Oil-bearing fluid inclusions: geochemical analysis and geological applications

含油流体包裹体:地球化学分析与地质应用[*]

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Abstract   Reliable geochemical information of similar quality to conventional analyses of crude oils and source rocks can be obtained from oil-bearing fluid inclusions (FI). Carefully controlled analytical procedures including sample clean-up, procedural blanks and attention to detail are essential for the successful analysis of inclusion oils. The procedures are technically challenging, but if they are carefully followed, successfully analysed samples can include not only those with high abundances of oil inclusions, such as in current or palaeo oil reservoirs, but also samples with low amounts of oil inclusions, such as those from oil migration pathways or from very ancient rocks. A full range of hydrocarbons can be measured from inclusions, including low molecular weight hydrocarbons, n-alkanes, isoprenoids, biomarkers and aromatic hydrocarbons.

There are many geological applications of the analysis of FI oils. These include better constraining oil charge histories of reservoirs and identifying active source rocks previously unknown in a particular basin. The effects of oil-alteration by biodegradation and/or water washing in the reservoir can be removed, mixing episodes in reservoirs can be deconvoluted, and the effects of drilling mud additives or other contaminants can be eliminated. Furthermore, the hydrocarbon composition and diversity of Earth's early biosphere can be constrained, and secondary migration pathways can be mapped across prospects or basins.
Key words   Oil-bearing fluid inclusion, Geochemical analysis, Application

摘 要   利用含油流体包裹体可以获得与原油和源区常规分析同等质量的可靠地球化学数据。细致而又小心谨慎地对待各测试步骤(如样品清洗、背景空白等)是成功进行包裹体油气成分分析的基础。从技术上来说,每一分析步骤都具有挑战性,但如果我们能按步骤循序渐进,就不仅能够分析那些含有大量石油包裹体的样品(如当今或古油藏样品),而且可以测试含极少量石油包裹体的样品(如迁移路径或极古老岩石样品)。包裹体中可被测试的碳氢化合物多种多样,包括低分子量的碳氢化合物、n-链烷、类异戊二烯、生物标志物、芳香族碳氢化合物等。

流体包裹体内石油成分分析在地质上有广泛应用,比如可以更好地重建储集区石油重注史、确定盆地中以前未知的活性源岩。在储集区内由生物降解造成的石油再造和(或)水洗作用经常被抹去,流体包裹体分析则可以解释储集区复杂成油阶段,当然更可以去除钻孔泥浆添加剂或其他污染物的影响。此外,也可以获知地球早期生物圈碳氢化合物的组成及多样性,以及在勘探区或盆地进行二次迁移路径填图。

关键词   含油流体包裹体;地球化学分析;应用
中图法分类号   P618.130.1

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1　Introduction

Oil-bearing fluid inclusions (FI) are small samples, often < 10 μm in diameter, of pore fluid trapped during the crystallisation of minerals such as quartz, feldspar and carbonate. Oil inclusions typically occur in diagenetic cements, such as quartz overgrowths, and in healed microfractures within detrital grains, diagenetic cements, or both. Oil inclusions form during the crystallisation of diagenetic minerals and through the fracturing during burial compaction of framework minerals (detrital or diagenetic). In most cases, if oil saturation was high in a reservoir, oil inclusions were formed. The presence of oil inclusions in water-wet reservoir sandstones provides a record of palaeo-oil migration (e. g. Burruss, 1981; McLimans, 1987; Eadington et al., 1991).

The tiny amounts of oil trapped in FIs can be analysed using gas chromatography-flame ionisation detection (GC-FID; e. g. Horsfield and McLimans, 1984; Jensenius and Burruss, 1990; Jochum 2000; Volk et al. 2002b) and gas chromatography-mass spectrometry (GC MS; e. g.; Karlsen et al., 1993, 2004; Lisk et al., 1996; George et al., 1996; Volk et al., 2002b; Jones and Macleod, 2000). Data from oil inclusion geochemistry can be used in petroleum systems analysis, to compare present and palaeo oils and to examine migration events and alteration processes that have affected oil composition over time. The advantage of using FIs is that once oil is trapped within mineral grains, it is physically isolated from the main pore system of the reservoir rock. Therefore, subsequent events in the reservoir such as loss of charge, water-washing, biodegradation and drilling do not affect the composition of the inclusion oil. Furthermore, oil inclusions survive within fractured core and within cuttings, even if these materials are dried by heating, subjected to experiments such as corefloods or stored for several years.

The purpose of this paper is firstly to review the analytical methodologies that are applicable to describing the geochemical composition of oil inclusions. Particular attention will be applied to the techniques that have been developed and refined at CSIRO, which enable direct comparison between inclusion oil geochemistry and crude oils or source rocks. Secondly, several geological applications arising from the knowledge of the chemical composition of oil inclusions will be discussed; these will be illustrated with reference to previously published examples by CSIRO.

2　Screening of samples

Prior to geochemical analysis of oil inclusions, it is advisable to ascertain that sufficient oil inclusions are present for analysis. This can be achieved by using various petrographic or geochemical methods, some of which are described in the next two sections.

2. 1　Grains containing Oil Inclusions (GOI) method

The distribution of oil inclusions is determined using the GOI method (Lisk and Eadington, 1994; Eadington et al.,

1996; Lisk et al., 2002). In brief, this petrographic method, designed for analysis of sandstones, measures the abundance of quartz and feldspar grains containing oilbearing FIs in sandstone samples and relates this parameter to an empirical database of GOI values from known oil fields to determine the extent of oil saturation in the geological past. Oil accumulation in the geological past can generally be differentiated from oil on migration pathways, irrespective of the current fluid phase. GOI values > 5% are indicative of palaeo oil zones (Lisk and Eadington, 1994; Lisk et al., 1998), whilst GOI values between 0. 1 and 5% usually indicate oil migration pathways (Lisk et al., 2000, 2001; Liu et al., 2004). If no oil has been present in a reservoir, GOI values are generally < 0. 1%.

Note, however, that GOI values provide only a rough guide to the amount of oil that can be expected to be extracted from oil inclusions (George et al., 2001a). This is because (1) GOI deliberately does not count total numbers of oil inclusions (as it an oil saturation-related parameter), and (2) no reference is made in GOI to the size of the oil inclusions. Because of the cube root factor, one 20 μm diameter inclusion contains the same amount of oil as 8000 1 μm diameter inclusions (George et al., 2001a). Most inclusion oils previously analysed at CSIRO have contained 100 – 4000 ng *n*-alkanes /g quartz crushed, and any recovery >40 ng/g is generally regarded to be reliable and easily interpretable (George et al., 2001a). Recent work on oil migration pathways succeeded in analysis of very low GOI samples (< 1. 5% GOI), with 7 – 23 ng/g quartz recovery of interpretable oil from inclusions (Liu et al., 2004; George et al., 2004b).

2. 2　Other screening techniques

Limited geochemical data on FI oils can be obtained from bulk-crushing mass spectrometric techniques (Barker and Smith, 1986) such as "Fluid Inclusion Stratigraphy" (FIS; Barclay et al., 2000) and can indicate transient oil migration (Liu et al., 2004). The FIS data can be used to screen many samples in a well, so as to select the best intervals for detailed geochemical analysis of inclusion oils. The FIS method, however, does not involve chromatographic separation prior to mass spectrometry and only analyses the low molecular weight hydrocarbon range. Consequently, this method provides none of the biomarker data typically used to make oil-source rock and oil-oil correlations.

Another way of screening samples is using the quantitative grains with fluorescence (QGF) method (Liu et al., 2003). This technique uses UV spectroscopy to assess the content of adsorbed and included oil in reservoir sandstones, and thus can be used to assess which reservoirs are most appropriate for detailed geochemical analysis of the inclusion oils.

3　Geochemical analysis of oil inclusions

The oil trapped within FIs in the quartz grains of the sandstones is extracted and analysed according to the Molecular Composition of Inclusions (MCI) protocols, a detailed description of which has been provided previously in George et al. (1998a). The MCI protocols have been developed at CSIRO from 1993 to present, building on early experience from other laboratories using GC-FID and GC MS for the analysis of oil

inclusions（e. g. Horsfield and McLimans, 1984; Jensenius and Burruss, 1990; Karlsen *et al.*, 1993; Jones *et al.*, 1996）.

