



Evaluating Re–Os systematics in organic-rich sedimentary rocks in response to petroleum generation using hydrous pyrolysis experiments

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Abstract

Successful application of the ^{187}Re – ^{187}Os geochronometer has enabled the determination of accurate and precise depositional ages for organic-rich sedimentary rocks (ORS) as well as establishing timing constraints of petroleum generation. However, we do not fully understand the systematics and transfer behaviour of Re and Os between ORS and petroleum products (e.g., bitumen and oil). To more fully understand the behaviour of Re–Os systematics in both source rocks and petroleum products we apply hydrous pyrolysis to two immature hydrocarbon source rocks: the Permian Phosphoria Formation (TOC = 17.4%; Type II-S kerogen) and the Jurassic Staffin Formation (TOC = 2.5%; Type III kerogen). The laboratory-based hydrous pyrolysis experiments were carried out for 72 h at 250, 300, 325 and 350 °C. These experiments provided us with whole rock, extracted rock and bitumen and in some cases expelled oil and asphaltene for evaluation of Re–Os isotopic and elemental abundance.

The data from these experiments demonstrate that the majority (>95%) of Re and Os are housed within extracted rock and that thermal maturation does not result in significant transfer of Re or Os from the extracted rock into organic phases. Based on existing thermodynamic data our findings suggest that organic chelating sites have a greater affinity for the quadrivalent states of Re and Os than sulphides.

Across the temperature range of the hydrous pyrolysis experiments both whole rock and extracted rock $^{187}\text{Re}/^{188}\text{Os}$ ratios show small variations (3.3% and 4.7%, for Staffin, respectively and 6.3% and 4.9% for Phosphoria, respectively). Similarly, the $^{187}\text{Os}/^{188}\text{Os}$ ratios show only minor variations for the Staffin and Phosphoria whole rock and extracted rock samples (0.6% and 1.4% and 1.3% and 2.2%). These isotopic data strongly suggest that crude oil generation through hydrous pyrolysis experiments does not disturb the Re–Os systematics in ORS as supported by various studies on natural systems.

The elemental abundance data reveal limited transfer of Re and Os into the bitumen from a Type III kerogen in comparison to Type II-S kerogen (0.02% vs. 3.7%), suggesting that these metals are very tightly bound in Type III kerogen structure. The $^{187}\text{Os}/^{188}\text{Os}$ data from the pyrolysis generated Phosphoria bitumens display minor variation (4%) across the experimental temperatures, with values similar to that of the source rock. This indicates that the isotopic composition of the bitumen reflects the isotopic composition of the source rock at the time of petroleum generation. These data further support the premise that the Os isotopic composition of oils and bitumens can be used to fingerprint petroleum deposits to specific source rocks.

Oil generated through the hydrous pyrolysis experiments does not contain appreciable quantities of Re or Os (~120 and ~3 ppt, respectively), in contrast to natural oils (2–50 ppb and 34–288 ppt for Re and Os, respectively), which may suggest

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that kinetic parameters are fundamental to the transfer of Re and Os from source rocks to oils. From this we hypothesise that, at the temperatures employed in hydrous pyrolysis, Re and Os are assimilated into the extracted rock as a result of cross-linking reactions.

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1. INTRODUCTION

The application and analytical advancements of the rhenium–osmium (Re–Os) geochronometer has permitted the determination of accurate and precise ($\leq \pm 1\%$) depositional ages for organic-rich sedimentary rocks (ORS), which have been invaluable for timescale calibration of sedimentary horizons lacking more established chronostratigraphic markers (Ravizza and Turekian, 1989; Cohen et al., 1999; Selby and Creaser, 2003, 2005a; Kendall et al., 2004, 2006, 2009a,b; Anbar et al., 2007; Selby, 2007; Turgeon et al., 2007; Yang et al. 2009; Rooney et al., 2010, 2011). These studies also demonstrate that petroleum generation, flash pyrolysis and/or polyphase metamorphism do not significantly affect the Re–Os ORS systematics. Specifically, the Re–Os ORS systematics have been shown to remain undisturbed at pressures up to 6 kbar and temperatures $>650^\circ\text{C}$ resulting from contact and regional metamorphism (Rooney et al., 2010, 2011). In contrast, interactions with low temperature ($\sim 100^\circ\text{C}$) hydrothermal fluids have been shown to disturb Re–Os systematics in ORS (Cooke et al., 1998; Kendall et al., 2009b; Rooney et al., 2011).

Crude oil generated from ORS through the maturation of organic matter is enriched in Re and Os, which has been transferred from source rocks (Barre et al., 1995; Woodland et al., 2001; Selby and Creaser, 2005b; Selby et al., 2007; Finlay et al., 2010). Applying Re–Os geochronology directly to crude oil has yielded ages that are in excellent agreement with basin models and are suggested to constrain petroleum generation events (Selby et al., 2005; Selby and Creaser, 2005a; Finlay et al., 2011a). Our present understanding suggests that Re and Os may be bound in crude oil by heteroatomic ligands or other metallo–organic complexes (Selby et al., 2007). However, we do not fully understand the elemental and isotopic behaviour of Re and Os in the ORS–crude oil system. Specifically, we have a limited understanding of the complexation and transfer of Re and Os and the Re–Os isotope systematics in and from ORS to crude oil as a result of petroleum generation.

To improve our understanding of Re and Os complexation in ORS and their transfer behaviour and the Re–Os isotope systematics from ORS to crude oil it is crucial to fully understand Re–Os systematics during petroleum generation. Laboratory-based hydrous pyrolysis experiments allow us to mimic natural petroleum generation of source rocks on a suitable timescale. Herein, we use this technique to evaluate the complexation of Re and Os in ORS and their transfer behaviour from ORS to crude oil.

Hydrous pyrolysis is an experimental technique that simulates the maturation, generation and expulsion of immiscible oil that is physically and chemically similar to natural crude oils (Lewan, 1979, 1985, 1997; Ruble et al., 2001; Lewan and Ruble, 2002). Hydrous pyrolysis

experiments provide realistic conditions for the generation of immiscible oil under laboratory conditions primarily because it involves the generation of an intermediate bitumen component during maturation (Lewan and Ruble, 2002). The generation of this intermediate bitumen component permits the separation and expulsion of oil from the polar-rich, water-saturated bitumen. The experiments result in the generation of three organic phases; bitumen, immiscible oil and gas (Ruble et al., 2001).

We present results from a series of hydrous pyrolysis experiments on immature Phanerozoic ORS, designed to mimic natural petroleum generation in an effort to evaluate Re and Os location in ORS and the transfer mechanisms of Re and Os in ORS to crude oil. Furthermore, this work enables us to enhance our understanding of the Re–Os isotope systematics of crude oil, in particular, the use of the Re–Os isotope system for fingerprinting oils. In addition to hydrous pyrolysis experiments on immature ORS, a hydrous pyrolysis experiment on a naturally occurring Phosphoria oil was carried out to assess the effects of this procedure on Re and Os abundances and isotopic data on natural oils.

2. SAMPLES

2.1. Staffin and Phosphoria Formations

The Jurassic Staffin and Permian Phosphoria Formations were selected for hydrous pyrolysis experiments as each formation is composed of a distinct kerogen type (Type III and II-S, respectively), have elevated total organic carbon (TOC) values and are immature with respect to petroleum generation (Table 1). These two samples provide an ideal opportunity to evaluate the occurrence of Re and

Table 1
Geochemical parameters of starting rocks used in the hydrous experiments.

Sample	TOC (wt.%)	T_{max} ($^\circ\text{C}$)	S1	S2	Bitumen (wt.%)	Asphaltene (wt.%)
Staffin Shale Formation ^a	2.5	431	0.03	4.05	0.03	7.9
Phosphoria Formation ^b	17.4	418	2.46	101.42	1.60	34

TOC = total organic carbon.

T_{max} = temperature ($^\circ\text{C}$) of the maximum formation of hydrocarbons by cracking of kerogen and has an uncertainty of $\pm 1\text{--}3^\circ\text{C}$ (Peters, 1986; Behar et al., 2001).

S1 = mg of hydrocarbons (free and thermovapourisable) per gram of rock.

S2 = mg of hydrocarbons (cracking of kerogen) per gram of rock (Peters, 1986).

^a Type III kerogen.

^b Type II-S kerogen.

Os in organic phases of immature ORS and the effect of petroleum generation on Re–Os systematics in ORS.

2.1.1. Jurassic Staffin Formation

Approximately 6 kg of the Jurassic Staffin Formation was sampled from a bed ~15 cm thick at Staffin Bay, Skye, Scotland (57°39'42.00"N, 6°14'45.26"W). The sample consists of dark grey and black clays and silty-shales from Bed 35 of the Flodigarry Shale Member (Matyja et al., 2006; Selby, 2007). In addition to the 6 kg sample, three other samples from Bed 35 were taken along its strike to provide an insight on the naturally occurring variation in Re and Os abundances in ORS from the same stratigraphy (Staffin 182-5, Staffin DSa, and DSb). A Re–Os age of 154.1 ± 2.2 Ma (2σ) provides accurate geochronology for the Oxfordian–Kimmeridgian boundary marked by the Flodigarry Shale Member (Selby, 2007). The thermal maturity, TOC and hydrogen and oxygen index values were determined (see Section 3). The samples are thermally immature with respect to petroleum generation with a T_{\max} value of 431 °C (Table 1). The samples have TOC values of approximately 2.5 wt.% and extractable organic matter

(bitumen) constituting 0.01 wt.% (Table 1). The hydrogen and oxygen index values of 176 and 23, respectively, indicate that the Staffin Formation contains a gas-prone Type III kerogen (Tissot and Welte, 1984; Peters, 1986; Vandenbroucke, 2003). The Staffin samples are enriched in Re and Os: ~14 ng/g and ~200 pg/g, respectively, (Table 2) relative to average continental crust (~0.2–2 ng/g Re and 30–50 pg/g Os; Esser and Turekian, 1993; Peucker-Ehrenbrink and Jahn, 2001; Hattori et al., 2003; Sun et al., 2003). Bed 35 has $^{187}\text{Re}/^{188}\text{Os}$ ratios of 355 and radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios of 1.477 (Selby, 2007; this study).

