Role of water in hydrocarbon generation from Type-I kerogen in Mahogany oil shale of the Green River Formation

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ABSTRACT

Hydrous and anhydrous closed-system pyrolysis experiments were conducted on a sample of Mahogany oil shale (Eocene Green River Formation) containing Type-I kerogen to determine whether the role of water had the same effect on petroleum generation as reported for Type-II kerogen in the Woodford Shale. The experiments were conducted at 330 and 350 °C for 72 h to determine the effects of water during kerogen decomposition to polar-rich bitumen and subsequent bitumen decomposition to hydrocarbon-rich oil. The results showed that the role of water was more significant in bitumen decomposition to oil at 350 °C than in kerogen decomposition to bitumen at 330 °C. At 350 °C, the hydrous experiment generated 29% more total hydrocarbon product and 33% more C_{15+} hydrocarbons than the anhydrous experiment. This is attributed to water dissolved in the bitumen serving as a source of hydrogen to enhance thermal cracking and facilitate the expulsion of immiscible oil. In the absence of water, cross linking is enhanced in the confines of the rock, resulting in formation of pyrobitumen and molecular hydrogen. These differences are also reflected in the color and texture of the recovered rock. Despite confining liquid-water pressure being 7–9 times greater in the hydrous experiments than the confining vapor pressure in the anhydrous experiments, recovered rock from the former had a lighter color and expansion fractures parallel to the bedding fabric of the rock. The absence of these open tensile fractures in the recovered rock from the anhydrous experiments indicates that water promotes net-volume increase reactions like thermal cracking over net-volume decrease reactions like cross linking, which results in pyrobitumen. The results indicate the role of water in hydrocarbon and petroleum formation from Type-I kerogen is significant, as reported for Type-II kerogen.

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1. Introduction

Closed-system pyrolysis experiments have shown that liquid H_2O has a significant effect on petroleum generation from Type-II kerogen in oil-prone source rocks. Lewan (1997) demonstrated that pyrolysis of Type-II kerogen in the Woodford Shale generated more liquid petroleum products in the presence of water than in its absence. The initial overall reaction of kerogen decomposition to polar-rich, high-molecular-weight bitumen was not affected by the presence of water as much as the subsequent overall reaction of bitumen decomposition to hydrocarbon-rich oil. In the absence of water, this latter overall reaction appears to have been diminished by the effect of cross-linking reactions, which resulted in the lower liquid yield (Lewan, 1997). Additional experiments with D_2O, Ga–In liquid alloy, isolated kerogen and various pressured gases showed that water dissolved in the bitumen network of

the source rock acted as a source of hydrogen to promote thermal cracking over cross linking, and was also an important component that contributed to the immiscibility and expulsion of the hydrocarbon-rich oil from the polar-rich bitumen retained in the rock.

In another comparative study, Behar et al. (2003) pyrolyzed Type-III kerogen in lignite with and without the addition of water. The experiments showed differences in the amount of polar-rich compounds generated (NSOs) and in maturity parameters (vitrinite reflectance and atomic H/C ratio) of the recovered lignite. Although no significant difference was observed in the quantity of C_{14+} saturates generated, 29% more C_{8+} hydrocarbons (i.e. saturates and aromatics) were generated in the hydrous experiments. The study also noted that the amount of water generated from the lignite in the intended anhydrous experiments was sufficient to form a saturated steam phase during pyrolysis. This saturated-steam condition did not constitute a true anhydrous experiment, so was referred to as nonhydrous pyrolysis. Realizing that appreciable quantities of water were generated and released by lignite and low rank coals led Behar et al. (2003) to conclude that the lack of differences, with and without added water, in petroleum products generated in confined Au tubes by Michels and Landais

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(1994) and Monthioux et al. (1983) could be explained by hydrous conditions existing in the confined gold tubes with no initially added water.

These comparative pyrolysis studies with and without water are extended in this study to Type-I kerogen in the Mahogany oil shale of the Green River Formation (Eocene). Type-I kerogen is an important component of lacustrine source rocks in Brazilian basins (Mello et al., 1988) and in the Uinta Basin of Utah (Tissot et al., 1978), where subsurface water is ubiquitous. It is also the common kerogen type in vast quantities of oil shales in the Green River Formation of the Piceance Basin, Colorado (Johnson et al., 2010), where *in situ* retorting without water is being tested (e.g. Brandt, 2008). The objective of this study was to determine differences between hydrous and anhydrous conditions in experiments at 330 and 350 °C for 72 h for Type-I kerogen. These temperature/time conditions respectively represent kerogen decomposition to polar-rich bitumen and bitumen decomposition to hydrocarbon-rich oil (Ruble et al., 2001).

2. Methods

The sample, 930923-8, is from the Mahogany oil-shale zone in the Parachute Creek Member of the Green River Formation. Details of the collection site are given by Ruble et al. (2001). The sample was crushed and sieved to a size range from 0.5 to 2.0 cm. Hastelloy C276 reactors (1 l) were loaded with 200 g crushed rock, with a Ni–Cr screen (18 mesh) placed over the rock to keep it in place during product collection at the end of the experiments. No water was added to the anhydrous experiments. Water generated from a Fisher Assay of the sample was 2.8 wt% of the rock. Calculations using ASME steam tables as described by Lewan (1993) indicated that only an undersaturated steam would occur in the reactor during heating at 330 and 350 °C. This was confirmed by initial steam pressures <1.4 MPa in both experiments, which is considerably lower than the 12.86 and 16.54 MPa required for steam saturation at 330 and 350 °C, respectively. Therefore, these experiments can be classified as anhydrous because the steam pressure is <20% of the saturated steam pressure as defined by Lewan (1992).

In addition to the crushed rock, the hydrous experiments were loaded with 400 g distilled water. This amount insured that all of the crushed rock was in contact with liquid water before, during and after the experiments. Calculations using ASME steam tables as described by Lewan (1993) indicate that, with a measured rock bulk density of 1.95 g/cm^3, the reactors were 67% and 73% filled with liquid water at 330 and 350 °C, respectively. The headspace in all of the loaded reactors was evacuated to at least 4.1 kPa for several minutes and then filled with 6.9 MPa of He to check for leaks with a Gow-Mac leak detector. If no leaks were observed, the He pressure was reduced to between 170 and 180 kPa. The reactors were weighed to within 0.1 g and placed in an electric heater. They were brought up to temperature within 55 min for the hydrous experiments and within 79 min for the anhydrous experiments. The experimental duration of 72 h was started from the time the reactors reached the designated temperatures. The higher thermal conductivity of water gave better temperature control with a standard deviation less than ±0.5 °C for the hydrous experiments vs. standard deviation within ±1.4 °C for the anhydrous experiments., The specific amounts of water and rock are given in Table 1.

At the end of the experiments, the electric heaters were turned off and the reactors were pulled out of the electric heaters within 1 h to allow them to cool to room temperature by the next day for unloading. The room-temperature reactors were weighed within 0.1 g and were compared with their original weights to determine whether leakage had occurred during the experiment. Gas

Table 1
Mass balance of recovered products from anhydrous- and hydrous-pyrolysis experiments with Mahogany oil shale (930923-8) from Green River Formation.

	Anhydrous		Hydrous	
Experiment	HP-3318	HP-3319	HP-3321	HP-3322
Conditions (°C/h)	330/72	350/72	330/72	350/72
Initial rock (g)	200.3	200.2	200.1	200.0
Added water (g)	0.0	0.0	400.3	400.0
Final pressure (MPa)[a]	1.46	2.56	13.7	18.63
Collected products (g)				
Recovered rock	191.4	187.5	183.8	172.2
Expelled oil[b]	0.573	0.570	5.05	14.32
Total gas	2.8	3.8	3.9	5.7
Water recovered	3.9	5.8	398.1	399.4
Total recovered	198.7	197.7	590.9	591.6
% Total recovered	99.2	98.7	98.4	98.6

[a] Final recorded pressure at experimental temperature.
[b] Expelled oil for anhydrous experiments is volatile liquid petroleum that condensed on the upper portion of reactor walls after cooling to room temperature. Expelled oil for hydrous experiments is summation of free oil floating on the water surface and free-oil rinse. Free oil quantities have been corrected for minor amounts of entrained water and rock dust, but equipment rinse has not been corrected for light oil (C_{14-}) loss during solvent blowdown.

pressures were measured using a calibrated pressure transducer to within 0.1 psia and two 50 cm^3 gas samples were collected for molecular composition and stable carbon isotope analyses. After venting the remaining gas, the reactor was weighed to determine by difference the amount of gas generated in the experiment (Table 1). The reactors were then opened and the head space depth to the top of the water or oil in the hydrous experiments was measured to within 1 mm. The moles of gas at the end of the experiments were calculated using the Ideal Gas Law with recorded room temperature, headspace volume and pressure. Molecular composition of the generated gases was analyzed with a Hewlett Packard 6890 gas chromatograph with seven columns, two thermal conductivity detectors and one flame ionization detector configured by Wasson-Ece Instrumentation.