3. 1 Sample preparation

A prerequisite for the successful analysis of the tiny amounts of oil trapped in FIs is the complete removal of oil and any contaminants from the outside of the grains. Outcrop samples, cuttings, rotary cores or sidewall cores can equally well be used for MCI analysis. A greater weight of cuttings samples is required, as more is lost due to removal of non-reservoir lithologies and drilling mud additives. Samples are gently disintegrated using a pestle and mortar, and cleaned from drilling and reservoir fluids by ultrasonication with organic solvents, replicate treatments with hydrogen peroxide and strong acids. These acids include hydrochloric acid for the removal of carbonates, boiling Aqua Regia（3：1 vol mix of conc. hydrochloric acid and nitric acid）to remove sulphides and Fe/ Mn oxides, and chromic acid to oxidise organic matter exterior to mineral grains. Chromic acid residues are removed by rinsing in hot, concentrated nitric acid（70%）. The samples are then washed with water and dried.

Note that if oil inclusions are hosted in carbonates, different procedures must be followed which do not remove the carbonate by acid treatment. In this case, only solvents can be used to clean up the outside of grain surfaces.

After these initial clean-up procedures, quartz and feldspar grains are separated from other mineralogies by a combination of wet and dry sieving followed by magnetic and heavy liquid separation. All shaly fragments must be removed from the sample. Commonly the < 425 μm > 180 μm fraction contains predominantly single quartz grains and is selected for geochemical analysis. The mineral concentrates are then again treated with hot hydrogen peroxide until any reaction ceases, washed in water and then treated with freshly prepared, hot chromic acid for 2 hours. The quartz concentrate is then thoroughly washed in distilled water and the fine silt fraction is discarded with the decanted water. These treatments are designed to effectively oxidise/eliminate any residual organic matter from the samples.

To ensure thorough cleanliness, the mineral concentrates are then subjected to solvent cleaning using triplicate 10 min sonications in 30 mL of methanol, followed by a triplicate 10 min sonication in 30 mL blends of dichloromethane（DCM）and methanol（93：7 vol%）and a triplicate 10 min sonication in 30 mL of DCM（all discarded）. This is followed by collection of a further triplicate rinse in 30 mL of DCM as outside rinse blanks for each sample. These outside rinse blanks are spiked with an internal standard（squalane）, concentrated, and then checked for cleanliness by GC MS analyses（see 3. 2）. Once the outside rinse blanks are deemed clean, the mineral concentrate is then ready for extraction using on and offline crushing techniques.

3. 2 Off-line Crushing

Before the FI extractions by offline crushing are started, system blank experiments using the same experimental conditions as detailed below（including the same amount of solvent）are carried out in order to determine the extent of any hydrocarbon contribution from the crushing cylinder and any carryover from the previously analysed sample. If system blanks are deemed to
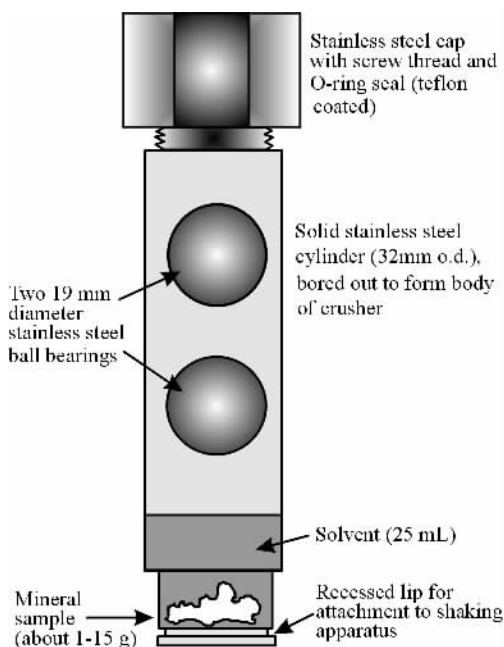

Fig. 1　Diagram of the 55 mL stainless steel crushing cylinder used for off-line crushing.

be sufficiently clean, then samples are crushed on the next day using exactly the same glassware, crushing cylinder, stainless steel balls, *etc*.

Aliquots of the cleaned mineral concentrates are crushed to a fine paste under DCM using a stainless steel crushing cylinder with a 55 mL capacity（Fig. 1）. Two stainless steel balls are placed in the cylinder above the sample and 25 mL of DCM is added before closure of the cylinder in air at atmospheric pressure. The cylinder is vigorously shaken for 2 x 10 mins in a vertical motion with a throw of about 40 mm, using a modified piston pump. This procedure crushes the mineral grains and releases the trapped oil, which partitions into the solvent. In between the two crushing phases, the crusher is allowed to cool in order to minimise evaporative loss of the leached FI oil. The resultant suspension of finely crushed quartz in solvent is poured into a beaker, and the crushing bomb is rinsed with an additional 25 mL of solvent. The solution in the beaker is then ultrasonicated for 10 mins, allowed to settle for a few minutes and then the supernatant solvent layer, containing the FI extract and traces of floating quartz grains, is transferred to a round bottom flask. The residual mineral powder is ultrasonicated twice with fresh DCM（25 mL）, and the supernatant is transferred into a round bottom flask. The solvent containing the oil extracted from the FIs（total = 100 mL）is reduced in a rotary evaporator and by blowing down with purified nitrogen. Suspended rock powder is removed by passing the extract reduced to ~ 2 mL through a short Pasteur pipette plugged with glass wool and packed with silica gel（C60：60210 μm）. Particular care is taken to avoid blowing the sample dry, so as to preserve the low molecular weight hydrocarbons（see Ahmed and George, 2004）. Generally, hydrocarbons down to ~ C_8 are recovered using this technique, those from C_{12} to C_{36} quantitatively. The amount of oil obtained from each FI oil is determined by adding small amounts（~0. 6 μg）of an internal standard（squalane）, since the yields are too small for gravimetric determination.

3. 3 Gas Chromatography Mass Spectrometry（GC – MS）

GC – MS of the FI oils is performed on a Hewlett Packard 5890 II gas chromatograph interfaced to a VG AutoSpecQ Ultima（electron energy 70 eV；electron multiplier 250 V；filament current 200 μA；source temperature 250℃）tuned to 1000 resolution. Chromatography is 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，J&W），using a splitless injection technique. The oven is programmed in two ways for different GC – MS runs：（a：for most hydrocarbons）for an initial temperature of 40℃ for 2 mins，followed by heating at 4℃ min^{-1} to 310℃，and（b：for biomarkers）for an initial temperature of 40℃ for 2 mins，followed by heating at 20℃ min^{-1} to 200℃ and then a second heating ramp at 2℃ min^{-1} to 310℃. The samples are run using single ion monitoring（SIM）programmes and metastable reaction monitoring（MRM）programmes，which are written specifically for optimal analysis of the main aromatic and saturated hydrocarbon biomarkers of interest to petroleum geochemists.

3. 4 FI oil fractionation

Usually at CSIRO，FI oils are measured by GC – MS as whole oils（i. e. without prior fractionation）. However，FI oils can be fractionated into total hydrocarbon fractions and NSO fractions to avoid unwanted interference of NSO compound peaks with aliphatic and aromatic hydrocarbon peaks. Furthermore，samples that have a significant *n*-alkane interference，in particular in their biomarker distributions，can be further fractionated into *n*-alkanes（not recovered）and branched and cyclic fractions.

All materials used for fractionations are heated at 400℃ overnight to remove any adsorbed organic contaminants，and blank experiments are conducted to ensure the integrity of data acquired on the fractionated FI oils. To produce a total hydrocarbon fraction，a short Pasteur pipette plugged with glass wool is packed with silica gel（4. 5 cm）and topped with alumina oxide（0. 5 cm）. The column is purged with two column heights of 1：4 petroleum ether（PE）：DCM v/v. The FI whole oil extract is then introduced on top of the column in a minimum volume of solvent（100 – 200 μL）. The hydrocarbon fraction is subsequently eluted with 3 mL 1：4 mixture of PE：DCM，adding the solvent drop-wise at first，and is collected in a 4 mL vial. The total hydrocarbon fraction is then concentrated to 100 – 200 μL by heating（45℃）and by blowing with gentle stream of dried and filtered nitrogen.

