Oil charge and biodegradation history in an exhumed fractured reservoir, Devonian, UK

Mas'ud Baba, John Parnell, David Muirhead and Stephen Bowden

School of Geosciences, University of Aberdeen, Aberdeen AB24 3UE, UK

Abstract

The distribution of oil residues in fractured Upper Devonian reservoir sandstones of Caithness help us to understand relationships between oil charge and episodes of fracturing. The sandstones are cut by an extensive set of tightly cemented deformation bands in the vicinity of the Brough Fault, and calcite-mineralized open fractures. The deformation bands compartmentalized the reservoir, which subsequently was charged by oil to varying extent in different compartments. Petrographic and biomarker data distinguish two charges of oil. The first charge of oil was unaltered. The later mineralized fractures introduced a heavier biodegraded oil that spread into the sandstone pores and displaced/overprinted the earlier oil. Two distinct oil charges are also evident from two generations of oil fluid inclusions, firstly in overgrowths on quartz grains, and secondly in the calcite veins, exhibiting distinct fluorescence characteristics. Migration and trapping of oil depended on the combination of two fracturing episodes of different character, in which the first episode created sealed compartments which were then filled by oil introduced by the second episode.

Key Words: Oil charge; biodegradation; fractured reservoir; Devonian; Caithness

Introduction

Fractured reservoirs are of increasing interest as possible hydrocarbon plays (Nelson 2001, Lonergan et al. 2007, Spence et al. 2014). The formation of fractured reservoirs is commonly associated with tectonic activity, involving uplift and deformation (Nelson 2001). This setting has a potential bearing on the distribution of oil in the reservoir, mechanism for filling or depleting the reservoir, and the likelihood of degradation of oil in the reservoir. In this study, we use petrographic, fluid inclusion and organic biomarker data to assess these aspects of reservoir history in an exhumed onshore oil reservoir.

This case study investigates a Devonian sandstone reservoir at Dunnet Head, Caithness, UK. These rocks are well-exposed (Parnell et al. 2004). Their proximity to the offshore Clair Field, West of Shetland, UK, which includes sandstone reservoirs of comparable age and setting, has made them an analogue for Clair Field studies, including fractured reservoir evaluation (Coney et al. 1993, Parnell et al. 2004, Barr et al. 2007).

Geological Setting

The sandstones at Dunnet Head are Upper Devonian (Upper Old Red Sandstone, UORS) continental deposits of mixed fluvial-aeolian origin (Trewin & Thirlwall 2002). The sandstones are mainly medium-grained, trough cross-bedded and locally pebbly with numerous clasts of green mudrock. These deposits are within the Orcadian Basin, with established hydrocarbon source rock potential in the underlying lacustrine rocks of the Middle Devonian (Middle Old Red Sandstone, MORS) (Marshall et al 1985, Parnell & Rahman 1990). Burial history modelling suggests that hydrocarbons were generated before and after Carboniferous basin inversion (Astin 1990, Hillier & Marshall 1992, Parnell et al. 1998, Ghazwani et al. 2018). Near the base of the UORS are extrusive volcanic rocks (lavas), with associated volcanic vents (Halliday et al. 1977). All of these rocks are cross-cut by an igneous dyke swarm dated as Permian (Lundmark et al. 2011). The UORS sandstones are especially well exposed and accessible at Brough (pronounced 'broch'). They are separated from the underlying MORS lacustrine deposits by a major lineament, the Brough Fault (Fig. 1), juxtaposing source rocks and reservoir rocks. Proximity to the fault, which was believed to be active in Devonian time and then reactivated subsequently during basin inversion (Astin 1985, Seranne 1992) has contributed to a complex fracturing history. The fault zone itself is not exposed at Brough, but beach blocks in the vicinity of the fault trace show brecciated bedrock cross-cut by calcite veins with traces of galena and sphalerite. The sulphide mineralization is typical of calcite veins in the region, many with bitumen, throughout the Devonian of Caithness (Gallagher et al. 1971, Dichiarante et al. 2016). The mineralization has been dated as Permian (Dichiarante et al. 2016). Some of the veins are associated with the intrusion of a suite of Permian dykes, evidencing a brief episode of high heat flow.

