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**Formation of bitumen in the Elgin/Franklin complex, Central Graben, North Sea:
Implications for hydrocarbon charging**

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Abbreviated title: *Bitumens of the Elgin/Franklin complex*

Abstract

The Elgin/Franklin complex contains gas condensates in Upper Jurassic reservoirs in the North Sea Central Graben. Upper parts of the reservoirs contain bitumens, which previous studies have suggested were formed by the thermal cracking of oil as the reservoirs experienced temperatures $>150^{\circ}\text{C}$ during rapid Plio-Pleistocene subsidence. Bitumen-stained cores contaminated by oil-based drilling muds have been analysed by hydrolysis. Asphaltene-bound aliphatic hydrocarbon fractions were dominated by *n*-hexadecane and *n*-octadecane originating from fatty acid additives in the muds. Uncontaminated asphaltene-bound aromatic hydrocarbon fractions however contained a PAH distribution very similar to normal North Sea oils, suggesting that the bitumens may not have been derived from oil cracking.

1-D basin models of well 29/5b-6 and a pseudowell east of the Elgin/Franklin complex utilise a thermal history derived from the basin's rifting and subsidence histories, combined with the conservation of energy currently not contained in the thermal histories. Vitrinite reflectance values predicted by the conventional kinetic models do not match the measured data. Using the pressure-dependent PresRo[®] model, however, a good match was achieved between observed and measured data. The predicted petroleum generation is combined with published diagenetic cement data from Elgin/Franklin to produce a composite model for petroleum generation, diagenetic cement and bitumen formation.

The Elgin/Franklin Fields are located between the Forties-Montrose and Josephine Highs in the high temperature-high pressure (HPHT) area of UK Central Graben, North Sea (Fig. 1). The fields were formed by faulting associated with NE-SW extension during the Upper Jurassic, and contains deeply buried (>5 km) Upper Jurassic shallow marine sandstone reservoirs (Fulmar Formation) in a westerly dipping fault block separated by a large NW-SE fault from a deep source kitchen to the east (Fig. 2) (Vandenbroucke et al. 1999). The presence of sandstones with up to 30% porosity and 2 Darcy permeabilities at depths below 5 km, coupled with the presence of significant diagenetic cementation and secondary porosity generation (Haszeldine et al. 1999; Lasocki et al. 1999) show that the post depositional history was complex.

The fields contain 60 million cu. m³ of gas condensate and 50 billion cu. m³ of gas, with both phases currently understood to have formed mainly by the cracking of oil as the temperature of the reservoir increased during the Neogene and Quaternary (Lasocki et al. 1999; Vandenbroucke et al. 1999). Apart from the present day high reservoir temperatures (190°C) and the high maturities of the reservoired hydrocarbons, the only evidence for hydrocarbon cracking is the occurrence of (pyro)bitumen. Visual examination of recovered cores has shown a concentrated zone of bitumen in the upper part of the reservoir (Isaksen 2004), with the bitumen occupying <2% of the total rock volume in Elgin and Franklin Fields (Lasocki et al. 1999). The bitumen therefore should show evidence of its elevated thermal maturity/aromaticity resulting from the high temperature treatment that cracked the oil. While the study by Vandenbroucke et al. (1999) provides a detailed kinetic evaluation of both the rate of liquid/gas product generation from a Kimmeridge Clay Formation (KCF) sourced oil and the composition of the conversion products, it does not include any details of the composition of the bitumens generated by this reaction. Indeed, tar mats and pyrobitumens often contain little in the way of free hydrocarbons and consequently little information exists on the source and chemical nature of these ubiquitous solids (Curiale 1985), although such information is essential to confirm the proposed formation mechanism. The analytical problem is also complicated by the use of 'oil-based' muds during drilling, which contaminate the samples and make analysis by conventional techniques particularly difficult (Wenger et al. 2004).

The driving mechanism for the oil-to-gas cracking hypothesis is the rapid increases in temperature and pressure that occurred as a result of rapid subsidence during the Plio-Pleistocene (Figs. 3a and 3b respectively) to give a present day temperature and pressure of ~190°C and 100 MPa (Lasocki et al. 1999; Vandenbroucke et al. 1999; Isaksen 2004; Hendry et al. 2000a). Thermal oil cracking involves the redistribution of hydrogen from the precursor oil to the hydrogen rich, thermodynamically stable methane and other low molecular mass gaseous hydrocarbons, leaving a hydrogen-poor (carbon-rich) solid-phase sometimes referred to as bitumen or coke in the laboratory and more frequently as bitumen or tar mats in geological reservoirs. Numerous studies using a variety of oils have been conducted into the thermal stability of oils in reservoirs, with particular emphasis being attached to the temperature at which oil becomes unstable. Initially oil was thought

to be unstable at temperatures above 150°C (Ungerer et al. 1988), although more recent work has shown that oils can be stable to temperatures as high as 200°C over geological periods (Hill et al. 2003). Both of these estimates of thermal stability ignore the effects that high water pressure has on such endothermic cracking reactions, with recent investigations having shown that such reactions are significantly retarded by high water pressures (Uguna et al. 2016; Xie et al. 2016).

The experimentation used as the basis for the oil-to-gas cracking hypothesis involves either vapour pressures or expandable gold-bags in which both vapour and liquid hydrocarbons and non-hydrocarbons are retained inside the gold-bag. Vapour is compressible and volume expansion produced by the solid to liquid/gas conversion is relatively easy and requires only minor expenditure of energy. However, volume expansion against the forces offered by incompressible pressurised water and mineral phases involves the expenditure of larger amounts of thermal energy, or in the case of thermally constrained systems such as geological basins, reduced amounts of reaction as required by the conservation of energy. If the oil-to-gas cracking is retarded by water pressure, then the other main residual product of this cracking process (pyrobitumen) cannot have formed by cracking, and a new formation mechanism that accounts for both the hydrocarbon types and the bitumens that are present in the reservoirs is required.

In addition to thermal maturation and cracking mechanisms, biodegradation and phase separation processes such as deasphalting, gravitational segregation, incompatible oil mixing and thermal convection can generate insoluble hydrocarbons such as tar-mats and bitumens (Wilhelms & Larter 1994). A further potential mechanism is via combination reactions, promoted by high reservoir pressures, which have recently been observed in laboratory simulations (Uguna et al. 2016). Combination reactions involve the reduction in the number of moles in the products compared with the reactions. Such reactions are exothermic, and are favoured under high pressures (Uguna et al. 2016). This study showed that high liquid water pressures could result in the formation of high molecular weight *n*-alkane hydrocarbons, and an increase in the amount of high molecular weight unresolved complex material (UCM) and the asphaltene content in a light API gravity North Sea oil from the Norwegian Oseberg field. The Oseberg oil is a highly paraffinic, low sulphur North Sea oil that appears to have been deasphalted by a later gas charge to form a tar mat at the

oil water contact by gravity segregation, yielding a tar-mat at the base of the reservoir (Dahl & Speers 1985). Furthermore, as a natural analog, an insoluble bitumen from a high-pressure Gulf of Mexico well was found to possess similar characteristics to the laboratory oils pyrolysed under high-pressure (Uguna et al. 2016).

The concentration of bitumen in the upper 2 m of the Elgin/Franklin reservoir with smaller amounts occurring below this zone is difficult to reconcile with the oil cracking model for either bitumen or gas condensate formation in the reservoir. Pyrobitumen, due to its asphaltic insoluble nature, must be located near to the point where oil cracking occurs, and the volume of gas condensate far exceeds the volume that 2 m section of bitumen in question could generate. The location of this bitumen near the top of the reservoir suggests that gravitational segregation cannot have occurred, since the higher density bitumen should sink as opposed to rise in a low-density gas condensate column. The bitumen formation mechanism is therefore a key event in the geological history of the Elgin/Franklin reservoir, and any model for the bitumen formation must account for both its geochemical character as well as its non-uniform distribution throughout the reservoir.

Hydropyrolysis and the scope of the investigation

Conventional geochemical tools (e.g., solvent extraction, biomarker analysis, etc.) are routinely applied in the oil industry to characterise the organic matter type and maturity of oils and source rocks, their depositional environments, and for establishing oil-oil and oil-source rock correlations. Such approaches in petroleum geochemistry make extensive use of the hydrocarbons (alkanes and aromatics) and low-molecular mass functionalised lipids (carboxylic acids *etc.*) that can be easily extracted from source rocks and crude oils using common organic solvents for characterisation by GC-MS (e.g., Mackenzie 1984; Peters et al. 2004). As tar mats and pyrobitumens generally contain little in the way of free hydrocarbons, little information exists on the source of these ubiquitous solids. Furthermore, for source rocks or reservoir cores contaminated with mineral oil-based drilling muds (OBM) and for severely biodegraded oils, the conventional approach can fail,

either because the biomarkers present are masked by those in the OBM, and or are irretrievably altered by microbial degradation. Thus, in these instances, petroleum geochemists currently have no molecular “fingerprints” at hand to aid basin modelling.