A branched and cyclic fraction is produced by trapping *n*-alkanes in a molecular sieve（ZSM5 silicalite）. The fractionation is conducted in a Pasteur pipette plugged with glass wool and dry-packed with 5 cm of silicalite（about 650 mg）. To ensure adequate packing the pipette is gently tapped while loading，since too rapid elution results in incomplete removal of *n*-C$_{15+}$ alkanes. Again，the sample hydrocarbon fraction is introduced to the column in a minimum amount of solvent and allowed to sink in，before adding solvent drop-wise at first. The branched and cyclic fraction is then slowly eluted with 4 mL of PE.

Pre-fractionation of FI oils is particularly useful when compound-specific carbon isotope data（CSI）on *n*-alkanes and isoprenoids in inclusion oils is needed，as this enables better and
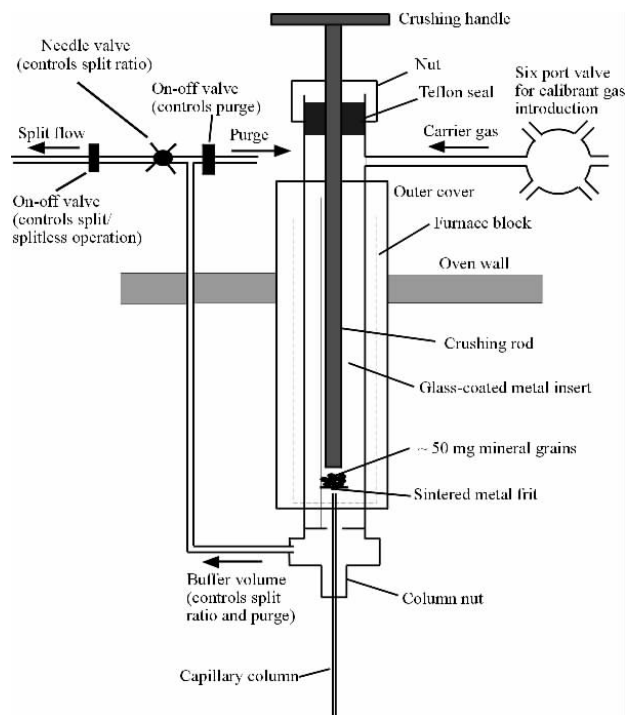

Fig. 2   Diagram of the Quantum MSSV1 Thermal Analysis System used for the on-line crushing of quartz grains containing oil inclusions directly onto a GC MS capillary column.

cleaner resolution of these compounds（Volk *et al.*，2004a；also see George *et al.* 1997b for CSI data on unfractionated FI oil）.

3. 5 Online crushing

Gasoline range hydrocarbons（C$_5$ – C$_9$）are analysed using an online crushing GC – MS method. This method utilises a device mounted on the GC – MS which allows crushing of mineral grains and release of volatile products from the FIs directly onto the chromatography column via the carrier gas. Small amounts of cleaned mineral concentrate are hand crushed in the glass-lined metal insert of a Quantum MSSV – 1 Thermal Analysis System（GC^2 Chromatography，Cheshire）using a metal plunger. The thermal analysis port（Fig. 2）is mounted on the same Hewlett Packard 5890 gas chromatograph interfaced to a VG AutoSpecQ as described in Section 3. 3. The port is held at 300℃ and carrier gas（helium；90 KPa head pressure）is passed through it in splitless mode during the crushing. Chromatography is carried out on a fused silica column（25 m x 0. 32 mm i. d.）coated with BPX5（5% phenyl 95% methyl silicone，0. 50 μm film thickness，SGE）. Oil and gases liberated during crushing are cryogenically trapped by passing a loop of the column through a liquid nitrogen bath. The oven is programmed from an initial temperature of – 20℃ at the start of the crushing（4 min. hold），followed by heating at 4℃ min^{-1} to 30℃，with a 8 min. hold，followed by heating at 4℃ min^{-1} to 300℃，with a 15 min. hold. After 2 mins the cryogenic trap is removed，and the thermal analysis port is switched into split mode（30 mL/min）to clean the port of residues. Products liberated from the inclusions are analysed using a two function SIM programme and by magnet

scanning. Note that areas of peaks in mass chromatograms have to be converted to TICequivalent areas and then to FIDequivalent data using response factors before data manipulation (e. g. George et al. , 2004a), so as to enable comparison of these type of data with conventional whole oil GC-FID analyses.

4 Geological applications of oil inclusion analysis

4. 1 Composition of early oil charge compared with current charge

Reservoir filling histories can be refined by understanding the composition of FI oils, because these often reflect earlier oil charge than is now present in a reservoir. Quartz cementation is a slow process that is strongly temperature controlled (Walderhaug, 1994a, b), and it may take several millions of years for oil inclusions within quartz overgrowths to be formed. However, oil inclusions in healed fractures are likely to be sealed and encapsulated much quicker than in overgrowths. Previous geochemical analyses of oil inclusions from current oil columns have provided data that suggest that most oil inclusions are trapped during the early stages of trap filling (e. g. Karlsen et al. , 1993; Lisk et al. , 1996; George et al. , 1997a, 1997b, 1998b; Isaksen et al. , 1998; Bhullar et al. , 1999; Pan and Yang, 2000; Volk et al. , 2001, 2002a). This is consistent with diagenetic studies showing that the rate of quartz diagenesis (and hence the rate of inclusion entrapment) slows down markedly once oil saturation increases in an oil reservoir (e. g. Worden et al. , 1998; Worden and Morad, 2000). Thus, the oil inclusion record is biased towards the composition of the earlier charge into a reservoir, so geochemical analysis of the oil trapped in inclusions provides a powerful technique for understanding the evolution of petroleum within a reservoir. For example, work by George et al. (1997b) showed that at the Jabiru oilfield in the Timor Sea, northern Australia, the thermal maturity of a FI oil, based on the more sensitive aromatic hydrocarbon ratios, was slightly lower than that of the co-existing crude oil (Fig. 3), although both were generated in the peak oil window (VRE [vitrinite reflectance equivalent] for FI oil = 0. 84% , for crude oil = 0. 92%).
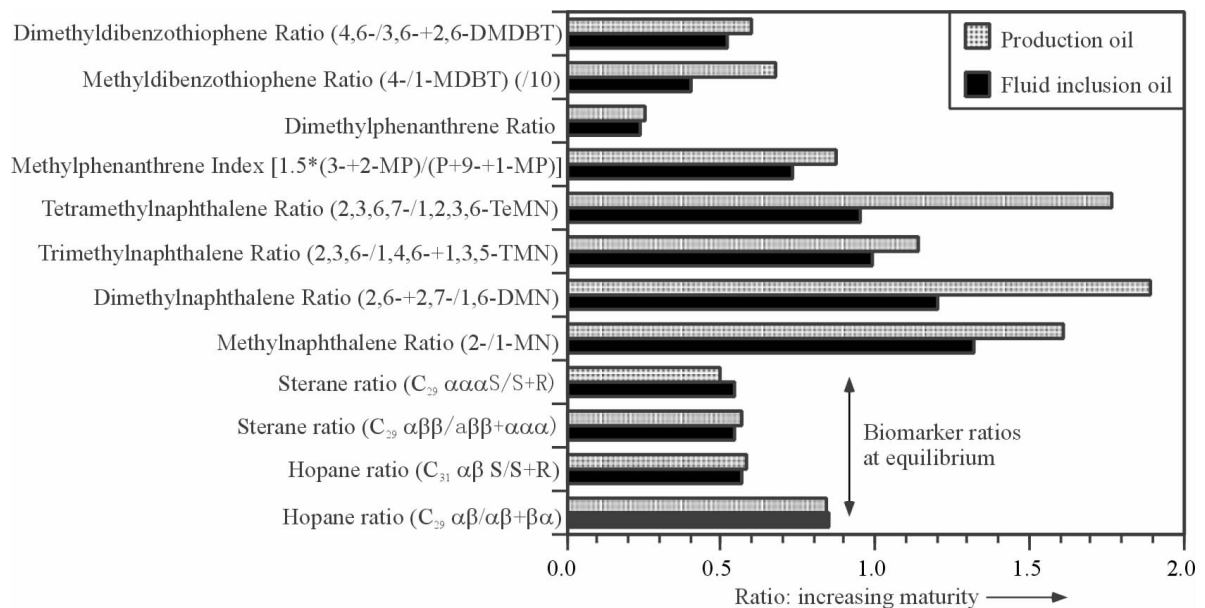

Fig. 3　Bar chart of maturity ratios for the FI oil and the crude oil from Jabiru-1A. From George et al. , 1997b.