2.1.2. Permian Phosphoria Formation

Approximately 20 kg of the Permian Phosphoria Formation was sampled from a bed ~16 cm thick at Retort Mountain quarry, Beaverhead, Montana, USA. (Lewan, 1978, 1985). The Phosphoria Formation is a fine-grained argillaceous phosphatic claystone with minor amounts of pyrite (Lewan et al., 1986). The Phosphoria samples have elevated TOC values of 17.4 wt.% and extractable bitumen constituting 1.6 wt.%, of which 34 wt.% is asphaltene (this study; Table 1). The samples are thermally immature with

Table 2
Re and Os abundance data of the original rock, recovered rock, extracted rock and bitumen for the Staffin Formation.

Fraction	Re (ng/g fraction)		Re (ng/g orig rock)	Re $D\%$ ^a	Os (pg/g fraction)		Os (pg/g orig rock)	Os $D\%$ ^a
	Mean	±			Mean	±		
Original rock								
Staffin 182-5	14.9	0.05	14.9		189.8	1.1	189.8	
Staffin DSa	13.4	0.08	13.4		193.9	0.6	193.9	
Staffin DSb	13.2	0.04	13.2		199.1	0.8	199.1	
Recovered rock								
Average	13.8	0.05	13.8		219.4	1.1	219.4	
Extracted rock	13.8	0.02	13.8		200.6	0.2	200.6	
Extracted rock								
Bitumen	14.0	0.05	14.0		224.4	1.1	224.4	
Total ^b	3.8	0.31	0.001		194.9	10.4	0.053	
			14.0	1.8			224.4	2.2
250 °C for 72 h								
Recovered rock	14.0	0.05	13.0		219.3	1.1	204.7	
Extracted rock	13.8	0.05	12.9		220.1	1.1	205.3	
Bitumen	1.1	0.18	0.001		8.2	3.9	0.004	
Total ^b			12.9	−1.0			205.3	0.3
300 °C for 72 h								
Recovered rock	13.6	0.05	12.6		224.7	1.1	208.2	
Extracted rock	13.5	0.05	12.5		231.7	1.1	214.4	
Bitumen	1.4	0.07	0.002		2.1	1.6	0.0003	
Total ^b			12.5	−0.5			214.4	2.9
325 °C for 72 h								
Recovered rock	13.6	0.05	12.5		224.7	1.1	207.0	
Extracted rock	14.2	0.06	13.0		229.8	1.1	211.1	
Bitumen	2.1	0.06	0.003		3.9	1.3	0.005	
Total ^b			13.0	4.0			211.1	1.9
350 °C for 72 h								
Recovered rock	13.3	0.04	12.2		226.4	1.1	206.9	
Extracted rock	14.5	0.05	13.2		222.7	1.1	203.0	
Bitumen	0.4	0.07	0.001		0.3	1.7	0.001	
Total ^b			13.2	7.9			203.0	−1.9

Sample Staffin 182-5 is from Bed 35 of Matyja et al. (2006) and Selby (2007); DSa and DSb are from Selby (2007).

^a DRe and DOs = total metal (extracted rock + bitumen)/recovered rock × 100.

^b Total = extracted rock + bitumen.

Table 3

Re and Os abundance data of the original rock, recovered rock, extracted rock and bitumen for the Phosphoria Formation.

Fraction	Re (ng/g fraction)		Re (ng/g orig rock)	Re <i>D</i> % ^a	Os (pg/g fraction)		Os (pg/g orig rock)	Os <i>D</i> % ^a
	Mean	±			Mean	±		
Original rock								
Aliquot 1	504.9	1.6	504.9		3377	16	3377	
Aliquot 2	469.8	1.5	469.8		3267	12	3267	
Aliquot 3	452.6	1.5	452.57		3122	9	3122	
Aliquot 4	477.1	1.5	477.1		3295	11	3295	
Average	476.1	21.8	476.1		3265	106	3265	
Extracted rock	486.5	1.5	478.7		3116	11	3065	
Bitumen	61.0	0.2	1.0		145	2	2	
Total ^b			479.68	0.5	3260		3068	−7.4
250 °C for 72 h								
Recovered rock	440.2	1.5	427.1		3215	11	3119	
Extracted rock	401.1	1.5	380.5		2838	11	2692	
Bitumen	115.0	0.4	2.5		228	2	5	
Total ^b			382.97	−11.5	3269		2697	−15.7
300 °C for 72 h								
Recovered rock	457.3	1.5	434.5		3209	11	3049	
Extracted rock	443.2	1.5	374.7		3419	11	2891	
Bitumen	133.9	0.4	14.0		314	3	33	
Total ^b			388.69	−11.8	3743		2923	−4.3
325 °C for 72 h								
Recovered rock	554.4	1.5	504.0		3496	11	3178	
Extracted rock	484.3	1.5	396.6		3568	11	2922	
Bitumen	93.7	0.3	8.5		188	2	17	
Total ^b			405.02	−24.4			2939	−8.1
350 °C for 72 h								
Recovered rock	547.3	1.5	478.0		3814	11	3331	
Extracted rock	501.7	1.5	413.3		3442	11	2835	
Bitumen	3.9	0.03	0.2		34	1	2	
Asphaltene of oil	0.1	0.002			5.6	0.7		
Total ^b			413.5	−15.6			2837	−17.4

^a DRe and DOs = total metal (extracted rock + bitumen)/recovered rock × 100.^b Total = extracted rock + bitumen.

respect to petroleum generation with a T_{\max} value of 418 °C (Table 1). The extracted rock of the Phosphoria Formation is predominantly amorphous organic matter with a sulphur content of 1.8 wt.%, and hydrogen and oxygen index values of 582 and 9, respectively (Lewan, 1985). These values indicate that this Phosphoria Formation sample possesses an oil-prone Type II-S kerogen (Tissot and Welte, 1984; Lewan, 1985; Orr and Sinninghe Damste, 1990; Vandenbroucke, 2003). The Phosphoria samples are also greatly enriched in Re and Os with abundances of ~470 ng/g and ~3300 pg/g, respectively (this study; Table 3) and possess elevated $^{187}\text{Re}/^{188}\text{Os}$ ratios of 988 and radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratios of 3.314 (this study).

3. METHODOLOGY

The entire Staffin and Phosphoria Formation sample sets were crushed, without metal contact, to small rock fragments (~1 × 1 × 1 cm), with any weathered surface material removed. Randomly selected 400 g aliquots of the rock fragments constituted the material for the 10 individual experiments. One subset from the Staffin (and Staffin

samples Staffin 182-5, DSa, DSb) and from the Phosphoria set were analysed to establish the variation in Re and Os abundance and isotopic compositions of the non-pyrolysed rock and for the hydrous pyrolysis experiments. The non-pyrolysed samples were analysed for TOC and T_{\max} parameters. The pyrolysed samples were analysed for their Re and Os abundances and isotopic compositions. The bitumen fraction of the Staffin and Phosphoria pyrolysed and non-pyrolysed samples was extracted for Re–Os analysis. Fig. 1 outlines the major analytical and experimental procedures employed during this study.

3.1. TOC and T_{\max} analysis

TOC values and thermal maturity data for the Phosphoria Formation were determined using Rock–Eval pyrolysis (Peters, 1986; Hunt, 1996) at the TOTAL Geochemistry and Fluids Laboratory (Pau, France). The TOC values and thermal maturity data for the Staffin samples were generated using a SR Analyser machine by Weatherford, Houston, USA. T_{\max} is a laboratory temperature that represents the temperature of maximum hydrocarbon

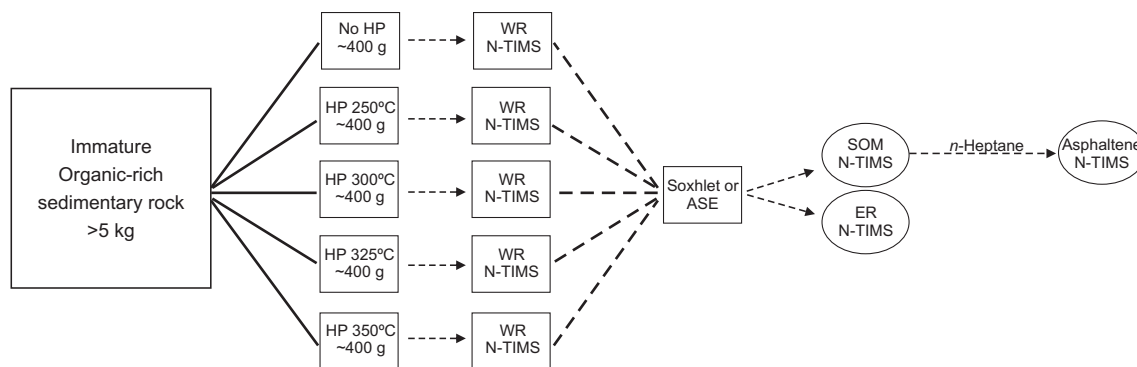


Fig. 1. Schematic flowchart outlining the hydrous pyrolysis and Re–Os analytical techniques employed in this study. The term WR denotes whole rock and each of the ten aliquots (two sample sets at five various temperatures) underwent Negative-Thermal Ionisation Mass Spectrometry (N-TIMS) to gain Re–Os isotopic composition and abundance. Extraction of the soluble organic matter (SOM) was carried out using Soxhlet or ASE on the Staffin and Phosphoria samples, respectively. The extracted rock (ER) and SOM then underwent N-TIMS whilst the asphaltene was isolated using *n*-heptane and analysed using N-TIMS, where possible. See text for discussion and complete methodology.

release by kerogen cracking in the SR Analyzer and Rock–Eval pyrolyser (Peters, 1986; Behar et al., 2001).