The sandstones are good reservoirs (typically 25 to 30 % porosity where not fractured), and locally contain much oil residue, giving them a black colour. Studies of the UORS reservoir sandstones at Brough were undertaken to assess:

(i) Whether the sandstones were charged with oil before or after fracturing, or both.
(ii) Consequent of the above, whether oil was imported or exported by fractures.
(iii) Following the above, the timing of oil degradation relative to fracturing.
(iv) Whether oil charge occurred during deep burial (maximum temperature) or during/after uplift.

Methodology

Sampling

Samples were collected for determination of paragenesis, fluid inclusion microthermometry and analysis of oil composition, from *in situ* exposures and beach cobbles on the foreshore at Brough, on the western side of the Brough Fault. The beach cobbles can be confidently matched with oil-charged sandstones in the exposures. The sequence of events was investigated in detail using the Brough material. Closely comparable UORS sandstones of similar petrography were also sampled at other localities in a similar stratigraphic position, also close to the Brough Fault at Dwarwick (Dunnet Head), and Sands Geo and Pegal Bay, Orkney (Fig. 1). Oil-bearing UORS sandstone was additionally sampled from *in situ* exposures at Ashy Geo (Dunnet Head), 4 km from the fault (Fig. 1). Middle ORS lacustrine shales on the footwall, eastern side of the Brough Fault were sampled for measurement of thermal maturity.

Fluid inclusions

Fluid inclusion studies were performed on doubly polished wafers using a Linkam THMS-600 heating–freezing stage mounted on a Nikon Labophot transmission light microscope. The instrument was equipped with a range of objective lenses including a 100× lens, calibrated against synthetic H_2O (374.1 and 0.0 °C) and CO_2 (− 56.6 °C) standards (Synthetic Fluid Inclusion Reference Set, Bubbles Inc., USA). The petrography of fluid inclusion assemblages was first examined at low magnifications using a NIKON Eclipse E600 microscope equipped with both transmitted white and incident ultraviolet light (UV) sources. Ultraviolet light, with an excitation wavelength of 365 nm, was provided by a high pressure mercury lamp with a 420nm barrier epi-fluorescence filter that allows only the long-wavelength UV to reach the sample.

Biomarkers

Rock samples of UORS sandstones for biomarker analysis were chosen from beach cobbles, which are fresher than the *in situ* exposures which are altered by surface water flow. The MORS source rock was sampled *in situ*. Samples were prepared by rinsing with distilled water two times, and again with dichloromethane (DCM). The dry rocks were crushed and extracted using a soxhlet apparatus for 48 hours. Solid bitumen and tar samples were ultrasonicated with DCM and methanol (MeOH). All glassware was thoroughly cleaned with a 93:7 mixture of DCM/MeOH. Crushed samples were weighed, recorded and transferred into pre-extracted thimbles. The extracts were then dried down using a rotary evaporator, separated into aliphatic, aromatic and polar fractions via a silica column chromatography using hexane, hexane/DCM in the ratio 3:1 and DCM/MeOH respectively. Prior to gas chromatography-mass spectrometry (GC-MS) analysis, an internal standard (5β-Cholane, Agilent Technologies) was added to the saturate fraction before injection into the GC-MS machine, and subsequent biomarker identification. This was done using an Agilent 6890N gas chromatograph fitted with a J&W DB-5 phase 50m MSD and a quadruple mass spectrometer operating in SIM mode (dwell time 0.1 s per ion and ionisation energy 70eV). Samples were injected manually using a split/splitless injector operating in splitless mode (purge 40ml min-1 for 2min). The temperature programme for the GC oven was 80-295 °C, holding at 80 °C for 2min, rising to 10 °C min^{-1} for 8min and then 3 °C min-1, and finally holding the maximum temperature for 10 min^{-1}. Quantitative biomarker data were obtained for isoprenoids, hopanes, steranes and diasteranes by measuring responses of these compounds on m/z 85, 125, 191, 217, 218, and 259 mass chromatograms and comparing them to the response of the internal standard. Biodegradation was assessed using the ratio of phytane to the C_{18} *n*-alkane (Ph/*n*C_{18}) which increases with degradation as *n*-alkanes are altered more rapidly (Peters & Moldowan, 1993). Biodegradation also causes the breakdown of steranes at a faster rate than diasteranes, including in the shallow subsurface in aerobic conditions, thus the diasterane/sterane ratio (D/S) can be elevated due to shallow biodegradation (Seifert & Moldowan, 1979), but is also controlled by thermal maturity and source rock lithology (Burton et al. 2018). Thermal maturity was estimated from the 20S/20S + 20R ratio for C_{29} steranes, based on the increasing proportion of the S isomer with maturation (Peters & Moldowan, 1993). Thermal maturity was also determined from the relative proportions of hopane peaks Ts (C27 18α (H)-22, 30-trisnorneohopane) and Tm (C27 17α(H)-22,30-trisnorhopane) peaks.