The FI analysis technique is particularly useful when multiple sources have generated and expelled petroleum (e. g. Karlsen et al. , 1993; Lisk et al. , 1996; George et al. , 1997a, 1998b, 1998c; Isaksen et al. , 1998). One example is the gas-leg FI oil from South Pepper-1, in the Barrow Sub-basin, West Australia (Fig. 4; Lisk et al. , 1996; George et al. , 1998b). The spider diagram (Fig. 4) shows various source-related parameters that are discussed in more detail in George et al. (1998b). The gas-leg FI oil from South Pepper-1 has Ts/Tm and C_{29}/C_{30} $\alpha\beta$ hopane ratios of ~ 1 and the C_{35} homohopanes are a significant proportion of the extended homohopanes. It has lower Pr/Ph and diasterane/sterane ratios than the currently reservoired crude oil, and contains gammacerane, a series of peaks tentatively identified as C_{30} to C_{34} 17α(H)-30-norhopanes and a large amount of 2α-methylhopanes. Collectively, geochemical analysis of the gas-leg FI oil suggests that it was generated from a less mature, more calcareous source rock, deposited under more reducing conditions than the Upper Jurassic Dingo Claystone, the main source of the crude oil in this well (Lisk et al. , 1996; George et al. , 1998b). Although this calcareous source rock has not been identified, other evidence from nearby oils (e. g. North Herald) has supported the presence of a family of vagrant oils in this region (Summons et al. , 1998). The relatively common finding that palaeo oils represented by FI oils were generated from geochemically different source rock facies compared to currently reservoired oil implies that (1) generation, filling, leakage and continued recharge are common in petroleum systems over geological time, and (2) newly arrived crude oil in a reservoir is not always trapped in large amounts in FI oils.
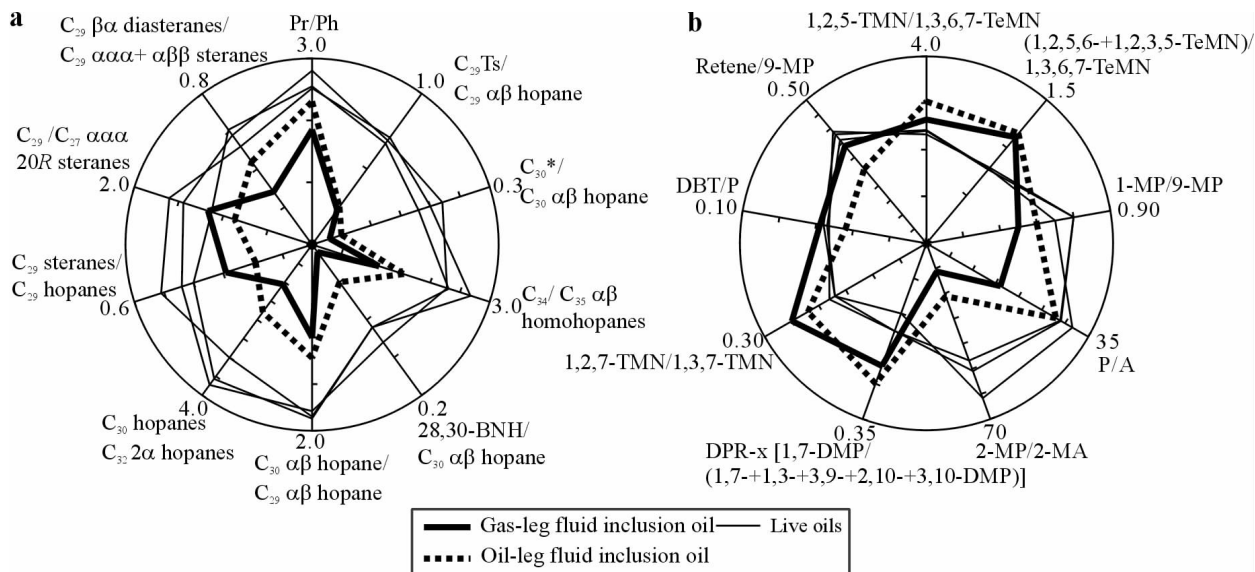
Fig. 4 Spider diagrams showing the variation in source-controlled parameters for (a) aliphatic hydrocarbons and (b) aromatic hydrocarbons for FI oils and crude oils from South Pepper. All parameters are scaled from 0 to the value on the axis, except for 1-MP/9-MP (0.8 to 0.9) and DPR-x (0.25 to 0.35). The aliphatic ratios are configured so that oils derived from more reducing, more calcareous and less terrestrial source rocks plot towards the middle of the diagram. From George et al. , 1998b.
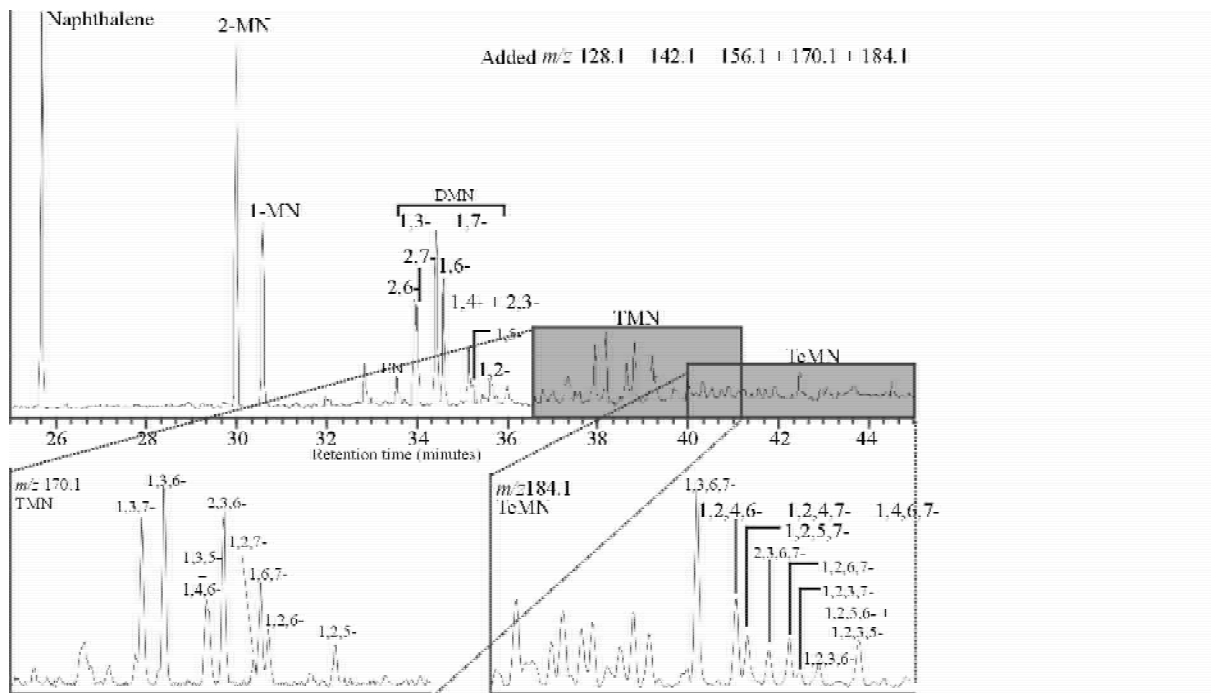

Fig. 5 Partial added m/z 128.1 + 142.1 + 156.1 + 170.1 + 184.1 mass chromatogram of the FI oil from Octavius-2 (3,200 m), showing the distribution of alkylnaphthalenes. The enlargements show details of the partial m/z 170.1 and 184.1 mass chromatograms over the indicated retention times. MN = methylnaphthalene, DMN = dimethylnaphthalene, EN = ethylnaphthalene, TMN = trimethylnaphthalene, TeMN = tetramethylnaphthalene. From George et al. , 1998a.

