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Gas:Oil Ratios for Source Rocks Containing Type-I, -II, -IIS, and -III Kerogens

as Determined by Hydrous Pyrolysis

by

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INTRODUCTION

Predicting the gas:oil ratio (GOR) of a petroleum play or prospect is important in evaluating the economics of an exploration venture and in assessing petroleum resources. Estimates of the GOR of prospects in well-drilled areas can typically be determined with analogs from neighboring production in the same play. In poorly drilled areas, GOR of prospects may be estimated by using analogs from more distant well-drilled plays that have similar geological settings or by models based on oil and gas generation from potential source rocks (e.g., Mackenzie and Quigley, 1988; and Kuo and Michael, 1994). GORs have also been determined by hydrous pyrolysis of potential source rocks in an exploration play or petroleum system (e.g., Noble and others, 1991; and Lillis and others, 1999). Unlike open- or closed-system anhydrous pyrolysis, hydrous pyrolysis generates an expelled oil that is physically and chemically similar to natural crude oil (Lewan, 1993a; 1997). As a result, the quantity of this expelled oil and the gas generated allows one to calculate GORs of a particular source rock at hydrous-pyrolysis temperatures representing different stages of oil generation.

The objectives of this report are to present GORs from hydrous pyrolysis experiments conducted on immature source rocks and report how they are affected by kerogen type and thermal maturity during petroleum generation. The source rocks used in this study contain the major kerogen types, including Type-I, -II, -IIS, and -III. Thermally immature samples were used to provide a complete understanding of changes in GOR from incipient petroleum generation through peak petroleum generation.

METHODS

Source Rock Samples: Experimental data were available on five immature source rocks, which are described in Table 1. The major kerogen types in these source rocks include Type-I, -II, -IIS, and -III. Collaborators that collected and pyrolyzed aliquots of these samples are also referenced in Table 1. With respect to vitrinite reflectance (%Ro), all of these sample have initial random mean %Ro values equal to or less than 0.5 or atomic H/C and O/C ratios indicative of pre-catagenesis (i.e., diagenesis) according to Tissot and Welte (1984; Fig. II.5.1, p.161).

Hydrous Pyrolysis Experiments: Complete details of hydrous pyrolysis experiments are given by Lewan (1993a). Briefly, the experiments consist of isothermally heating several hundred grams of gravel-sized immature source rock in the presence of liquid water in one-liter stainless-steel reactors at subcritical-water temperatures (<374°C) for several days (2-10 days). After the experiment is completed and allowed to cool to room temperatures (20-25°C), the gas pressure and temperature are recorded and a gas sample is collected in 30-cm^3 stainless-steel cylinders. Gas compositions were determined by mass spectometry according to an enhanced version of the ASTM D2650-88 method. The remaining gas is vented and the reactor is opened to quantitatively collect the expelled oil, which floats on the water surface above the submerged source rock. All of the experiments considered in this study were conducted for 72 hours at temperatures ranging from 160 to 365°C (Table 2). These experimental conditions simulate thermal maturities associated with oil generation. Atomic H/C and O/C ratios of kerogens at temperatures equal to or less than 355°C for 72 hours indicate that the samples have only been

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subjected to catagenesis according to Tissot and Welte (1984, Fig. II.5.1, p.161). Low-rank coals (< 0.5%Ro) subjected to hydrous pyrolysis at 355°C for 72 hours obtain random mean vitrinite reflectance values of 1.55 %Ro (Lewan, 1993b).

Gas Volume Calculations: The first step in calculating a gas volume is to determine the number of moles of hydrocarbon gas generated, which consists of methane, ethane, propane, n-butane, i-butane, n-pentane and i-pentane. The number of moles of total gas at the end of each experiment, n_{tot}, was calculated by the ideal gas law :

$$n_{tot} = (PV)/(RT) , \qquad (1)$$

where P is the measured cool-down pressure, T is the measured cool-down temperature, V is the head-space gas volume, and R is the ideal gas constant. The number of moles of each of the component hydrocarbon gases is calculated using gas analyses, which are reported in mole percent of the total gas. The number of moles of each hydrocarbon gas is summed to give the number of moles of hydrocarbon gas generated in the experiment, n_{HC}. Assuming that these gases behaved ideally at room temperatures, the volume of hydrocarbon gas at 14.7 psi and 288.71 K, V_{HCgas}, was determined by rearranging the ideal gas equation:

$$V_{HC} = (n_{HC}RT)/P , \qquad (2)$$

where P is 14.7 psia, T is 288.71 K, $n_{HC} = n_{methane} + n_{ethane} + n_{propane} + n_{n\text{-}butane} + n_{i\text{-}butane} + n_{n\text{-}pentane} + n_{i\text{-}pentane}$, and R is 1206.00 (cm^3·psi)/(mol·K). Equation 2 gives the volume in cubic centimeters. This quantity is multiplied by 3.5314667 x 10^{-5} to give the volume of hydrocarbon gas in standard cubic feet (scf):

$$V_{HC} (ft^3) = V_{HC} (cm^3) \times 3.314667 \times 10^{-5} . \qquad (3)$$

In this report, gas volumes are given in units of mcf/kg TOC (e.g., Table 3 and Figure 1). For clarification, mcf is milli-standard cubic feet (i.e., scf x 10^{-3}) and kg TOC is the mass of total organic carbon (TOC) in the original unheated sample.

Oil Volume Calculations: The volume of oil generated in each experiment was calculated by dividing the total mass of oil in grams, m_{oil}, by its density in grams per cubic centimeter, d_{oil}:

$$V_{oil} (cm^3) = (m_{oil}) / (d_{oil}) . \qquad (4)$$

The resulting cubic centimeters of oil is divided by 158982.84 to convert the volume of oil to barrels:

$$V_{oil} \text{ (bbls)} = V_{oil} \text{ (cm}^3\text{)} / 158982.84 . \tag{5}$$

Densities of all the expelled oils (d_{oi}) generated by hydrous pyrolysis were not determined, but typically their API gravities range between 25° and 42°, which equates to densities of 0.904 and 0.816 g/cm^3/, respectively. For this study, a density of 0.876 cm^3/g (30.0° API gravity) was used to calculate volumes for all the oils generated by hydrous pyrolysis.

Gas to Oil Ratio (GOR) Calculations: GORs in scf/bbl were calculated by dividing the volume of hydrocarbon gas by the volume of oil generated in the experiment.

$$GOR \text{ (ft/bbl)} = V_{HC} \text{ (ft}^3\text{)} / V_{oil} \text{ (bbls)} \tag{6}$$

A sensitivity test was conducted to evaluate the effect a range of API gravities between 25° and 42° had on calculated GORs. The average difference in GORs calculated with densities of 0.816 and 0.904 g/cm^3 for all the experiments considered in this study is 84 ± 57 scf/bbl. This difference in GORs indicates that the use of a constant oil density of 0.876 g/cm^3 (30.0°API gravity) has no significant effect on the calculated GORs presented in this study. As indicated in Table 3, GORs are only calculated for experiments in which an expelled oil is generated. Therefore, no GORs are calculated at temperatures below 270°C.

RESULTS

The amount of hydrocarbon gas generated from the source rocks containing the different kerogen types is given in Table 3. Figure 1 shows an exponential increase in hydrocarbon gas generated with increasing experimental temperature for all the source rocks. The two source rocks containing Type-IIS kerogen generate the most hydrocarbon gas, which at 350°C is more than twice that generated by the Type-III kerogen in the lignite (Table 3). Source rocks containing Type-I and -II kerogens generate similar amounts of hydrocarbon gases, which at 350°C are slightly less than that generated by the Type-IIS kerogens but nearly twice that generated by the Type-III kerogen in the lignite (Table 3).

The GORs for the source rocks containing the different kerogen types are given in Table 3. Figure 2 shows a curvilinear decrease in GOR with increasing experimental temperature for all the source rocks, with the exception of the slight increase at temperatures greater than 340°C for the Type-IIS kerogens. At 350°C for 72h, the GORs for the Type-IIS and -I kerogens are similar and range between 401 and 527 scf/bbl (Table 3). Type-II and -III kerogens at these same experimental conditions have significantly higher GORs of 935 and 883 scf/bbl, respectively. These two kerogen types also have consistently higher GORs at the lower experimental temperatures with the exception of the Type-II kerogen at 285°C for 72h. Overall, GORs during oil generation are between 500 and 1500 scf/bbl irrespective of kerogen type.