Carbon isotope values of natural gas components were determined using gas chromatography–isotope ratio monitoring mass spectrometry (GC–IRMS) methodology after Baylis et al. (1994). A natural gas sample was introduced into a HP 6890 gas chromatograph via an autosampler through a sample-loop injector. Natural gas components were separated using a Varian PoraBond-Q column (50 M × 0.32 mm × 5 μm). Typical GC conditions were: He carrier gas @ 1.5 ml/min; 40 °C (6 min) to 150 °C at 15 °C/min; ramp to 250 °C (held 5 min) at 30 °C/min. Components were combusted in the He stream (with a trickle of O$_2$) at 1050 °C in an in-line Alsint-99.7 ceramic reactor (0.5 mm i.d. × 6 mm o.d. × 500 mm length). The combustion products (primarily CO$_2$ and H$_2$O) were passed through an in-line Nafion drier and the final analyte CO$_2$ was passively drawn via open split into the source of a GV-Elementar Isoprime isotope-ratio mass spectrometer for subsequent carbon isotope analysis. The final carbon isotope values represent the average of multiple replicate analyses (typically 3) with a standard deviation of ±0.2‰. The $\delta^{13}C$ values are reported relative to the international Vienna Pee dee Belemnite (VPDB) standard.

The expelled immiscible oil floating on the water surface of the hydrous experiments was collected with a Pasteur pipette, weighed in a tared glass vial and designated as free floating oil. An aliquot was filtered through a 0.45 μm PTFE cartridge with a 5 ml glass syringe. The remaining expelled immiscible oil occurring as a thin film on the surface of the water, reactor headspace walls and collection pipette was collected with ca. 300 ml benzene and designated as free-oil rinse. The benzene with its free-oil rinse was filtered through a 0.45 μm PTFE filter in an all glass filter apparatus. The benzene was allowed to evaporate under a fume hood until the wt change was <3 mg within 30 min. As described by

Lewan (1993), the mathematical sum of the free floating oil and the free-oil rinse constitutes the expelled oil. Ca. 100 mg of the free oil was deasphaltened with iso-octane and fractionated on a silica–alumina column into saturates with iso-octane, aromatics with CH_2Cl_2 and resins with a mixture of CH_2Cl_2 and MeOH. The complete procedure is available at http://energy.cr.usgs.gov/gg/geo-chemlab/current_sops/columchromsop.html.

For the anhydrous experiments, no liquid petroleum was observed on the rock chips but a thin film of what appeared to be oil vapor that condensed at the top of the reactor during cooling at the end of the experiment was present. With the Ni–Cr screen holding the crushed rock in place at the bottom of the reactor, this oil film was rinsed off the upper reactor walls with benzene by holding the reactor in an inclined position over a wide-mouth separatory funnel. The benzene was removed as for the free-oil rinse in the hydrous experiments. This free-oil rinse of condensed oil vapor is the only component that constitutes expelled oil in the anhydrous experiments and is referred to as volatile oil.

Water was decanted from the reactors in the hydrous experiments and filtered through a 0.45 μm GN-6 Metricel filter in an all-glass vacuum filter apparatus. The filtered water weights were recorded. The spent rocks for both hydrous and anhydrous experiments were collected with a large spatula and placed in tared Petri dishes and weighed. The recovered rock was allowed to air dry in a fume hood until the weight became constant to within 0.1 g after at least 3 h. The weight loss gave the amount of water associated with the recovered rock, which was added to the weight of the filtered water for a mass balance calculation for the hydrous experiments. Recovered water for the anhydrous experiments only reflects the weight loss of the recovered rock after air drying in the fume hood.

A 20 g aliquot of pulverized dried recovered rock was extracted with $CHCl_3$ in a Soxhlet apparatus until the solvent filling the siphon tube was clear, which ranged from 24 to 66 h. The $CHCl_3$ was evaporated off under a fume hood until the change in wt was 3 mg or less within a 30 min interval. Bitumen from the original unheated rock was also extracted and blown down using the same procedure. Separation of asphaltenes, saturates, aromatics and resins was conducted as above.

3. Results

3.1. Overall mass balance

Table 1 gives a mass balance of the major recovered products. The overall mass balance is at or greater than 98.4 wt%. This is based on the original rock mass used in the anhydrous experiments and the original rock plus added water mass in the hydrous experiments. The anhydrous experiments generate some water, which is expected to be from early kerogen decomposition, as discussed by Colburn et al. (1989). This generated water cannot be differentiated from the added water in the hydrous experiments and, as a result, is included with the recovered water mass. The mass of total gas is determined by taking the reactor mass difference before and after gas collection and venting. Total gas increases from the 330 to 350 °C experiments with the increase being greater in the hydrous experiments. As expected, the mass of recovered rock decreases from the 330 to 350 °C experiments, but because of more expelled products (i.e. oil and gas) in the hydrous experiments the decrease in recovered rock is greater than in the anhydrous experiments.

3.2. Visual rock description

The recovered rock from all the experiments remained essentially intact and maintained its original gravel size and angular shapes. However, notable differences in color and texture were observed. The overall color darkened from 330 to 350 °C in the hydrous and anhydrous experiments, but the anhydrous recovered rock was distinctly darker than in its corresponding hydrous experiment (Fig. 1). The other distinct difference between the recovered rock from hydrous and anhydrous experiments is in the texture. The darker recovered rock from the anhydrous experiments has a texture similar to the original rock, with a bedding fabric highlighted by lamina with subtle compositional differences (Fig. 2a and b). The lighter recovered rock from the hydrous experiments also has laminae with subtle compositional differences but prominent lenticular expansion fractures parallel to the bedding fabric are common (Fig. 2c and d). These fractures can be open by as much as 0.2 mm and can extend 1–6 mm through portions of the rock chips. In the 330 °C experiment, the fractures contain bitumen and the rock surfaces sometimes show bitumen balls that appear to have been extruded from the rock via the fractures. In the 350 °C experiment, the fractures are open, with no apparent filling, but have some thin bitumen lining. These expansion fractures have been reported by Lewan (1987), being attributed to tensile stress generated by expansion associated with kerogen conversion to bitumen and bitumen conversion to oil. The significance of these expansion fractures is especially noteworthy considering the rock chips in the hydrous experiments experienced a uniform hydrostatic (i.e. liquid water) pressure 7–9 times greater than the vapor pressure experienced by the rock chips in the anhydrous experiments (Table 1). The presence of these fractures in the recovered rock from the hydrous experiments and their scarcity in the recovered rock from the anhydrous experiments attests to significant physiochemical differences in petroleum-generation reactions with and without water.

3.3. Leco TOC and Rock Eval

Leco total organic carbon (TOC) contents and Rock-Eval pyrolysis parameters are given in Table 2. The original TOC (15.83 wt%) was reduced to essentially the same value at 330 °C in the hydrous and anhydrous experiments (11.7 and 11.4 wt%, respectively). However, at 350 °C the TOC of the recovered rock was 10.47 wt% for the anhydrous experiment and 7.53 wt% for the hydrous experiment. A more accurate assessment of TOC loss can be made by recalculating the values on the basis of the original TOC content (i.e. mg/g orig. TOC) by using the recovered rock weights in Table 1. The TOC values in these units show more of a TOC loss in the hydrous experiments than in the anhydrous experiments for both temperatures. The differences are greater at 350 °C than at 330 °C (Table 2). At 350 °C, 59% of the original TOC was lost from the rock in the hydrous experiments and 38% was lost in the anhydrous experiment.