Data

Petrography

Two sets of fractures cut the sandstones (Figs. 2,3). Over at least 50 m from the fault plane at Brough, the UORS is cut by a dense anastomosing network of deformation bands (Parnell et al. 2004), whose spatial density increases with proximity to the fault. The bands are typically 1 to 3 mm wide, and show cross-cutting relationships with each other which compartmentalize the sandstone

(Fig. 3), but do not show any preferred orientation. The deformation bands are further cross-cut and displaced by brittle fractures mineralized by veins of calcite and/or solid bitumen (Figs. 3,4). The calcite-bitumen veins occur widely across the Orcadian Basin, and post-date the tilting and folding of the rocks attributed to the inversion episode.

The deformation bands are tightly cemented by quartz and illite. The sandstone not cemented in deformation bands exhibits later quartz cementation as overgrowths. Feldspars, especially in the vicinity of the Brough Fault, were partially leached to form intragranular porosity, which was then infilled by kaolinite. Following a charge of oil into pore space (see below), further cementation by carbonates and pyrite occurred (Fig. 5). The carbonate cement is variably ferroan calcite and dolomite. The brittle fractures post-date cementation. The integrated paragenetic sequence for diagenesis, oil charge and fracturing is summarized in Fig. 4.

Oil Charge

The sandstones contain distinctive zones coloured brown to black. The black colour is due to pervasive intergranular bitumen, representing a solid black oil residue. Data from the extraction of organic matter by solvents showed that the brown colour also represents a weak charge of oil, but without an extensive solid residue. Thus we distinguish two oils, represented by the brown and black residues. Examination of 200 UORS beach cobbles larger than 10 cm size, representing all the cobbles in a section of beach and enough to be typical of the immediately adjacent UORS outcrop, suggest about 50 % of the sandstone porosity was charged with oil. The MORS outcrop on the opposite, footwall side of the Brough Fault consists of very distinct lacustrine siltstones. Volumetrically, this is dominated by the black oil. Petrographic studies constrain the relative timing of oil emplacement:

(i) Black oil infills intragranular porosity within altered feldspar grains.

(ii) Cemented deformation bands lack oil impregnation (Fig. 3).

(iii) Some compartments defined by deformation bands are empty of oil, while adjacent compartments are filled by oil (Fig. 3).

(iv) In some samples, most compartments defined by deformation bands contain a brown oil stain, but only a few contain black oil (Fig. 3).

(v) Veins of solid bitumen cross-cut and displace cemented laminae, cemented deformation bands, and oil-charged compartments (Fig. 3).

(vi) In many samples, black oil is distributed selectively about the veins of solid bitumen (Fig. 2B). In contrast, the brown oil-stained sandstone does not show any preferred relationship with the veins.