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DISCUSSION

Amounts of Gas Generated: Type-III kerogen is typically described as a gas-prone source (Hunt, 1996, and references therein). Although Type-III kerogen has the highest GOR during catagenesis (Figure 2), it generates the lowest amounts of hydrocarbon gas compared with the oil-prone kerogens (i.e., Type-I, -II, and -IIS). Previously reported hydrous pyrolysis results have also shown that Type-I and -II kerogens generate significantly more gas than Type-III kerogen (Lewan, 1993c; Hunt, 1996, p. 601, Table 16-3). These results are also in general agreement with open-system pyrolysis results as modeled by Behar and others (1997) and the composite- pyrolysis model by Pepper and Corvi (1995). An implication of these results is that oil-prone kerogens can be the source of more hydrocarbon gas during catagenesis than so called gas-prone Type-III kerogen.

The only notable contradiction between the hydrous pyrolysis and the open-system pyrolysis by Behar and others (1997) is that the Type-IIS kerogen does not generate the highest amount of hydrocarbon gas in the open-system pyrolysis as observed in hydrous pyrolysis (Figure 1). However, the composite-pyrolysis model by Pepper and Corvi (1995) predicts that Type-IIS kerogen generates the most hydrocarbon gas, which is in agreement with the hydrous pyrolysis results. Hydrous pyrolysis experiments conducted by Seewald and others (1998) also showed that Type-IIS kerogen in a sample of Monterey Shale generated four times as much hydrocarbon gas as Type-III kerogen in samples of the Smackover and Eutaw shales. These experimental observations suggest that petroleum systems that produce high-sulfur oils from Type-IIS kerogen should also have appreciable quantities of hydrocarbon gas associated with them.

The exponential increase in hydrocarbon generation with increasing temperature (Figure 1) raises the questions whether this increase in gas generation continues through metagenesis and what is the maximum amount of gas that can be generated from a source rock. It should be noted that the results from the hydrous pyrolysis experiments represent a closed-system in which gas may be generated from the decomposition of kerogen or bitumen retained in a rock, as well as from the expelled oil on the water surface within the closed reactor. It is interesting that with all these possible sources for gas, there are no obvious breaks in the slope of gas generation that would suggest changes in the source of gas with increasing temperature. Additional experiments are needed to determine the extent of this exponential increase in hydrocarbon gas and the maximum amount of hydrocarbon gas that can be generated from different source materials (i.e., kerogen, bitumen, and oil).

Clay-mineral catalysis has been suggested to play an important role in petroleum generation (Johns and Shimoyama, 1972; Goldstein, 1983). However, experimental pyrolysis results indicate that the presence of clay minerals has no significant effect on generation of methane and ethane from kerogen (Tannenbaum and Kaplan, 1985). Although results from our study are not unequivocal in indicating that clay-mineral catalysis is not important in gas generation, they do suggest that clay minerals in a source rock are not essential to hydrocarbon gas generation. Specifically, the two source rocks containing Type-IIS kerogen in this study are limestones and generate the most hydrocarbon gas despite their low clay-mineral content. In addition, the claystone with Type-II kerogen does not generate significantly greater amounts of hydrocarbon gas than

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the marlstone with Type-I kerogen despite the higher clay-mineral content of the former (Table 3).

Gas:Oil Ratios (GORs): Figure 3 shows that hydrous-pyrolysis GORs during oil generation are between 400 and 3000 scf/bbl. These GORs are within the range of values (<5000 scf/bbl) prescribed by Larter and Mills (1991) for petroleum expelled from source rocks based on pyrolysis-gas chromatography. England and Mackenzie (1989) refer to these expelled GORs as "feedstock" GORs, which they suggest range between 1000-2500 scf/bbl. Although these GOR ranges are in agreement with those derived from hydrous pyrolysis (Table 3 and Figure 2), there is a major difference in the way these GORs change with maturation during oil generation. Figure 2 shows GORs derived from hydrous pyrolysis decrease during oil generation. The more gas-prone Type-III kerogen in the Wilcox lignite decreases from 2831 scf/bbl at 280°C for 72h to 883 scf/bbl at 350°C for 72h. The oil-prone Type-I, -II, and -IIS kerogens decrease from 2381scf/bbl at 270°C for 72h to 401-935 scf/bbl at 350°C for 72h. As shown in Figure 3, these decreasing hydrous-pyrolysis GORs are contrary to the increasing GORs derived from closed-system anhydrous pyrolysis as reported by Quigley and Mackenzie (1988). These authors state that their trend is representative of most source rocks irrespective of differences in lithology.