4.2 Composition of oil charge prior to seal or fault breach, or otherloss of charge

GOI data indicate that palaeo-oil columns are common not only below current oil columns, but also in wells that are completely dry now. For example, in the Timor Sea region of northern Australia there was an extensive period of fault-seal breach of oil reservoirs during Late Miocene/Early Pliocene fault reactivation, and this left many palaeo-oil columns in now water-filled reservoir sections (e. g. O'Brien et al. , 1996; Lisk et al. , 1998). In dry wells, the analysis of FI oils offers the possibility of understanding a petroleum system without having access to

currently reservoired fluids (e. g. Parnell *et al.*, 2001 ; Karlsen *et al.*, 2004 ; Volk *et al.*, 2004a, 2004b), and potentially then being able to predict where the oil may have leaked to, or where it may be trapped in non-breached structures.

A good example of this application is the dry Octavius-2 well in the Vulcan Sub-basin, northern Australia (Fig. 5 ; George *et al.*, 1998a). Octavius FI oil is pristine, rich in aliphatic hydrocarbons and high maturity. A full range of C_5 to C_{37} hydrocarbons, including nalkanes, isoprenoids, alkylcyclohexanes, hopanes and aromatic hydrocarbons were detected by the off-line and on-line crushing techniques. Alkylnaphthalene distributions of Octavius FI oil contain relatively large amounts of the more thermally-stable ? - substituted isomers (e. g. 2-MN ; 2,6- and 2,7-DMN ; 2,3,6- TMN ; Fig. 5), indicating high maturity (George *et al.*, 1998a). Approximate calibrations of alkylnaphthalene ratios suggest that the Octavius FI oil has a maturity in the range 1.0 to 1.3% VRE, and this is corroborated by the methylphenanthrene ratio and by the alkylbiphenyl maturity ratios. Biomarkers are in very low abundance owing to thermal cracking, and any biologicallyinfluenced aromatic hydrocarbon distributions have been lost.

4.3 Composition of oil charge prior to gas charge

Currently gas-filled structures sometimes have GOI anomalies, and these may indicate the presence of a palaeo-oil zone prior to recharge with gas (e. g. George *et al.*, 1998b, 2002a, 2004c ; Bhullar *et al.*, 1999 ; Volk *et al.*, 2002a, 2004b). In these instances, analysing the oil in the FIs provides geochemical information on the original oil charge to the structure, which may aid in assessing from which source rock and when the oil was generated. Furthermore, comparison of the currently reservoired fluid (e. g. a gas condensate) and the FI oil allows conclusions regarding the transition mechanism from oil to gas to be made.

One example of this application is the Bayu-1 gas condensate field in the Timor Sea, which has a thin palaeo oil zone (George *et al.*, 2002a, 2004c). Compared to the condensate, the FI oil was generated from a more marine-influenced, less clay-rich source rock or source facies, which was deposited in a less oxic environment with greater eukaryotic input (Fig. 6). The source rock of the condensate was more terrigenous and had greater microbial input. The Bayu condensate has previously been attributed to mixed sourcing from the less terrestrially-influenced facies of the Jurassic Elang and Plover formations, together with the marine Flamingo Group (Preston and Edwards, 2000). Analysis of the FI oil confirms a more marine-influenced source facies of the palaeo-oil, with the Echuca Shoals Formation being the most likely source based on oil-oil and oil-source correlations (Fig. 6). The FI oil has a mid-oil window maturity (~ 0.75% VRE), whereas the currently reservoired condensate has a higher maturity (~ 0.9% VRE). These maturity data are consistent with early expulsion from the more labile, marine-derived organic matter in the Echuca Shoals Formation, followed by expulsion of large amounts of condensate from the more terrestrially-dominated Elang and Plover formations (George *et al.*, 2002a, 2004c).
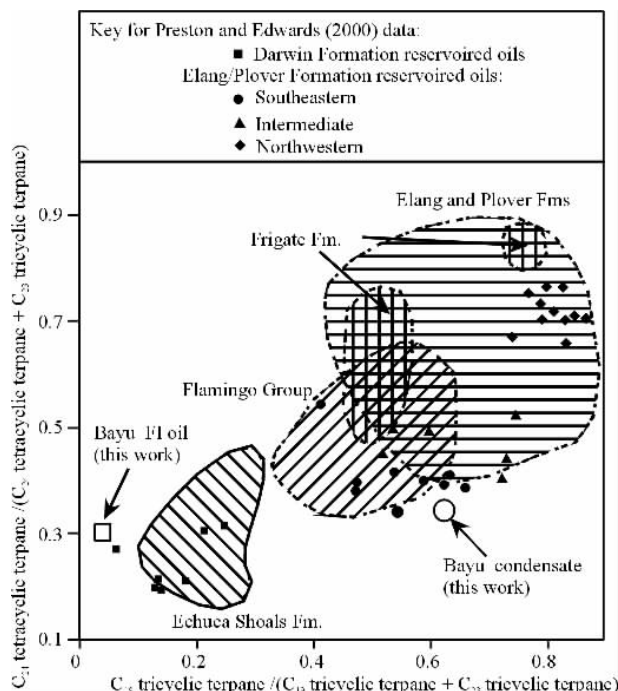

Fig. 6 Cross plot of C_{19} tricyclic terpane /(C_{19} tricyclic terpane + C_{23} tricyclic terpane) versus C_{24} tetracyclic terpane /(C_{24} tetracyclic terpane + C_{23} tricyclic terpane), calculated from the m/z 191 mass chromatograms, showing the greater marine influence for the source of the Bayu-1 FI oil compared to other oils in the Northern Bonaparte Basin, including Bayu-1 condensate. Oil and source rock fields are taken from Preston and Edwards (2000).
Fm. = formation. From George *et al.*, 2004c.

4.4 Composition of oil charge prior to biodegradation or water washing

The in-reservoir processes of biodegradation and water washing can alter the composition of oils in reservoirs significantly (e. g. Palmer, 1993). Although inclusion oils that may be biodegraded or contain an admixture of a biodegraded residue have occasionally been analysed (e. g. Jensenius and Burruss, 1990 ; George *et al.*, 2004b, Volk *et al.*, 2004b), it is more common to find relatively non-biodegraded FI oils in a reservoir where the free crude oil is biodegraded (e. g. Lisk *et al.*, 1996 ; George *et al.*, 1998b ; Bhullar *et al.*, 1999 ; Weiwei *et al.*, 2002). The reason for this is that FI oils predominantly get trapped early in the reservoir charge history, prior to pervasive biodegradation of the crude oil, and the FIs thus preserve pristine oil. This is an important application, as biodegradation can destroy important geochemical information about the source and maturity of the original oil charge.

Similarly, water washing can affect crude oils in reservoirs, and although some FI oils are water washed (e. g. Mauk and Burruss, 2002), FI oils may preserve the original non-water washed signature of the oil (George *et al.*, 2004a). For example, Laminaria High crude oils in the Timor Sea region are interpreted to have been waterwashed, resulting in partial loss of $C_1 C_3$ alkanes, benzene, toluene and xylenes (Fig. 7).
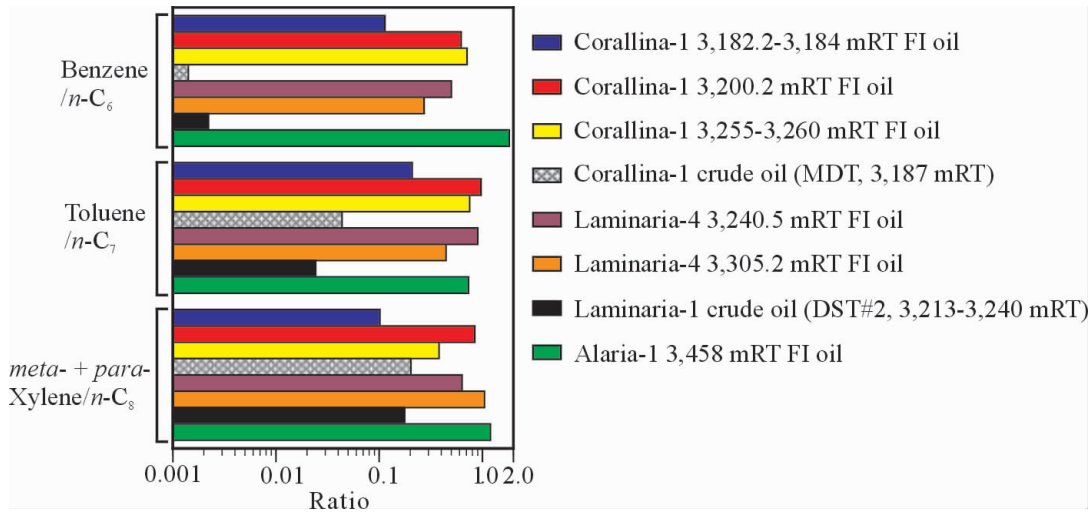
Fig. 7 Histogram of the benzene/nC$_6$, toluene/nC$_7$ and meta + paraxylene/nC$_8$ ratios for six FI oils and the two crude oils from the Laminaria High. From George et al., 2004a.