(vii) There is no spatial relationship between proportion of sandstone charged by pore-filling black oil and proximity to the Brough Fault.

(viii) Laminae and beds of sandstone exhibit lateral changes from oil-bearing (black-coloured) to oil-free, due to variations in cementation. The oil occurs selectively distributed in some laminae only (Fig. 2A). Sandstone stained brown (also oil-bearing) is not selectively distributed in some laminae only.

In summary, oil charge post-dated deformation bands, and left residues controlled by cementation and vein networks.

Fluid inclusions

Several populations of fluid inclusions can be recognized in the sandstone at Brough. Examination under ultra-violet light shows that both aqueous and hydrocarbon (oil) inclusions were entrapped. The quartz and calcite cements contain abundant aqueous fluid inclusions. They are two-phase, irregular in shape, 3-25 µm along maximum dimension, with liquid/vapour (L/V) ratios of 0.85 to 0.98. In other basins, calcite-hosted inclusions can be susceptible to stretching and leaking, and hence yield unreliable data (Prezbindowski & Larese 1987), but the consistent L/V ratios suggest that this has not happened here. Aqueous inclusions in quartz overgrowths were also measured in UORS sandstones from Dwarwick, Ashy Geo, Sands Geo and Pegal Bay (Fig. 1). Two-phase oil inclusions at Brough are distinguished from the aqueous inclusions by larger vapour bubbles, yellow-brown coloration in plane-polarized light, and fluorescence under ultra-violet light. The oil inclusions show no evidence of a free water phase, so were trapped as a homogenous fluid. They are 7 to 22 µm length, and commonly with irregular form.

The quartz cement in deformation bands lacks any oil inclusions, but the later overgrowths on quartz grains contain the earliest, primary oil inclusions recorded in the sandstones at Brough (Fig. 4). Primary oil inclusions were also found in quartz overgrowth cements at Ashy Geo and Pegal Bay. The oil inclusions occur along with aqueous inclusions in the overgrowths, suggesting that they were trapped penecontemporaneously. All primary oil inclusions in the overgrowths fluoresce yellow, typical of relatively immature oil (Bodnar 1990). The homogenization temperatures for all inclusions are in the range 103 to 147 °C. Primary oil inclusions also occur in calcite cement at Brough, fluorescing yellow. Two homogenization temperatures were measured, at 132 to 136 °C. Rare blue-fluorescing inclusions typical of relatively mature oil (Bodnar 1990) occur in the calcite veins containing bitumen and in secondary trails cross-cutting quartz grains and overgrowths, yielding lower temperatures in the range 88 to 112 °C. Microthermometry data are summarized in Table 1.

Biomarkers

Samples for biomarker analysis were selected to allow resolution of data from brown oil staining, pore-filling black oil, and veins of solid bitumen. Soluble fractions were successfully extracted from each of the 3 components, and also the MORS lacustrine shale from the footwall side of the Brough Fault. Data for biomarker compositions are reported in Table 2, and representative chromatograms shown in Fig. 6. The sterane thermal maturity parameter is at about maximum value of ~0.55 in all samples, typical of oil window conditions. All samples contain relatively high levels of the C_{28} sterane (Fig. 7), and the alkane β-carotane. The Ph/$n$$C_{18}$ ratio is higher in the samples of black sandstone and bitumen veins than in samples of brown oil staining (Fig. 8).