These conflicting results can be explained by differences in the products generated by closed-system anhydrous and hydrous pyrolysis. In hydrous pyrolysis, only the expelled oil and generated gas are used in the calculation of the GOR. In anhydrous pyrolysis, no expelled oil is generated, so GORs are calculated with the generated gas and solvent-soluble or thermally-labile bitumen in the rock. In addition, Lewan (1997) shows that cross-linking reactions resulting in the formation of pyrobitumen (i.e., insoluble char or inert carbon) are more prevalent in closed-system anhydrous pyrolysis than in hydrous pyrolysis. Therefore, the anhydrous-pyrolysis GORs increase with temperature as soluble or labile bitumen decreases and generated gas increases to a greater extent than in hydrous pyrolysis. The contrary GOR trends determined by these two different pyrolysis methods are shown in Figure 4, which is based on closed-system anhydrous and hydrous pyrolysis experiments conducted on aliquots of the same sample of Woodford Shale (Lewan, 1997). An important implication of this difference is that GORs derived from hydrous pyrolysis indicate that source rocks in the early stages of oil generation can generate accumulations with GORs between 1500 and 3000 scf/bbl. Conversely, GORs derived from closed-system anhydrous pyrolysis indicate source rocks in the early stages of oil generation can only generate accumulations with GORs less than 1000 scf/bbl.

Although the hydrous-pyrolysis GORs decrease during most of oil generation, it is expected that this GOR trend will reverse and increase after oil generation. This increase would not be the result of additional oil generation but of additional gas generation from the thermal decomposition of the remaining kerogen and bitumen within the source rock and the expelled oil on the water surface. Source rocks with Type-IIS kerogen show a distinct GOR increase at the higher temperatures (>340°C) that suggests the start of this anticipated increase (Figure 2). An important question that remains is whether the gas generated after oil generation is from the kerogen and bitumen remaining in the source

rock or from the expelled oil? Additional hydrous-pyrolysis experiments on oil and mature source rock are needed to resolve this question.

CONCLUSIONS

GORs for a given source rock can be derived from hydrous pyrolysis experiments. During oil generation, source rocks with oil-prone kerogen (i.e., Type-I, -II, and -IIS) generate hydrous-pyrolysis GORs between 382 and 2381 scf/bbl. Source rocks with Type-III kerogen generate higher GORs (883-2831 scf/bbl) than source rocks with more oil-prone kerogen (i.e., Type-I, -II, and -IIS) during catagenesis (oil generation). However, the more oil-prone kerogens can generate twice as much hydrocarbon gas per gram of organic carbon as the more gas-prone Type-III kerogen .

During oil generation, GORs determined by closed-system anhydrous pyrolysis increase with increasing temperature, and GORs determined by hydrous pyrolysis initially decrease with increasing temperature. As a result, hydrous-pyrolysis GORs indicate that petroleum accumulations with GORs between 1500 and 3000 scf/bbl can be generated during the early stages of oil generation. Conversely, anhydrous-pyrolysis GORs indicate that petroleum accumulations with GORs greater than 2000 scf/bbl can only be generated near the end of oil generation.

In conjunction with the recommendations made by Henry and Lewan (1999), more hydrous-pyrolysis experimental work is needed to quantitatively understand the controls on gas generation from source rocks and expelled oil. These experiments should be designed to determine if the exponential increase in hydrocarbon-gas generation and an increase in GORs occurs past oil generation and into metaganesis. Experiments should also be designed to evaluate whether this late-stage hydrocarbon gas is generated from organic components retained in the source rock or from expelled oil.

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Table 1: Description of immature source rocks subjected to hydrous pyrolysis.

