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Supplementary information for

Rhenium-Osmium geochronology of UK Atlantic Margin oil: Implications for global petroleum systems

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Geology

The West of Shetland Basin petroleum system is a rifted fault block and graben province of Tertiary to Mesozoic age running along the UK Atlantic margin between the West Shetland platform and Faeroe Islands (Carruth et al 2003; Mark 2010; Spencer et al 1999). A large body of geochemical and basin modelling research indicate a significant Upper Jurassic marine source with minor Middle Jurassic terrestrial input for UK Atlantic margin oils (Spencer et al., 1999; Mark et al., 2008; Scotchman et al., 2006; Leach et al., 1999; Lamers and Carmichael, 1999; Scotchman and Carr, 2005; Parnell et al., 2005; Hols et al., 1999; Rooney et al., 1998; Cornford et al., 1998; Scotchman et al., 1998; Mark et al., 2005; Scotchman et al., 2006). Reservoirs are found in fractured basement, Devonian (e.g. structural trapped Clair field; Spencer et al., 1999; Carruth et al., 2003), Jurassic and Palaeogene sediments (e.g. Stratigraphically trapped Foinaven and Schiehallion fields; Fig.1; Fig. DR1; Spencer et al., 1999; Mark et al., 2010).

The Devonian and Early Carboniferous collapse of the Caledonian orogenic belt formed deep, sinistral transtensional basins. Faulting reversed in the Carboniferous and transpression, lead to basin inversion (De Paola et al., 2005; Carruth et al 2003). Boreal rifting in the Permian and Triassic reactivated existing faults and lead to the deposition of fluvial clastics and evaporates. Jurassic marine transgression lead to localised early Jurassic deposition, however, the majority of Middle Jurassic costal sediments lie uncomfortably on Triassic deposits. Late Jurassic/ Early Cretaceous central Atlantic rifting formed the, Westray, Flett and Rona Ridge fault blocks and surrounding sub-basins (Fig. 1). Continued transgression lead to anoxic conditions within these sub-basins and the deposition of an organic rich marine shale, equivalent to the North Sea Kimmeridge Clay Formation (Carruth et al 2003, Spencer et al 1999 Scothchman et al., 2006). Thermal subsidence ensured continued sediment deposition which, by the end of the Cretaceous, caused buried Jurassic sediments to become mature (Carruth et al 2003, Spencer et al 1999, Scotchman et al., 2006). The Early Palaeocene Icelandic plume lead to the formation of the Faeroes Platform through flood volcanism as well as uplift of the Shetland Platform. Denudation of the Shetland Platform formed coarse turbidites in the Foinaven Sub-basin and periodic deposition, during marine lowstands, in the Flett Sub-basin (Carruth et al 2003). Decreased subsistence rates in the Late Palaeocene / Eocence drove marine regression which, combined with filling of accommodation space, lead to the deposition of fluvial / deltaic sediments sourced from the eroding east Shetland Platform (Carruth et al 2003). These sediments form a ~3 km thick Palaeocene sedimentary succession containing present day reservoirs (Spencer et al 1999). Oligocene/Miocene north-south compressions reactivated major NW/SE trending faults and inverted Palaeocene basins. Miocene thermal cooling lead to the subsidence and collapse of the Atlantic margin and present day deep sea floor levels (Carruth et al 2003, Spencer et al 1999 Mark 2010).

Re – Os analytical methodology

Rhenium and Os analysis was conducted at the Northern Centre for Isotopic and Elemental Tracing facility at Durham University following the analytical protocols of Selby and Creaser (2003); Selby (2007) and Selby et al. (2007).

Asphaltene was separated for from 18 oils from the UK Atlantic Margin (Fig.1) using the *n*–heptane based methodology of Speight (1998) and Selby et al. (2007). In summary, in a 60 ml glass vial, 40 ml of *n*–heptane was added to 1 g of oil. The contents were thoroughly mixed and agitated for ~12 hrs. The contents of the vial were then transferred to a 50 ml centrifuge tube and centrifuged at 4000 rpm for 5 minutes to ensure complete separation of the soluble maltene and insoluble asphaltene fractions. The maltene fraction was decanted to waste and the asphaltene fraction was dried on a hot plate at ~60˚C.