The Rock-Eval hydrogen index (HI, Table 2) indicates that the recovered rock at 330 °C maintained a higher generation potential in the hydrous experiment than in the anhydrous experiments in spite of the similar TOC values. The higher generative potential in the recovered rock from the hydrous experiment relative to the anhydrous experiment is also observed at 350 °C. This indicates that, in spite of more TOC being lost from the rock in the hydrous experiments, the remaining TOC has a higher hydrocarbon potential than that of the higher TOC remaining in the rock of the anhydrous experiment. Conversely, the S_1 component is reversed, with the recovered rock from the anhydrous experiments at both temperatures being greater than that of the recovered rock from the hydrous experiments. This higher S_1 component of the recovered rock from the anhydrous experiments is also reflected in the higher production index (PI) values.

The temperature at maximum S_2 generation (T_{max}) remains at 442 °C in both hydrous experiments, as observed for Green River
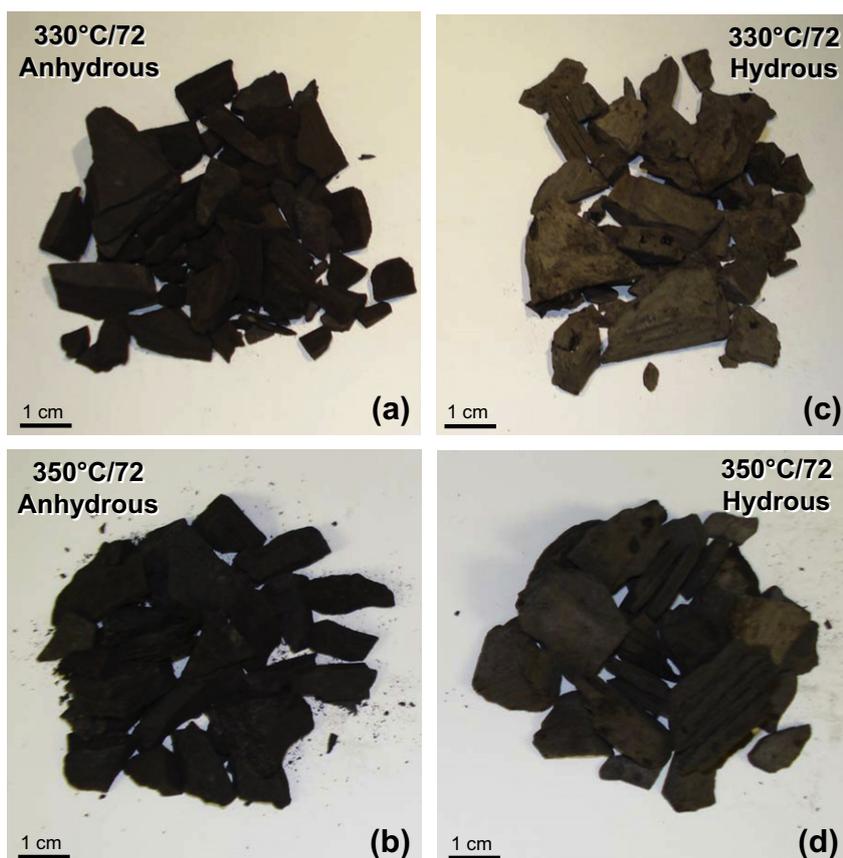
Fig. 1. Aliquots of gravel-sized rock recovered from anhydrous experiments at (a) 330 °C for 72 h and (b) 350 °C for 72 h, and from hydrous experiments at (c) 330 °C for 72 h and (d) 350 °C for 72 h.

Fig. 2. Photomicrographs taken with a binocular microscope of rock-chip surfaces perpendicular to bedding fabric of recovered rock from anhydrous experiments at (a) 330 °C for 72 h and (b) 350 °C for 72 h and from hydrous experiments at (c) 330 °C for 72 h and (d) 350 °C for 72 h.

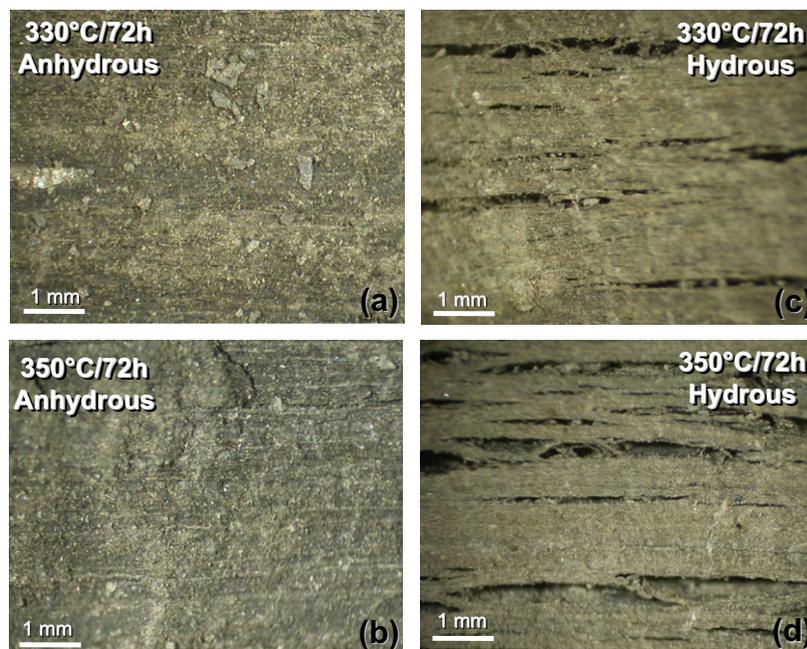Type-I kerogen in other hydrous experiments (Huizinga et al., 1988) and naturally matured source rocks (Tissot et al., 1987).

The T_{max} values of the rock recovered from the anhydrous experiments decrease with increasing temperature relative to that of

Table 2
TOC and Rock-Eval parameters for original sample and pyrolyzed aliquots of Mahogany oil shale (930923-8) from Green River Formation.

	Original spl.	330 °C/72 h		350 °C/72 h	
Experiment	930923-8	HP-3318	HP-3321	HP-3319	HP-3322
Conditions (°C/h)	Unheated	Anhydrous	Hydrous	Anhydrous	Hydrous
TOC (wt% recovered rock)	15.8	11.4	11.7	10.5	7.5
(mg/g original TOC)	1000.0	714.4	679.5	619.4	409.6
Rock Eval analysis					
S_1 (mg/g recov. rock)	3.7	40.3	23.6	53.9	14.1
(mg/g original TOC)	23.2	242.9	136.6	318.9	76.6
S_2 (mg/g recov. rock)	134.3	70.5	85.1	29.6	33.4
(mg/g original TOC)	846.8	425.3	493.3	175.2	181.6
S_3 (mg/g recov. rock)	5.4	3.4	1.4	3.3	1.2
T_{max} (°C)	442	438	442	432	443
HI (mgS_2/TOC)[a]	848.3	618.1	726.8	282.9	443.8
OI (mgS_3/TOC)[a]	34.2	29.6	12.2	31.1	16.2
PI ($S_1/S_1 + S_2$)[b]	0.03	0.36	0.22	0.65	0.3

[a] HI, hydrogen index; OI, oxygen index, based on TOC of recovered rock.
[b] PI, production index.

the original unheated rock, which has not been reported for naturally matured Type-I kerogen. The oxygen index (OI) is less in all the experiments relative to the original unheated rock (Table 2), but is significantly higher in the recovered rock from the anhydrous experiments than that from the hydrous experiments.

3.4. Extracted bitumen

The amount and composition of extractable bitumen from the original unheated sample and the recovered rock from the anhydrous and hydrous experiments are given in Table 3. Total bitumen from the anhydrous experiments was consistently greater than in the corresponding hydrous experiments. However, the difference at 330 °C is less than that at 350 °C. This is similar to comparisons between hydrous and anhydrous experiments with source rocks containing Type-II kerogen (Lewan, 1997). Within the context of the full temperature range (160–365 °C for 72 h) of hydrous experiments on the same sample by Ruble et al. (2001), the amounts of bitumen generated can be explained by the two overall reactions: (i) kerogen to bitumen and (ii) bitumen to oil. The initial increase in bitumen from the original unheated sample to 330 °C for anhydrous and hydrous experiments is attributed to the kerogen partially decomposing to bitumen. In the 350 °C experiment, the decrease in bitumen is attributed to its decomposition to

immiscible oil in the hydrous experiment and to pyrobitumen in the anhydrous experiment.