Kerogen Type	Type-I	Type-II	Type-IIS	Type-IIS	Type-III
Rock Unit	Green River Fm.	New Albany Sh.	Ghareb Limestone	Ghareb Limestone	Wilcox Gp.
Sub-Rock Unit	mahogany shale	Clegg Creek Mbr.	"oil shale"	"oil shale"	Calvert Bluff Fm.
Geologic Age	Eocene	Mississippian	Cretaceous	Cretaceous	Paleocene
Sample Number	930923-8	931026-3	930616-9	930608-6	WX-3
Location	Utah	Indiana	Israel	Jordan	Texas
Basin	Uinta	Illinois	Dead Sea	Dead Sea	Gul Coast
TOC (wt. %)	15.23	14.34	14.14	16.63	61.53
Lithology	marlstone	claystone	limestone	limestone	lignite
Collaborators*	Ruble[1]	Guthrie[2]	Tannenbaum[3]	Ramini[3]	Dias[4]; IFP[5]

*Collaborator references are [1] Ruble and others (1994); [2] Lewan and others (1995); [3] Lewan and others (1997); and [4] Dias and others (1997).
[5] F. Behar and F. Lorant (in preparation)

Table 2: Hydrous-pyrolysis experimental numbers and conditions considered in this study. All experiments were conducted for 72 hours.

Temperature (°C)	Experiment (HP-) Number Designation				
	Type-I 930923-8	Type-II 931026-3	Type-IIS 930616-9	Type-IIS 930608-6	Type-III WX-3
160.0	2186	NE	NE	NE	NE
180.0	2187	NE	NE	NE	NE
200.0	2188	NE	2318	2351	2399
220.0	2189	NE	NE	NE	NE
240.0	2190	NE	2319	2352	2400
270.0	2109	2066	NE	NE	NE
280.0	NE	NE	2320	2353	2667
285.0	2110	2073	NE	NE	NE
300.0	2111	2067	2326	2344	2635
307.5	2114	NE	NE	NE	NE
310.1	NE	2074	2337	2354	2396
315.0	2115	NE	NE	NE	NE
320.3	NE	2068	2336	2361	NE
322.5	2116	NE	NE	NE	NE
330.0	2117	2075	2335	2362	2637
337.5	2118	NE	NE	NE	NE
340.2	NE	2076	2334	2363	NE
345.0	2119	NE	2321	2368	NE
350.0	2107	2070	2317	2348	2398
355.1	2108	2078	2316	2347	NE
360.3	2113	2071	2327	2345	NE
365.0	2112	2085	2314	2346	NE

NE = No experiment was conducted at this temperature for 72 hours.

Table 3: Volume of hydrocarbon-gas (C$_1$-C$_5$) generated and calculated GOR for source rocks subjected to hydrous pyrolysis experiments for 72 hours. Type IISi denotes Israeli Ghareb Limestone and Type IISj denotes Jordanian Ghareb Limestone.