3.2. Bitumen and asphaltene extraction and isolation

Bitumen (the soluble organic matter extracted from ORS) was extracted from both the non-pyrolysed and pyrolysed Staffin samples (~100 g) using Soxhlet apparatus for 24 h with chloroform. The refluxed solvent was filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter and the bitumen was concentrated by rotary vacuum evaporation. Bitumen from the Phosphoria non-pyrolysed and pyrolysed samples was extracted using an ASE 200 at the Total Laboratory for Fluids and Geochemistry (Pau, France) with dichloromethane using 15 g of sample at 100 °C and 100 bars.

For asphaltene separation, ~1 g of bitumen was placed in a 60 ml glass vial with 40 ml of *n*-heptane and sealed with a PTFE lined cap. The contents were agitated to ensure the bitumen and *n*-heptane were thoroughly mixed. The glass vial was then placed on a vari-mix rocker overnight. After ~12 h contact time the contents were centrifuged at 4000 rpm for 5 min. The asphaltene was separated using filtration on a 0.45 µm PTFE membrane. The *n*-heptane containing the maltene was placed into clean 22 ml glass vials and evaporated at room temperature to recover the maltene fraction.

3.3. Hydrous pyrolysis experiments

Randomly selected rock fragments (~400 g) of the Phosphoria and Staffin samples were matured at various stages of petroleum generation by isothermal hydrous pyrolysis (Lewan, 1985). Hydrous pyrolysis experiments were conducted in Hastelloy C-276 reactors with carburised surfaces. The rock fragments from the Staffin and Phosphoria sample sets were immersed in 400 ml distilled water which is sufficient to maintain a liquid water phase. The reactors were sealed and filled with ~6.9 MPa of He and leak-checked using a thermal conductivity leak detector. Temperatures were monitored with Type J thermocouples, which are

calibrated against national standards, and remain within ±0.5 °C of the desired temperature. The hydrous pyrolysis experiments were carried out at 250, 300, 325 and 350 °C for 72 h. These temperatures were selected as they represent various stages of oil generation: (1) start of bitumen generation, (2) peak bitumen generation, (3) early oil generation and (4) peak oil generation of a Type II source rock (Lewan, 1985). These temperatures also provide the best conditions to gain sufficient quantities of asphaltene and maltene fractions from the organic-rich Phosphoria samples. Precise Re and Os isotopic analysis of the asphaltene and maltene fractions requires >200 mg of bitumen.

After the experiments had cooled to room temperature, pressure and temperature values were recorded and a sample of head-space gas was collected in an evacuated 30 cm³ stainless-steel cylinder. Expelled oil generated in the hydrous pyrolysis experiments was collected in three steps. First, any expelled oil was collected from the surface of the water in the reactor with a Pasteur pipette. Second, the water and minor amounts of expelled oil not collected with the pipette were decanted into a glass separatory funnel. The separated oil was concentrated at the funnel stopcock, where it was collected with the same Pasteur pipette used to collect the oil on the water surface. Third, the thin film of expelled oil on the reactor walls, separatory funnel, Pasteur pipette, and rock fragments were rinsed with benzene at room temperature. This benzene rinse was filtered through a 0.45 µm PTFE filter and the expelled oil was concentrated by rotary vacuum evaporation of the benzene. Expelled oil collected with a Pasteur pipette as described above, is called “free oil”, whereas expelled oil rinsed from the equipment with benzene is called “equipment rinse”. The decanted water was filtered through a 0.45 µm cellulose–acetate/nitrate filter. Rock fragments were removed from the reactor and dried at room temperature (~20 °C) in a HEPA fume hood until their weight was constant (<1% change).

3.4. Re–Os analysis

Rhenium–osmium isotopic analyses were carried out at Durham University’s Total Laboratory for Source Rock

Geochronology and Geochemistry at the Northern Centre for Isotopic and Elemental Tracing (NCIET). In this study Re–Os analyses were conducted on the non-pyrolysed and recovered pyrolysed rock fragments as well as all organic fractions e.g., oils, bitumens, asphaltenes and maltenes (Fig. 1). For clarity the term ‘non-pyrolysed’ rock refers to the original rock that has not experienced hydrous pyrolysis. Rhenium–Os analysis was conducted on an aliquot (~0.2–0.5 g) of the powdered rock fragments (~50 g) of the non-pyrolysed and recovered pyrolysed samples. These whole rock analyses reflect the total organic matter within the rock matrix, which constitutes the kerogen and bitumen fractions. Rhenium–Os analyses were also conducted on solvent-extracted (or bitumen free) rocks. The isolated bitumen and separated asphaltene fractions, hydrous pyrolysis generated expelled oil and water used in the pyrolysis experiments were also analysed.

For whole rock and extracted rock analyses, between 0.2 and 0.5 g of sample material was placed into a Carius tube with a known amount of a tracer solution of ^{185}Re – ^{190}Os , plus 8 ml of a Cr^{VI} – H_2SO_4 solution (made from 0.25 g of CrO_3 per 1 ml of 4 N H_2SO_4) and heated to 220 °C for ~48 h (Selby and Creaser, 2003). For analysis of bitumen and asphaltene, fractions and organic precipitates between 0.1 and 0.2 g together with a known amount of ^{185}Re – ^{190}Os mixed tracer solution were dissolved in inverse *aqua-regia* (8 ml ~14 N HNO_3 and 3 ml ~10 N HCl) in Carius tubes at 220 °C for ~48 h (Selby et al., 2007). Inverse *aqua-regia* is used to digest the bitumen and asphaltene fractions to ensure complete sample digestion and sample–spike equilibration.

Osmium was extracted from the Cr^{VI} – H_2SO_4 and *aqua-regia* solutions using solvent extraction (Chloroform) and purified by micro-distillation, with the Re fraction purified using anion column chromatography (Selby and Creaser, 2003). Determination of Re–Os isotopic composition and abundances was achieved using ID-NTIMS (Creaser et al., 1991; Völkening et al., 1991; Walczyk et al., 1991; Selby and Creaser, 2003).

Procedural blanks during this study were 2 ± 0.12 pg Re and 0.2 ± 0.08 pg Os (1 SD, $n = 3$, *aqua-regia*), and 16.8 ± 0.4 pg Re and 0.4 ± 0.1 pg Os (1 SD, $n = 4$, Cr^{VI} – H_2SO_4 solution). The blank $^{187}\text{Os}/^{188}\text{Os}$ isotopic composition for *aqua-regia* are 0.27 ± 0.51 (1 SD, $n = 3$) and 0.25 ± 0.21 (1 SD, $n = 4$) for the Cr^{VI} – H_2SO_4 solution. Uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios are determined by error propagation of uncertainties in Re and Os mass spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and reproducibility of standard Re and Os isotopic values.

To ensure and monitor long-term mass spectrometry reproducibility, in-house standard solutions of Re and Os are repeatedly analysed at NCIET. This work was carried out concomitantly with work by Rooney et al. (2010) and Finlay et al. (2010) with the standard data reported below identical, within uncertainty. The Re standard analysed during the course of this study is made from 99.999% zone-refined Re ribbon and is considered to be identical to that of AB-1 (Creaser et al., 2002; Selby and Creaser, 2003; Kendall et al., 2004). The NCIET Re standard yields

an average $^{185}\text{Re}/^{187}\text{Re}$ of 0.59772 ± 0.00172 (1 SD, $n = 114$). This paper details further use of the Durham Romil Osmium Standard (DROsS) for monitoring the mass spectrometry reproducibility of osmium isotopic compositions. The DROsS recorded during this study yield an average $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.16093 ± 0.00008 (1 SD, $n = 36$).

4. RESULTS

Rhenium and Os abundance data from the hydrous pyrolysis experiments were mass-balanced and are reported as ng/g of original rock and pg/g of original rock, respectively, using the equation:

$$\{M_i\} = [(A_i * g_i)/1000]/G \quad (1)$$

where the subscript ‘i’ refers to the material (non-pyrolysed/pyrolysed rock, extracted rock, bitumen, etc.) being analysed, A is abundance in ppb or ppt, g is weight of material in grams and G is weight of starting rock in grams. Presenting the data in this format allows the evaluation of the Re and Os abundances located in the various fractions and to more accurately interpret the transfer behaviour and mechanisms of Re and Os in the ORS and crude-oil system. Data for Re and Os of the Staffin and Phosphoria Formation non-pyrolysed and pyrolysed samples are presented in Tables 2 and 3, respectively. The $^{187}\text{Re}/^{188}\text{Os}$ ratios of the whole rock, extracted rock and bitumen for the Staffin non-pyrolysed are found in Table 4.