Discussion

Temperatures

Anomalously high heat flow during burial is inferred from vitrinite reflectance studies (Hillier & Marshall 1992, Marshall 1998) and apatite fission track studies (Thomson et al. 1999), and implied by volcanic activity (lava flows) during Devonian sedimentation. The sequence would have cooled following Carboniferous basin inversion (Hillier & Marshall 1992). New temperature data is available from fluid inclusion homogenization temperatures and organic biomarker maturity parameters. The biomarker and reflectance data indicate maximum temperatures achieved, while the fluid inclusion data can distinguish temperature conditions for mineral phases precipitated at different times. However, all of the fluid inclusion temperatures (deformation band quartz, overgrowth quartz, calcite cement) at Brough are over 100 °C, up to 150 °C, and no relatively low temperatures were measured. These temperatures are consistent with oil generation temperatures and comparable with fluid inclusion data in other basins (e.g. Walderhaug 1994). Such temperatures suggest burial depths of 2 to 4 km for typical geothermal gradients. The biomarker data for the MORS immediately adjacent to the Brough Fault indicates oil window temperatures, and vitrinite reflectance data for the MORS at this locality (Hillier & Marshall 1992) is relatively high at 1.4 % (uppermost oil window to gas window), implying that the fluid inclusions in the UORS were entrapped at/near maximum burial. As the fracturing episodes (deformation bands, calcite veins + fractured grains) are closely associated with cements yielding 100+ °C temperatures, we infer that the fractures were formed during deep burial. However, the fluid inclusion data show that there was a 20 to 40 °C fall in temperature between the deformation bands of the first fracturing episode and the calcite veins of the second episode. The history of basin inversion, and predicted time of oil generation at about the time of inversion, suggest that the second fracturing episode occurred following at least partial inversion. This timing is further suggested by the veins cutting folds and tilted rocks attributed to inversion. Homogenization temperatures for quartz overgrowths at other localities are also in the range 90 to 141 °C, but relatively high values of 179 to 195 °C are recorded at Sands Geo. At Sands Geo, the UORS is cross-cut by Permian igneous dykes, which may have caused localized, anomalous high-temperature cementation. The data for the other localities are at the upper end of the range determined for quartz cementation in other basins (Walderhaug 1994).

Oil charge and fracturing

At a specimen scale, the distribution of oil shows spatial relationships with the distribution of fractures. The intersection of deformation bands in three dimensions isolated volumes of sandstone, some of which were not charged by oil, as observed elsewhere (Pittman 1981, Antonellini et al. 1999). The proportion of sandstone charged by oil is quite constant across the outcrop (100 m width at Brough), suggesting a large-scale sweep of oil through the reservoir. Although there is an increase in spatial density of the deformation bands with proximity to the fault plane, as observed in other cases (e.g. Antonellini & Aydin 1995, Ogilvie & Glover 2001), there is no evidence for preferential channelling of oil along the Brough Fault. The later cross-cutting brittle fractures commonly contain bitumen, representing the local movement of oil between sandstone pores and the new fracture porosity. The common occurrence of pore-filling black oil selectively distributed around bitumen-bearing veins indicates that the veins introduced this charge of oil to the rock.

The composition of oil has evolved through time, as shown by the distinct oil charges. Several lines of evidence indicate that the oil charge responsible for brown oil staining predated the charge represented by the black oil. Bitumen veins pass through compartments charged with brown oil and compartments charged with black oil, but only appear to be conduits for the black oil, which must therefore be later. Some compartmentalized sandstones have brown oil in most compartments, with a few compartments containing black oil, but the opposite distribution does not occur, suggesting that the brown oil was displaced by the black oil. The spatial relationship between bitumen veins and black oil in selected sandstone layers (Fig. 2A) indicates that where the fracture system cut through the most porous layers, matrix flow took over from fracture flow. The limited penetration in some cases (Fig. 2B) may reflect the relatively viscous nature of the heavy oil. The black oil appears to be a heavier oil than the brown oil, as its distribution is more controlled by variations in cementation. This is supported by biomarker data (below). In summary, the heavy oil charge occurred subsequent to the brown oil.

A residue of viscous oil may alternatively be a consequence of asphaltene phase transition rather than biodegradation (Pfieffer et al. 2017). However, no cavities representing oil droplets or exsolved gas were observed in the oil residue in electron micrographs, that might have resulted from this process.