Experimental Temperature (°C)	Type I Volume (mcf/kg TOC)	Type I GOR (ft³/bbl)	Type II Volume (mcf/kg TOC)	Type II GOR (ft³/bbl)	Type IISi Volume (mcf/kg TOC)	Type IISi GOR (ft³/bbl)	Type IISj Volume (mcf/kg TOC)	Type IISj GOR (ft³/bbl)	Type III Volume (mcf/kg TOC)	Type III GOR (ft³/bbl)
160.0	2.4	NO	—	—	—	—	—	—	—	—
180.0	3.5	NO	—	—	—	—	—	—	—	—
200.0	5.1	NO	—	—	13.3	NO	5.0	NO	3.3	NO
220.0	6.4	NO	—	—	—	—	—	—	—	—
240.0	13.8	NO	—	—	55.8	NO	21.1	NO	22.0	NO
270.0	45.0	NO	112.9	2381	—	—	—	—	—	—
280.0	—	—	—	—	205.1	1262	112.5	1513	86.4	2831
285.0	81.5	1240	129.9	1037	—	—	—	—	—	—
300.0	161.7	801	232.6	1522	410.8	923	297.5	832	162.9	2621
307.5	234.6	924	—	—	—	—	—	—	—	—
310.1	—	—	339.6	1243	517.1	754	422.3	639	230.2	2393
315.0	307.7	922	—	—	—	—	—	—	252.6	1799
320.3	—	—	495.5	1122	795.4	606	667.0	503	—	—
322.5	454.4	714	—	—	—	—	—	—	—	—
330.0	584.8	648	726.3	978	1033.5	559	1004.0	481	373.4	1325
337.5	704.6	687	—	—	—	—	—	—	—	—
340.2	—	—	967.0	992	1438.6	509	1473.5	382	—	—
345.0	1047.3	458	—	935	1581.9	505	1549.8	389	—	—
350.0	1340.8	401	1374.8	935	1861.9	527	1865.1	408	755.8	883
355.1	1533.2	463	1582.9	768	2117.7	606	2123.8	439	—	—
360.3	1710.9	434	1850.8	944	2409.1	716	2349.6	522	—	—
365.0	1898.3	492	2030.9	1006	2688.8	757	2942.8	630	—	—