The saturate/aromatic ratio and normalized % of hydrocarbons (i.e. saturates + aromatics) are consistently higher in the anhydrous experiments than those of the corresponding hydrous experiments. GC traces of the bitumen extracts are shown in Fig. 3 and characteristic indices are given in Table 3. The pristane/phytane (Pr/Ph) ratio values are greater in all of the experiments relative to the original bitumen, but the values for the anhydrous experiments are higher than for the hydrous experiments. Conversely, the Pr/n-C_{17} and Ph/n-C_{18} ratios are lower in all of the experiments relative to the original bitumen, and those for the hydrous experiments are greater than those for the anhydrous experiments. The odd predominance in the n-C_{27} to n-C_{31} range remains more pronounced in the bitumen from the hydrous experiments than from the anhydrous experiments. The unresolved complex mixture (UCM) area relative to n-C_{28} is the greatest in the original unheated sample, and higher in the hydrous experiments than in the anhydrous experiments (Table 3). Overall, these chromatographic attributes indicate the anhydrous bitumens have a more mature appearance than those of the hydrous experiments.

All the saturate, aromatic, resin and asphaltene (SARA) fractions of the experimental bitumens are greater than those of the original bitumen (Table 3). Saturate and aromatic fractions increase from 330 to 350 °C in the anhydrous experiments, but decrease in the

Table 3
Bitumen extract of original sample and recovered rock from anhydrous and hydrous pyrolysis experiments with Mahogany oil shale (930923-8) from Green River Formation (930923-8).

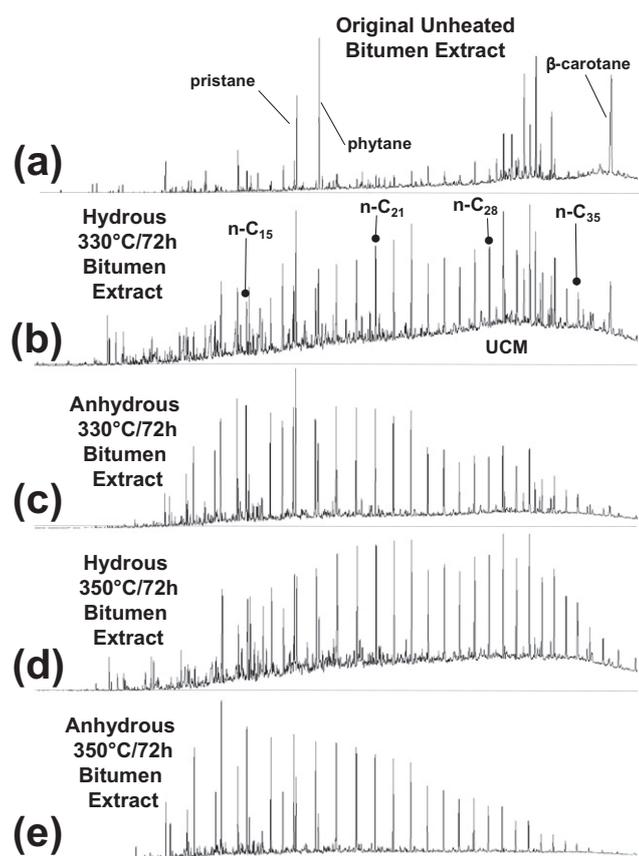|	Original	Anhydrous	Hydrous	Anhydrous	Hydrous
Experiment		HP-3318	HP-3321	HP-3319	HP-3322
Conditions (°C/h)	Unheated	330/72	330/72	350/72	350/72
Bitumen extract (mg/g orig. TOC)					
Saturates (Sat)	24.9	136.8	86.0	176.7	59.0
Aromatics (Arom)	21.8	80.4	72.7	92.4	44.9
Resins	92.4	124.0	114.8	97.7	47.2
Asphaltenes	12.5	300.2	340.7	90.7	58.1
Total	151.6	641.4	614.3	457.4	209.1
Sat/Arom	1.1	1.7	1.2	1.9	1.3
% Hydrocarbons	30.8	33.9	25.8	58.8	49.7
% Polars	69.2	66.1	74.2	41.2	50.3
Gas chromatography					
Pr/Ph	0.63	2.10	1.92	1.94	1.76
Pr/nC_{17}	3.19	1.37	2.13	0.64	0.97
Ph/nC_{18}	15.92	0.74	1.26	0.36	0.53
OEP (nC_{27} to nC_{31})[a]	2.51	1.26	1.44	1.15	1.20
UCM/(n-C_{28} + UCM)	0.44	0.21	0.39	0.16	0.25

[a] Scalan and Smith (1970).

Fig. 3. FID gas chromatograms of bitumen extracted from (a) original unheated sample and samples subjected to (b) hydrous pyrolysis at 330 °C for 72 h, (c) anhydrous pyrolysis at 330 °C for 72 h, (d) hydrous pyrolysis at 350 °C for 72 h and (e) anhydrous pyrolysis at 350 °C for 72 h (UCM, unresolved complex mixture).

Fig. 4. Ternary plot of saturate, aromatic and polar (resin + asphaltene) fractions of C_{15+} component of bitumen extracted from original unheated rock and recovered rock aliquots, and generated oil from hydrous and anhydrous experiments at 330 and 350 °C for 72 h.

hydrous experiments (Table 3). Resin and asphaltene fractions decrease from 330 to 350 °C in hydrous and anhydrous experiments, but the decrease is greater in the former. The proportionality of these fractions is shown in the ternary diagram in Fig. 4, with resin and asphaltene fractions combined under the heading of polars. Relative to the original bitumen, the bitumen from the 330 °C experiments is slightly enriched in polars for the hydrous experiment and slightly depleted in polars for the anhydrous experiment. The 350 °C experiments show appreciable depletion in the polars for the hydrous and anhydrous bitumens. Although the anhydrous bitumen at 350 °C shows more polar depletion than that of the hydrous bitumen, the differences between that of the 330 °C experiments is similar (Fig. 4). However, the anhydrous bitumen shows a slight saturate enrichment relative to aromatics compared to the hydrous bitumen, which is reflected in the saturate/aromatic values in Table 3.

3.5. Generated oil

Two types of generated oil were distinguished. In anhydrous experiments, volatile components condense at the top of the reactor as it cools to room temperature at the end of the experiment. This condensed volatile oil occurs as fingers of thin films that start at the reactor head and extend down the reactor wall and end ca. 7 cm above the screen overlying the rock chips. It can only be collected with benzene and is referred to as volatile free-oil rinse. As shown in Table 4, the amounts of this volatile oil is essentially the same in both anhydrous experiments (330 and 350 °C). In hydrous experiments, immiscible oil is expelled from the water-submerged
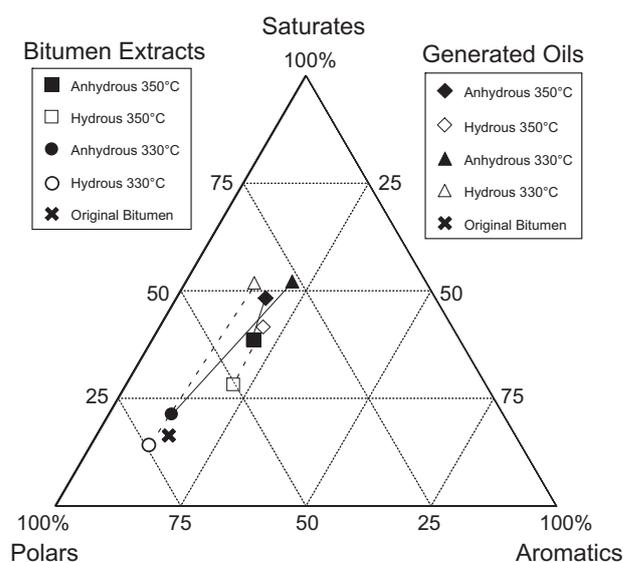
rock and collects on the surface of the water during the experiment (Lewan, 1997). Some of it may also volatilize in the water vapor or dissolve in the liquid water at the experimental temperatures and pressures, but a significant portion remains as a liquid oil phase, as indicated by oil-layer staining on the reactor walls and thermal well at the expanded water levels. As noted by Lewan (1993), this oil layer is particularly notable when borosilicate glass liners are used. The majority of it (Table 4) is collected with a pipette and referred to as free floating oil. The oil remaining on the reactor walls, reactor head and collection pipette is collected with benzene and referred to as free-oil rinse. Although the quantities of free-oil rinse from the hydrous experiments and the volatile oil rinse from the anhydrous experiments are under the same row heading in Table 4, they are actually different collection products (i.e. liquid oil vs. condensed oil vapor). The summation of free floating oil and free-oil rinse is collectively referred to as total oil (C_{5+}). As shown in Table 4, the amount of total immiscible oil (C_{5+}) in the hydrous experiments increases nearly threefold from 330 to 350 °C. The total volatile oil (C_{5+}) generated in the anhydrous experiments remains essentially the same from 330 to 350 °C and is less than the total immiscible oil generated in the 350 °C hydrous experiment by more than one order of magnitude.