The evolution of oil charge is also reflected by the change in fluid inclusion fluorescence colour from yellow in quartz and calcite cement to blue in calcite veins, which represents an increase in oil maturity (Bodnar 1990). The distinct fluorescence colours imply a break in time and conditions between the two episodes of precipitation. The change from yellow to blue fluorescence is similarly recognised in oil fluid inclusions in the Clair Field (Baron et al. 2008, Blamey et al. 2009). The predominant source rock for the Clair Field is probably Jurassic, rather than Devonian, so the similar fluorescence trend reflects a universal feature of oil maturity evolving over time.

Although the major faults in the region are thought to have been active during Devonian sedimentation, their current displacements probably date to Carboniferous basin inversion (Coward et al. 1989, Seranne 1992, Hippler 1993). Thus, in the case of the Brough Fault, downthrow to the east during Devonian sedimentation was followed by downthrow to the west during Carboniferous inversion (Coward et al. 1989) and at present.

Biomarker data

All samples show relatively high levels of the C_{28} sterane, which is characteristic of lacustrine organic matter (Huang & Meinschein 1979), and implies that the oil residues were derived from the Devonian lacustrine source rocks. The occurrence of β-carotane is also typical of lacustrine organic matter, and is recorded in previous studies in the Orcadian Basin (Irwin & Meyer 1990; Othman Wilson et al. 2014; Ghazwani et al. 2018). Biomarker data for the brown- and black-coloured sandstones indicate that both represent oil residues, but with distinct compositions (Fig. 8). All samples have relatively low D/S ratios, which we do not interpret further. However, the brown oils have lower Ph/nC_{18} ratios compared with the black oils. The vein bitumen plots with the black sandstones, suggesting that they are closely related. The Ph/nC_{18} values suggest that the brown-stained sandstones experienced little or no biodegradation, while the black sandstones and bitumen veins contain oil that had experienced significant biodegradation.

Oil degradation

The temperatures determined from the fluid inclusions in the quartz overgrowths are higher than those known to support life (Takai et al. 2008) and much higher than the 70-80 °C temperature above which reservoir sterilization is known to occur (Wilhelms et al. 2001). As oil is normally generated at a temperature of 120 °C or lower, the high temperatures recorded by oil inclusions in the overgrowths suggest either movement into hotter conditions due to continued burial after oil generation, or generation at high temperatures due to rapid burial. The fluid inclusion temperatures were obtained from the UORS, stratigraphically overlying the MORS source rock, further emphasizing their anomalously high values. Regardless of why the values are high, the lack of biodegradation in the first oil is consistent with the high temperatures of 103 to 147 °C, probably during maximum burial.

The biodegraded second charge of black oil also experienced temperatures (88 to 112 °C) at which sterilization is expected, although lower than the temperatures experienced by the first oil. The temperatures recorded by the bitumen-bearing calcite veins are likely to represent a relatively short pulse of fluid that is hotter than the ambient rock temperature (Parnell 2010). If these 88-112 °C temperatures were short-lived, only recorded in the calcite veins, microbial activity in the reservoir might have survived unscathed. However, the relationship of the black oil to the bitumen in the calcite veins suggests that the black oil migrated at high temperatures. Biodegradation of this oil was probably pre-emplacement in the sandstone at Brough, as the earlier brown oil is not affected. At other localities in the basin, sandstones exhibit secondary oxidative reddening, dated palaeomagnetically as Permian (Robinson 1985), which has altered pore-filling oil. Permian reddening in Britain extends to depths of over 500 m (Wang 1992), so some subsurface oil reservoirs in the Orcadian Basin are likely to have been altered at that time. In deep oxidizing conditions, alteration could include biodegradation. At Brough, the altered oil was able to enter the sandstone pores during the subsequent veining episode.