The FI oils, in contrast, are not waterwashed, indicating that this event post-dated the original oil charge (Fig. 7). Water washing has been invoked as a mechanism to explain the significant under-filling of these traps (Newell, 1999), but for this process to achieve the level of volume reduction needed to account for the current column heights, the traps needed to have been initially filled to spill with gas-condensate. Petrographic and geochemical evidence, however, shows that FIs trapped in these fields contain oil and not gas-condensate. Consequently, loss of oil charge from the Laminaria High through fault seal leakage is suggested to be the more likely explanation for the majority of the observed volume loss (George et al., 2004a).

4.5 Composition of oil charge prior to drilling contamination

A common problem with many oil exploration wells is that they are drilled with oil-based drilling muds, or are contaminated with other anthropogenic substances. These can make evaluation of oils recovered from tests or by solvent extraction of reservoir lithologies very difficult, due to overprinting of the crude oil. Analysis of oil inclusions can avoid these problems, because the FIs are trapped before drilling, so extraneous or drilling contaminants can be removed by careful clean-up of the reservoir samples prior to inclusion oil analysis.

For example, geochemical evidence for a previously unrecognised light oil or gascondensate source rock in the Nancar Trough area of the Timor Sea was found by analysis of FI oil from the Ludmilla-1 well (George et al., 2002b). This has an unusually high abundance of midchain substituted monomethylalkanes relative to n-alkanes (Fig. 8), and was derived from an unknown source rock deposited in a marine environment under suboxic to oxic conditions with limited sulphur content, a low contribution of terrestrial organic matter and a high contribution of organic matter from bacterial activity, particularly cyanobacterial organic matter (George et al., 2002b). This information was only revealed following FI analysis, because recovered oils and core extracts from this and nearby wells were heavily contaminated by alkene-based drilling mud additives.
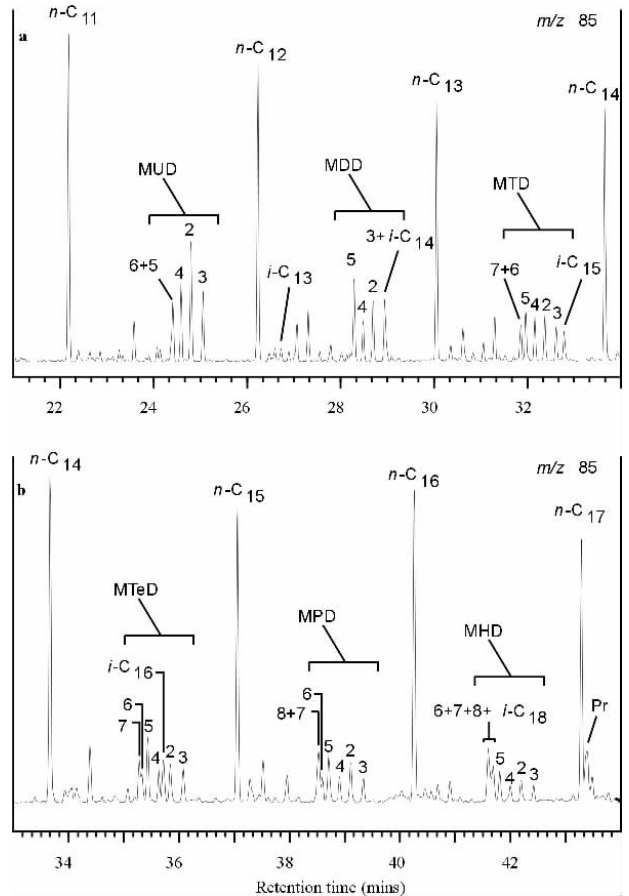

Fig. 8 Partial m/z 85 mass chromatograms of the Ludmilla1 FI oil, showing the distribution of nalkanes, monomethylalkanes and isoprenoids. Numbers refer to n-alkane carbon number, MUD = methylundecanes, MDD = methyldodecanes, MTD = methyltridecanes, MTeD = methyltetradecanes, MPD = methylpentadecanes, MHD = methylhexadecanes, Pr = pristane. From George et al., 2002b.
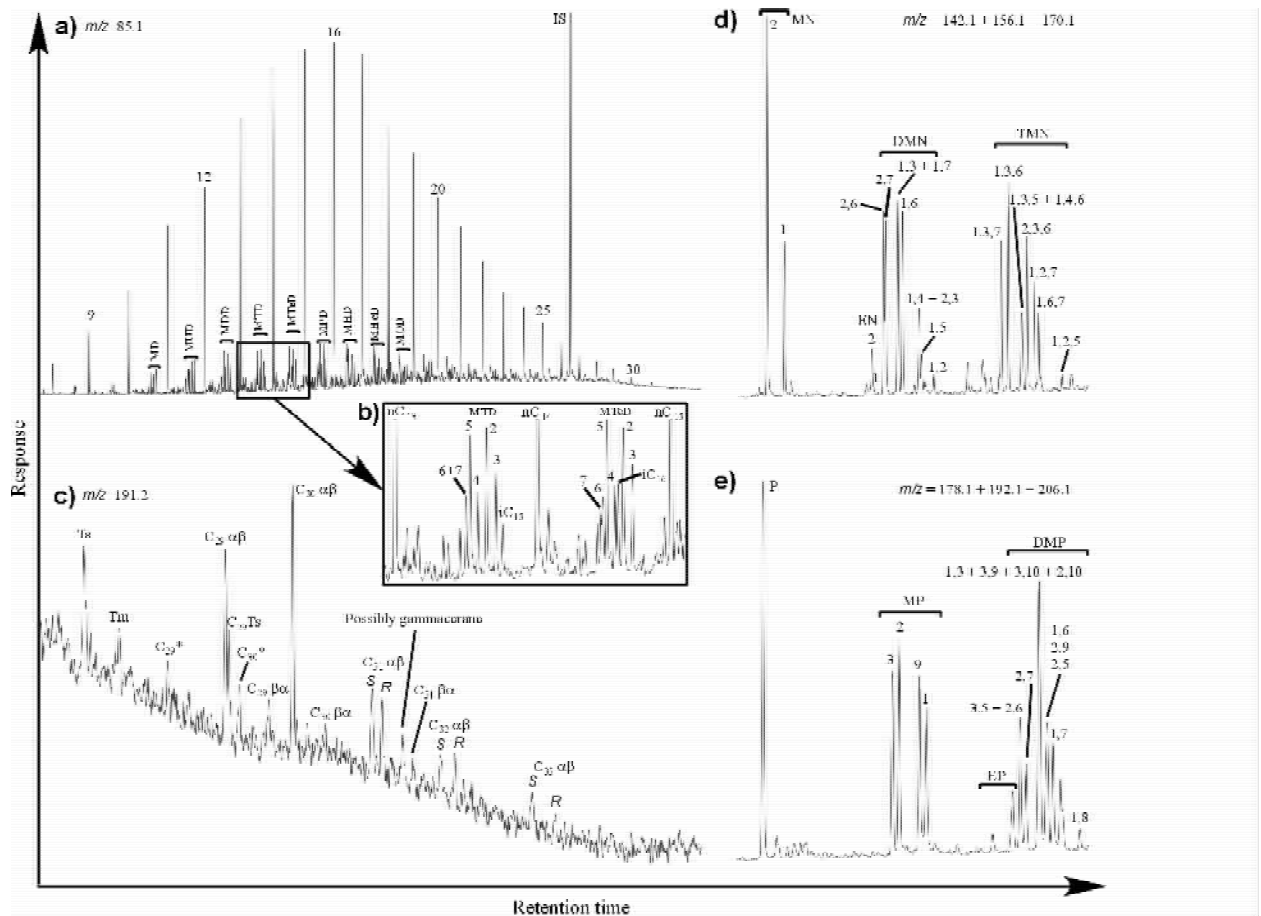
Fig. 9　Partial mass chromatograms of Bessie Creek Sandstone inclusion oil. A: Alkane distribution (m/z = 85. 1); bracketed peaks are branched alkanes, predominantly monomethylalkanes. MD = methyldecanes; MHeD = methyheptadecanes; MOD = methyloctadecanes; IS = internal standard; other identities see Fig. 8. B: Detail of methyltridecane and methyltetradecane isomeric distribution in m/z = 85. 1; n-C_x refers to n-alkanes, i-C_x refers to isoprenoids. C: Pentacyclic triterpane distribution (m/z = 191. 2); Ts = C_{27}18α(H), 22,29,30-trisnorneohopane; Tm = C_{27}17α,22,29,30-trisnorhopane; C_{29} * = C_{29} 17α-diahopane; C_{29} αβ = 17α,21β(H)-30-norhopane; C_{29} Ts = 18α(H)-30-norneohopane; C_{30} * = C_{30} 17α-diahopane; C_{29} αβ = 17α,21β(H)-30-norhopane; C_{30} αβ = 17α,21β(H)-hopane; C_{30-31} αβ = 17α,21β(H)-hopane and homohopane; C_{31-33} αβ 22S and R = 17α(H),21β(H)-homo-, bishomo-, and trishomohopane (22S and R). D: Alkylnaphthalenes (added m/z = 142. 1 + 156. 1 + 170. 1). E: P = Phenanthrene; MP = methylphenanthrenes; EP and DMP = ethyl- and dimethylphenanthrenes (added m/z = 178. 1 + 192. 1 + 206. 1). From Dutkiewicz et al. , 2003b.

