = diahopane and 2 α (Me) = methylhopane. Numbers in italics refer to relative abundance of chromatograms.

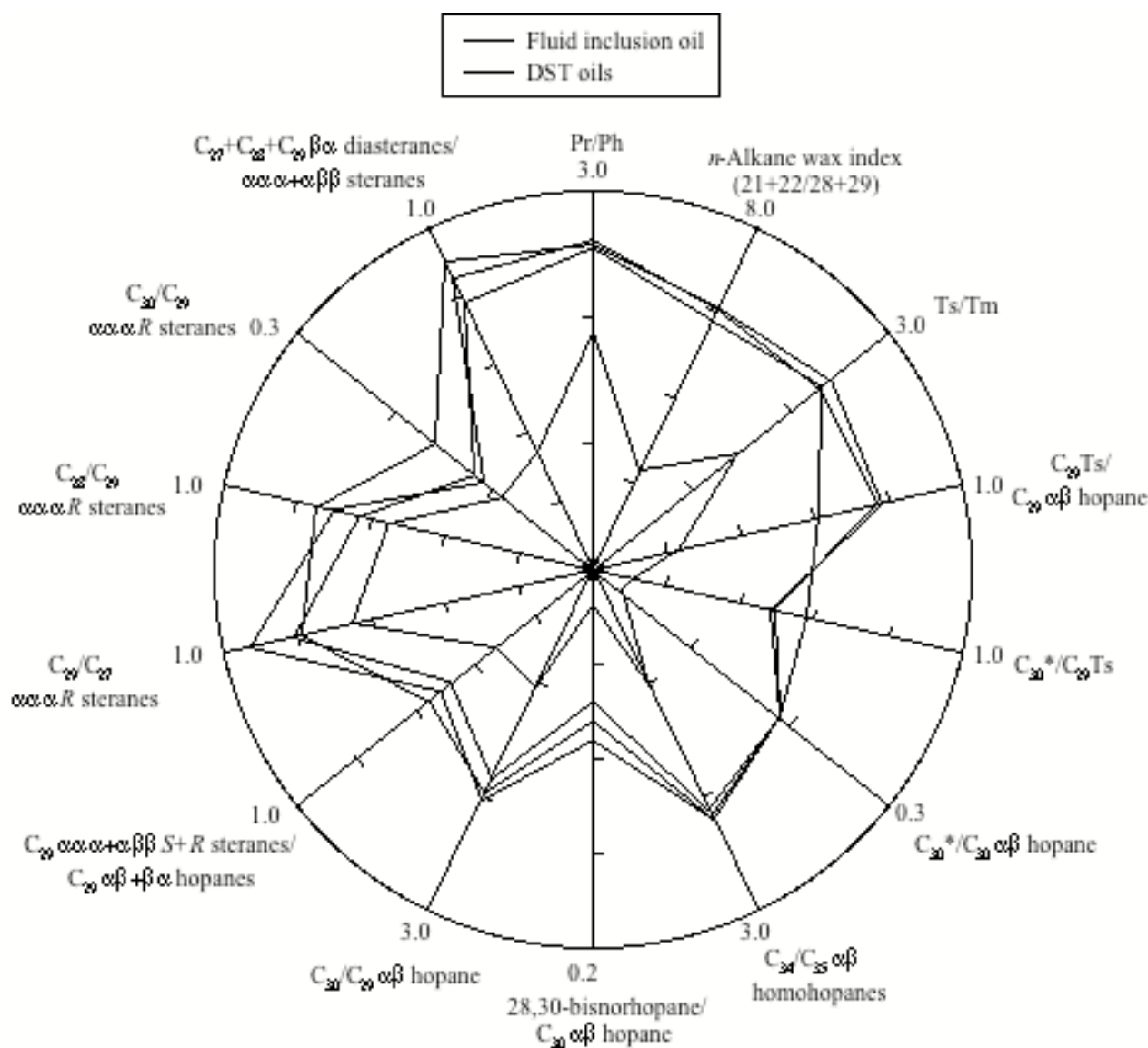


Fig. 8.—Spider diagram of source-related biomarker parameters for the South Pepper fluid inclusion oil (1220m) and the three DST oils. Ratios are configured so that oils derived from more anoxic, more calcareous and less terrestrial source rocks plot towards the middle of the diagram. This diagram clearly shows that the fluid inclusion oil was derived from a different source rock facies compared to the oil currently reservoirized at South Pepper.