Catalytic hydrolysis (HyPy) refers to pyrolysis assisted by high hydrogen gas pressures (>10 MPa). It has been developed as an analytical pyrolysis technique that possesses the unique ability to produce high yields of biomarkers from petroleum source rocks and oil asphaltenes while minimising alteration of their isomeric distributions (Love et al. 1995; Grotheer et al. 2015; Robert et al. 2016). Bitumens obtained from the Fulmar Formation from three wells (22/30c-13, 29/5b-6 and 29/5b-8) in the Elgin/Franklin complex (Fig. 1), have been analysed using HyPy, which in conjunction with vitrinite reflectance data from these wells, has been combined with a burial-thermal history to produce an integrated model for the origin of both the bitumen and hydrocarbon charge. A key element of this model is the temperature history of the Elgin/Franklin reservoirs and the associated Kimmeridge Clay (KCF) and Pentland source rocks. Petroleum system modellers currently derive thermal histories of basins and potential hydrocarbon exploration prospects using tectonic and kinetic models calibrated using present day corrected well temperature records (Harris & Peters 2012). Both tectonic and kinetic models assume the conservation of thermal energy and use of increased heat flow during uplift and erosion. The imposition of full conservation of energy requires the incorporation of mechanical movement into the temperature history calculations, which produces additional thermal energy during both subsidence and uplift. In the case of basin uplift (such as the generation of the Base Cretaceous unconformity in the Central Graben), the generation of the upward push that created the uplift and erosion between the depositional of the Upper Jurassic and Lower Cretaceous rocks always produces additional heat compared with that occurring during the preceding and succeeding phases of subsidence. Although the increase in temperatures produced by energy conservation means that petroleum generation starts earlier than currently believed by petroleum system modellers, the rate of petroleum generation is slowed by the higher pV (mechanical) work (and therefore higher E_a) required by endothermic chemical reactions such as petroleum generation. The inclusion of the pressure effect in kinetic modelling is necessary for petroleum system models to conserve energy.

The separation and subsequent characterisation of the bitumens by HyPy has been complicated severely by the extremely high levels of oil based drilling mud in the samples investigated. This has made it impossible to characterise extractable biomarkers and has made bulk characterisation of the bitumen asphaltenes unreliable. When neat bitumen is available, it is relatively straightforward to perform bulk characterisation, such as using solid state ^{13}C NMR and elemental compositions (e.g., Huc et al. 2000). As a further complication, components in the drilling mud may partition into the asphaltene phase during solvent extraction and asphaltene isolation, and give rise to aliphatic biomarkers during HyPy that interfere with the analysis of those generated from the bitumen. Therefore, the aromatic fractions in the hydropyrolysates have been used to assess the thermal maturity and origin of the bitumen using a combination of GC-MS and ^1H NMR analyses.

Geological setting

The Central Graben is part of failed rift system that initially developed during the Triassic, followed by further extension during the Middle Jurassic that may have extended until early/mid-Cretaceous (Sclater & Christie 1980; Barton & Wood 1984; Thorne & Watts 1989). The amount of extension (β) in the South-Central Graben (SCG) is between 1.5 and 2 (Sclater & Christie 1980). The geological setting of the Elgin and Franklin Fields was described in detail by Lasocki et al. (1999), and readers are referred to this paper for the details of the geological history. The stratigraphic column and cross section show an unconformity between the Lower Cretaceous shales that form the seal and the underlying Jurassic rocks (Fig. 4). The structure formed by uplift and rotation associated with underlying salt movements during the early Cretaceous (Lasocki et al. 1999). The uplifted footwalls were affected by minor phases of reactivation, and during the Lower Cretaceous the structure appears to have been submerged, and a continuous sequence of Upper Cretaceous and Tertiary sediments were then deposited. The rate of subsidence suddenly increased during Plio-Pleistocene, and this was attributed to thermal rejuvenation, as evidenced by the high heat flows and low flexural rigidity of the crust during the late Cenozoic (Thorne & Watts 1989). The heat flow history will be considered in more detail in the Discussion section. The

KCF and Heather Formation shales, together with the coals and shales of the Middle Jurassic Pentland Group, form the main source rocks for the hydrocarbons (Lasocki et al. 1999; Vandembroucke et al. 1999), although Isaksen (2004) suggested that the Middle Jurassic sources were not present in the source kitchens for the Elgin/Franklin Fields.

Methodology

Five samples from the Elgin well 22/30c-13, and two from the Franklin well 29/5b-8 were subjected to solvent extraction and HyPy (Table 1), as summarised in Fig. 5. The cores samples were first ground to a powder with the 106-250 μm fraction used for the investigation. The ground samples (approximately 100 g) were extracted successively via a Soxhlet apparatus for 48 hours each with *n*-heptane, toluene and dichloromethane (DCM)/methanol. Sequential solvent extraction has been previously demonstrated to yield petroleum fluids that are the least altered in terms of biodegradation or thermal evolution (Wilhelms et al. 1996; Russell et al. 2004).

The *n*-heptane extract of each core comprises the “free” phase of the oil which is adsorbed in the rock pores leaving the bulk of the bitumen to be extracted successively with toluene and DCM/methanol. The “bound” phase is generated by subjecting the asphaltenes isolated from the DCM/methanol fraction to HyPy. The asphaltenes were recovered by dissolving the DCM/MeOH extracts in a minimum amount of DCM. To this solution, a 40-fold excess of chilled *n*-heptane was added, and stirred for approximately 30 minutes. The solution was then transferred to centrifuge tubes where the suspension was spun for 5 minutes (Russell et al. 2004). The *n*-heptane supernatant, containing the dissolved maltene fraction, was then decanted. This process was repeated a minimum of 4 times, or until the *n*-heptane supernatant appeared colourless. The quantities of asphaltenes obtained from the various samples were between 5 and 50 mg.

HyPy tests were conducted on the asphaltenes as described by Meredith et al. (2004). To prevent reactor blockage and aid catalyst impregnation, the asphaltenes were first mixed with acid washed (dilute HCl) and pre-extracted (DCM/methanol) sand; the mixture was loaded with the Mo catalyst using an aqueous/methanol solution of ammonium dioxodithiomolybdate $[(\text{NH}_4)_2\text{MoO}_2\text{S}_2]$ to give a nominal molybdenum loading of 1 wt. % sample. The samples were pyrolysed in a fixed-bed reactor

with resistive heating from 50°C to 250°C at 300°C min⁻¹, and then from 250°C to 520°C at 8°C.min⁻¹, under a hydrogen pressure of 15 MPa. A hydrogen sweep gas flow of 5 L min⁻¹, measured at ambient temperature and pressure, ensured that the products were quickly removed from the reactor vessel, with the hydropyrolysates collected in a dry ice cooled silica trap. To ensure that there was no contamination of the products, the silica used for trapping (35-70 mesh) was pre-extracted with *n*-hexane in a Soxhlet extraction apparatus for 24 hours, and then with DCM/methanol (93:7 v/v) for 48 hours, and dried in a muffle furnace at 600°C for 4 hours.

The aliphatic, aromatic and polar (NSO) fractions from the heptane soluble “free”, and the asphaltene hydropyrolysate “bound” phases were separated by silica gel adsorption chromatography with successive elutions of *n*-hexane, *n*-hexane/DCM (4:1 v/v) and DCM/methanol (1:1 v/v). The yields of each fraction were determined by evaporation under a stream of dry nitrogen in pre-weighed vials. GC-MS analyses of the aliphatics and aromatics (1 µl in DCM) were performed on a Fisons Instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer (ionising energy 70 eV, source temperature 280°C). Separation was achieved on a DB-1 fused silica column (50 m x 0.32 mm; film thickness 0.25 µm), with helium as the carrier gas and an oven programme of 50°C (2 min) to 300°C (28 min) at 5°C min⁻¹. The selected ions monitored included *m/z* 83 (*n*-alk-1-enes), *m/z* 85 (*n*-alkanes), *m/z* 191 (hopanes) and *m/z* 217 (steranes), with the areas of individual peaks integrated to calculate compound ratios. Where there was sufficient sample the aromatic hydrocarbon fractions (0.3-2.5 mg) were analysed by ¹³C NMR and ¹H NMR to assess aromaticity. Approximately, 2 mg of sample was dissolved in 0.5 chloroform-d and the spectra were obtained using a Bruker 500 MHz instrument.

The thermal maturities of 11 samples from the Franklin well 29/5b-6 were determined by vitrinite reflectance using kerogen preparations obtained by acid washing of the original samples (Fig. 5). Prior to reflectance measurements, the samples were ground and polished using successively finer grades of silicon carbide and colloidal silica to produce a scratch free polish. Measurements were made on a Leitz Orthoplan microscope fitted with an MPV photometer using incident light illumination. The microscope is also fitted with a mirror box, xenon lamp and appropriate barrier filters, such that UV illumination could be used before any VR measurements were made on a particle. The samples were examined in white light using oil immersion objectives, while reflectance was measured using a green filter with a peak transmission of 546 nm and a 16 µm measuring

aperture. The vitrinite reflectance (mean VR) values were based on variable numbers of vitrinite particles in the different samples, and the numbers of particles measured are also shown. Strewn kerogen mounts from two Kimmeridge Clay samples (5114.6 and 5132.9 m) were also prepared for use under transmitted light illumination. The strewn mounts were then used to assess the spore colours of the kerogens in these samples.

Results

Solvent extractable (free) phase hydrocarbon biomarkers

The solvent extract yields for the Elgin/Franklin cores are shown in Table 1. They are highly variable across the seven samples and appear to be related to the grainsize and hence porosity of the samples. The two Franklin mudstone samples showed a relatively low yield (<4.0 mg/g), while four Elgin sandstone samples yielded >24.3 mg/g, but an Elgin mudstone yielded only 3.7 mg/g. The total ion chromatogram (TIC) from the GC-MS of the *n*-heptane soluble free oil extract of one of the five Elgin samples from well 22/30c-13 is shown in Fig. 6a. This can be seen to be dominated by *n*-alkanes in the range *n*-C₁₃ to *n*-C₂₁, maximising at *n*-C₁₈, with these *n*-alkanes apparently derived from diesel-based drilling mud (Wenger et al. 2004), although small amounts of higher molecular weight components were also present. The free heptane extracts from the two Franklin samples were compositionally different, although probably still impacted by drilling mud contamination. These extracts contain a low boiling fraction dominated by *n*-alkanes (*n*-C₁₁ to *n*-C₂₀ with a maximum at *n*-C₁₄), together with a higher boiling fraction composed largely of a unresolved complex mixture (UCM) that elutes over the range of *n*-C₂₀ to *n*-C₃₂ (Fig. 6a).