4.1. Organic phases

The hydrous pyrolysis experiments on the Staffin and Phosphoria samples generated bitumen, oil and gas (Table 5). The experiments at 350 °C for the Staffin and Phosphoria samples generated the maximum amount of gas and oil, (3.4 and 16 g of gas and 1.1 and 13.8 g of oil, respectively; Table 5). Both the Staffin and Phosphoria experiments yield a mass balance of ~98% based on original rock plus added water mass. Table 6 illustrates the volume of organic phases generated from the hydrous pyrolysis experiments with respect to grams of original TOC. The clay-rich Staffin Formation released 6–10 g of water during hydrous pyrolysis and, as a result of the breakdown of a gas-prone Type III kerogen generated 340 mg/g original TOC of gas at 350 °C (Tables 4 and 5). The Phosphoria Formation generated slightly less gas (230 mg/g original TOC) and released a comparable volume of water (0–8 g) at 350 °C (Tables 4 and 5).

4.2. Re–Os data of the Staffin Formation

The Re and Os abundances in the Staffin Formation non-pyrolysed rock taken from the 6 kg sample are very similar to those in other sections of Bed 35 from the Staffin Formation (Table 2). The Staffin whole rock pyrolysed samples display a constant but small (6%) decrease in Re abundance throughout the hydrous pyrolysis temperature range (Table 2). Similarly, the Os abundance in the pyrolysed whole rock displays a small (5%) decrease through the range of hydrous pyrolysis temperatures. These decreases

Table 4
Staffin and Phosphoria Formation $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ data for original rock, recovered rock, extracted rock, bitumen and where applicable, asphaltene.

Fraction	Staffin Formation				Phosphoria Formation			
	$^{187}\text{Re}/^{188}\text{Os}$		$^{187}\text{Os}/^{188}\text{Os}$		$^{187}\text{Re}/^{188}\text{Os}$		$^{187}\text{Os}/^{188}\text{Os}$	
	Mean	±	Mean	±	Mean	±	Mean	±
Original rock	355.2	2.1	1.477	0.009	988.0	3.4	3.314	0.005
Extracted rock	353.5	2.1	1.470	0.009	1113.6	3.9	3.164	0.006
Bitumen	116.4	17.5	2.001	0.303	3571.4	83.9	5.979	0.143
Asphaltene	ND		ND		4218.3	85.5	5.024	0.140
250 °C for 72 h								
Recovered rock	359.8	2.1	1.454	0.009	925.0	3.2	3.208	0.005
Extracted rock	354.5	2.1	1.443	0.009	952.1	3.2	3.178	0.005
Bitumen	815.5	1119.2	2.405	3.339	3573.9	51.1	3.730	0.054
Asphaltene	ND		ND		3798.9	29.1	3.794	0.030
300 °C for 72 h								
Recovered rock	342.1	2.0	1.470	0.009	959.2	3.2	3.169	0.004
Extracted rock	330.1	1.9	1.466	0.009	883.7	3.2	3.310	0.006
Bitumen	4150.6	9232.6	1.920	4.385	3045.7	39.8	3.819	0.051
Asphaltene	ND		ND		3158.8	33.8	3.890	0.043
325 °C for 72 h								
Recovered rock	341.2	2.0	1.453	0.009	1070.2	3.7	3.199	0.005
Extracted rock	348.0	2.2	1.429	0.009	912.0	3.1	3.156	0.004
Bitumen	2891.8	2352.6	0.890	0.809	3465.7	72.7	3.510	0.074
Asphaltene	ND		ND		3745.7	54.1	3.602	0.053
350 °C for 72 h								
Recovered rock	333.2	2.0	1.450	0.009	974.8	3.3	3.269	0.004
Extracted rock	369.6	2.2	1.473	0.009	988.8	3.4	3.256	0.005
Bitumen	10072.7	149295.4	2.739	41.121	780.6	70.9	3.502	0.348
Asphaltene	ND		ND		578.0	8.9	2.735	0.048

Table 5
Hydrous pyrolysis conditions for the Staffin and Phosphoria Formations and details of products yielded.

Sample and temperature (°C)	Rock at start (g)	Water in reactor (g)	Recovered rock (g)	Water recovered (g)	Generated gas (g)	Expelled oil (g)	Total recovery (%)
Staffin Formation							
SK-1 250	400.2	410.3	373.5	420.6	1.7	0.02	98.2
SK-1 300	400.1	410.3	370.7	416.3	2.7	0.58	97.5
SK-1 325	400.1	410.3	368.6	419.1	3.3	0.89	97.7
SK-1 350	400.1	410.3	365.7	419.9	3.4	1.09	97.5
Phosphoria Formation							
Phosph. 250	400.4	375.1	388.5	374.6	2.1	0.10	98.7
Phosph. 300	400.4	375.8	380.4	377.8	4.8	1.34	98.5
Phosph. 325	400.6	375.0	364.2	374.7	9.1	6.70	97.3
Phosph. 350	400.4	375.4	349.7	383.7	16.0	13.76	98.4

are within the range of variation in Re and Os abundances of other samples also from Bed 35 (Table 2).

The Re and Os abundance in the extracted rock from the non-pyrolysed Staffin sample are similar although slightly lower than those of the extracted rock of pyrolysed samples at all temperatures (Table 2). The extracted rock Re and Os abundance data for the Staffin pyrolysed samples are similar across the range of hydrous pyrolysis temperatures (~4% variation for both Re and Os). The Staffin bitumens show an extremely minor increase in Re abundance peaking at 300 °C although this value is still lower than the Re

abundance of the non-pyrolysed bitumen. The Os abundance in the Staffin bitumen decreases from the non-pyrolysed value of 195 pg/g to a low of 0.3 pg/g in the 350 °C experiment (Table 3).

The non-pyrolysed rock contains 0.03% of bitumen relative to TOC or 0.01 g of the whole rock. This bitumen contains Re and Os abundances of 3.8 ng/g and 194.9 pg/g, respectively. Hydrous pyrolysis of the Staffin samples generated minor amounts of bitumen for the experiments (<0.1 g; Table 6). Bitumen from the pyrolysed rock possess a Re abundance that is slightly less than that of the

Table 6

Amounts of organic phases extracted or generated from the samples of Staffin and Phosphoria Formations.

Sample and temperature (°C)	Bitumen (mg/g orig. TOC)	Expelled oil (mg/g orig. TOC)	Generated gas (mg/g orig. TOC)	Total (mg/g orig. TOC)
Original	10.4	0.0	0	10.4
SK-1 250	20.8	2.2	170	193.0
SK-1 300	48.2	57.7	270	375.9
SK-1 325	51.7	89.4	330	471.1
SK-1 350	88.6	109.3	340	537.9
Original	133.3	0.0	0	133.3
Phosph. 250	213.4	1.4	30	244.9
Phosph. 300	735.3	19.2	69	823.5
Phosph. 325	706.0	96.2	131	933.0
Phosph. 350	267.4	197.7	230	695.0

non-pyrolysed sample and similarly, Os abundances for the bitumen of pyrolysed samples are lower than that of the bitumen from the non-pyrolysed sample (Table 2).

It must be noted that many of the bitumen samples have large uncertainties ($\pm > 1000$) associated with them. The large uncertainties also reflect the blank correction associated with measuring these small (<0.05 g) samples for analysis and the minor abundance of Re and Os in the bitumen. The significance of the bitumen $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ will be discussed below.

The $^{187}\text{Os}/^{188}\text{Os}$ ratios of the non-pyrolysed and pyrolysed whole rock, extracted rock and bitumen can be found in Table 4. As noted for the $^{187}\text{Re}/^{188}\text{Os}$ ratios above, many of the bitumen $^{187}\text{Os}/^{188}\text{Os}$ ratios have large uncertainties ($\pm 3.3\text{--}41.1$) associated with them related to the small (<0.05 g) sample size and very small (<10 pg/g) Os abundance in the bitumen fraction.

The hydrous pyrolysis experiments on the Staffin Formation did not generate any free oil although an equipment rinse did provide a small quantity (<1.09 g) of expelled oil at 350 °C. This equipment rinse was sufficient for Re–Os analyses but does not contain any measurable amounts of Re or Os and was not included in the mass balance calculations.

4.3. Re–Os data of the Phosphoria Formation

The non-pyrolysed Phosphoria Formation whole rock sample contains 477 ng/g and 3295 pg/g of original rock, of Re and Os, respectively. There are slight variations in Re and Os abundances of multiple aliquots of the non-pyrolysed Phosphoria Formation displaying a coefficient of variation of 7.9% and 3.8%, respectively (Table 3). The slight variations in Re and Os abundances of the Phosphoria pyrolysed samples are comparable to natural variations inherent in varying aliquots as seen in the non-pyrolysed samples. The pyrolysed whole rock and non-pyrolysed extracted rock fractions have comparable Re and Os abundances (Table 3).

The non-pyrolysed Phosphoria sample contains 0.13 g of naturally-occurring bitumen per gram original TOC, and this bitumen has Re and Os abundances of 61 ng/g and 145 pg/g, respectively (Tables 3 and 5). In comparison, the pyrolysed samples contain a greater amount of bitumen

per gram original TOC for the range of hydrous pyrolysis experiments (Table 6). The Re and Os abundances for these pyrolysed bitumens are displayed in Table 3. The greater bitumen content of the Phosphoria samples (1.6 vs. 0.03 wt.% for the Staffin Formation) permits the extraction of an asphaltene fraction from the bitumen component. The extracted maltene fraction was not analysed as the small (<0.01 g) amounts inhibited precise ID-NTIMS analysis and previous work has shown that the maltene contains very minor amounts of Re and Os (<14% of total extract; Selby et al., 2007). The asphaltene abundance is not mass balanced as together with the maltene it represents 100% of the bitumen. The amount of asphaltene in the bitumen peaks in the 300 °C experiment however, this does not appear to be the controlling factor in Re and Os abundances of these fractions (Table 7).