Using the carius tube technique (Shirey and Walker, 1995) ~0.1 – 0.2 g of asphaltene was dissolved with a known volume of ^{190}Os and ^{185}Re spike solution in 9 ml of inverse *aqua regia* (6 ml of 16 N HNO_3 and 3 ml of 12 N HCl) at 220°C for 24 hrs. Osmium was purified from the inverse *aqua regia* solution using solvent extraction ($CHCl_3$) and micro-distillation methods. After the removal of Os, the Re bearing inverse *aqua regia* solution was evaporated to dryness at 80˚C and then re-dissolved in 3 ml 0.2 N HNO_3 in preparation for Re anion exchange chromatography. The purified Re and Os were loaded onto a Ni and Pt filaments respectively, and analysed for their isotopic compositions using Negative Thermal Ionisation Mass Spectrometry (NTIMS; Volkening et al., 1991; Creaser et al., 1991) on a ThermoElectron (TRITON) mass spectrometer. Re was measured using Faraday collectors and Os in peak hopping mode using a secondary electron multiplier.

Total procedural blanks for Re and Os 2.4 and <0.7 pg, respectively, with $^{187}Os/^{188}Os$ value of ~0.18 (n = 2). Raw Re and Os oxide values were corrected for oxygen contribution and mass fractionation. The Re and Os isotopic values and elemental abundances are calculated by full propagation of uncertainties from Re and Os mass spectrometer measurements, blank abundance and isotopic composition, spike calibration and sample and spike weights. Throughout the period of this study, in house Re and Os standard solutions were repeatedly analysed to monitor instrument reproducibility. The Re standard runs produced average $^{185}Re/^{187}Re$ values of 0.59838 ± 0.00185 (1S.D. n = 41) identical to the reported values of Selby (2007; 0.5977 ± 0.0012). The NCIET Re standard is made from zone-refined Re ribbon in the same way to the in house Re standard (AB1) of the Department of Earth Sciences, University of Alberta, and the $^{185}Re/^{187}Re$ values are indistinguishable to AB1 values reported by Selby and Creaser (2003; 0.59863 ±0.00062) and Selby et al. (2005; 0.5986 ± 0.0006). The measured difference between our reported $^{185}Re/^{187}Re$ values and the accepted $^{185}Re/^{187}Re$ value (Gramlich et al., 1973) is used to correct for sample mass fractionation. The Os (AB2) standard, is made from ammonium hexachloro-osmate. The average $^{187}Os/^{188}Os$ AB2 ratio, using the electron multiplier, is 0.10678 ± 0.00037 (1 S.D. n = 45), identical to AB2 values reported by Selby and Creaser (2003; 0.106838 ±0.000029), Selby et al. (2005; 0.10684 ± 0.00009) and Selby (2007; 0.10679 ± 0.00007).

Two Re-Os ages in UKAM oils?

This study presents Re-Os asphaltene data that regress to form a 68 ± 13 Ma generation age (see main text). Interestingly the majority of the samples (n = 16) yield Os_i that form two distinct families that possess values of ~1.02 and 1.11. When these data are regressed separately they produce precise ages of 64.3 ± 3.9 Ma (MSWD = 2.1) and 71.9 ± 5 Ma (MSWD 1.02), suggesting the possibility that these samples record two separate generation events. However, because these dates overlap within uncertainty these separate ages must be treated with caution.

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Figure Caption

Figure DR1. Geological column for the UK Atlantic margin compiled from Nadin et al., 1997; Spencer et al., 1999; Carruth, 2003; Scotchman et al., 2006; and Mark et al., 2010.