The SARA fractions of the C_{15+} portion of the generated oils are given as mg/g of original TOC in Table 4. These fractions for the C_{15+} portion of the volatile oils from the anhydrous experiments have similar quantities at 330 and 350 °C. The proportionality of the fractions is different, with saturates increasing slightly relative to aromatics and hydrocarbons (saturates and aromatics) decreasing relative to polars (resins and asphaltenes) from 330 to 350 °C (Table 4). The proportionality of hydrocarbons to polars for the immiscible oils generated from the hydrous experiments is approximately the same at 330 and 350 °C. However, saturates relative to aromatics decrease from 330 to 350 °C (Table 4). The overall proportionality among saturates, aromatics and polars (resins + asphaltenes) is shown in Fig. 4. This ternary diagram includes the bitumen extracts for comparison. All the generated oils are more enriched in saturates and aromatics than their corresponding bitumen extracts, but to different degrees. The greatest differences are at 330 °C for both the hydrous and anhydrous experiments (Fig. 4). The least difference is seen for the 350 °C anhydrous

Table 4
Oil generated as volatiles from anhydrous experiments and immiscible phase from hydrous experiments on aliquots of Mahogany oil-shale sample (930923-8) from Green River Formation.

	Anhydrous	Hydrous	Anhydrous	Hydrous
Experiment	HP-3318	HP-3321	HP-3319	HP-3322
Conditions (°C/h)	330/72	330/72	350/72	350/72
Generated oil (mg/g orig. TOC)	Volatile oil	Immiscible oil	Volatile oil	Immiscible oil
Free floating oil (C_{5+})	0.0	98.0	0.0	356.8
Free floating oil (C_{15+})	0.0	82.2	0.0	282.6
Free-oil rinse (C_{15+})	18.1	61.4	18	95.6
Free-oil rinse (C_{5+})[a]	21.5	73.2	22.7	120.8
Total C_{15+} oil	18.1	143.7	18.0	432.5
Total C_{5+} oil[a]	21.5	171.2	22.7	477.5
SARA C_{15+} (mg/g orig. TOC)				
Saturates (Sat)	9.4	74.5	8.7	179.8
Aromatics (Arom)	3.8	19.8	3.2	89.6
Resins	3.7	34.2	4.7	117.9
Asphaltenes	1.1	15.2	1.4	45.2
Total (C_{15+})	18.1	143.7	18.0	432.5
Sat/Arom	2.5	3.8	2.7	2.0
% C_{15+} Hydrocarbons	73.2	65.6	65.8	62.3
% C_{15+} Polars	26.8	34.4	34.2	37.7
% C_{5+} Hydrocarbons[b]	77.5	71.2	72.9	65.8
% C_{5+} Polars	22.5	28.8	27.1	34.2
GC ratios (peak heights)				
Pr/Ph	1.97	2.13	1.86	2.13
Pr/nC_{17}	1.54	2.61	0.68	1.04
Ph/nC_{18}	0.76	1.39	0.36	0.51
OEP (nC_{27} to nC_{31})[c]	1.30	1.47	1.13	1.19

[a] Anhydrous values for C_{14-} fraction lost during column chromatography assumed to be the same percentages as determined for corresponding hydrous experiments.
[b] Assuming all of C_{14-} fraction is undifferentiated hydrocarbon (saturates + aromatics).
[c] Scalan and Smith (1970).

experiment, with the difference for the 350 °C hydrous experiment being intermediate. GC traces of the generated oils are shown in Fig. 5. The isoprenoids are more apparent in the hydrous than in the anhydrous experiments. As expected in typical thermal maturation trends, the *n*-alkanes become more prominent at 350 °C, as indicated by Pr/*n*-C_{17} and Ph/*n*-C_{18} (Table 4). Pr/Ph remains the same from 330 to 350 °C in the hydrous experiments, but decreases slightly in the anhydrous experiments. The odd *n*-alkane dominance in the C_{27}–C_{31} range decreases as expected (Hunt, 1996) from 330 to 350 °C in hydrous and anhydrous experiments

(Table 4), but the decrease is less in the hydrous experiments. Overall, the generated oils from the hydrous experiments have a more thermally immature character than the volatile oils generated from the anhydrous experiments (Fig. 5).

3.6. Generated gas

The compositions of the generated head gas in the anhydrous and hydrous experiments are given in Table 5. CO_2 is the major gas generated in hydrous and anhydrous experiments at both
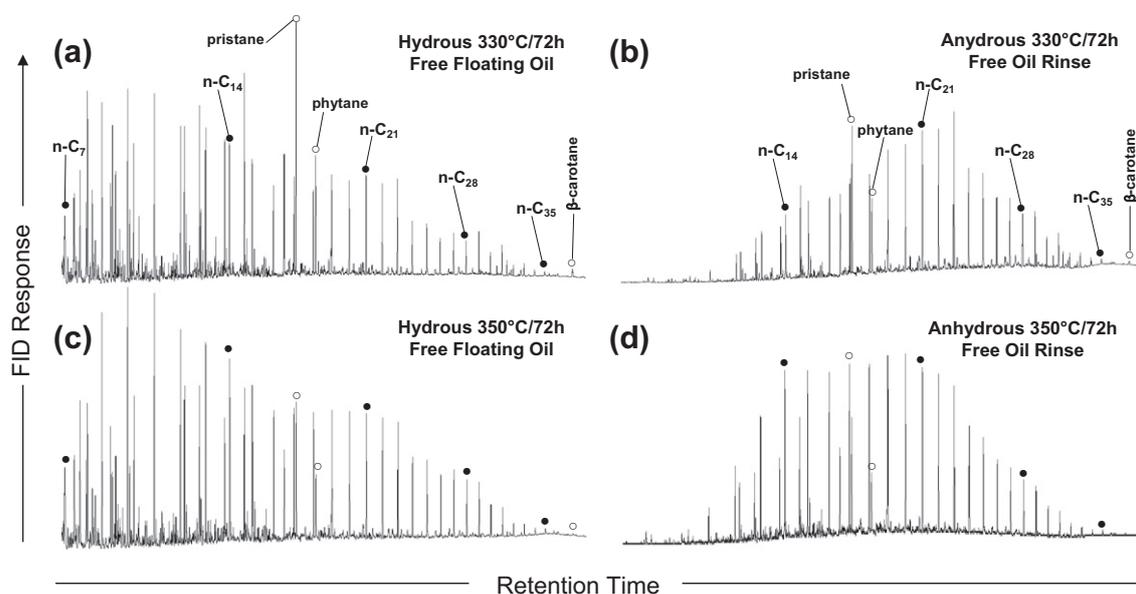

Fig. 5. FID gas chromatograms of generated oil from (a) hydrous pyrolysis at 330 °C for 72 h, (b) anhydrous pyrolysis at 330 °C for 72 h, (c) hydrous pyrolysis at 350 °C for 72 h and (d) anhydrous pyrolysis at 350 °C for 72 h.

temperatures. Unlike in Lewan (1997), no attempt was made to do a mass balance on its occurrence because of the possibility of carbonate mineral contributions. Even without taking into account the large amounts of CO_2 that can be dissolved in the water (e.g. Lewan, 1997), the amounts of generated CO_2 are significantly higher in the hydrous experiments. Conversely, H_2 is higher in the anhydrous experiments, also reported by Lewan (1997) for Type-II kerogen in the Woodford Shale. H_2S is essentially the same in the hydrous and anhydrous experiments, with the latter having slightly higher quantities. Again, this comparison does not take into account the dissolved H_2S in the water of the hydrous experiments, which can be appreciable depending on pH (Lewan, 1997). CO did not occur in notable quantities in the hydrous or anhydrous experiments (Table 5). The quantities of non-hydrocarbon gases increased in the hydrous experiments from 330 to 350 °C (Table 5). Likewise, H_2S and H_2 increased in the anhydrous experiments from 330 to 350 °C, but the increase in CO_2 was small.