Although concentrated in the relatively low boiling fraction, the drilling mud present in both well cores clearly extends into the higher boiling range, and so may well impact on the biomarker distribution of the sample. An example of the *m/z* 217 mass chromatograms from the heptane soluble fraction from one of the Elgin sandstones and one of the Franklin mudstones is shown in Fig. 7a. It is unclear whether the mature sterane profile, with the S and R epimers of the homologs with the 5 α ,14 α ,17 α configuration of equivalent abundance seen in the Franklin sample is derived from

the free phase of the bitumen itself, or from the drilling mud (for ratios see Table 1). The higher relative abundance of steranes in the Franklin cores may be due to the higher boiling range of the drilling mud used in this well as shown in Fig. 6a. The sterane distributions are typical of those for North Sea oils with C₂₇-C₂₉ regular steranes (isomerisation ratios shown in Table 1), together with earlier eluting diasteranes evident (Fig. 7a). This was also reflected in the *m/z* 191 mass chromatograms (not shown), which revealed the level of side chain isomerisation of the hopanes (22S/S+R) to be approaching equilibrium (Table 1). Due to the likelihood of drilling mud contamination it is not possible to use the biomarker profiles as a reliable indication of the thermal maturity of these samples.

Generally, the yields of DCM/methanol extracts were greater than those for toluene extracts, providing qualitative evidence that the bitumen phase was concentrated in the DCM/methanol extracts. The composition of both the toluene and DCM/methanol extracts was similar to the heptane fraction indicating that a small proportion of the drilling mud carried over into these fractions during extraction (GC-MS not shown). The asphaltene fraction was isolated from the DCM/methanol fraction from each sample (Table 1), with the highest amounts of bitumen asphaltenes, both proportionally and in absolute terms found in the four Elgin sandstone cores.

Asphaltene (bound) phase hydrocarbon biomarkers

The yields from the HyPy tests on the asphaltenes are presented in Table 1. Between 3 and 45 mg of asphaltene were subjected to HyPy, and overall product yields were in the range 140-425 mg/g. For the asphaltenes investigated, the aliphatic yields range between 60 and 250 mg/g, and the aromatics between 20 and 120 mg/g. As will be described, the aliphatic yields are heavily influenced by *n*-alkanes believed to be derived from some of the constituents in the drilling mud.

HyPy aliphatic hydrocarbons

The TIC from the aliphatic hydrocarbon fractions of the hydropyrolysates of the asphaltenes isolated from the DCM/methanol extract from an example of both the Elgin and Franklin cores are shown in

Fig. 6b. It was hoped that these would produce hydrocarbon distributions that were clear of drilling fluid contaminants as previously shown for oil reservoir core samples, contaminated with synthetic α -olefins (Russell et al. 2004). However, for both the Elgin and Franklin cores these samples were dominated by *n*-octadecane, and to a lesser extent *n*-hexadecane, which are clearly not reflective of pristine hydrocarbon distributions as generated from the bound phase of mature oil asphaltenes (Meredith et al. 2008). These *n*-alkanes are thought to arise from fatty acid components employed as emulsifiers or lubricants in the drilling fluid which are dominated by stearic and palmitic acid salts (Wenger et al. 2004; Fink 2015). Due to their high polarity these compounds would partition with the asphaltene fraction during precipitation in *n*-heptane, and then be decarboxylated to their corresponding hydrocarbons during HyPy (Sephton et al. 2005a; Meredith et al. 2006). However, other *n*-alkanes extending beyond *n*-C₂₅ are still evident for both samples that are typical distributions for asphaltene hydropyrolysates. Note that earlier work on HyPy has shown conclusively that asphaltenes are largely immune from biodegradation so that when free *n*-alkanes have been biodegraded, *n*-alkyl moieties bound within the asphaltenes are preserved (Sonibare et al. 2009).

Evidence of drilling mud contamination is also apparent in the distribution of biomarkers in the hydropyrolysate aliphatic fractions, with the *m/z* mass 217 chromatogram of the steranes seen to be dominated by C₂₉ $\alpha\alpha\alpha$ R isomer (Fig. 7b). This is suggestive of a very low degree of thermal maturity with the C₂₉ $\alpha\alpha\alpha$ S/S+R ratio seen to be <0.20 for all seven samples investigated, and <0.10 for four of them (Table 1). Due to their relatively low abundance it is not possible to get reliable isomerisation data for the C₂₇ and C₂₈ sterane homologs. While it is known that the isomerisation of biomarkers bound within the macromolecular asphaltene structure and then released by HyPy is somewhat retarded relative to those in the free phase across a wide range of thermal maturity (Murray et al. 1998; Lockhart et al. 2008), the highly immature sterane signal is not consistent with that from either the free phase (although that may also reflect the drilling mud) or the current day temperature conditions of the Elgin/Franklin complex. It is more likely that the high abundance of the C₂₉ $\alpha\alpha\alpha$ R ethylcholestane is due to an impurity, possibly arising from sterols present in the drilling mud (Bennett & Larter 2000; Russell et al. 2004), which as seen for the fatty acids above would be reduced to their corresponding sterane during HyPy (Sephton et al. 2005b). Apart from this compound the distribution of the steranes in the bound phase is consistent with what you would expect from the HyPy of mature oil asphaltenes, in particular the absence of rearranged

compounds such as the diasteranes (Sonibare et al. 2009), and possible co-elution of $\beta\alpha\alpha$ isomers with the $\alpha\beta\beta$ steranes (Russell et al. 2004).

The abundance of bound hopanes within the asphaltenes was very low for all seven samples analysed. This extremely high sterane to hopane ratio also points towards the C_{29} $\alpha\alpha\alpha$ R isomer being a contaminant, and means that it is not possible to use the hopanes to assess the thermal maturity of the samples.

HyPy aromatic hydrocarbons

In view of the difficulties encountered with the aliphatic fraction from drilling mud-derived products, the aromatic fractions from the HyPy were used to assess maturity for the bitumens since these are believed to be contaminant free. While oil-based drilling muds may contain some aromatic species, these are restricted in modern muds used offshore (Wenger et al. 2004), and will likely be limited to the free phase. The maturity assessment was accomplished by comparing aromatic ring size distribution by GC-MS, and hydrogen aromaticity by $^1\text{H-NMR}$.

The use of bound aromatic biomarkers for the assessment of thermal maturity is not as well understood as for their aliphatic counterparts. Lockhart (2010) reported that the methylphenanthrene index (MPI-1) of Radke & Welte (1983) increased with thermal maturity as expected for Type III kerogen-bound aromatic assemblages up to a VRo of 1.5%. While this is a greater maturity range than is applicable for the hopane and sterane biomarker ratios, the parameters based on alkylphenanthrene rearrangements break down beyond the oil window. Wu et al. (2015) found similar results for both a natural and artificial maturity sequence up to a VRo of 1.75%, with samples of greater maturity having bound aromatics that were increasingly dominated by parent PAHs (a decrease in the relative abundance of alkyl substituted structures), together with an overall increase in the number of rings present (Grotheer et al. 2015).

Fig. 8 presents the TIC for the HyPy aromatic hydrocarbons from a typical North Sea oil asphaltene (Blake Field, Russell et al. 2004) and a representative example from each of the Elgin and Franklin samples. With increasing maturity, the carbon aromaticity increases in both vitrinite and liptinites, Types III and II kerogens (Carr & Williamson 1990; Suggate & Dickenson 2004), with the increased aromaticity occurring as expected alongside the gradual increase in the size of the aromatic clusters in the kerogen. Thus, single isolated aromatic rings are common in immature oil-prone kerogens (Vandenbroucke & Largeau 2007), through 3 and 4 ring aromatics in clusters in the oil window as exemplified by the development of phenanthrenes, methylphenanthrenes and triaromatic steranes (Radke & Welte 1983). Ultimately large polyaromatic 'graphitic' sheets are formed at high maturities, e.g., pyrobitumen and petroleum coke. The bound aromatics from the HyPy of the asphaltenes extracted by DCM/methanol from both the Elgin and Franklin wells are dominated by 3 and 4 ring compounds and have a similar overall aromatic distribution to that of the North Sea oil asphaltene. Maturity dependant aromatic compound ratios such as MPI-1 are presented in Table 2, together with ratios to assess the degree of alkylation and ring size distribution of these aromatic fractions, which together show that these bitumens are of a broadly similar maturity to a typical North Sea oil asphaltene. There is no evidence from GC-MS that significant levels of drilling mud derived aromatics are present. Fig. 9 compares the ¹H-NMR spectra chromatograms for hydropyrolysate aromatics from one of the Franklin samples (a), and a typical North Sea oil asphaltene (b). The aromatic fractions have very similar hydrogen distributions with ~30% of the total hydrogen being aromatic, this being considerably less than seen for an over mature pyrobitumen. Therefore, this presents strong evidence that the bitumens analysed have maturities more broadly similar to that of the North Sea oil asphaltene than an over mature pyrobitumen. As with the GC-MS data, there is no evidence from ¹H-NMR that significant levels of drilling mud derived aromatics are present.