4. 6　Composition of very ancient oils

Small numbers of oil inclusions are sometimes detected in unusual geological environments, for example, in hydrothermal systems (Hoffmann et al. , 1988), veins (Volk et al. , 2002b), crystalline basement (Munz et al. , 1995, 2002) and in Archaean and Proterozoic rocks (Dutkiewicz et al. , 1998, 2003, 2004; Volk et al. , 2003). Oil inclusions can evidently survive temperatures of up to 300 C (Dutkiewicz et al. , 2003). A very exciting application is to obtain detailed molecular geochemical information on small numbers of oil inclusions in Archaean rocks, which are likely to contain biomarkers that provide information on the early evolution of life. Preserved organic matter in Archean sedimentary rocks is usually metamorphosed kerogen and pyrobitumen(Buick et al. , 1998), which have only rarely yielded indigenous soluble or bound

hydrocarbons (Brocks et al. , 1999, 2003a, 2003b). Biomarkers indicate that the biota was more diverse than the fossil record suggests, but whether these biomarkers are syngenetic with the rocks needs to be carefully assessed in view of molecular mobility and contamination (Hayes et al. , 1983). A syngenetic relationship between included biomarkers and their source rock is evident where the timing of fluid-inclusion entrapment is constrained, as was shown for recent studies of Mesoproterozoic oil inclusions from which detailed geochemical information (e. g. Fig. 9) was obtained (Volk et al. , 2003; Dutkiewicz et al. , 2003, 2004). For example, n-alkanes, monomethylalkanes, alkylnaphthalenes and alkylphenanthrenes could readily be detected in the Bessie Creek Sandstone FI oil (Fig. 9), and this also contained traces of hopanes (although no steranes were detectable). Oil inclusions thus hold the promise of providing relatively pristine and robust data for the composition and diversity of Earth's early biosphere.
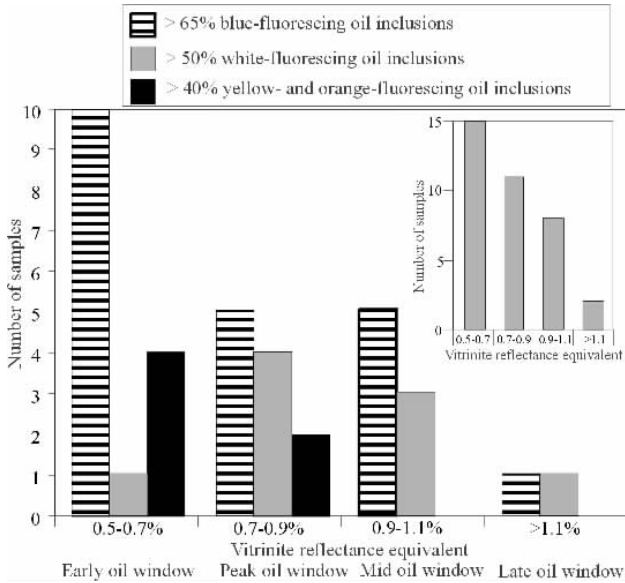
Fig. 10　Histogram showing the thermal maturity (vitrinite reflectance equivalent) derived from molecular thermal maturity parameters for samples containing FI oils with different fluorescence colour populations. The inset shows all samples in each maturity range as a single column. From George *et al.*, 2001b.

4.7　Application of fluorescence colours of oil-bearing FIs

For several years the fluorescence colours of oil inclusions have been used as a qualitative thermal maturity guide of migrating oil, and have also been related to API gravity (e.g. Burruss *et al.*, 1985; McLimans, 1987; Bodnar, 1990; Earnshaw *et al.*, 1993; Stasiuk and Snowdon, 1997; Parnell *et al.*, 2001). It is generally believed that inclusion oils of higher API gravity and maturity fluoresce in the blue end of the visible spectrum, whereas inclusion oils of lower API gravity and maturity fluoresce in the red region. For a more comprehensive review of the literature on this subject see George *et al.* (2001b, 2001c). In a study to test this relationship, the geochemically-derived thermal maturity of oils extracted from inclusions and the fluorescence colours of oil-bearing FIs were measured in 36 sandstone samples from Australasian oil fields (George *et al.*, 2001b).

The results showed that samples containing mainly blue-fluorescing oil inclusions have thermal maturities anywhere within the oil window, including relatively low maturities (VRE $< 0.65\%$; Fig. 10), contrary to the widely applied assumption that blue fluorescence colours indicate high maturities (George *et al.*, 2001b). Samples containing mainly white-fluorescing oil inclusions have maturities anywhere within the oil window and cannot be distinguished using molecular geochemical parameters from samples containing mainly blue-fluorescing oil inclusions (Fig. 10). Though few in number, samples with mainly yellow and orange-fluorescing oil inclusions tend to have maturities in the lower half of the oil window (Fig. 10).

Table 1　Peak assignments for steranes and diasteranes in the m/z 217 mass chromatograms in Fig. 11.