The $^{187}\text{Re}/^{188}\text{Os}$ ratios for the whole rock, extracted rock and bitumen fractions of the pyrolysed Phosphoria Formation samples are comparable to values for the non-pyrolysed samples. However, there is a greater range in the $^{187}\text{Os}/^{188}\text{Os}$ ratios for the whole rock, extracted rock and bitumen fractions of the pyrolysed Phosphoria Formation (Table 4).

The hydrous pyrolysis experiments on the Phosphoria Formation yielded quantities of expelled oil (Table 5). However, the generated oils from the 300 and 325 °C experiments do not contain significant amounts of Re or Os and are not considered in the mass balance calculations. In contrast, the asphaltene component of the 350 °C oil was analysed for Re and Os abundance and isotopic composition and contains very minor abundances although the isotopic ratios are pertinent to the discussion below. The asphaltene component of the oil contains 130 ppt of Re and 5.6 ppt of Os with a $^{187}\text{Re}/^{188}\text{Os}$ ratio of 163 and a radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratio of 3.595 (Table 7).

The organic precipitates from the decanted hydrous pyrolysis waters of both the Staffin and Phosphoria Formation experiments are only slightly enriched in Re and Os (0.1–10 ppb and 1–224 ppt, respectively) though these abundances do have significant uncertainties (>10%) associated with the blank correction. As a result, we do not consider these precipitates to be relevant to the discussions concerning Re and Os transfer in maturing ORS.

Table 7

Isotopic composition and elemental abundance data for the asphaltenes of the Phosphoria Formation original rock and experiment aliquots.

Sample and temperature (°C)	Asphaltene in bitumen (%)	Re (ng/g)	±	Os (pg/g)	±	¹⁸⁷ Re/ ¹⁸⁸ Os		¹⁸⁷ Os/ ¹⁸⁸ Os	
						Mean	±	Mean	±
Original rock Asphaltene	34	236.77	0.78	443.2	7.5	4218	85	5.024	0.140
250 Asphaltene	36.4	265.89	0.86	498.6	3.7	3799	29	3.794	0.030
300 Asphaltene	53.7	252.67	0.83	574.6	5.1	3159	34	3.890	0.043
325 Asphaltene	43.4	225.60	0.75	421.8	4.3	3746	54	3.602	0.053
350 Asphaltene	22.3	11.75	0.10	131.3	1.4	578	9	2.735	0.048
350 Asphaltene of oil from rock	–	0.13	0.002	5.6	0.7	163	59	3.595	1.360

5. DISCUSSION

5.1. Complexation behaviour and location of Re and Os in ORS

Although the specifics of where Re and Os reside in sedimentary rocks requires further research, some discussion on this topic is warranted from the results of this study. As Re and Os are known to exhibit chalcophilic, siderophilic and organophilic behaviour it is essential that we determine whether these metals reside in organic or mineral phases. In this study, we have assumed that Re and Os in these samples resides in organic matter. This assumption can be considered to be valid as Re and Os in ORS have been shown to be hydrogenous in origin and are complexed into organic matter under reducing conditions (Ravizza and Turekian, 1989; Ravizza et al., 1991; Colodner et al., 1993; Ravizza and Esser, 1993; Cohen et al., 1999; Morford and Emerson, 1999; Morford et al., 2005). Studies working on source rocks and crude oil products have also recorded enrichments of Re and Os in organic matter (Selby and Creaser, 2003, 2005a; Selby et al., 2005, 2007; Finlay et al., 2010, 2011a). This assumption also holds for the bitumen extracted from the whole rocks as chloroform will only extract the soluble organic matter upon which the Re and Os determinations of bitumen are conducted. The insoluble organic matter remaining in the solvent-extracted (bitumen-free) rock is, by definition, extracted rock. Further, the assumption that Re and Os concentrations determined on the solvent-extracted rock are exclusively within the extracted rock comes with the caveat that pyrite digested by either the Cr^{VI}–H₂SO₄ or inverse *aqua-regia* medium does not contribute significant concentrations to the Re and Os budget of the solvent-extracted rock (Cohen et al., 1999; Selby and Creaser, 2003). This last assumption can also be quantified experimentally as diagenetic pyrite in the samples used in this study is <1 wt.% (as determined by XRD). Both disseminated and cubic pyrite found in ORS have Re and Os concentrations of <2.6 and 0.11 ng/g, respectively. This is in comparison to ORS with concentrations of 15–60 and 0.3–1.0 ng/g, respectively (Cohen et al., 1999).

Analyses of the thermally immature Staffin and Phosphoria samples indicate that the extracted rocks are enriched in Re and Os with abundances that are broadly similar to those of the whole rocks (1.4% and 2.3% variation for Re and Os, respectively from Staffin and 0.3% and 6.9%, respectively, from Phosphoria; Tables 2 and 3). These data alone suggest that the vast majority of the Re

and Os budget in immature ORS is complexed within this kerogen fraction (pre-extracted whole rock). Although the samples are still considered thermally immature based on laboratory thermal maturation analysis, the ORS used in this study have experienced burial resulting in the generation of an extractable bitumen fraction (Table 1). The Staffin sample contains very small amounts of bitumen (0.01%), in comparison to the Phosphoria sample (1.6%). This is a function of, in part, the higher TOC content (17.4% [Phosphoria] vs. 2.5% [Staffin]) and earlier bitumen generation from a Type II-S kerogen to that of a Type III kerogen (Lewan et al., 2006).

The higher Re and Os concentrations in the Phosphoria sample with Type II-S kerogen relative to those in the Staffin sample with Type III kerogen is possibly related to preservation of higher concentrations of chelating precursors or a longer period of pore-water openness during sedimentation. As described for nickel and vanadium their concentration in organic matter is a result of chelating tetrapyrrole complexes derived from chlorophyll being preserved and slow sedimentation rates maintaining an open sediment pore-water system for scavenging of metals from the overlying water body (Lewan and Maynard, 1982). However, unlike the recognized tetrapyrrole sites for preferential chelation of V and Ni in ORS, the specific chelating sites for Re and Os in ORS are not yet known (Lewan and Maynard, 1982; Selby et al., 2007).

Although attributing the higher Re and Os concentrations in the Phosphoria samples relative to the Staffin samples to the preservation of chelating precursors or prolonged open pore-water systems remains equivocal, it should be noted that Re and Os concentrations in coals which are predominantly Type III kerogen, are typically <1 ng/g (Orem and Finkelman, 2003; Baioumy et al., 2011). This suggests that Type III kerogen may not retain the needed organic chelating sites for preferentially binding Re and Os. The same is true for V and Ni in Type III kerogen as a result of tetrapyrrole precursors (i.e., chlorophyll) which are not preserved in sedimentary vascular-plant debris (Lewan and Maynard, 1982). These data suggest that kerogen type and the unique chemical makeup of kerogen is a major controlling factor in Re and Os concentrations in ORS. However, many source rocks have large variations in Re and Os concentrations despite consisting of Type II kerogen (ranges of >100 ng/g Re and >1400 pg/g Os; Creaser et al., 2002). We suggest that ultimately, the uptake of Re and Os into ORS will be controlled by factors such as sedimentation rates and pore-water chemistry as well as kerogen type.

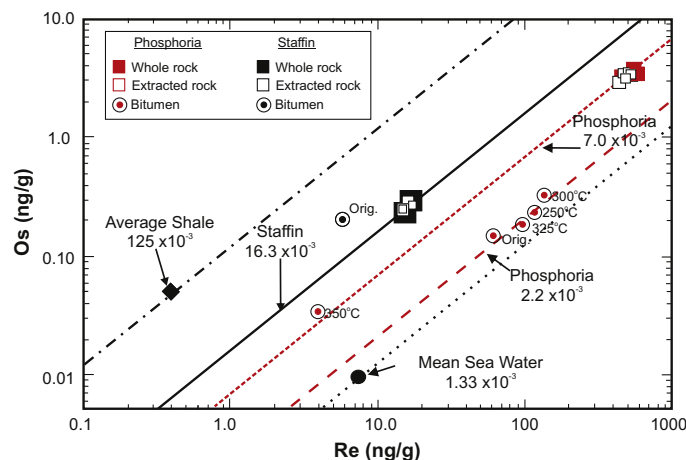


Fig. 2. Log plot of Re and Os concentrations on an original-rock basis of original (orig.) and pyrolysed Staffin and Phosphoria whole rock and extracted rock, and Phosphoria bitumen with pyrolysis temperatures. Mean sea water value from [Bruland and Lohan \(2003\)](#) and average shale value from [Li and Schoonmaker \(2003\)](#). Whole rock and extracted rock values for Staffin and Phosphoria demonstrate small variations within the relevant sample set and thus overlap. No hydrous pyrolysis generated Staffin bitumens plot on the diagram due to low Os abundances, see text for discussion. Phosphoria symbols are in red and Staffin in black. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

As shown in [Fig. 2](#), the elemental Re–Os ratio of the Staffin and Phosphoria whole rock and extracted rock components remains, essentially, the same at all maturation temperatures (coefficient of variation of 2.7% and 3.5% for the Staffin and 5.5% and 7.1% for the Phosphoria, respectively). The elemental Re–Os ratios of 61 and 62 for the Staffin components, and 146 and 141 for the Phosphoria whole rock and extracted rock are much lower than the value for seawater (~ 4500 ; [Peucker-Ehrenbrink and Ravizza, 2000](#)). The Phosphoria samples display Os enrichment by more than two orders of magnitude and Re less than two orders of magnitude compared with the Staffin samples. For both rocks, Os at a significantly lower concentration appears to have a great affinity for the organic chelating sites than Re. Further work on the valance state/species and organic chelating sites is needed to resolve these issues.