Higher quantities of hydrocarbon gases were generated in the anhydrous experiments than in the corresponding hydrous experiments (Table 5). Methane enrichment as determined by the methane/ethane (C_1/C_2) ratio and the dryness index ($C_1/\sum[C_1$ to $nC_5]$) indicates that methane is more enriched in the hydrous experiments than in the corresponding anhydrous experiments (Table 5). The quantities of hydrocarbon gases and their mole ratios with one another indicate that the apparent methane enrichment in the hydrous experiments is a result of greater quantities of the heavier hydrocarbons being generated in anhydrous experiments relative to the hydrous experiments. The dryness index ($C_1/\sum[C_1$ to $nC_5]$) and the C_1/C_2 ratio either stay the same or decrease from 330 to 350 °C in both the hydrous and anhydrous experiments (Table 5). Although methane enrichment is generally considered to increase with the maturity of a source rock, Whiticar (1994) notes that this prescribed trend is not as well established for Type-I and Type-II

kerogen as it is for Type-III kerogen. The greater enrichment of methane in natural gases vs. gases generated by pyrolysis remains an issue (Mango, 1992; Price and Schoell, 1995), but the proportionality of the heavier hydrocarbon gases in natural and pyrolysis gases is similar. The typical range of C_2/C_3 and C_3/C_4 ratios for natural gas according to Nikonov (1972) is from 1.5 to 5 and 1 to 3, respectively. As shown in Table 5, these ratios for the gases generated in the hydrous and anhydrous experiments occur within these natural ranges.

The stable carbon isotope ratio (i.e. $\delta^{13}C$) of the gases shows small differences between hydrous and anhydrous experiments and between 330 and 350 °C (Table 5). The values are similar to those reported by Ruble et al. (2001) for methane and ethane. Methane shows the greatest difference between hydrous and anhydrous experiments, with a 0.5‰ difference at 330 °C and a 0.9‰ difference at 350 °C. Differences in the other gases occur within the analytical error of 0.2‰. All the gases show "dogleg" trends on plots of $\delta^{13}C$ vs. carbon-number reciprocal, as reported for other hydrous experiments and some natural samples (e.g. Kotarba et al., 2009).

4. Discussion

Table 6 presents a summary of the data for the hydrous and anhydrous experiments. Similar to the comparative study by Lewan (1997) of Type-II kerogen in the Woodford Shale, there are significant differences between hydrous and anhydrous closed-system pyrolysis. The differences are most evident for the experiments at 350 °C, which represent polar-rich bitumen decomposition to hydrocarbon-rich oil (Ruble et al., 2001). Totals of C_{15+} products plus hydrocarbon gas (C_{6-}) show that hydrous experiments are 12.9% and 28.8% greater than anhydrous experiments at 330 and 350 °C, respectively (Table 6). The largest yield

Table 5
Characterization of generated headspace gas from pyrolyzed aliquots of Mahogany oil shale (930923-8) from Green River Formation (IS, insufficient sample).

	330 °C/72 h		350 °C/72 h	
Experiment	HP-3318	HP-3321	HP-3319	HP-3322
Conditions	Anhydrous	Hydrous	Anhydrous	Hydrous
Molecular analysis (mg/g orig TOC)				
Hydrogen	1.10	0.52	1.65	0.74
Hydrogen sulfide	3.19	3.28	5.63	5.56
Carbon dioxide	62.68	93.16	66.85	119.6
Carbon monoxide	0.00	0.00	0.00	0.00
Methane	9.97	6.98	17.6	15.05
Ethane	6.20	3.57	12.27	8.24
Ethene	0.07	0.03	0.08	0.04
Propane	5.35	3.08	10.38	6.70
Propene	0.16	0.06	0.30	0.12
n-Butane	2.17	1.36	4.06	2.50
i-Butane	1.74	1.25	2.74	2.08
Butenes	0.15	0.07	0.28	0.11
n-Pentane	0.89	0.60	1.56	0.90
i-Pentane	0.85	0.62	1.30	0.89
Undifferentiated C_{5+}	0.42	0.26	0.66	0.35
Total gas	94.9	114.9	125.4	162.9
Total hydrocarbons	27.97	17.90	51.24	36.98
Mole ratios				
$C_1/\Sigma(C_1-nC_5)$	0.62	0.66	0.60	0.66
C_1/C_2	3.01	3.66	2.69	3.42
C_2/C_3	1.70	1.70	1.73	1.80
C_3/C_4	1.80	1.55	2.01	1.93
i-C_4/nC_4	0.80	0.91	0.68	0.83
$\delta^{13}C$ *(‰ vs. PDB)*				
Methane	−46.6	−46.1	−46.9	−46.0
Ethane	−36.8	−36.6	−36.5	−35.9
Propane	−37.0	−36.8	−36.7	−36.8
n-Butane	IS	IS	−35.0	−34.9
Carbon dioxide	−0.8	0.0	−1.1	−1.8

difference between hydrous and anhydrous experiments at 350 °C is less than the 68% difference reported by Behar et al. (2003) for Type-III kerogen in the Wilcox lignite and the 102% difference reported by Lewan (1997) for Type-II kerogen in the Woodford Shale. This may in part be related to more hydrogen being available in the original Type-I kerogen or more likely that the condition at 350 °C for 72 h does not give the maximum yield under hydrous conditions. Totals for Type-III kerogen are considered maximum yields by Behar et al. (2003) at 350 °C for 96 h and the total for Type-II kerogen at 350 °C for 72 h is at the maximum oil yield according to Lewan and Ruble (2002). However, the maximum oil yield for Type-I kerogen in this sample of Mahogany shale is at 360 °C for 96 h (Lewan and Ruble, 2002). At 350 °C for 72 h, the oil yield would be only 78% of the maximum, and greater differences between hydrous and anhydrous experiments may occur at experimental conditions closer to the maximum oil yield.

The C_{6-14} fraction, not measured in the bitumen extracts, can be taken into account by using the Rock-Eval S_1 yields on the recovered rock as a proxy for the total C_{6+} bitumen. As shown in Table 6, significantly greater product yields are still observed for the hydrous experiments. Although more TOC remains in the recovered rock from the anhydrous experiments because of less expelled product, the generating potential of this residual TOC is significantly less than that of the remaining TOC in the hydrous experiments. At 350 °C, 62 wt% of the original TOC remains in the recovered rock from the anhydrous experiment, with a HI value of 283 mg/g TOC. The recovered rock from the hydrous experiment at 350 °C retained only 41 wt% of the original TOC and the HI is 444 mg/g TOC (Table 6). These differences are most readily interpreted by way of cross-linking reactions being more dominant under anhydrous conditions than hydrous conditions. As proposed by Lewan (1997), more pyrobitumen is formed as a result of cross-linking reactions under anhydrous than hydrous conditions because in the latter, dissolved water in the bitumen of the rock serves as a source of hydrogen. Molecular hydrogen is more abundant for the anhydrous experiments, which is indicative of cross linking dominating thermal cracking. In addition, the expulsion of the oil from the confines of the bitumen impregnated rock under hydrous conditions also minimizes cross-linking reactions, which are sometimes referred to as recombination reactions that result in formation of pyrobitumen. The ability of water dissolved in the bitumen to provide a source of hydrogen and facilitate expulsion of immiscible oil is attributed to thermal cracking reactions dominating cross-linking reactions in hydrous experiments. This ability of hydrous pyrolysis to expel generated oil similar to natural crude oil from a source rock is an exceptional attribute originally reported by Lewan et al. (1979).

The net volume of products generated via thermal cracking typically increases and, conversely, decreases via cross-linking reactions. The expansion fractures in the recovered rock from the hydrous experiments indicate an internal net-volume increase in the hydrous experiments, which also generated the most liquid product (bitumen + oil). Conversely, the scarcity of expansion fractures and less hydrocarbon potential remaining in residual organic matter of the rock recovered from the anhydrous experiments and lower liquid product indicates cross-linking reactions were more dominant than in the hydrous experiments. The tensile stress generated within the rock of the hydrous experiments is especially noteworthy considering the liquid-water confining pressure (13.70 and 18.63 MPa) surrounding the rock chips was 9–7 times greater than the water vapor confining pressure (1.46 and 2.56 MPa) surrounding the rock chips in the anhydrous experiments, which did not exhibit expansion fractures. The results are in agreement with previous comparative studies (Lewan, 1997; Lewan et al., 1979) that indicate that water has a critical role in the generation and expulsion of oil from a source rock, and that the latter is a consequence of the former, as proposed by Momper (1978).