| Peak	Sterane and diasterane assignments	Abbreviation
a	13β(H),17α(H)-diacholestane (20S)	C_{27} βα20S diasterane
b	13β(H),17α(H)-diacholestane (20R)	C_{27} βα20R diasterane
c	13α(H),17β(H)-diacholestane (20S)	C_{27} αβ20S diasterane
d	13α(H),17β(H)-diacholestane (20R)	C_{27} αβ20R diasterane
e	5α(H),14α(H),17α(H)-cholestane (20S)	C_{27} ααα20S sterane
f	5α(H),14β(H),17β(H)-cholestane (20R)	C_{27} αββ20R sterane
g	5α(H),14β(H),17β(H)-cholestane (20S)	C_{27} αββ20S sterane
h	5α(H),14α(H),17α(H)-cholestane (20R)	C_{27} ααα20R sterane
i	24methyl13β(H),17α(H)-diacholestane (20S)*	C_{28} βα20S diasterane
j	24methyl13β(H),17α(H)-diacholestane (20R)*	C_{28} βα20R diasterane
k	24methyl13α(H),17β(H)-diacholestane (20S)	C_{28} αβ20S diasterane
l	24methyl13α(H),17β(H)-diacholestane (20R)*	C_{28} αβ20R diasterane
m	24methyl5α(H),14α(H),17α(H)-cholestane (20S)*	C_{28} ααα20S sterane
n	24methyl5α(H),14β(H),17β(H)-cholestane (20R)	C_{28} αββ20R sterane
o	24methyl5α(H),14β(H),17β(H)-cholestane (20S)	C_{28} αββ20S sterane
p	24methyl5α(H),14α(H),17α(H)-cholestane (20R)	C_{28} ααα20R sterane
q	24ethyl13β(H),17α(H)-diacholestane (20S)	C_{29} βα20S diasterane
r	24ethyl13β(H),17α(H)-diacholestane (20R)	C_{29} βα20R diasterane
s	24ethyl13α(H),17β(H)-diacholestane (20S)	C_{29} αβ20S diasterane
t	24ethyl13α(H),17β(H)-diacholestane (20R)	C_{29} αβ20R diasterane
u	24ethyl5α(H),14α(H),17α(H)-cholestane (20S)	C_{29} ααα20S sterane
v	24ethyl5α(H),14β(H),17β(H)-cholestane (20R)	C_{29} αββ20R sterane
w	24ethyl5α(H),14β(H),17β(H)-cholestane (20S)	C_{29} αββ20S sterane
x	24ethyl5α(H),14α(H),17α(H)-cholestane (20R)	C_{29} ααα20R sterane

＊　= isomeric peaks (24S and 24R).
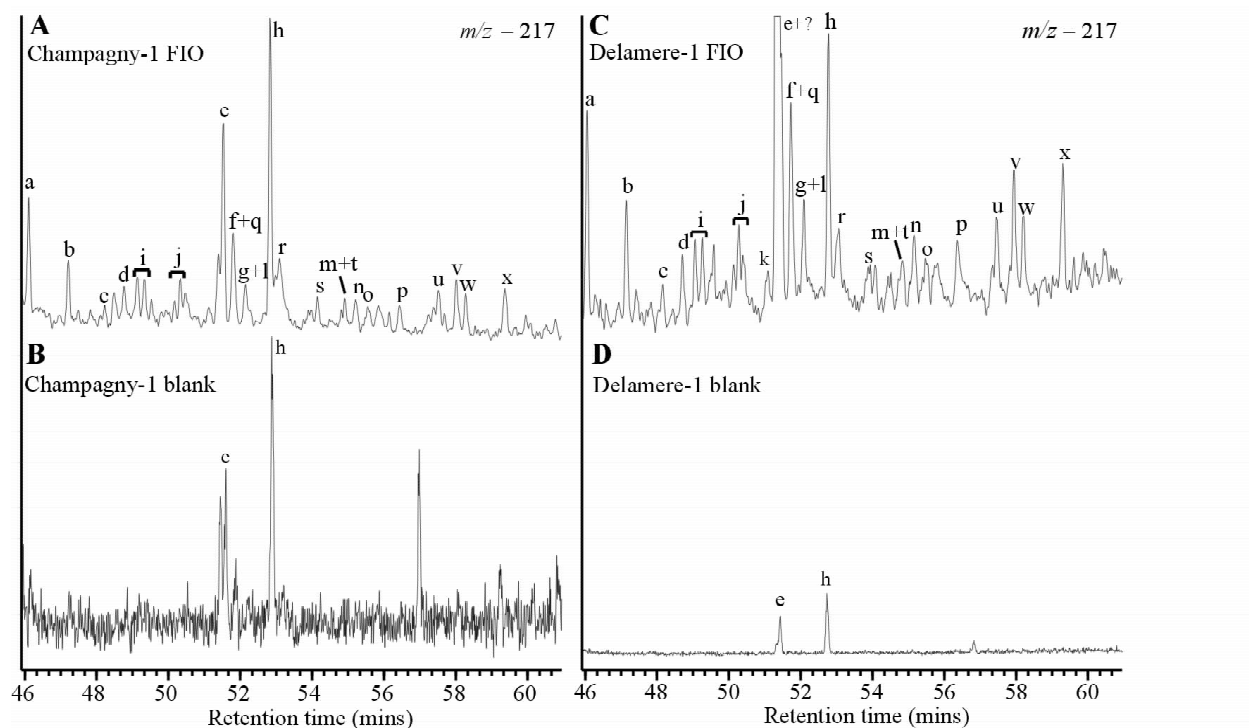
Fig. 11   Partial m/z 217 mass chromatograms showing the distribution of steranes and diasteranes in（a）Champagny-1 FI oil，（b）the system blank associated with the Champagny-1 FI oil，（c）Delamere-1 FI oil，and（d）the system blank associated with the Delamere-1 FI oil. The blanks are drawn to the same scale as the FI oil chromatograms. Peak assignments are defined in Table 1. From George et al. , 2004b.

Thus，fluorescence colours did not show a clear correlation with the molecular maturities of the samples described in this study（George et al. , 2001b）. It is thought that fractionation of the gross composition of oil during the inclusion trapping process may also be a significant controlling process on the fluorescence colours of oil inclusions，due to the preferential adsorption of polar compounds onto charged mineral surfaces. A trapping control is strongly supported by synthetic oil inclusion work. Care should be taken when interpreting the charge history of samples containing oil inclusions with mixed fluorescence colour populations，because it is possible that the different colour populations represent a single oil charge，with oil inclusions trapped under slightly different conditions or at slightly different mineralogical boundaries，rather than multiple migration events（George et al. , 2001b）.

4.8   Composition of oil on secondary migration pathways

During secondary migration，there is an opportunity for oil to be trapped as FIs within framework grains such as quartz and within diagenetic cements that have a crystalline structure. Oil saturation on migration pathways remains relatively low，so typically，less oil inclusions get trapped when compared with samples from an oil column（Liu et al. , 2004）. It is likely that the oil inclusions reflect an average of all the oil that has passed through the migration conduit，although it is possible that periodic selective or non-trapping may bias the inclusion record. Until recently the small volume of oil recovered from the low numbers of oil inclusions on secondary migration pathways has precluded their detailed chemical analysis，although their

presence has been noted（Bhullar et al. , 2000；Lisk et al. , 2000，2001；Parnell et al. , 2001）.

In a recent study in the Timor Sea region（George et al. , 2004b），reliable geochemical data were acquired from very small numbers of oil inclusions on migration pathways that were significantly above the levels detected for the system and outside-rinse blanks（Fig. 11）. The FI oil trapped on the interpreted oil migration pathway in Champagny-1 was generated from clay-rich marine source rock with little terrigenous organic matter input. It was generated at peak oil window maturity and correlates best with oils derived from the Late Jurassic Lower Vulcan Formation. In contrast，the Delamere-1 FI oil contains evidence of greater input of terrigenous organic matter，and was generated at early oil window maturity. These data indicate that it is feasible to geochemically map migration pathways across prospects or basins，and to analyse palaeo-oil compositions in oil zones where few inclusions get trapped（George et al. , 2004b）.

5   Conclusions

（1）The MCI protocols have been tried，tested and maybe perfected over more than 10 years at CSIRO，and have been shown to enable very good quality geochemical data to be acquired on oil trapped in FIs.

（2）Petrographic and/or geochemical techniques should be used to screen samples before attempting molecular geochemical characterisation of FI oils.

（3）It is essential to completely remove oil and any contaminants from the outside of grains prior to FI analysis. This

should be monitored by repeated analysis of outside rinse and system（procedural）blanks.

（4）The off-line crushing technique is usually suitable for analysis of C_{12}-C_{36} hydrocarbons, whilst the on-line crushing technique is reliable for C_5 to C_9 hydrocarbons.

（5）The hydrocarbons detected by the MCI protocols include low molecular weight hydrocarbons, n-alkanes, isoprenoids, biomarkers and aromatic hydrocarbons.

（6）Geological applications of FI analysis include better constraining oil charge histories of reservoirs, identifying previously unknown active source rocks in petroliferous basins, and removing the effects of oil-alteration or contamination episodes in reservoirs.

（7）Small numbers of oil inclusions from secondary migration pathways and from Proterozoic rocks can also be analysed, and these applications are at the forefront of current research to develop and improve interpretational methodologies.

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