We can gain some insights into the behaviour of Re and Os at seawater activities by using Eh–pH diagrams. Examples of these diagrams are shown in [Fig. 3](#) with conditions of 25 °C and 1 bar for seawater activities of Re, Os and S according to mean values given by [Bruland and Lohan \(2003\)](#). Superimposed on these diagrams is the Eh–pH field for marine and marginal marine sediments (ms; [Baas Becking et al., 1960](#)). This field is divided into oxidizing and reducing sediments at an Eh of zero ([Lewan, 1984; Lewan et al., 2008](#)). Within the reducing portion of the sediment field, Re and Os occur predominantly in the form of a sulphide. ReS_2 accounts for 66% and OsS_2 accounts for 57% of the reducing sediment field. For Re, the remaining reducing-sediment field consists of 29% trivalent and quadravalent oxides (Re_2O_3 and ReO_2 , respectively) and 5% as a ReO_4^- anion. The remaining 43 percent of the reducing field for the Os occurs in the native state (Os^0).

These diagrams are based solely on available thermodynamic data and do not consider kinetic aspects or organic chelating sites for reactions involving Re and Os.

Nonetheless, they provide some interesting insights and implications on the reducing-sediment field within which Re and Os chelation may occur. Solid species of both metals occur in at least 95% of the reducing-sediment field. The areas of Re- and Os-sulphides overlap with ReS_2 extending only 9% beyond the OsS_2 boundary into the reducing-sediment field ([Fig. 3](#)). This similarity is possibly related to their chalcophilic nature as quadravalent metals. Within the remaining reducing-sediment field the differences between Re and Os become more pronounced. Osmium only occurs in its native state whereas Re occurs as oxides in +3, +4 and +7 valance states. In the presence of organic matter, Re and Os appear to prefer organic chelating sites over their thermodynamically possible solid sites. It remains to be determined whether the valance states of Re and Os are the controlling factors over their affinity for the organic chelating sites outside their sulphide fields. Based on available data indicating low concentrations of Re and Os in pyrite in ORS (e.g., [Cohen et al., 1999; Liu et al., 2008](#)), it is suggested that organic chelating sites have a greater affinity for the quadravalent states of Re and Os than sulphides.

5.2. Whole rock abundances per gram of TOC

The bitumen fractions from the immature Staffin and Phosphoria samples contain considerable concentrations of Re (3.8 and 61 ng/g, respectively). This represents a significant percentage of the whole rock Re content (Staffin = 28% and Phosphoria = 13%; [Tables 2 and 3](#)). For Os, the bitumen of the Staffin and Phosphoria samples contain 195 and 145 pg/g, respectively. These abundances, again, represent a significant percentage of the whole rock Os content, especially for the Staffin sample (Staffin = 89% and Phosphoria = 4%). However, if we assume that Re and Os in ORS are associated entirely with the organic matter

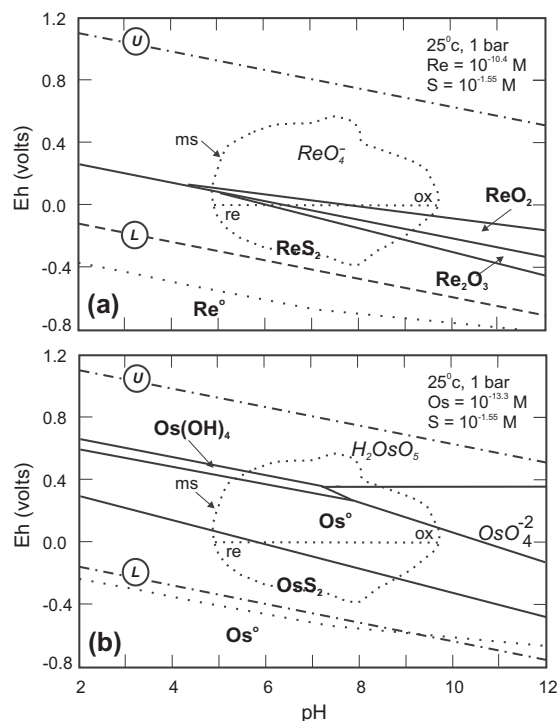


Fig. 3. Eh–pH diagrams constructed for 25 °C, 1 bar, and seawater concentrations of Re, Os, and S according to Bruland and Lohan (2003). Broken dotted lines labeled U and L represent respectively upper and lower stability limits for water as described by Garrels and Christ (1965). Dashed outline labeled *ms* represents field for marginal marine and marine sediments as reported by Baas Becking et al. (1960). Dashed horizontal line at an Eh of zero denotes boundary between reducing (Re) and oxidizing (Ox) sediment fields. (a) Diagram for Re using free energy of formation of species given by De Zoubov and Pourbaix (1966) with the ReS_2 value used by Brookins (1978). (b) Diagram for Os using free energy values from compilation by Brookins (1988).

then the whole rock value of ~ 480 ng/g is a considerable underestimate of the true Re abundance for the Phosphoria sample. We can calculate a Re and Os abundance (T_A) based on original rock TOC using the equation:

$$T_A = (100/TOC) * \text{Re Content of whole rock} \quad (2)$$

Based upon a TOC of 17.4% and a whole rock Re content of 477 ng/g TOC the Re abundance of the Phosphoria sample is closer to 2742 ng/g TOC. This equation is equally valid for the Os component and the true Os abundance of the Phosphoria is 18,939 pg/g TOC. Thus, the bitumen component represents only 2.2% of total Re and 0.8% of total Os found in the immature Phosphoria sample. Likewise, the Staffin samples also show that the Re and Os content of the bitumen is only a minor component of the whole rock Re and Os budget. For example, the Staffin bitumen contains 3.8 ng/g TOC of Re from a T_A of 550 ng/g TOC and for Os the bitumen has 195 pg/g TOC from a T_A of 8760 pg/g TOC thus representing 0.7% of total Re and 2.2% of total Os found in this sample. This further illustrates that $>95\%$ of the Re and Os budget is housed within the kerogen fraction.

5.3. Re and Os elemental abundance data of whole rock, extracted rock and bitumen components as a function of hydrous pyrolysis temperature

Previous studies have shown that the Re–Os geochronometer is not adversely disturbed by thermal events such as hydrocarbon maturation, flash pyrolysis or metamorphism (Creaser et al., 2002; Kendall et al., 2004; Selby and Creaser, 2005a; Rooney et al., 2010, 2011). As such, the Re–Os ORS geochronometer records the timing of sediment deposition and not the age of post-depositional events. Although current evidence suggests that the Re–Os system is not adversely affected by these events, we do know that natural crude oils are enriched in Re and Os that have been transferred from the source rock (Selby et al., 2005, 2007; Selby and Creaser 2005b; Finlay et al., 2010, 2011b). However, we have a very limited understanding of the mechanisms and magnitude of elemental transfer from a source rock to the generated crude oil.

The experimental conditions used in this study are based on a more complete set of hydrous pyrolysis experiments published by Lewan (1985, Fig. 2 in that paper). Experiments at 250 and 300 °C for 72 h represent the initial thermal decomposition of kerogen to bitumen, followed by the thermal decomposition of bitumen to oil in experiments at 325 and 350 °C for 72 h. For both of these overall reactions, the Staffin samples with gas-prone Type III kerogen displayed no appreciable transfer of the Re and Os in the extracted rock to the bitumen (Table 2). This indicates that the bonding sites of Re and Os in the Staffin samples are robust at the experimental temperatures. Conversely, the Phosphoria sample with Type II-S kerogen shows slight transfer of Re and Os from the extracted rock to the bitumen (4.6% and 1.3% of total whole rock Re and Os, respectively, Table 3 and Fig. 2). As shown in Fig. 2, both Re and Os increase with rising bitumen generation from kerogen to 300 °C. These concentrations then fall at 325 and 350 °C as the bitumen thermally decomposes to oil. Relative to the extracted rock which contains more than 91% of Re and 88% of Os throughout the hydrous pyrolysis experiments (Table 3), Re is preferentially released from the extracted rock to the bitumen with a near constant elemental Re–Os ratio of 470 (Fig. 2). The notable exception is the bitumen at 350 °C, which has an elemental Re–Os ratio of 113 which is closer to that of the extracted rock and whole rock ratio of 140. As shown in Table 3, essentially all of the Re and Os in bitumen occurs in the asphaltene fraction, which comprises the most significant portion of the bitumen as observed in naturally generated crude oil (Lewan, 1993; Selby et al., 2007). As the extracted rock decomposes in part to bitumen with increasing thermal maturation, more Re- and Os-rich portions of the extracted rock are converted until the end of bitumen generation at 300 °C in these hydrous pyrolysis experiments. This is followed by a decrease in Re and Os in the bitumen as it degrades into oil and pyrobitumen. The absence of Re and Os in the expelled oils suggests that their loss from the bitumen is a result of their assimilation into the pyrobitumen through cross-linking reactions, as opposed to partitioning into the expelled oil through thermal cracking (Lewan, 1997).

The lack of Re and Os in expelled oil from the hydrous pyrolysis experiments is unexpected from the standpoint that these metals are observed in natural crude oils (Woodland et al., 2001; Selby and Creaser, 2005a; Selby et al., 2007; Finlay et al., 2010, 2011a) and have been measured in crude oils from Phosphoria source rocks (Lillis and Selby, 2010). Other experimental pyrolysis results using Woodford Shale with Type II kerogen also report a lack of Re and Os partitioning into oils from source rocks (Reisberg et al., 2008).