Conclusions

Petrographic and geochemical studies help to elucidate the relationship between fracturing and oil charge in an exhumed fractured reservoir at Brough (Fig. 9):

(i) The pervasive development of deformation bands in the vicinity of the fault pre-dated oil charge into the sandstones, and created a compartmentalization into which the oil could partially penetrate. (Earliest Carboniferous)

(ii) The compositions of brown oil-staining and black oil are distinct, implying that there were two distinct charges of oil. The brown oil-staining represents the first charge. (Mid Carboniferous)

(iii) Cross-cutting fractures contain bitumen with a composition comparable to that of the black oil/sandstone, and show evidence for acting as conduits to supply the black pore-filling oil. By implication, these fractures post-dated the first oil charge. (Mid-Late Carboniferous)

(iv) The second oil charge was biodegraded before emplacement in the sandstones. (Late Carboniferous – Permian)

Migration and trapping of oil depended on the combination of two fracturing episodes of different character, in which the first episode created sealed compartments which were then filled by oil introduced by the second episode. These findings emphasize that the type and timing of fracturing episodes influence the detailed nature of oil charge into fractured reservoirs.

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Figure Captions

Fig. 1. Map for localities in vicinity of Brough Fault, separating Middle Devonian (Middle Old Red Sandstone) lacustrine rocks and Upper Devonian (Upper Old Red Sandstone) sandstone reservoir rocks. AG, Ashy Geo; B, Brough; D, Dunnet; PG, Pegal Bay; SG, Sands Geo.

Fig. 2. Field photographs of sandstone exposures, Brough foreshore, showing selective distribution of oil. A, oil impregnations (black) along porous layers, controlled by selective cementation along some laminae, and early cemented concretions. B, Pore-filling black oil distributed selectively around vein of solid bitumen.

Fig. 3. Cross-sections through sandstone samples, Brough, showing selective distribution of oil in compartments. Note cemented deformation bands lack impregnation by pore-filling black oil. A, First oil charge (brown) more pervasive than second oil charge (black), separated by unfilled deformation band (arrowed). B, Phases of fracturing and oil charge, numbered as in sequence shown in Fig. 8. Cemented deformation band (1), sandstone with first oil charge (2), bitumen-bearing veins (4a), sandstone with second oil charge (4b). Some compartments defined by deformation bands are empty of pore-filling bitumen. Samples are beach cobbles representative of adjacent exposures.

Fig. 4. Paragenetic sequence for diagenetic events including oil charge, Upper Devonian sandstones, Brough. Two fracturing episodes included as vertical bars; two oil charges as solid black bars. Temperatures determined from fluid inclusions (data from oil inclusions in brackets).

Fig. 5. Scanning electron micrograph of sandstone, Brough, showing quartz grains with oil residue (bitumen B, black) between pores, and cement by calcite (C, light grey) and pyrite (P, bright).

Fig. 6. Representative chromatograms for brown oil, black oil and vein bitumen, Brough. (a) m/z 85 and 125 highlighting n-alkanes; (b) m/z 217 highlighting steranes.

Fig. 7. Sterane compositions (percentage C_{27}, C_{28}, C_{29}) for samples from Brough. Data show all bitumens share a high C_{28} content, typical of non-marine samples in the Orcadian Basin.

Fig. 8. Cross plot of diasterane/sterane ratio against Ph/nC$_{18}$ ratios for Brough samples. Four samples of black oil and vein bitumen have elevated Ph/nC$_{18}$ ratios, indicating greater biodegradation.

Fig. 9. Schematic sequence of cross-sectional stages of fracturing and oil charge, in relation to burial history of MORS (M) and UORS (U), based on Hillier & Marshall (1992) and Parnell et al. (1998). Deformation bands and first oil charge occurred during burial. Fracturing and second oil charge occurred following inversion.

Table 1. Fluid inclusion data for samples from Brough and other localities adjacent to Brough Fault.