Figure DR1 Finlay et al., 20XX

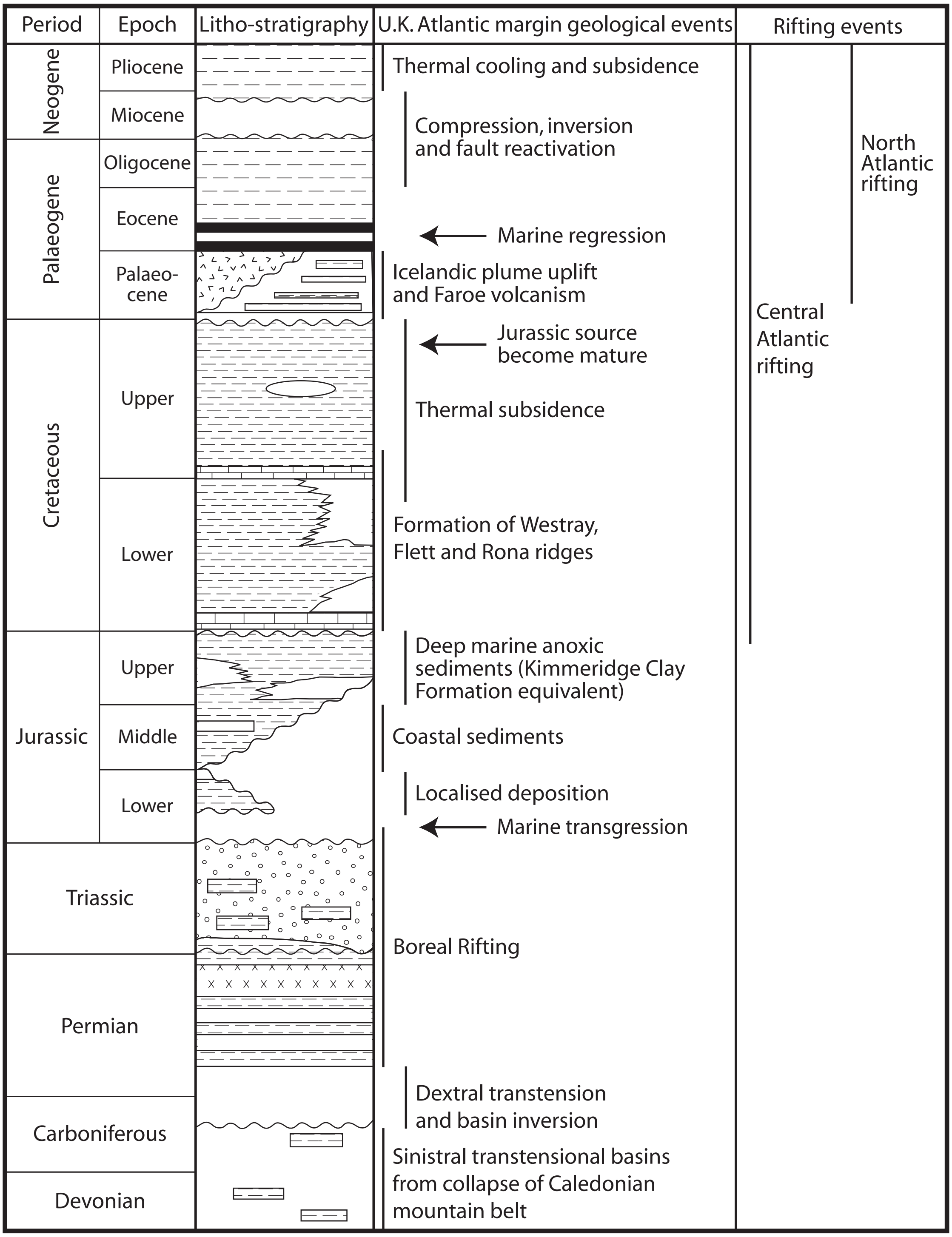

TABLE DR1. GEOCHEMISTRY DATA FOR UK ATLANTIC MARGIN OIL.