The generated bitumen from the Staffin samples do not contain significant concentrations of Re or Os (0.4–2.1 ng/g and 0.3–8.2 pg/g, respectively) suggesting that these metals are very tightly bound in Type III kerogen structure. As the thermal parameters of the hydrous pyrolysis experiments were identical for the Staffin and Phosphoria samples it can be proposed that kerogen type is the controlling factor for the transfer of Re and Os from kerogen into bitumen. This would agree with experimental and natural data which shows that greater thermal stress is required to crack Type III kerogens in comparison with Type II/II-S (Lewan, 1985; Lewan and Ruble, 2002), and Type III kerogen produces mostly gas whereas Type II/II-S kerogen produces mostly oil.

The results from hydrous pyrolysis experiments on the Phosphoria Formation define small variations in Re and Os abundance (8% and 4%, respectively) of the whole rock fractions. These variations can be attributed to the natural variations inherent in the Phosphoria Formation as seen in the non-pyrolysed samples (Table 3). Likewise, the Re–Os abundance data from the Phosphoria extracted rock samples reveals only small variations in Re or Os abundance (4%). The Phosphoria bitumen samples display an enrichment in Re and Os that is correlative with the peak bitumen generation temperature for a Type II-S kerogen (300 °C; Table 3; Lewan, 1985). Additionally, the Re and Os abundances for the Phosphoria bitumen illustrate an excellent linear relationship ($r^2 = 0.989$; Fig. 4). This would suggest that these metals reside in similar organic hosts within the bitumen and are transferred consistently in terms of amount and the destination throughout maturation.

If we consider the Phosphoria bitumens which have generated both the greatest amounts of bitumen and contain the highest abundances of Re and Os, we see that these bitumens contain between 0.1% and 4.6% of Re and 0.1% and 1.3% of Os, respectively, of the total whole rock values. This reveals minimal transfer of Re and Os from the extracted rock to the bitumen resulting from hydrous pyrolysis experiments. Ultimately, this strongly suggests that hydrous pyrolysis and by inference natural thermal maturation, does not result in any significant mobilisation of Re and Os from ORS and thereby increasing our confidence that Re–Os systematics are not disturbed during natural maturation.

Analysis of the Staffin and Phosphoria bitumen and asphaltene fractions from both non-pyrolysed and pyrolysed samples indicate that the asphaltene contains >90% of the bitumen Re and Os budget. These findings are in agreement with studies on asphaltene fractions of whole oils suggesting that Re and Os in natural and pyrolysis generated

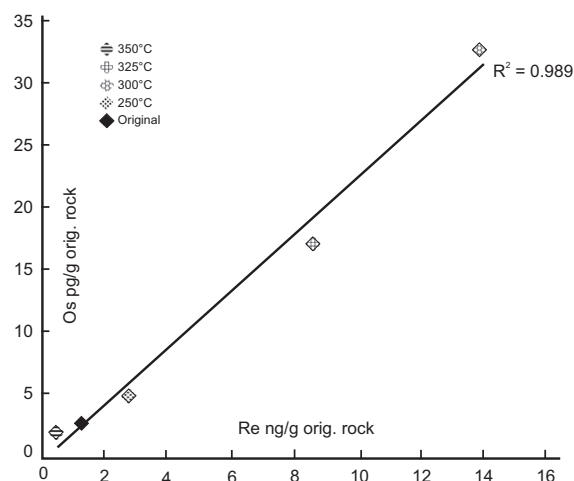


Fig. 4. Re and Os abundances for pyrolysis generated and natural Phosphoria bitumens. The data reveal a clear linear relationship suggesting that these metals reside in similar organic hosts within the bitumen. This also infers that Re and Os are transferred consistently in both amount and destination throughout maturation stages until peak bitumen generation temperature is reached (300 °C). After this stage, the abundances decrease as the metals are transferred from bitumen to petroleum products e.g., in natural systems or they are retained in the insoluble organic matter e.g., pyrobitumen. See text for discussion.

bitumens are bound in heteroatomic ligands, preferentially found in asphaltenes (Selby et al., 2007).

We demonstrate that in both natural and pyrolysis generated bitumen, Re and Os is present, which originated from the transformation of kerogen. In contrast to natural oils, the oil generated from hydrous pyrolysis of the Phosphoria samples does not contain significant quantities of Re or Os above blank levels (Selby et al., 2007; this study). The asphaltene from the 350 °C free oil portion of the expelled oil did contain Re and Os but this abundance was several orders of magnitude lower than asphaltenes of naturally occurring oils generated from the Phosphoria Formation (Table 7).

The lack of Re and Os transfer from the bitumens to the oils indicates that hydrous pyrolysis may not completely mimic natural crude oil generation with respect to Re and Os transfer from source rocks to oils. However, there are two major differences between natural systems and the hydrous pyrolysis experiments. Principally, the temperatures of hydrous pyrolysis are much greater than that of natural generation. The higher temperatures involved in hydrous pyrolysis may induce the transfer of Re and Os from the kerogen into an insoluble phase such as pyrobitumen. Current techniques for the isolation of pyrobitumen rely on the use of HF which has been shown to artificially disturb Re–Os systematics by leaching Re preferentially over Os (Selby and Creaser, 2003). Secondly, the distinct time differences for maturation in natural systems in contrast with hydrous pyrolysis experiments may be vital to the transfer of Re and Os from bitumen to oil (10^6 to 10^8 years and hours and days, respectively). The issue is whether an experimental observation contrary to conventional wisdom is an artefact of the higher temperatures employed or a new insight too

subtle to be recognised in the limited data and coarseness of natural observations.

Appreciable amounts of Re and Os of the bitumens have not been transferred to the oil despite reaching the peak oil generation temperature and they are not found in the water used in the hydrous pyrolysis experiments. We hypothesise that the Re has been taken up into the extracted rock as a form of pyrobitumen, which is insoluble and cannot be analysed without adversely affecting the Re–Os systematics. This lack of Re and Os being partitioned into the expelled oil brings into question how one interprets their presence and isotopic signatures observed in natural crude oils. If one takes the tenet that the presence and isotopic signatures of Re and Os are introduced into an oil after it has been expelled from a source rock, the values would be determined by the carrier rocks the oil migrated through or the reservoir rocks in which the oil accumulated (Curiale, 2002). This complicates their interpretation because of the uncertainty in the mechanism, proportionality, and isotopic fractionation by which the exogenous Re and Os are acquired by the oil. Assuming the simplest case that the natural Re and Os contamination from carrier or reservoir rocks was totally reflective of their age, the age determination on an oil would reflect the age of these rocks. The 111.6 Ma for the Athabasca sands based on Re–Os dating (Selby and Creaser, 2005a) would suggest that this age is a collective age of the Paleozoic and Mesozoic carrier and reservoir rocks. The main reservoir rocks are in the Lower Cretaceous Manville Group, which has assigned ages from 105 to 119 Ma (Higley et al., 2009). In addition, this rock unit overlies the main unconformity along which migration of the original oil occurred (Higley et al., 2009). The Athabasca tar sands cover an area in excess of 140,000 km², have a complicated geological history and although there is one predominant source rock a number of other units in this region have matured and generated hydrocarbons. As a result, a variety of studies have attempted to understand and constrain the generation history of these deposits with often contrasting results (Riediger et al., 1999; Selby and Creaser, 2005a; Higley et al., 2009 and references therein). Ultimately, it is highly implausible that a carrier bed could transmit proportionally enough Re and Os to yield an Os isotopic composition of the oil which was identical to the source rock at the time of generation e.g., Selby and Creaser (2005a) and Finlay et al. (2011a,b). Average continental crustal rocks have Re and Os abundances ranging from 80–600 and 30–50 pg/g, respectively (Peucker-Ehrenbrink and Jahn, 2001 and references within). These values are more than an order of magnitude lower than ORS of this study or natural oils (Selby and Creaser, 2005a; Selby et al., 2007; Finlay et al., 2010, 2011a). Therefore, liberating these metals from typical carrier or reservoir beds such as sandstones and carbonates is extremely implausible as leaching would require high temperatures and acidic fluids. In addition, Re and Os transferring into oil would have very radiogenic ¹⁸⁷Os/¹⁸⁸Os ratios as a result of the decay of ¹⁸⁷Re from detrital minerals from ca. 2 Ga crust. The two major differences, time and temperature, lead us to suggest that the transfer of Re and Os from kerogens to bitumens and into oil is kinetically controlled. The

kinetic parameters of hydrous pyrolysis, namely high temperatures over short periods of time are not conducive to the transfer of Re and Os from source rock kerogens to bitumens and into oils. Thus, it can be postulated that these metals reside in very stable functional groups that, despite the elevated temperatures, do not undergo significant transfer on a short timescale.

Complicated scenarios involving multi-stage generation from a number of source rock horizons are entirely plausible and care is needed for interpretation of geochronology data. As an example, the oils generated from Permian Phosphoria source rocks in eastern Idaho migrated into the Wyoming Bighorn Basin through the Tensleep Sandstone and accumulated in both Phosphoria and Tensleep reservoirs (Maughan, 1984). These two formations span an age from approximately 250–295 Ma, and work in progress shows a comparable scatter in the Re–Os ages of the crude oils (260 ± 37 Ma; Lillis and Selby, 2010). Although these two cases suggest that Re–Os geochronology of crude oil may be influenced by contamination during migration, Re–Os geochronology from oils of the UK Atlantic Margin yield ages that are in excellent agreement with Ar–Ar geochronology of feldspar cements and oil fluid inclusions as well as basin modeling of crude oil generation (Mark et al., 2005; Selby et al., 2005; Scotchman et al., 2006; Finlay et al., 2011a).