Additional insights into the differences between hydrous and anhydrous experiments can be obtained from SARA data. Table 7 presents the summation of SARA data for the C_{15+} component of bitumen and oil from Tables 3 and 4. The table also includes a % difference between hydrous and anhydrous experiments at 330 and 350 °C for each fraction and their proportionality. All four fractions are greater in the hydrous experiments but the proportions at which they are greater differ. At 330 °C, resin and asphaltene fractions are greater in the hydrous experiments by 16.7% and 18.7%, respectively, and the saturate and aromatic fractions are greater by 9.8% and 9.9%, respectively (Table 7). At 350 °C, the asphaltene fraction is only greater in the hydrous experiment by 12.2% and the resin fraction is higher by 61.2%. The saturate and aromatic fractions are greater in the hydrous experiment by 28.8% and 40.7%, respectively (Table 7). Although C_{15+} hydrocarbons (saturate + aromatic fractions) and polars (resin + asphaltene fractions) are respectively 33% and 61% greater in the hydrous experiments at 350 °C, the normalized % values are similar (Table 7). Therefore, comparisons between hydrous and anhydrous pyrolysis based on normalized hydrocarbon percentages are misleading in that more hydrocarbons (saturates plus aromatics) are generated in hydrous than anhydrous pyrolysis.

As noted by Lewan (1997), it is not the amount of water that is important in the experiments, but rather the presence of sufficient liquid water to maintain dissolved water in the bitumen of a rock during thermal maturation. It is this dissolved water within the bitumen that differentiates hydrous from anhydrous pyrolysis.

Table 6
Yields from original sample and from anhydrous and hydrous pyrolysis experiments with Mahogany oil shale (930923-8) from Green River Formation.

	Original	Anhydrous	Hydrous	Anhydrous	Hydrous
Experiment		HP-3318	HP-3321	HP-3319	HP-3322
Conditions (°C/h)	Unheated	330/72	330/72	350/72	350/72
Product yield (mg/g orig. TOC)					
Bitumen extract (C_{15+})	151.6	641.4	614.3	457.5	209.1
Generated oil (C_{15+})	0.00	18.1	143.7	18.0	432.5
Hydrocarbon gas (C_{6-})	0.0	28.0	17.9	51.2	37.0
Total	151.6	687.4	775.9	526.7	678.6
Δ_{Total}[a] = ([H − A]/A)100			12.90%		28.80%
Rock-Eval parameters (mg/g orig. TOC)					
Hydrocarbon gas (C_{6-})	0.0	27.9	17.9	51.2	37.0
S_1	23.2	243.0	136.6	318.8	76.6
Generated oil (C_{5+})	0.0	21.5	171.2	22.7	477.5
Total	23.2	292.5	325.7	392.8	591.1
Δ_{Total}[a] = ([H − A]/A)100			11.40%		50.50%

[a] $\Delta_i = ([H_i − A_i]/A_i)100$; where H = hydrous parameter i and A = anhydrous parameter i.

Table 7
SARA C$_{15+}$ yields of bitumen and oil generated from anhydrous and hydrous pyrolysis experiments with Mahogany oil shale (930923-8) Green River Formation.

	Anhydrous	Hydrous	Anhydrous	Hydrous
Experiment	HP-3318	HP-3321	HP-3319	HP-3322
Conditions (°C/h)	330/72	330/72	350/72	350/72
SARA (mg/g orig. TOC)				
Saturates	146.2	160.5	185.4	238.8
Δ_{sat}		9.8%		28.8%
Aromatics	84.2	92.5	95.6	134.5
Δ_{aro}		9.9%		40.7%
Resins	127.7	149	102.4	165.1
Δ_{res}		16.7%		61.2%
Asphaltenes	301.3	355.9	92.1	103.3
Δ_{asph}		18.1%		12.2%
Hydrocarbons[a]	230.4	253.0	281.0	373.3
Δ_{HC}		9.8%		32.8%
Polars[b]	429.0	504.9	194.5	268.4
Δ_{Polars}		17.7%		38.0%
Mass ratio and percentsaturates/aromatics	1.7	1.7	1.9	1.8
$\Delta_{S/A}$		−0.1%		−8.4%
% Hydrocarbons	34.9	33.4	59.1	58.2
% Polars	65.1	66.6	40.9	41.8
$\Delta_{\%HC}$		2.40%		2.3%

$\Delta_i = ([H_i - A_i]/A_i)100$, where H_i is the hydrous value of i and A is the anhydrous value i.

[a] Hydrocarbons = saturate + aromatic fractions.
[b] Polars = resin + asphaltene fractions.

The liquid water surrounding and overlying the rock chips in the reactor during hydrous pyrolysis serves only to maintain dissolved water in the bitumen of the rock and to provide a medium of higher density than the expelled oil to facilitate its buoyancy upwards as in natural secondary petroleum migration. It is envisaged that the same subsurface water in the fractures and adjacent rocks of a maturing source rock that facilitates secondary migration of expelled oil is also responsible for maintaining dissolved water in the bitumen of the maturing source rock. Water in sedimentary basins is ubiquitous and critical for subsurface chemical reactions during diagenesis through high-grade metamorphism (e.g. Weaver and Beck, 1971; Winkler, 1974; Rumble et al., 1982; Ferry, 1983; Whitney, 1990; Yardley, 2009; Ireland et al., 2010; Jamtveit and Austrheim, 2010). Deeper crustal waters also exist and play an important role in the formation and composition of magmas (e.g. Goranson, 1931, 1932; Tuttle and Bowen, 1958; Mysen, 2009).

Although the presence of water during petroleum formation in sedimentary basins is likely and important, extending its role to oil shale retorting has notable limitations. It has long been known that injecting steam into surface retorts improves the quality and quantity of the vaporized oil generated during the process (Gavin, 1922). Comparative experiments have also shown that steam pyrolysis gave a total yield 47% more than anhydrous pyrolysis, but the yield was 42% less than in hydrous pyrolysis (Lewan, 1997, Table 9). Therefore, to take advantage of liquid water in oil shale retorting, a retort must be able to maintain high pressures >13 MPa at retorting temperatures equal to or greater than 350 °C. As noted by Lewan and Cox (2008), these conditions for surface retorts would be prohibitively expensive, but *in situ* retorting at depths >850 m would allow liquid water to exist in contact with the oil shale at 360 °C. These deeper depths limit suitable areas for *in situ* retorting of high grade oil-shale occurrences, but would reduce cross-linking reactions, enhance oil generation and expulsion, improve thermal conductivity and make use of formation waters not in contact with shallower ground waters. Overall viability of *in situ* retorting with water at greater depths will depend on economic and environmental considerations for specific sites.

5. Conclusions

Results of this comparative study on Mahogany oil shale from the Green River Formation indicate that there are significant differences in the types of products and their yield under hydrous and anhydrous pyrolysis conditions. In agreement with previous comparative studies on oil-prone source rocks (Lewan, 1997), the differences are more pronounced in the conversion of bitumen to oil at 350 °C after 72 h than in the conversion of kerogen to bitumen at 330 °C after 72 h. Volatile oil that condenses at the top of the reactor during cooling of the anhydrous 350 °C experiment represents only 4% of the immiscible oil expelled during the hydrous 350 °C experiment. Part of this difference is accounted for by more bitumen being retained in anhydrous recovered rock than in hydrous recovered rock. However, summation of the C$_{15+}$ component of bitumen and oil is 50% higher in the hydrous experiment than in the anhydrous experiment. This total C$_{15+}$ component in the hydrous experiment has 33% more hydrocarbons than that of the anhydrous experiment. Rock-Eval S$_1$ values for the recovered rocks indicate that the lighter C$_6$–C$_{14}$ component of the products retained in the recovered rocks cannot be responsible for the difference. The amount of TOC remaining in the recovered rock from the hydrous 350 °C experiment is 34% lower than that in the recovered rock from the anhydrous 350 °C experiment. Although the TOC content of the recovered rock from the anhydrous experiment is greater, the Rock-Eval HI value is 36% lower than that of the lower TOC content of the recovered rock from the hydrous experiments. These differences and the greater molecular hydrogen generated in the anhydrous experiment indicates that more cross linking occurs in the anhydrous experiment than in the hydrous experiment. In contrast to net-volume increases associated with thermal cracking, cross linking results in a net-volume decrease. The greater proportionality of thermal cracking to cross linking in the hydrous experiments is reflected in the expansion fractures of the recovered rock, which are not observed in the recovered rock from the anhydrous experiments. These results indicate that water provides a source of hydrogen to promote thermal cracking over cross linking and facilitates the generation of expelled hydrocarbon-rich oil that is immiscible in the water-saturated, polar-rich bitumen in the rock. The ubiquity of water in the subsurface of sedimentary basins ensures a source of water during thermal maturation of oil-prone source rocks. However, *in situ* retorting of oil shale requires deeper depths to ensure sufficient pressures to maintain liquid water in contact with the heated oil shale. Economic and environmental considerations remain to be determined in order to assess the viability of deeper hydrous *in situ* retorting.