Well* G Number[†§] Oil field	206/8-2 G5400[§] G	206/8-2 5401[§] G01	206/8-3A 24[†] G01 Clair S	206/8-3A 204/ 23[†] G2	20-5 851[§] G2	204/20-5 851[§] G27 chiehallion	204/19-3A 204/ 49[§] G	19-3A 2750[§] G27 Cuillin	204/19-3A 62[§] G	PFJ-1160 5234[§] G	PFJ-1187 5271[§] G	PFJ-1247 5306[§] G Foinaven	204/24A-1 20 2075[†] G27	4/24A-1 63[†]	Mean S	.D.	Range for KCF sourced oils[§§]
Saturates (%)	39.6	39.8	46.5	39.0	59.9	70.1	47.3	51.5	54.2	62.0	N.D.[††]	61.8	63.9	58.6	53.4	10.3	N.D.[††]
Aromatics (%)	41.4	42.7	37.1	40.0	30.9	25.5	42.0	39.6	37.7	34.3	N.D.[††]	34.9	32.7	37.1	36.6	4.9	N.D.[††]
Residual (%)	19.1	17.5	16.4	21.0	9.2	4.4	10.7	8.9	8.1	3.7	N.D.[††]	3.3	3.4	4.3	10.0	6.4	N.D.[††]
Saturates/Aromatic s	1.0	0.9	1.3	1.0	1.9	2.8	1.1	1.3	1.4	1.8	N.D.[††]	1.8	2.0	1.6	1.5	0.48	0.6 − 8.0
δ^{13}C Whole Oil	-29.5	-29.5	-29.5	-29.7	-29.5	-29.5	-29.4	-29.4	-29.4	-29.6	N.D.[††]	-29.6	-29.6	-29.5	-29.5	0.1	-27.1 − -30.4
δ^{13}C Saturates	-30.2	-30.3	-30.2	-30.2	-30.3	-30.1	-29.7	-30.0	-30.1	-30.2	N.D.[††]	-30.1	-30.1	-30.1	-30.1	0.2	N.D.[††]
δ^{13}C Aromatics	-29.0	-29.0	-28.8	-28.9	-29.1	-29.3	-29.1	-28.9	-29.2	-29.0	N.D.[††]	-28.9	-28.8	-28.8	-29.0	0.2	N.D.[††]
Pr[#]/Ph[**]	1.9	1.9	N.D.[††]	N.D.[††]	1.5	1.4	f	1.9	1.5	1.7	N.D.[††]	1.6	N.D.[††]	N.D.[††]	1.7	0.2	0.6 − 1.9
Pr/nC_{17}	0.5	0.5	N.D.[††]	N.D.[††]	1.0	1.0	f	0.8	0.7	1.6	N.D.[††]	1.4	N.D.[††]	N.D.[††]	0.9	0.4	0.3 − 1.0
Ph/nC_{18}	0.3	0.3	N.D.[††]	N.D.[††]	0.7	0.7	f	0.5	0.5	1.0	N.D.[††]	0.9	N.D.[††]	N.D.[††]	0.6	0.2	0.2 − 1.1
C_{27} sterane (%)	N.D.[††]	N.D.[††]	29.5	33.0	35.0	33.7	33.7	N.D.[††]	31.4	N.D.[††]	35.0	N.D.[††]	33.1	33.7	33.1	1.7	N.D.[††]
C_{28} sterane (%)	N.D.[††]	N.D.[††]	33.0	26.6	29.0	29.6	28.7	N.D.[††]	36.4	N.D.[††]	30.0	N.D.[††]	28.3	27.9	30.0	3.0	N.D.[††]
C_{29} sterane (%)	N.D.[††]	N.D.[††]	37.5	40.4	36.0	36.7	37.6	N.D.[††]	32.2	N.D.[††]	35.0	N.D.[††]	38.6	38.4	36.9	2.4	N.D.[††]