At present, Re–Os oil geochronology has only been applied to a limited number of regions and further work is necessary to more fully elucidate what event the geochronometer is recording. It is plausible that in certain systems there are significant time lags between the generation of bitumen from kerogen and the generation of crude oil from bitumen. In these examples, Re–Os geochronology may be recording the initial stages of petroleum generation and thus yield ages seemingly in stark contrast to those from basin models.

5.4. Implications of Re and Os isotopic data of pyrolysed whole rock, extracted rock and bitumen

Both whole rock and extracted rock ¹⁸⁷Re/¹⁸⁸Os ratios across the temperature range of the hydrous pyrolysis experiments show very small variations (3.3% and 4.7% for Staffin, respectively and 6.3% and 4.9% for Phosphoria, respectively, Table 4). Similarly, the ¹⁸⁷Os/¹⁸⁸Os ratios show only minor variations for the Staffin and Phosphoria whole rock and extracted rock samples (0.6% and 1.4% and 1.3% and 2.2%; Table 4). These isotopic data strongly suggest that crude oil generation through hydrous pyrolysis experiments does not disturb the Re–Os systematics in ORS as supported by various studies on natural systems (Creaser et al., 2002; Kendall et al., 2004; Selby and Creaser, 2005a; Rooney et al., 2010). This lack of disturbance in the isotopic ratios suggests that Re–Os geochronology of overmature ORS is viable because Re and Os are not significantly removed from the extracted rock fraction of the source rock during petroleum generation. Minute variations in ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios in ORS of varying maturity and any fractionation that occurs during maturation may result from the minor transfer of Re and

Os from kerogen to bitumen to crude oil. These small variations and any associated fractionation could be one of the factors that control the uncertainties presented for Re–Os ORS geochronology.

The Staffin bitumen samples have very large uncertainties associated with the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios related to the blank correction on these very small (<0.05 g) samples with low Re and Os abundances that are not conducive to precise analysis (Tables 2 and 6). As a result, it is extremely difficult to evaluate the Re–Os isotopic data for the pyrolysed Staffin bitumen fractions with any confidence so we do not discuss these findings further. The non-pyrolysed Staffin bitumen sample does provide precise $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ data. The bitumen fraction possesses a much lower $^{187}\text{Re}/^{188}\text{Os}$ ratio compared with the whole rock. The significance of results such as these will be discussed more fully using the Phosphoria dataset below.

The bitumen components for the Phosphoria samples yield precise data which permit discussion of the isotopic composition and transfer of Re and Os from extracted rock to bitumen. Bitumen generated from pyrolysis at 250, 300 and 325 °C have broadly similar $^{187}\text{Re}/^{188}\text{Os}$ ratios (~3200–3800; Table 4). In contrast, the bitumen from the 350 °C experiment has a much lower $^{187}\text{Re}/^{188}\text{Os}$ ratio (781). This is inferred to relate to the significantly lower Re abundance in comparison with the Os abundance in the 350 °C generated bitumen. The $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Phosphoria bitumens also display a considerable variation (26%). The majority of this variation is centred on the contrast in $^{187}\text{Os}/^{188}\text{Os}$ ratios from the non-pyrolysed bitumen sample to the pyrolysed bitumen samples (5.979 vs. 3.640, respectively). All the pyrolysed bitumen samples possess similar $^{187}\text{Os}/^{188}\text{Os}$ ratios (4% variation) across the range of hydrous pyrolysis temperatures (Table 4).

The bitumen of the non-pyrolysed rock was generated through burial of the Permian Phosphoria Formation. This bitumen contains significant enrichment of Re (0.98 ng/g) over Os (2.3 pg/g), which is reflected in the very high $^{187}\text{Re}/^{188}\text{Os}$ ratio (>3500) and is in agreement with our understanding of Re and Os fractionation in bitumens (Selby et al., 2007; Turgeon et al., 2008). Due to the in-growth of radiogenic ^{187}Os , this natural bitumen has a much more radiogenic value than that of the whole rock. In contrast, the pyrolysed rock bitumen has no time to produce radiogenic ^{187}Os thus the $^{187}\text{Os}/^{188}\text{Os}$ ratio is much lower, and reflects that of the whole rock and extracted rock ratios (Table 4).

Analysis of the asphaltene from the oil generated from the Phosphoria 350 °C experiment yields an $^{187}\text{Os}/^{188}\text{Os}$ ratio that is comparable with that of the bitumen for the pyrolysed samples. Although this is only one analysis, and the small amount of asphaltene provides imprecise data, the results do agree with previous studies which show the $^{187}\text{Os}/^{188}\text{Os}$ ratio of oils and asphaltenes can be used as a technique for correlating an oil to its source (Selby and Creaser, 2005a; Finlay et al., 2010, 2011a,b). The variation in $^{187}\text{Os}/^{188}\text{Os}$ ratios between the non-pyrolysed rock bitumen and pyrolysed rock bitumens has profound implications for employing the Re–Os system as a tool for fingerprinting oils within petro-

leum systems (e.g., Selby and Creaser, 2005b; Selby et al., 2007; Finlay et al., 2011a,b).

The Phosphoria bitumens produced through hydrous pyrolysis all have $^{187}\text{Os}/^{188}\text{Os}$ ratios that closely reflect the $^{187}\text{Os}/^{188}\text{Os}$ ratios of the source rock and that any fractionation is extremely minor (Table 4). Additionally, some oils generated in natural systems have high $^{187}\text{Re}/^{188}\text{Os}$ ratios relative to the source rock and other oils have low $^{187}\text{Re}/^{188}\text{Os}$ ratios, but both types have $^{187}\text{Os}/^{188}\text{Os}$ ratios that are comparable to the source rock (Selby and Creaser, 2005a; Selby et al., 2007; Finlay et al., 2011a). Further studies are required to better constrain the behaviour of Re and Os in both source rocks and oils from a variety of kerogens.

6. CONCLUSIONS

Hydrous pyrolysis experiments were employed to improve our understanding of how Re and Os in ORS are affected by hydrocarbon maturation and gain an improved insight to the Re–Os systematics of the ORS–crude oil system. The experiments were designed to allow us to evaluate how Re and Os are transferred from source rock kerogen to bitumen and into oils. The experiments provide the results on Re and Os isotopic abundance and isotopic data from the first attempt to monitor the transfer of Re and Os from source rocks into oils on a laboratory timescale.

Following extraction of bitumen from two immature Phanerozoic source rocks Re–Os isotopic analyses indicate that the extracted rock component has Re and Os abundances which are very close to the whole rock values. In addition, the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios of the extracted rock and whole rock components of these immature source rocks are very similar. Thus Re and Os are predominantly bound in the extracted rock component and the isotopic ratios show minimal variation.

Although there are significant (up to 27%) variations in Re and Os abundances between the pyrolysed whole rock and extracted rock components, the $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios of the extracted rocks and whole rock components display much smaller variations. Importantly, the non-pyrolysed and pyrolysed whole rocks and extracted rock $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ ratios vary less than the abundances (17% and 4%, respectively). These results demonstrate minimal transfer of Re–Os from extracted rock to the bitumen fraction. The dataset from these hydrous pyrolysis experiments allows us to conclude that Re and Os remain complexed in whole rock “kerogen” even after polyphase metamorphism. This is probably a result of the Re and Os being complexed within very stable functional groups that are associated with insoluble organic matter. Furthermore, it can be hypothesised that the hydrocarbon maturation process does not adversely upset the Re–Os system as observed in natural systems and thus further demonstrates that Re–Os geochronology is feasible on petroleum mature, overmature and metamorphosed ORS.

The peak bitumen generation temperature of Type II-S kerogens occurs at 300 °C and correlates with the peak Re and Os abundance of this bitumen. This suggests that as the kerogen cracks to bitumen, Re and Os are mobilised

and transferred from the complexation site in kerogen to the related site in bitumens.

The Phosphoria bitumens from the non-pyrolysed samples have $^{187}\text{Os}/^{188}\text{Os}$ ratios that are much more radiogenic than those of the non-pyrolysed whole rock. In contrast, the pyrolysis-generated bitumens have $^{187}\text{Os}/^{188}\text{Os}$ ratios which are comparable with the relevant whole rock values. If the isotopic composition of the bitumen is transferred to the oil with limited fractionation then the isotopic composition of oil represents a very useful fingerprinting tool as suggested by previous work (Selby and Creaser, 2005a; Finlay et al., 2011a,b). As with other geochemical fingerprinting techniques such as Ni/V and organic geochemistry, the Re–Os geochronometer requires that the oils or bitumens display a range in $^{187}\text{Re}/^{188}\text{Os}$ that are positively correlated to $^{187}\text{Os}/^{188}\text{Os}$ ratios.

After bitumen generation, the source rocks produce immiscible oil with generation peaking at 355 for Type II-S (Lewan, 1985). However, in contrast with natural systems these oils do not contain any measurable amounts of Re and Os. From this we can suggest that laboratory-based hydrous pyrolysis experiments do mimic natural systems with regard to Re–Os transfer during bitumen generation. However, the lack of transfer of Re and Os from the bitumen to the oils demonstrates that hydrous pyrolysis experiments do not fully mimic natural systems with respect to Re and Os transfer from source rocks to oil. This lack of transfer of Re and Os to the oils from bitumens in the experiments may be a result of the high experimental temperatures and short time frames resulting in the formation of insoluble phase such as pyrobitumen. This pyrobitumen phase is insoluble and impossible to isolate without disturbing Re–Os systematics. This lack of Re and Os in the oils from these experiments strongly suggests that the transfer of Re and Os is kinetically controlled with time possibly being the most important factor.

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