Vitrinite reflectance and petroleum system modelling

In the 29/5b-6 (Elgin) well, the samples chosen for VR measurement are from the depth interval of 914.4 m (Pleistocene) to 5132.9 m (Kimmeridge Clay Formation, Late Jurassic) (Table 3). The main characteristic is the relatively low reflectance values (<0.8% Ro) in the Jurassic sediments at depths

greater than 4500 m (~14750 ft., Table 3). This low maturity is especially interesting given the present day high temperatures (180 to 190°C) in the Fulmar Sandstone Formation reservoirs, and the temperature history presented by Vandenbroucke et al. (1999) that shows the reservoir temperatures have exceeded 100°C throughout the Tertiary. A transmitted light view of the Upper Jurassic shale at 5114.3 m (16780 ft.) shows a mixture of black humic kerogen with orange-brown oil-prone palynomorph and amorphous kerogens (Fig. 10). The orange-brown colours indicate optimum oil generation consistent with a source rock maturity of 0.7 to 0.8% Ro (Smith 1983; Waples 1985). The vitrinite reflectance data were used for the thermal history derivation during petroleum system modelling undertaken using Platte River's 1D BasinMod software.

Discussion

The model for bitumen generation requires the thermal history to be defined, so that the timing of oil charge can be determined, because the presence of oil in the reservoir is a prerequisite for bitumen formation. Petroleum generation from the oil-prone (Type II kerogen) KCF source rock in the 29/5b-6 well and Ps-1 pseudowell (source kitchen) are controlled by the heat flow input into the model, and the burial history. The high reservoir permeabilities present in both Elgin and Franklin and other locations in the South Central Graben (SCB) have been discussed with regard to the diagenetic history, including the presence of bitumens (e.g., Darby et al. 1997; Haszeldine et al. 2003; Hendry et al. 2000a, 2000b; Lasocki et al. 1999; Wilkinson & Haszeldine 2011; Wilkinson et al. 1997, 2006, 2014). The implications of the timing of the different diagenetic events to the understanding of the mechanisms and timing of bitumen formation are described in the following sections.

Burial, thermal and maturation histories

The burial histories for both the 29/5b-6 well (Fig. 11a), and the Ps-1 pseudowell (Fig. 11b) show an initial period of rifting subsidence with the Pentland, Fulmar and Kimmeridge Clay Formations being deposited in a subsiding basin following Middle Jurassic rifting. The Middle and Upper Jurassic are then overlain by the angular Base Cretaceous Unconformity (BCU). Most published burial history models for the Central Graben model the unconformity as a hiatus (e.g., Jensen et al. 1985; Cornford 1994; Wilkinson et al. 1997;

Vandenbroucke et al. 1999; Rudkiewicz et al. 2000; Swarbrick et al. 2000). However, an angular unconformity requires that pre-existing rocks have been uplifted, tilted and eroded to varying degrees, prior to the deposition of younger Lower Cretaceous rocks above the unconformity. Angular unconformities are not represented by a hiatus, which is a period without deposition, uplift and erosion. This additional syn-rift subsidence and burial means that the Pentland and KCF source rocks were partly matured by high heat flow associated with Middle-Late Jurassic rifting. In the Ps-1 pseudowell in the half-graben to the east of the Elgin/Franklin structures, the amount of uplift and erosion during the formation of the BCU is lower than in the 29/5b-6 well, thereby preserving a greater thickness of Middle and Upper Jurassic in the source kitchen. After the unconformity, the basin started subsiding again and the Lower Cretaceous Cromer Knoll formation was deposited. Subsidence and deposition of chalk and shales largely continued throughout the Upper Cretaceous and Tertiary, respectively. However, there is some evidence of local inversion in the Central Graben during the very late Cretaceous to early Paleocene, the late Paleocene, and the Late Eocene (Zanella & Coward 2003). The stratigraphy of the 29/5b-6 well does not show any evidence of inversion events during the Paleocene to late Eocene, and no uplift events during these periods are included in the model.

Previous attempts to model the thermal history of the Central Graben have often used constant heat flow/geothermal gradient histories, (e.g., Barnard & Bastow 1991; Saigal et al. 1992; Vandenbroucke et al. 1999), while Jensen et al. (1985) used a constant heat flow to model the Aars-1 well in the adjacent Danish Central Graben to the southeast. The use of constant heat flow appears to be based on the work of Leadholm et al. (1995), who found that it is a reasonable assumption for the modelling of Upper Jurassic source rocks maturation in the North Sea. In contrast a variable thermal history was used by Cornford (1994), with a linear heat flow reduction from a peak of 90 mW/m² at 163 Ma to 45 mW/m² at 100 Ma, and then followed by a constant heat flow of 45 mW/m² from 100 to 0 Ma. When used with the burial history, this heat flow model gave good correlations between measured and predicted well temperature and VR data. Swarbrick et al. (2005) devised a heat flow history for the modelling of the Judy Field that continuously decreased from the peak during Middle Jurassic rifting to the present day.

The current kinetic models used to predict the rates of endothermic (e.g. maturation, petroleum generation and oil-to-gas cracking) reactions assume that the reaction rates are independent of pressure. The mechanical (pV) work forms part of the activation energy (E_a) of the reaction is the work done during the generation of the free radicals involved in the reactions. This pV work at activation forms part of the overall enthalpy change produced by the reaction, and the enthalpy change is generated from the thermal energy of the system (the geological basin in this case) in which the reaction occurs. In addition to the pV work, the thermal energy increases the kinetic and potential (which together give the internal) energies of particles required for the bond rupture in the reacting atoms/free radicals, and thus the internal energy increases with increasing temperature. Predicted reaction rates must conserve energy such that the predicted extent of any reaction cannot exceed the thermal energy of the rock that hosts the reaction. As the pore pressure increases, so the pV work required by each endothermic reactions also increases. In thermally constrained high-pressure systems, e.g., Central Graben, the amount of reaction is reduced (retarded) so as to conserve energy. In a pressurised constrained volume filled with highly incompressible phases (solid rock and water) that is at a fixed temperature, energy conservation means that any increase in the pressure produces a reduction in the generated volume.

The retardation of VR has been confirmed by experiments (Dalla Torre et al. 1997; Le Bayon et al. 2011; Uguna et al. 2012a; 2012b; 2015). Other maturation parameters are also retarded in high pressure systems, e.g., T_{max} in the Yinggehai Basin of China (Hao et al. 1995). The issue of pressure retardation is somewhat contentious with some workers claiming that overpressure does not retard vitrinite reflectance in some basins, e.g., Qiongdongnan Basin, South China Sea (Hao et al. 1995), Laramide Basin of Wyoming (Surdam et al. 1997), Barrow sub-basin, North West Shelf of Australia (He et al. 2002). In a study on the presence and mechanisms of overpressure retardation in petroleum basins in China, Hao et al. (2007) observed a hierarchy of overpressure retardation, with some basins showing strong evidence of overpressure retardation while others show little evidence of retardation. The variations in the effect of overpressure on maturation and hydrocarbon generation were thought to be due to the diversities of maturation reactions in kerogen, and the nature and timing of overpressure generation and development (Hao et al. 2007). However, the relation between overpressure and the presence/absence of retarded maturation is affected by the effect that erosional unconformities have on the heat flow, VR and overpressure histories. All the basins noted above that are considered not to show the effect of pressure retardation also contain unconformities in the later parts of their burial histories. As discussed above the modelling of uplift

and erosion to create the unconformity changes the heat flow history, and will therefore alter the thermal history from those used in the studies that claim that pressure has no effect of maturation and petroleum generation.

The models proposed by Carr (1999) and Zou & Peng (2001) assumed that vitrinite reflectance was retarded in overpressured basins, consistent with Le Chatelier's principle. However, vitrinite reflectance always increases with increasing depth in a reaction that is irreversible, and as Le Chatelier's principle applies to the chemical equilibrium of reversible reactions, then the effect of pressure is unimportant to the extent to which vitrinite reflectance increases with increasing temperature and time (Nielsen et al. 2017). However, between the reactant and either the transition state (Laidler & King 1983) or free radical formation and propagation, a pseudo-equilibrium state occurs, although Nielsen et al. (2017) are correct as regards the absence of equilibrium in the relationship between transition state-free radical intermediates and products. The pressure together with temperature therefore control the conversion between the reactant and the transition state or free radicals.

The thermal history used in this study shows reducing heat flow with time post-peak, but with variable rates of reduction, with the most rapid reductions occurring during periods of most rapid subsidence (Fig. 12). The decrease in heat flow following rifting is halted by a period of increasing heat flow during the period of uplift to produce the BCU. This increase in heat flow is necessary, otherwise the rocks being uplifted increase their potential energy (increased distance from the earth's gravitational centre) which without increased heat flow that is always generated during mechanical work (generation of upward push responsible for uplift). Following the period of exhumation and erosion, both the well and Ps-1 pseudowell start to subside again, and the heat flow also begins to reduce, with the heat flow reduction being greater during more rapid periods of subsidence (Carr & Uguna 2015). During the Plio-Pleistocene both the well (29/5b-6) and Ps-1 pseudowell show rapid subsidence, and Thorne & Watts (1989) suggested that this might be due to the onset of thermal rejuvenation as shown by the high heat flow and low flexural rigidity. The apparently high heat flows during the Plio-Pleistocene occurs partly due to the conversion of potential energy into thermal energy during the rapid Plio-Pleistocene subsidence.