*UK grid
[†]B.P. Unpublishe data
[§]Data from this study
[#]Pristane
**Phytane
[††]No Data
[§§]Cornford et al. (1998)

TABLE DR2. Re-Os ASPHALTINE RESULTS FOR UK ATLANTIC MARGIN OIL

Well*	"G" Number	Field co	Asphaltene ntent %	Re (ppb)			Os (ppt)			$^{187}Re/^{188}Os$			$^{187}Os/^{188}Os$			rho	Os$_i$†		
206/8-2	G5399	Clair	3.5	2.18	±	0.01	294.7	±	3.5	40.0	±	0.9	1.079	±	0.031	0.684	1.03	±	0.02
206/8-2	G5400	Clair	1.9	2.24	±	0.01	312.0	±	2.8	38.7	±	0.6	1.037	±	0.021	0.656	0.99	±	0.01
206/8-2	G5401	Clair	1.6	2.32	±	0.01	316.9	±	2.8	39.6	±	0.6	1.062	±	0.021	0.656	1.02	±	0.01
206/8-2	G5402	Clair	3.1	2.18	±	0.01	295.9	±	2.7	39.8	±	0.6	1.067	±	0.021	0.654	1.02	±	0.01
206/8-2	G5403	Clair	3.1	2.64	±	0.02	349.2	±	3.1	40.9	±	0.6	1.068	±	0.021	0.653	1.02	±	0.01
206/8-2	G5404	Clair	4.5	1.83	±	0.01	260.8	±	2.4	38.0	±	0.6	1.054	±	0.022	0.658	1.01	±	0.01
206/8-3A	G0124	Clair	8.0	1.39	±	0.04	68.8	±	1.7	111	±	6	1.22	±	0.08	0.688	1.09	±	0.05
206/8-3A	G0123	Clair	4.3	1.47	±	0.04	226.8	±	2.8	35.1	±	1.2	1.055	±	0.032	0.485	1.02	±	0.02
204/20-5	G2851	Schiehallion	1.2	2.80	±	0.02	180.3	±	3.8	84.7	±	3.7	1.14	±	0.07	0.719	1.04	±	0.04
204/19-3A	G2749	Cuillin	1.7	6.00	±	0.04	208.4	±	1.5	158	±	2	1.163	±	0.016	0.627	0.98	±	0.01
204/19-3A	G2750	Cuillin	1.6	20.8	±	0.1	180.0	±	1.6	673	±	9	1.741	±	0.026	0.740	0.98	±	0.01
204/19-3A	G2762	Cuillin	2.8	4.49	±	0.03	45.4	±	0.7	581	±	16	1.81	±	0.06	0.852	1.15	±	0.02
PFJ-1160	G5234	Foinaven	0.4	2.58	±	0.04	182.6	±	2.0	77.7	±	1.9	1.222	±	0.028	0.589	1.13	±	0.02
PFJ-1187	G5271	Foinaven	0.4	2.57	±	0.04	176.8	±	1.9	79.6	±	1.8	1.188	±	0.027	0.598	1.10	±	0.02
PFJ-1247	G5306	Foinaven	0.4	2.74	±	0.04	182.6	±	1.9	82.4	±	1.8	1.212	±	0.027	0.604	1.12	±	0.02
PFJ-1246	G5307	Foinaven	-	18.6	±	0.1	151.4	±	1.7	74.4	±	2.0	1.200	±	0.029	0.574	1.12	±	0.02
204/24A-1	G2075	Foinaven	1.2	1.63	±	0.04	62.1	±	1.2	142	±	7	1.08	±	0.05	0.731	0.92	±	0.03
204/24A-1	G2763	Foinaven	0.8	0.74	±	0.04	54.6	±	1.5	76	±	6	1.34	±	0.10	0.597	1.25	±	0.07

All uncertainties shown are 2σ.

*UK North Sea grid.

†Os$_i$ = 187Os/188Os calculated at the time of oil generation (68 Ma).