	Setting	Inclusion chemistry	Inclusion class	Th (°C) range	Tm (°C) range	Wt.% equiv. NaCl	L/V ratio	Inclusion size (µm)
Brough	Def. bands qtz cement	aqueous	S	103.0 to 132.0 (n=16)	-16.2 to -12.9	16.8 to 19.6	0.90-0.95	10-20
	Qtz overgrowth	aqueous	P	129.9 to 143.3 (n=13)	-4.8 to -3.4	5.6 to 8.1	0.93-0.97	5-10
	Qtz overgrowth	oil	P	125.9 to 146.6 (n=11)			0.75 - 0.80	5-25
	Calcite cement	aqueous	P	112.6 to 147.5 (n=13)	-18.9 to -14.4	18.1 to 21.6	0.94 - 0.96	10-18
	Calcite cement	oil	P	132.5 to 136.1 (n=2)			0.80	14-18
	Healed cracks in qtz grains	oil	S	102.6 to 112.1 (n=6)			0.80	14-19
	Calcite veins	aqueous	P	88.0 to 105.0 (n=13)			0.80	2-10
Ashy Geo	Qtz overgrowth	aqueous	P	90.1 to 112.5 (n=11)	-3.1 to -0.3	0.5 to 5.1	0.90-0.94	3-6
	Qtz overgrowth	oil	P	103.1 to 111.2 (n=7)			0.80-0.90	6-15
Dwarwick	Qtz overgrowth	aqueous	P	125.5 to 140.5 (n=11)	-1.8 to -0.1	0.2 to 3.1	0.93-0.95	4-10
Sands Geo	Qtz overgrowth	aqueous	P	179.4 to 194.4 (n=16)	-5.6 to -1.1	1.9 to 8.3	0.92-0.95	5-8
	Sand injection qtz cement	aqueous	P	115.5 to 124.6 (n=10)	-17.9 to -15.0	18.6 to 20.9	0.90-0.94	4-10
Pegal Bay	Qtz overgrowth	aqueous	P	94.9 to 107.4 (n=16)	-2.0 to -0.5	0.9 to 3.4	0.90-0.95	3-8

	Qtz overgrowth	oil	P	112.3 to 128.7 (n=12)			0.85-0.90	8-14

L/V, liquid/vapour ratio; P, Primary; S, Secondary; Th homogenization temperature; Tm, ice melting temperature

Table 2. Biomarker data for samples from Brough.

	Grid Reference	**EOM (%)**	**D/S (C_{29})**	**C_{29} 20S/(20S + 20R)**	**Ts/(Ts+Tm)**	**Pr/Ph**	**Pr/nC_{17}**	**Ph/nC_{18}**	**C_{27}S (%)**	**C_{28}S (%)**	**C_{29}S (%)**
Brown Oil 1	ND 220742	0.38	0.38	0.65	0.55	0.56	0.52	1.34	10	46	44
Brown Oil 2	ND 220742	1.37	0.57	0.60	0.62	0.70	0.63	0.82	12	49	39
Brown Oil 3	ND 220742	0.32	0.25	0.49	0.66	0.68	0.78	0.95	5	57	38
Brown Oil 4	ND 220742	1.21	0.32	0.58	0.63	0.66	0.74	1.19	5	55	40
Black Oil 1	ND 220742	1.52	0.12	0.59	0.54	0.47	4.07	3.31	13	46	41
Black Oil 2	ND 220742	1.28	0.23	0.60	0.59	0.92	0.67	0.91	10	45	45
Black Oil 3	ND 220742	0.75	0.08	0.54	0.58	0.71	2.50	6.40	8	58	34
Vein Bitumen 1	ND 220742	8.33	0.32	0.62	0.50	0.74	0.62	0.90	10	53	37
Vein Bitumen 2	ND 220742	7.59	0.17	0.52	0.45	0.66	4.68	7.15	9	56	35
Vein Bitumen 3	ND 220742	3.17	0.21	0.48	0.56	0.70	2.79	6.35	7	57	36
MORS Source Rock	ND 222740	1.98	0.38	0.52	nd	0.97	0.27	0.27	10	54	36

nd, no data