The burial and thermal histories were used to generate the temperature and pressure histories, with both being required to predict VR values that can be calibrated with the measured well data (Table 3). Although the measured VR values appear to be relatively low ($\sim 0.7\%$ Ro) at a depth of 5 km, this is consistent with the orange-brown palynomorph colours present in samples analysed at this depth (Fig. 10). The modelled VR- and pressure-depth plots for the 29/5b-6 well show good correlations between the measured values and predicted trends (Figs. 13a and b respectively). The temperature and pressure histories for the Fulmar formation in 29/5b-6 well are shown in Fig. 14. The pressure-depth plot (Fig. 13b) shows that the well becomes overpressured near the Upper-Lower Oligocene boundary. The VR-depth plot shows that the KCF is still mid-mature for oil generation (0.7 to 1.0% Ro) at the present day, although the base Pentland Formation is predicted to be very close to the late mature window (Fig. 13a). The VR trend predicted by the thermal history (Fig. 12) and conventional temperature-time kinetic Easy% Ro model (Sweeney & Burnham 1990) is shown by the dashed line in Fig. 13a, with the predicted trend being much higher than the measured values. In contrast, the values predicted by the PresRo[®] kinetic model are consistent with the measured values. In the 29/5b-6 well, the maturation history shows that the base Pentland Formation reaches 0.7% Ro, i.e. mid-mature for oil generation at 86 Ma (Fig. 15a), whereas in the Ps-1 pseudowell the Pentland Formation reached 0.7% Ro at 145 Ma, which is before the uplift associated with the BCU (Fig. 15b). In the Ps-1 pseudowell, the base Pentland Formation becomes late-mature for oil generation (1.0 to 1.3% Ro) at 142 Ma, and then finally becomes gas-mature (1.3 to 3.0% Ro) at 22 Ma (Fig. 15b). The Pentland Formation is a gas-prone source rock and is modelled to have been generating and expelling gas condensate from 145 Ma until the onset of gas generation at 22 Ma, with migration envisaged up the faults between the graben location of the Ps-1 pseudowell and the Elgin and Franklin reservoirs, charging the Elgin and Franklin reservoirs (Lasocki et al. 1999). The KCF in the Ps-1 pseudowell reached 0.7% Ro at 128 Ma, which is during the period when the Ps-1 pseudowell had been uplifted prior to the BCU formation, whereas in 29/5b-6 it only achieves a maturity of 0.7% Ro at 67 Ma.

The VR data obtained from the 29/5b-6 well in this study was compared with published datasets from the UK, Norwegian and Danish Central Grabens show that the VR data for the 29/5b-6 well (Fig. 13a, Table 3) appears to be slightly lower than the bulk of the values at depths of 5 km (Fig. 16). The VR values shown in Fig. 16 were obtained from published well results in a number studies, although the entire database presented by Isaksen (2004) for the UK Central Graben quadrants 22, 23, 29 and 30 (main HPHT area) is not shown. Only

the lowest and highest values at various depths throughout the analysed depth interval are shown to give an indication of the measured range of VR values presented in the Isaksen study. The entire Isaksen dataset had apparently been high-graded to only include autochthonous vitrinite. Some low values between 0.20% Ro and 0.30% Ro in the depth interval 3800 and 4200 m in the Isaksen data were not included in Fig. 16, as being anomalously low for some reason. While Isaksen did not consider the effects of pressure on VR, this effect was considered in Carr (1999), Carr (2003), Carr & Petersen (2004) and Petersen et al. (2012) studies on VR in the high-pressure areas of UK and (mainly) Danish Central Graben. Two values from UK 23/26-2z shows values of 0.54% Ro and 0.55% Ro in the depth interval between 4500 and 4700 m also suggest that lower values than bulk of the VR values at this depth in the Central Graben. Certainly, there is always the possibility that some non-vitrinitic kerogen, e.g. bitumen or liptinite (Hackley & Cardott 2016) was actually being measured in both 23/26-2z and 29/5b-6 wells. In the case of measurements undertaken on the 29/5b-6 well, UV light illumination was used to check each field of view that vitrinite was the kerogen being measured, since low reflectance bitumen and liptinite would be expected to fluoresce at VR values in the reflectance range 0.5 to 0.8% Ro. The low VR values measured in 29/5b-6 well at approximately 5 km were checked using kerogen spore colour (SCI) analysis, as was the entire 23/26-2z dataset in Carr (2003). The orange-brown coloured palynomorphs in the 5114.6 m sample from 29/5b-6 well are consistent with VR values in the range 0.7 to 0.8% Ro. The low numbers of readings taken from each sample arise from the use of small samples, and the rejection of possible vitrinite particles due either to poor morphology (e.g. rounded edges suggesting reworked vitrinite particles), or fluorescence that might produce suppressed low reflectance values (e.g. Buiskool Toxopeus 1983; George et al. 1994; Hao & Chen 1992; Petersen & Rosenberg 1998; Uguna et al. 2017). The low number of VR readings obtained from each sample in Table 3 potentially limits the validity of the measured values (Hackley & Cardott 2016), although the general consistency between the VR and spore colour data at 5 km depth suggests that although not precise it is sufficiently accurate enough for the purpose of calibrating the thermal history.

Petroleum charging and bitumen formation

The API and GOR values for the Elgin Field are 49° and 3800 respectively, while the values for the Franklin field are 50° and 8000, with the KCF being the source rock for the oil and the Pentland coals and shales being the gas source rock for the gas (Lasocki et al. 1999; Isaksen 2004). Peak hydrocarbon generation from the KCF in the south Central Graben occurred at about 40 Ma (Barnard & Bastow 1991). In the Judy and Joanne fields just to the south, oil generation from the KCF in the western kitchen (the location of the pseudo-well) commenced at 56.5 Ma and was completed (source rock exhausted) by Mid Miocene (10.4 Ma), whereas generation from the KCF was only just beginning at this time (Lines & Auld 2004). However, Hendry et al. (2000a) claimed that the Franklin Field was filled during the Miocene (23 to 5 Ma), although the Elgin Field was filled only within the last 5 Ma. These estimates of timing for the petroleum charge were obtained mainly from petroleum system modelling and in some cases from the diagenetic paragenesis sequence, e.g., Lasocki et al. (1999); Hendry et al. (2000b). The Miocene age for Franklin petroleum charge is consistent with the times given by Saigal et al. (1992) for the Ula field (Norwegian Central Graben), and by Cornford (1994) for the south Central Graben in general. Lasocki et al. (1999) state that the Elgin and Franklin hydrocarbons have always existed under monophasic conditions, with the initial 'oil' fill gradually becoming richer in gas until the system 'flipped' to gas condensate (Lasocki et al. 1999). There was also an earlier oil charge in the south Central Graben, which, based on K–Ar ages of authigenic illite, appears to have occurred between 84 and 59 Ma (Wilkinson et al. 2006). There is no K–Ar record of such an early oil charge in Elgin or Franklin, as all of the clays within the reservoir are illitized, which means that it is impossible to differentiate authigenic from detrital clays (Lasocki et al. 1999).

Bitumen formation is the last diagenetic event in the Elgin and Franklin Fields (Wilkinson et al. 1997; Lasocki et al. 1999; Hendry et al. 2000b). The bitumen occupies <10% of the pore volume, and the bitumen in the three wells involved in this study appears highly concentrated in the upper 2 m of the Fulmar reservoirs, observations that are consistent with those of Lasocki et al. (1999) and Isaksen (2004). The diagenetic studies provide the temperatures at which certain cements, e.g., ankerite and quartz were formed (Fig. 14). A modified diagenetic paragenetic sequence to those generated by Lasocki et al. (1999); Hendry et al. (2000a, 2000b) which retains the same relative sequence, but

with modified temperatures and timing (Fig. 17). The ankerite and quartz both contain aqueous fluid inclusions, i.e. without hydrocarbon, with ankerite mean homogenisation (T_h) temperatures of 143°C and 153°C from two Elgin cores (range 140 to 170°C), and 143°C (Franklin) and 163°C (Elgin) for quartz (Hendry et al. 2000a). In contrast, three aqueous inclusions containing hydrocarbons in late-stage albite cement gave T_h values of 155–160°C in 29/5b-6 well (Hendry et al. 2000a). The oxygen $\delta^{18}\text{O}$ (‰ SMOW) isotope data were interpreted by Hendry et al. (2000b) to indicate formation temperatures between 120 and 180°C.

Illite formation dates obtained using K–Ar radiometric dating cannot be used to date the timing of oil charge as all of the clays within the reservoir are illitized, which means that it is impossible to differentiate authigenic from detrital clays (Lasocki et al. 1999). The authigenic illite K–Ar dates of 84 to 59 Ma in the 29/10b-2 well just to the south of Elgin Field are thought to represent the timing of an early oil charge, as high oil saturations are believed to restrict access to aqueous pore waters which consequently prevents further cement formation (Wilkinson et al. 2006; Wilkinson & Haszeldine 2011). As the KCF in the Ps-1 pseudowell become mature for oil generation and expulsion in the graben from 128 Ma, there is a potential source for such an oil charge.

The bitumen in Elgin/Franklin Fields occurs predominantly in the upper 2 m of the reservoirs, which are also the zones of highest porosity and permeability, although some bitumen is dispersed throughout the reservoirs in both fields (Lasocki et al. 1999; Isaksen 2004). Oil-to-gas cracking during the rapid Plio-Pleistocene subsidence has been considered to be the main reason for the formation of the gas-condensates in the Elgin and Franklin Fields (Lasocki et al. 1999; Isaksen 2004) and in the Judy Field just to the south (Lines & Auld 2004). Oil was migrating into the Elgin/Franklin reservoirs starting at approximately 90 Ma, slightly earlier than in 29/10b-2 well to the south in which an early oil charge between 84 and 59 Ma was proposed by Wilkinson and Haszeldine (2014). This early oil was then possibly degraded via the combination reactions by the overpressure from about 60 Ma (Fig. 17). The evidence for this comes from the ^1H NMR analyses of the bitumen and comparisons with non-degraded North Sea oils, as both show structures composed predominately of 3-4 aromatic rings, and not the coke/graphitic structures produced by oil-to-gas cracking. However, if the pressure mediated combination reactions are invoked to produce the bitumen, then as such reactions are exothermic (as opposed to the endothermic petroleum generation and cracking reactions), and exothermic combination reactions are therefore unlikely to have occurred in high-