References

Baylis, S.A., Hall, K., Jumeau, E.J., 1994. The analysis of the C$_1$–C$_5$ components of natural gas samples using gas chromatography–combustion–isotope ratio mass spectrometry. Organic Geochemistry 21, 777–785.

Behar, F., Lewan, M.D., Lorant, F., Vandenbroucke, M., 2003. Comparison of artificial maturation of lignite in hydrous and nonhydrous conditions. Organic Geochemistry 34, 575–600.

Brandt, A.R., 2008. Converting oil shale to liquid fuels: energy inputs and greenhouse gas emissions of the Shell in situ conversion process. Environmental Science and Technology 42, 748–7495.

Colburn, T.T., Oh, M.S., Crawford, R.W., Foster, K.G., 1989. Water generation during pyrolysis of oil shales. 1. Sources. Energy and Fuels 3, 216–223.

Ferry, J.M., 1983. Regional metamorphism of the Vassalboro Formation, south-central Maine, USA: a case study in the role of fluids in metamorphic petrogenesis. Journal of the Geological Society, London 140, 551–576.

Gavin, M.J., 1922. Oil Shale: An Historical, Technical, and Economic Study. US Bureau of Mines Bulletin 210.

Goranson, R.W., 1931. The solubility of water in granite magmas. American Journal of Science 22, 481–502.

Goranson, R.W., 1932. Some notes on the melting of granites. American Journal of Science 23, 227–236.

Huizinga, B.J., Aizenshtat, Z.A., Peters, K.E., 1988. Programmed pyrolysis-gas chromatography of artificially matured Green River kerogen. Energy and Fuels 2, 74–81.

Hunt, J.M., 1996. Petroleum Geochemistry and Geology, second ed. W.H. Freeman and Company, New York.

Ireland, M.T., Goulty, N.R., Davies, R.J., 2010. Influence of pore water chemistry on silica diagenesis: evidence from the interaction of diagenetic reaction zones with polygonal fault systems. Journal of the Geological Society, London 167, 273–279.

Jamtveit, B., Austrheim, H., 2010. Metamorphism: the role of fluids. Elements 6, 153–158.

Johnson, R.C., Mercier, T.J., Brownfield, M.E., Pantea, M.P., Self, J.G., 2010. An Assessment of in-Place Oil Shale Resources in the Green River Formation, Piceance Basin, Oil-shale assessment of the Piceance Basin, Colorado, US Geological Survey Digital Data Series DDS–69–Y, Colorado, 187pp (Chapter 1).

Kotarba, M.J., Curtis, J.B., Lewan, M.D., 2009. Comparison of natural gases accumulated in Oligocene strata with hydrous pyrolysis gases from Menilite Shales of the Polish Outer Carpathians. Organic Geochemistry 40, 769–783.

Lewan, M.D., 1987. Petrographic study of primary petroleum migration in the Woodford Shale and related rock units. In: Doligez, B. (Ed.), Migration of Hydrocarbons in Sedimentary Basins. Editions Technip, Paris, pp. 113–130.

Lewan, M.D., 1992. Nomenclature for pyrolysis experiments involving H_2O. American Chemical Society Division of Fuel Chemistry Preprints 37 (4), 1545–1547.

Lewan, M.D., 1993. Laboratory simulation of petroleum formation – hydrous pyrolysis. In: Engel, M., Macko, S. (Eds.), Organic Geochemistry Principles and Applications. Plenum Press, New York, pp. 419–442.

Lewan, M.D., 1997. Experiments on the role of water in petroleum formation. Geochimica et Cosmochimica Acta 61, 3691–3723.

Lewan, M.D., Cox, D.O., 2008. Applying hydrous pyrolysis to in situ oil-shale retorting. In: Abstract. 28th Oil Shale Symposium Abstracts, Golden, CO, p. 14.1.

Lewan, M.D., Ruble, T.E., 2002. Comparison of petroleum generation kinetics by isothermal hydrous and nonisothermal open-system pyrolysis. Organic Geochemistry 33, 1457–1475.

Lewan, M.D., Winters, J.C., McDonald, J.H., 1979. Generation of oil-like pyrolysates from organic-rich shales. Science 203, 897–899.

Mango, F.D., 1992. Transition metal catalysis in the generation of petroleum and natural gas. Geochimica et Cosmochimica Acta 56, 553–555.

Mello, M.R., Telnaes, N., Gaglianone, P.C., Chicarelli, M.I., Brassell, S.C., Maxwell, J.R., 1988. Organic geochemical characterization of lacustrine and marine hypersaline environments from Brazilian sedimentary basins. In: Matavelli, L., Novelli, L. (Eds.), Advances in Organic Geochemistry. Pergamon Press, Oxford, pp. 31–45.

Michels, R., Landais, P., 1994. Artificial coalification: comparison of confined pyrolysis and hydrous pyrolysis. Fuel 73, 1691–1696.

Momper, J.A., 1978. Oil migration limitations suggested by geological and geochemical considerations. In: Physical and Chemical Constraints on Petroleum Migration, vol. 1. American Association of Petroleum Geologists Short Course Note Series #8, pp. B1–B60.

Monthioux, M., Landais, P., Monin, J.C., 1983. Comparison between natural and artificial maturation series of humic coals from the Mahakam delta, Indonesia. Organic Geochemistry 8, 275–292.

Mysen, B., 2009. Solution mechanisms of silicate in aqueous fluid and H_2O in coexisting silicate melts determined *in-situ* at high pressure and high temperature. Geochimica et Cosmochimica Acta 73, 5748–5763.

Nikonov, V.F., 1972. Distribution of methane homologs in gas and oil fields. Doklady Akademi Nauk SSSR 206, 234–236 (in Russian).

Price, L.C., Schoell, M., 1995. Constraints on the origins of hydrocarbons gas from compositions of gases at their site of origin. Nature 378, 368–371.

Ruble, T.E., Lewan, M.D., Philp, R.P., 2001. New insights on the Green River petroleum system in the Uinta basin from hydrous pyrolysis experiments. American Association of Petroleum Geologists Bulletin 85, 1333–1371.

Rumble III, D., Ferry, J.M., Hoering, T.C., Boucot, A.J., 1982. Fluid flow during metamorphism at the Beaver Brook fossil locality, New Hampshire. American Journal of Science 282, 886–919.

Scalan, R.S., Smith, J.E., 1970. An improved measure of the odd–even predominance in the normal alkanes of sediment extracts and petroleum. Geochimica et Cosmochimica Acta 34, 611–620.

Tissot, B., Deroo, G., Hood, A., 1978. Geochemical study of the Uinta basin – formation of petroleum from the Green River Formation. Geochimica et Cosmochimica Acta 42, 1469–1485.

Tissot, B.P., Pelet, R., Ungerer, P.H., 1987. Thermal history of sedimentary basins, maturation indices, and kinetics of oil and gas generation. American Association of Petroleum Geologists Bulletin 71, 1445–1466.

Tuttle, O.F., Bowen, N.L., 1958. Origins of granites in light of experimental studies in the system $NaAlSi_3O_8$–$KAlSi_3O_8$–SiO_2–H_2O. Geological Society of America Memoir 74.

Weaver, C.E., Beck, K.C., 1971, Clay Water Diagenesis During Burial: How Mud Becomes Gneiss, vol. 134. Geological Society of America Special Publication, 96pp.

Whiticar, M.J., 1994. Correlation of natural gases with their sources. In: Magoon, L.B., Dow, W.G. (Eds.), The Petroleum System – From Source to Trap, vol. 60. American Association of Petroleum Geologists Memoir, pp. 261–283.

Whitney, G., 1990. Role of water in the smectite-to-illite reaction. Clays and Clay Minerals 38, 343–350.

Winkler, H.G.F., 1974. Petrogenesis of Metamorphic Rocks, third ed. Springer-Verlag, New York.

Yardley, B.W.D., 2009. The role of water in the evolution of the continental crust. Journal of the Geological Society, London 166, 585–600.