temperature basins such as the present-day Central Graben. For this reason, bitumen formation is divided into parts 1 and 2, with 1 being bitumen generated by combination reactions, and 2 being the oil deasphalting mechanism proposed by Lasocki et al. (1999). Bitumen formation prevents further mineral diagenesis, and the range of temperatures shown for bitumen formation represents the various processes responsible for bitumen generation. Relying only on gas deasphalting to produce the bitumen would not seem to account for the high concentration of bitumen in the upper parts of the reservoir, and this is attributed to an early oil charge being degraded by combination reactions. The presence of bitumen throughout the reservoir is used as evidence for in-situ oil cracking occurring during the late 1 km of burial in both Elgin and Franklin Fields (Isaksen 2004). According to Isaksen (2004), the distribution of bitumen throughout the reservoir apparently precludes gas-deasphalting of oil as the mechanism for bitumen formation. If oil-to-gas cracking reactions occurred during the last 1 km of subsidence (4 Ma, Fig. 11a), then this would involve a relatively rapid reaction rate that experimental evidence provided by Uguna et al. (2016) and Xie et al. (2016) suggest is impossible due to the high pressures already present in the reservoirs before any pressure produced by oil-to-gas cracking occurred during the last 4 Ma of subsidence (Fig. 11a). The carbon isotope data for the Elgin/Franklin Fields shows heavier ^{13}C saturate and aromatic isotope values than occur in the KCF but similar to those in the Pentland Formation, and Isaksen (2004) suggested this the heavy ^{13}C isotope values occurred due to oil-to-gas cracking producing lighter values. However, combination reactions would also produce oils and bitumens with heavier isotopes, since the reaction rate of ^{13}C - ^{12}C bonds is faster than ^{12}C - ^{12}C bonds in combination reactions. A later oil charge into the highly permeable reservoirs is then degraded by the later gas migration from the Pentland into the reservoir, which is also consistent with the heavy ^{13}C isotope obtained from both Elgin/Franklin and Pentland gas-prone source rock. Currently there are no kinetic models available that can predict rates of oil degradation via combination reactions, and therefore it is impossible to assign the amounts of bitumen formed by combination as opposed to the amounts formed by gas de-asphalting. Further analysis will be required to determine whether it is possible to geochemically separate bitumens formed via combination reactions from those formed by oil-to-gas cracking or gas de-asphalting.

Conclusions

1. Characterisation of the hydropyrolysate aromatic hydrocarbons from the bitumen asphaltenes has shown that these are very similar compositionally to asphaltenes in North Sea oils with relatively low aromaticities, and such bitumens are therefore not pyrobitumens produced by the thermal cracking of oils.
2. The bitumen formed as a result of oil generation from the KCF prior to uplift and erosion that produced the base Cretaceous unconformity.
3. The early oil generation is a direct result of the elevated heat flows at the time of rifting.
4. The bitumen is possibly formed by two processes with the first being combination reactions induced by an early oil charge and the development of overpressure within the Fulmar reservoir, and the second being gas deasphalting produced by the later successive oil and gas charges into the reservoir.
5. Following the onset of renewed subsidence during the latter part of the Lower Cretaceous, oil and gas condensates generated from the KCF and Pentland source rocks charged the structure.

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References

Barnard, P.C. & Bastow, M.A. 1991. Petroleum generation, migration, alteration, entrapment and mixing in the Central and Northern North Sea. In: England, W. & Fleet, A. (eds) *Petroleum Migration*. Geological Society of London, Special Publication, 59, 167–190.

Barton, P. & Wood, R.J. 1984. Tectonic evolution of the North Sea basin: crustal stretching and subsidence. *Geophysical Journal of the Royal Astronomical Society*, 79, 987–1022.

Bennett, B. & Larter, S.R. 2000. Polar non-hydrocarbon contaminants in reservoir core extracts. *Geochemical Transactions*, 1, 34–37.

Buiskool Toxopeus, J.M.A. 1983. Selection criteria for the use of vitrinite reflectance as a maturity tool. In: Brooks, J. (ed) *Petroleum geochemistry and exploration of Europe*. Geological Society London Special Publication, 12, 295–307.

Carr, A.D. 1999. A vitrinite reflectance kinetic model incorporating overpressure retardation. *Marine and Petroleum Geology*, 16, 353–377.

Carr, A.D. 2003. Thermal history model for the South Central Graben, North Sea, derived using both tectonics and maturation. *International Journal of Coal Geology*, 54, 1–19.

Carr, A.D. & Williamson, J.E. 1990. The relationship between aromaticity, vitrinite reflectance and maceral composition of coals: implications for the use of vitrinite reflectance as a maturity parameter. *Organic Geochemistry*, 16, 313–323.

Carr, A.D. & Petersen, H.I. 2004. Modelling of the hydrocarbon generation history and volumetric considerations of the Lulita Field, Danish North Sea. *Petroleum Geoscience*, 10, 107–119.

Carr, A.D. & Uguna, C.N. 2015. Some thoughts on the influence of pressure and thermal history assumptions on the petroleum systems modelling. *Journal of Petroleum Geology*, 38, 459–465.

Cornford, C. 1994. The Mandal-Ekofisk(!) petroleum system in the Central Graben of the North Sea. In: Magoon, L.B. & Dow, W.G. (eds) *The Petroleum System - From Source to Trap*. AAPG Memoir, 60, 537–571.

Curiale, J. 1985. Origin of solid bitumens, with emphasis on biological marker results. *Organic Geochemistry*, 10, 559–580.

Dahl, B. & Speers, G.C. 1985. Geochemical characterization of a tar mat in the Oseberg Field Norwegian Sector, North Sea. *Organic Geochemistry*, 10, 547–558.

Dalla Torre, M., Mählmann, R.F. & Ernst, W.G. 1997. Experimental study on the pressure dependence of vitrinite maturation. *Geochimica et Cosmochimica Acta*, 61, 2921–2928.

Darby, D., Wilkinson, M., Haszeldine, R.S. & Fallick, A.E. 1997. Illite dates record deep fluid movements in petroleum basins. *Petroleum Geoscience*, 3, 133–140.

Fink, J.K. 2015. *Water-Based Chemicals and Technology for Drilling, Completion, and Workover Fluids*. Gulf Professional Publishing, Houston, 288.

George, S.C., Smith, J.W. & Jardine, D.R. 1994. Vitrinite reflectance suppression in coal due to a marine transgression: case study of the organic geochemistry of the Greta Seam, Sydney Basin. *Australian Petroleum Exploration Association Journal*, 34, 241–255.

Grotheer, H., Robert, A., Greenwood P.F. & Grice, K. 2015. Stability and hydrogenation of polycyclic aromatic hydrocarbons during hydropyrolysis (HyPy) – Implications of highly matured organic matter *Organic Geochemistry*, 86, 45–54.

Hackley, P.C. & Carbott, B.J. 2016. Application of organic petrography in North American shale petroleum systems: A review. *International Journal of Coal Geology*, 163, 8–51.

Hao, F. & Chen, J. 1992. The cause and mechanism of vitrinite reflectance anomalies. *Journal of Petroleum Geology*, 15, 419–434.

Hao, F., Sun, Y., Li, S. & Zhang, Q. 1995. Overpressure retardation of organic-matter maturation and petroleum generation: a case study from the Yinggehai and Qiongdongnan Basins, South China Sea. *AAPG Bulletin*, 79, 551–562.

Hao, F., Zou, H. Gong, Z., Yang, S. & Zeng, Z. 2007. Hierarchies of overpressure retardation of organic matter maturation: Case studies from petroleum basins in China. *AAPG Bulletin*, 91, 1467–1498.

Harris, N.B. & Peters, K.E. 2012. Analysing thermal histories of sedimentary basins: methods and case studies – introduction. In Harris, N.B. & Peters, K.E. (eds) *Analysing thermal histories of sedimentary basins: methods and case studies*. SEPM Special Publication No. 103. Oklahoma, USA.

Haszeldine, R.S., Wilkinson, M., Darby, D., Macaulay, C.I., Couples, G.D., Fallick, A.E., Fleming, C.G., Stewart, R.N.T. & McAulay, G. 1999. Diagenetic porosity creation in an overpressured graben. In: Fleet, A.J. & Boldy, S.A.R. (eds) *Petroleum Geology of Northwest Europe*. Proceedings of the 5th Conference, Geological Society of London, 1339–1350.

Haszeldine, R.S., Cavanagh, A.J. & England, G.A. 2003. Effects of oil charge on illite dates and stopping quartz cement: calibration of basin models. *Journal of Geochemical Exploration*, 78–79, 373–376.

He, S., Middleton, M., Kaiko, A., Jiang, C. & Li, M. 2002. Two case studies of thermal maturity and thermal modelling within the overpressured Jurassic rocks of the Barrow sub-basin, north west shelf of Australia. *Marine and Petroleum Geology*, 19, 143–159.

Hendry, J.P., Wilkinson, M., Fallick, A.E. & Haszeldine, R.S. 2000a. Ankerite cementation in deeply buried Jurassic sandstone reservoirs of the central North Sea. *Journal of Sedimentary Research*, 70, 227–239.

Hendry, J.P., Wilkinson, M., Fallick, A.E. & Haszeldine, R.S. 2000b. Disseminated ‘jigsaw piece’ dolomite in Upper Jurassic shelf sandstones, Central North Sea: an example of cement growth during bioturbation? *Sedimentology*, 47, 631–644.

Hill, R.J., Tang, Y. & Kaplan, I.R. 2003. Insights into oil cracking based on laboratory experiments. *Organic Geochemistry*, 34, 1651–1672.

Huc, A.Y., Nederlof, P., Debarre, R., Carpentier, B., Boussafir, M., Laggoun-Defarge, F., Lenail-Chouteau, A. & Bordas-Le Floch, N. 2000. Pyrobitumen occurrence and formation in a Cambro-Ordovician sandstone reservoir, Fahud Salt Basin, North Oman. *Chemical Geology*, 168, 99–112.

Isaksen, G. 2004. Central North Sea hydrocarbon systems: Generation, migration, entrapment, and thermal degradation of oil and gas. *AAPG Bulletin*, 88, 1545–1572.

Jensen, P.K., Holm, L. & Sahai, S.K. 1985. Modelling burial history, temperature and maturation. In: Thomas, B.M. (ed) *Petroleum geochemistry in exploration of the Norwegian shelf*. Graham and Trotman, London, 145–151.

Laidler, K.J. & King, M.C., 1983. The development of transition state theory. *Journal of Physical Chemistry*, 87, 2657–2664.

Lasocki, J., Guemene, J.M., Hedayati, A., Legorjus, C. & Page, W.M. 1999. The Elgin and Franklin Fields: UK Blocks 22/30C, 22/30b and 29/5b. In: Fleet, A.J. & Boldy, S.A.R. (eds) *Petroleum Geology of Northwest Europe*. Proceedings of the 5th Conference, Geological Society of London, 1007–1020.

Leadholm, R.H., Ho, T.Y. & Sahai, S.K. 1985. Heat flow, geothermal gradients and maturation modelling on the Norwegian continental shelf using computer methods. In: Thomas, B.M. (ed) *Petroleum geochemistry in exploration of the Norwegian shelf*. Graham and Trotman, London, 131–143.

Le Bayon, R., Brey, G.P., W.G. Ernst, W.G. & Mählmann, R.F. 2011, Experimental kinetic study of organic matter maturation: Time and pressure effects on vitrinite reflectance at 400 °C. *Organic Geochemistry*, 42, 340-355.

Lines, M.D. & Auld, H.A. 2004. A petroleum charge model for the Judy and Joanne Fields, Central North Sea: application to exploration and field development. *Geological Society Special Publication*, 237, 175–206.

Lockhart, R.S. 2010. Behaviour of kerogen-bound biomarkers at elevated levels of thermal maturity. PhD thesis, University of Nottingham.

Lockhart, R.S., Meredith, W., Love, G.D. & Snape, C.E. 2008. Release of bound aliphatic biomarkers via HyPy from Type II kerogen at high maturity. *Organic Geochemistry*, 39, 1119–1124.

Love, G.D., Snape, C.E., Carr, A.D. & Houghton, R.C. 1995. Release of covalently-bound alkane biomarkers in high yields from kerogen via catalytic hydrolysis. *Organic Geochemistry*, 23, 981–986.

Mackenzie, A.S. 1984. Applications of biological markers in petroleum geochemistry. In: Brooks, J. & Welte, D. (eds) *Advances in Petroleum Geochemistry*. Academic Press, London. pp. 115–214.

Meredith, W., Russell, C.A., Cooper, M., Snape, C.E., Love, G.D., Fabbri, D. & Vane, C.H. 2004. Trapping hydrolysis products on silica and their subsequent thermal desorption to facilitate rapid fingerprinting by GC-MS. *Organic Geochemistry*, 35, 61–72.

Meredith, W., Sun, C., Snape, C.E., Sephton, M.A. & Love, G.D. 2006. The use of model compounds to investigate the release of covalently bound biomarkers in hydrolysis. *Organic Geochemistry*, 37, 1705–1714.

Meredith, W., Snape, C.E., Carr, A.D., Nytoft, H.P. & Love, G.D. 2008. The occurrence of unusual hopenes in hydrolysis products generated from severely biodegraded oil seep asphaltenes. *Organic Geochemistry*, 39, 1243–1248.

Murray, I.P., Love, G.D., Snape, C.E. & Bailey, N.J.L. 1998. Comparison of covalently-bound aliphatic biomarkers released via hydrolysis with their solvent-extractable counterparts for a suite of Kimmeridge clays. *Organic Geochemistry*, 29, 1487–1505.

Nielsen, S.B., Clausen, O.R. & McGregor, E. 2017. Basin %Ro: A vitrinite reflectance model derived from basin and laboratory data. *Basin Research*, 29, 515–536.

Peters, K.E., Walters, C.C. & Moldowan, J.M. 2004. *The Biomarker Guide. Volume 2: Biomarkers and isotopes in petroleum systems*. Cambridge University Press. Cambridge.

Petersen, H.I. & Rosenberg, P. 1998. Reflectance retardation (suppression) and source rock properties related to hydrogen-enriched vitrinite in Middle Jurassic coals, Danish North Sea. *Journal of Petroleum Geology*, 21, 247–263.

Petersen, H.I., Andersen, C. Holme, A.C., Carr, A.D. & Thomsen, E. 2012. Vitrinite reflectance gradients of deep wells with thick chalk sections and high pressure: Implications for source rock maturation, Danish–Norwegian Central Graben, North Sea. *International Journal of Coal Geology*, 100, 65–81.

Radke, M.W. & Welte, D.H. 1983. The methylphenanthrene index (MPI). A maturity parameter based on aromatic hydrocarbons. In: Bjoroy, M. (ed) *Advances in Organic Geochemistry*. Wiley, Chichester, 504–512.

Robert, A.M., Grotheer, H., Greenwood, P.F., McCuaig, C.T., Bourdet, J. & Grice, K. 2016. The hydrolysis (HyPy) release of hydrocarbon products from a high maturity kerogen associated with an orogenic Au deposit and their relationship to the mineral matrix. *Chemical Geology*, 425, 127–144.

Rudkiewicz, J-L., Penteadó, H.L. De B., Vear, A., Vandenbrouke, M., Brigaud, F., Wendebourg, J. & Düppenbecker, S.J. 2000. Integrated basin modeling helps to decipher

petroleum systems. In: Mello, M.R. & Katz, B. (eds) *Petroleum Systems of South Atlantic Margins*. AAPG Memoir, 73, 27–40.

Russell, C.A., Meredith, W., Snape, C.E., Love, G.D., Clarke, E. & Moffatt, B. 2004. The potential of bound biomarker profiles released via catalytic hydrolysis to reconstruct basin charging history for oils. *Organic Geochemistry*, 35, 1441–1459.

Saigal, G.C., Bjørlykke, K. & Larter, S. 1992. The effects of oil emplacement on diagenetic processes - Examples from Fulmar reservoir sandstones, Central Graben, North Sea. *AAPG Bulletin*, 76, 1024–1033.

Slater, J.G. & Christie, P.A.F. 1980. Continental Stretching: An explanation of the Post-Mid-Cretaceous subsidence of the Central North Sea Basin. *Journal of Geophysical Research*, 85, 3711–3739.

Sephton, M.A., Meredith, W., Sun, C. & Snape, C.E. 2005a. Hydrolysis as a preparative method for the compound-specific carbon isotope analysis of fatty acids. *Rapid Communications in Mass Spectrometry*, 19, 323–325.

Sephton, M.A., Meredith, W., Sun, C. & Snape, C.E. 2005b. Hydrolysis as a preparative technique for compound-specific carbon isotope ratio measurement of endogenous steroids. *Rapid Communications in Mass Spectrometry*, 19, 3339–3342.

Smith, P.M.R. 1983. Spectral correlation of spore colour standards. In Brooks, J. (ed) *Petroleum geochemistry and exploration of Europe*. Geological Society London Special Publication, 12, 289-294.

Sonibare, O.O., Snape, C.E., Meredith, W., Uguna, C.N. & Love, G.D. 2009. Geochemical characterisation of heavily biodegraded oil sand bitumens by catalytic hydrolysis. *Journal of Analytical and Applied Pyrolysis*, 86, 135–140.

Suggate, R.P. & Dickinson, W.W. 2004. Carbon NMR of coals: the effects of coal type and rank. *International Journal of Coal Geology*, 57, 1–22.

Surdam, R.C., Jiao, Z.S. & Heasler, H.P. 1997. Anomalously pressured gas compartments in Cretaceous rocks of Laramide basins of Wyoming: A new class of hydrocarbon accumulation. In: Surdam, R.C. (ed) *Seals, traps, and the petroleum systems. AAPG Memoir*, 67, 199–222.

Swarbrick, R.E., Osborne, M.J., Grunberger, D., Yardley, G.S., Macleod, G., Aplin, A.C., Larter, S.R., Knight, I. & Auld, H. 2000. Integrated study of the Judy Field (Block 30/7a) - an overpressured Central North Sea oil/gas field. *Marine and Petroleum Geology*, 17, 993–1010.

Swarbrick, R.E., Seldon, B. & Mallon, A.J. 2005. Modelling the Central North Sea pressure history. In: Doré, A.G. & Vining, B.A. (eds) *Petroleum Geology: North-West Europe and Global Perspectives - Proceedings of the 6th Petroleum Geology Conference*. Geological Society of London, 1237–1245.

Sweeney, J.J., & Burnham, A.K. 1990. Evaluation of a simple model of vitrinite reflectance based on chemical kinetics. *AAPG Bulletin*, 74, 1559–1570.

Thorne, J.A. & Watts, A.B. 1989. Quantitative analysis of North Sea subsidence. *AAPG Bulletin*, 73, 78–116.

Uguna, C.N., Carr, A.D., Snape, C.E., Meredith, W. & Díaz, M.C. 2012a. A laboratory pyrolysis study to investigate the effect of water pressure on hydrocarbon generation and maturation of coals in geological basins. *Organic Geochemistry*, 52, 103–113.

Uguna, C.N., Snape, C.E., Meredith, W., Carr, A.D., Scotchman, I.C. & Davis, R.C. 2012b. Retardation of hydrocarbon generation and maturation by water pressure in geological basins: An experimental investigation. In: Peters, K.E. Curry, D.J. & Kacwicz, M. (eds) *Basin Modeling: New Horizons in Research and Applications*. AAPG Hedberg Series No. 4, 19–37.

Uguna, C., Carr, A.D., Snape, C.E. & Meredith, W. 2015. High pressure water pyrolysis of coal to evaluate the role of pressure on hydrocarbon generation and source rock maturation at high maturities under geological conditions. *Organic Geochemistry*, 78, 44–51.

Uguna, C., Carr, A.D., Snape, C.E. & Meredith, W. 2016. Retardation of oil cracking to gas and pressure induced combination reactions to account for viscous oil in deep petroleum basins: Evidence from oil and *n*-hexadecane pyrolysis at water pressures up to 900 bar. *Organic Geochemistry*, 97, 61–73.

Uguna, J.O., Carr, A.D., Marshall, C., Large, D.J, Meredith, W., Jochmann, M., Snape, C.E., Vane, C.H., Jensen, M.A. & Olausson, S. 2017. Improving spatial predictability of petroleum resources within the Central Tertiary Basin, Spitsbergen: A geochemical and petrographic study of coals from the eastern and western coalfields. *International Journal of Coal Geology*, 179, 278–294.

Ungerer, P., Behar, F., Villalba, M., Heum, O.R. & Audibert, A. 1988. Kinetic modelling of oil cracking. *Organic Geochemistry*, 13, 857–868.

Vandenbroucke, M. & Largeau, C. 2007. Kerogen origin, evolution and structure. *Organic Geochemistry*, 38, 719–833.

Vandenbroucke, M., Behar, F. & Rudkiewicz, J–L. 1999. Kinetic modelling of petroleum formation and cracking: implications from the high pressure/high temperature Elgin Field (UK, North Sea). *Organic Geochemistry*, 30, 1105–1125.

Waples, D.W. 1985. Geochemistry in petroleum exploration. Reidel Dordrecht, pp 232.

Wenger, L.M., Davis, C.L., Evensen, J.M., Gormly, J.R. & Mankiewicz, P.J. 2004. Impact of modern deepwater drilling and testing fluids on geochemical evaluations. *Organic Geochemistry*, 35, 1527–1536.

Wilhelms, A. & Larter, S.R. 1994. Origin of tar mats in petroleum reservoirs. Part II: Formation mechanisms for tar mats. *Marine and Petroleum Geology*, 11, 442–456.

Wilhelms, A., Horstad, I. & Karlsen, D. 1996. Sequential extraction - a useful tool for reservoir geochemistry? *Organic Geochemistry*, 24, 1157–1172.

Wilkinson, M. & Haszeldine, R.S. 2011. Oil charge preserves exceptional porosity in deeply buried, overpressured, sandstones: Central North Sea, UK. *Journal Geological Society of London*, 168, 1285–1295.

Wilkinson, M., Darby, D., Haszeldine, R.S. & Couples, G.D. 1997. Secondary porosity generation during deep burial associated with overpressure leak-off: Fulmar Formation, United Kingdom Central Graben. *AAPG Bulletin*, 81, 803–813.

Wilkinson, M., Haszeldine, R.S. & Fallick, A.E. 2006. Hydrocarbon filling and leakage history of a deep overpressured sandstone, Fulmar Formation, UK North Sea. *AAPG Bulletin*, 90, 1945–1961.

Wilkinson, M., Haszeldine, R.S., Morton, A. & Fallick, A.E. 2014. Deep burial dissolution of K-feldspars in a fluvial sandstone, Pentland Formation, UK Central North Sea. *Journal of the Geological Society*, 171, 635–647.

Wu, L., Liao, Y. & Geng, A. 2015. Investigation of hydrolysis released aromatic hydrocarbons from Permian kerogens at different maturities in the Sichuan Basin, China. *Journal of Analytical and Applied Pyrolysis*, 114, 47–59.

Xie, L., Sun, Y., Uguna, C.N., Li, Y., Snape, C.E. & Meredith, W. 2016. Thermal cracking of oil under water pressure up to 900 bar at high thermal maturities 1. Gas compositions and carbon isotopes. *Energy & Fuels*, 30, 2617–2627.

Zanella, E. & Coward, M.P. 2003. Structural Framework. In: Evans, D., Graham, C., Armour, A. & Bathurst, P. (eds) *The Millennium Atlas: Petroleum geology and the central and northern North Sea*. Geological Society, London.

Zou, Y-R. & Peng, P. 2001. Overpressure retardation of organic-matter maturation: a kinetic model and its application. *Marine and Petroleum Geology*, 18, 707–713.

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Figure captions

Fig. 1. Location map showing the location of the Elgin/Franklin complex and the wells in this study within the UK Central Graben (after Lasocki et al. 1999).

Fig. 2. Geological cross section based on the section of Vandenbroucke et al. (1999). 1 – Pentland Formation; 2 – Fulmar Sandstone; 3 – Kimmeridge Clay Formation; a-b Lower Cretaceous; c-d Upper Cretaceous; e-f – Paleogene; g-h – Neogene. A and B represent the location of well 29/4b-6 and Ps-1 pseudowell respectively.

Fig. 3. **(a)** Temperature; **(b)** Pressure history as used by Vandenbroucke et al. (1999) to model oil cracking in Elgin/Franklin Field.

Fig. 4. Stratigraphic column used for modelling (after Lasocki et al. 1999).

Fig. 5. Flow diagram of the experimental procedure.

Fig. 6. TIC of: **(a)** Free oil (*n*-heptane extract); **(b)** Asphaltene bound (HyPy generated) aliphatics (DCM/MeOH extract) from the core at 6390.3 m (well 22/30c-13) of the Elgin Field and 5768.3 m (well 29/5b-8) of the Franklin Field.

Fig. 7. *m/z* 217 showing: **(a)** Steranes present in the free oil (*n*-heptane extract); **(b)** Asphaltene bound (HyPy generated) aliphatics (DCM/MeOH extract) from the core at 6390.3 m (well 22/30c-13) of the Elgin Field and 5768.3 m (well 29/5b-8) of the Franklin Field.

Fig. 8. Comparison of the TIC (in full SCAN mode) of the aromatic fraction from the HyPy of DCM/MeOH extract asphaltenes from **(a)** Elgin Field (6322.6 m); **(b)** Franklin Field (18925.3 ft); **(c)** A typical North Sea oil asphaltene (Blake Field, Moray Firth).

Fig. 9. Comparison of ^1H NMR spectra for the hydropyrolysate aromatics from (a) Franklin Field bitumen sample (5768.3 m); (b) A typical North Sea oil asphaltene (Blake Field, Moray Firth).

Fig. 10. Transmitted slide of Franklin Field (well 29/5b-6) Kimmeridge Clay Formation (KCF) sample (depth 5114.6 m) showing a mixture of humic (black) and orange-brown oil-prone kerogen.

Fig. 11. Burial histories: (a) Well 29/5b-6; (b) Ps-1 pseudowell.

Fig. 12. Thermal history models of well 29/5b-6 and Ps-1 pseudowell as used for maturation and hydrocarbon generation modelling.

Fig. 13. (a) VR depth plot; (b) Pressure-depth plot for well 29/5b-6 showing good match between measured and predicted values using the PresRo[®] kinetic model.

Fig. 14. Temperature and overpressure histories of top and base Fulmar reservoir in 29/5b-6 well.

Fig. 15. Hydrocarbon generation histories: (a) Well 29/5b-6; (b) Ps-1 pseudowell derived using the PresRo[®] kinetic model.

Fig. 16. VR-depth plot for UK and Danish Central Graben dataset obtained from Carr (2003), Carr and Petersen (2004), Isaksen (2004), Petersen et al. (2012), and unpublished well data for the Danish, Norwegian and UK Central Grabens. Only some of the highest and lowest VR data at different depths from the Isaksen (2004) dataset are shown to illustrate the general consistency between VR data for the 29/5b-6 VR with the VR data from other Central Graben wells.

Fig. 17. Elgin/Franklin paragenetic sequence based on the sequences produced by Lasocki et al. (1999) and Hendry (2000a), modified to reflect the thermal history shown in Fig. 12a.

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Table 2. Aromatic hydrocarbon ratios from the HyPy of the Elgin/Franklin Field bitumen asphaltene compared to those from a typical North Sea oil asphaltene (Blake Field, Moray Firth)

Sample	North Sea oil	Elgin - 22/30c-13	Franklin - 29/5b-8	
	asphaltene	6322.6 m	5768.3 m	5854.6 m
MPI-1 *	0.78	0.89	0.90	1.03
MPI-3 *	1.92	1.83	1.63	1.76
m/z 178/192 †	0.93	0.74	0.65	0.56
m/z 178/252 ‡	1.41	1.01	2.32	1.02

* MPI (methylphenanthrene index) - Calculated from the intensities of the 4 methylphenanthrene isomers seen in the m/z 192 mass chromatogram and the intensity of phenanthrene in the m/z 178 mass chromatogram (from Radke & Welte 1983).

† The abundance of phenanthrene in the m/z 178 mass chromatogram / the total abundance of the 4 methylphenanthrene isomers in the m/z 192 mass chromatogram.

‡ The abundance of phenanthrene (3 rings) in the m/z 178 mass chromatogram / the total abundance of benzopyrene (5 rings) in the m/z 252 mass chromatogram.

Table 3. *Vitrinite reflectance data from well 20/5b-6, Franklin Field*

Depth (m)	Vitrinite reflectance (% Ro)	No. of measurements	Standard deviation
914.4	0.26	6	0.026
1371.6	0.30	4	0.063
1828.8	0.31	7	0.031
2743.2	0.38	2	0.070
3078.5	0.47	3	0.084
3200.4	0.54	6	0.073
3322.4	0.48	3	0.019
3417.5	0.51	5	0.031
4968.3	0.64	3	0.037
5114.6	0.72	1	-
5132.9	0.66	3	0.033

