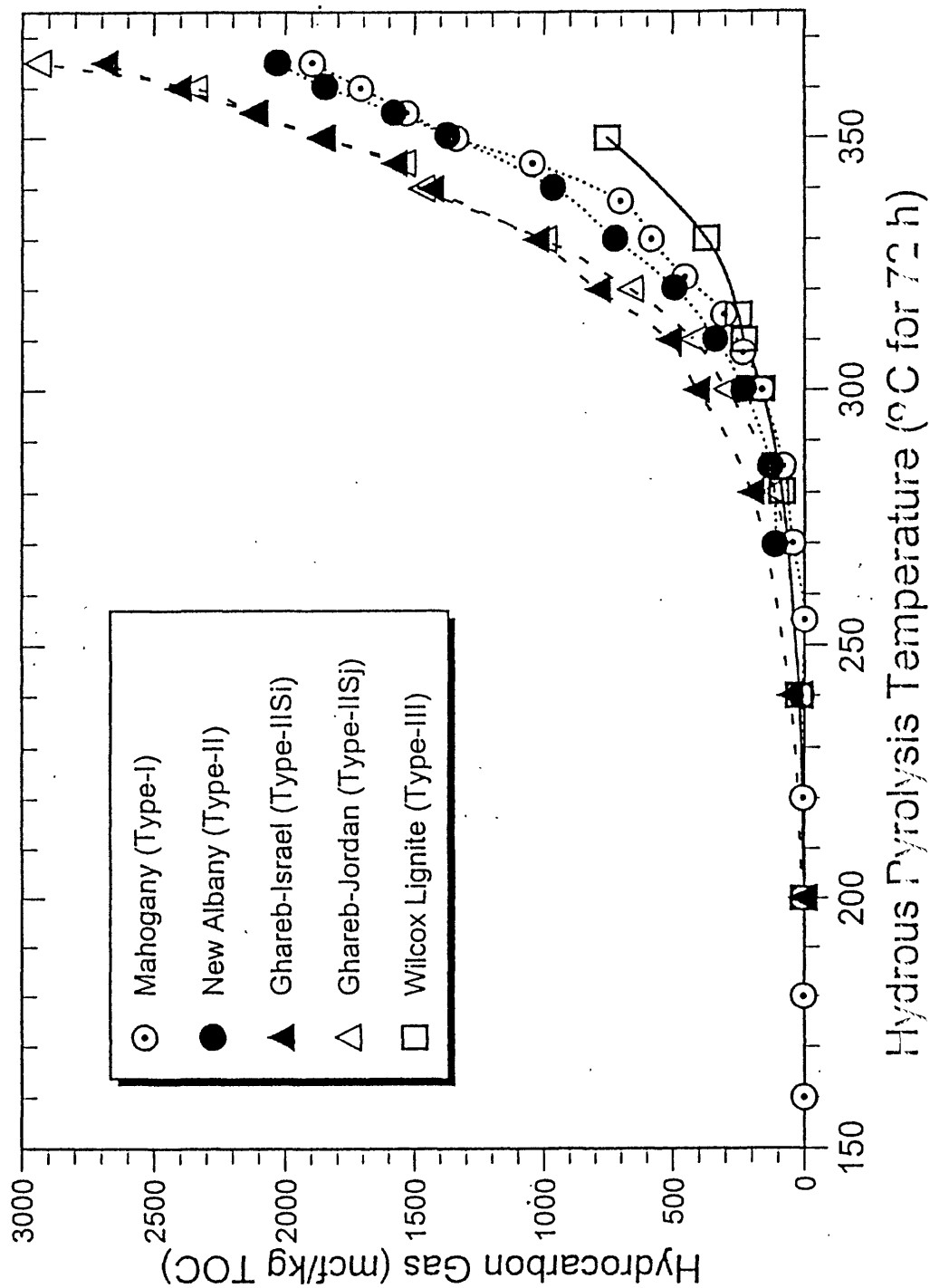
Figure 1: Volume of gas generated from source rocks with different kerogen types subjected to hydrous-pyrolysis temperatures between 270 and 365°C for 72 hours.
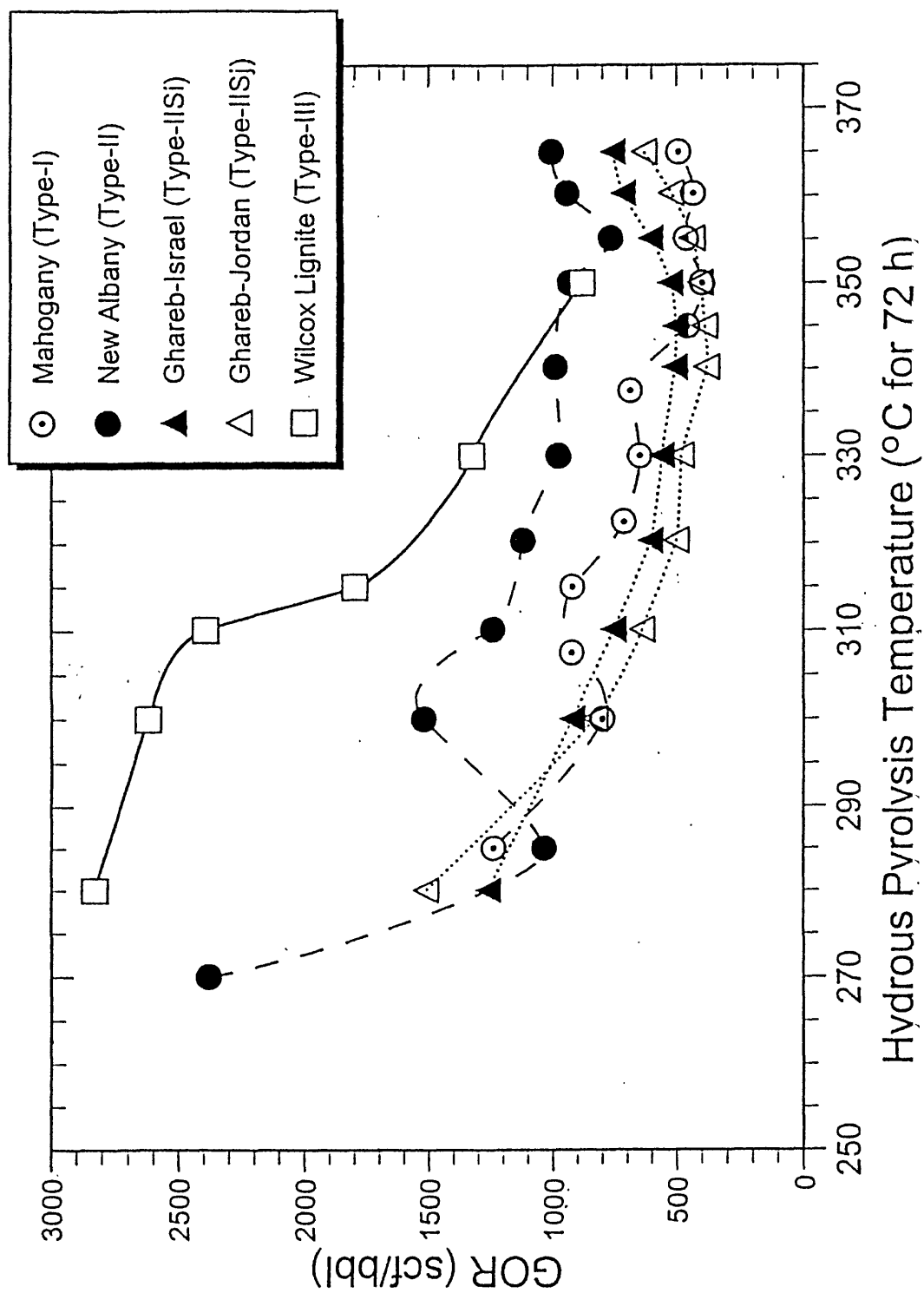
Figure 2: Gas:oil ratios (GOR) for source rocks with different kerogen types subjected to hydrous-pyrolysis temperatures between 270 and 365°C for 72 hours.
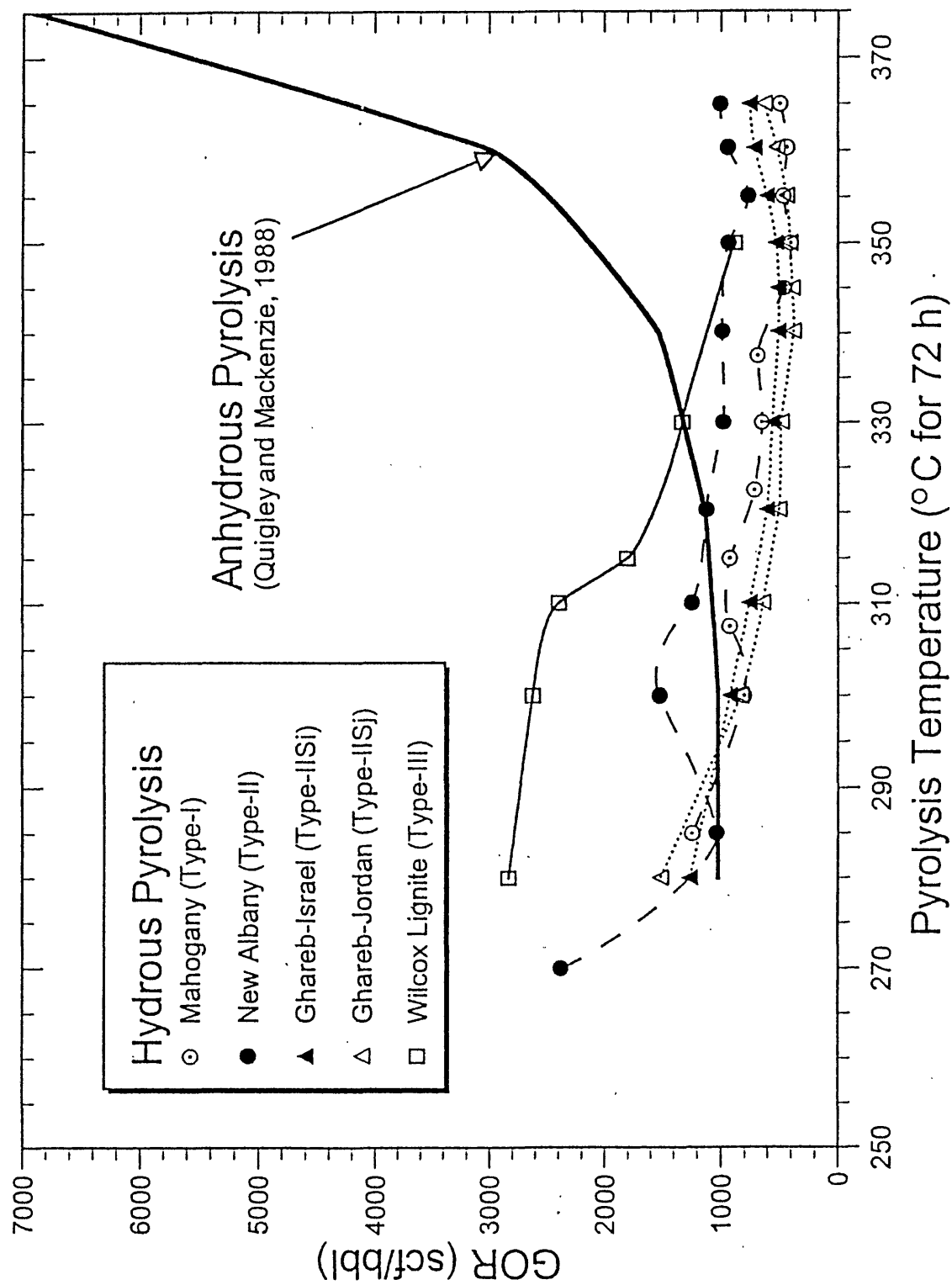
Figure 3: Comparison of gas:oil ratios (GOR) for source rocks with different kerogen types subjected to hydrous- and anhydrous-pyrolysis temperatures between 270 and 365°C for 72 hours.
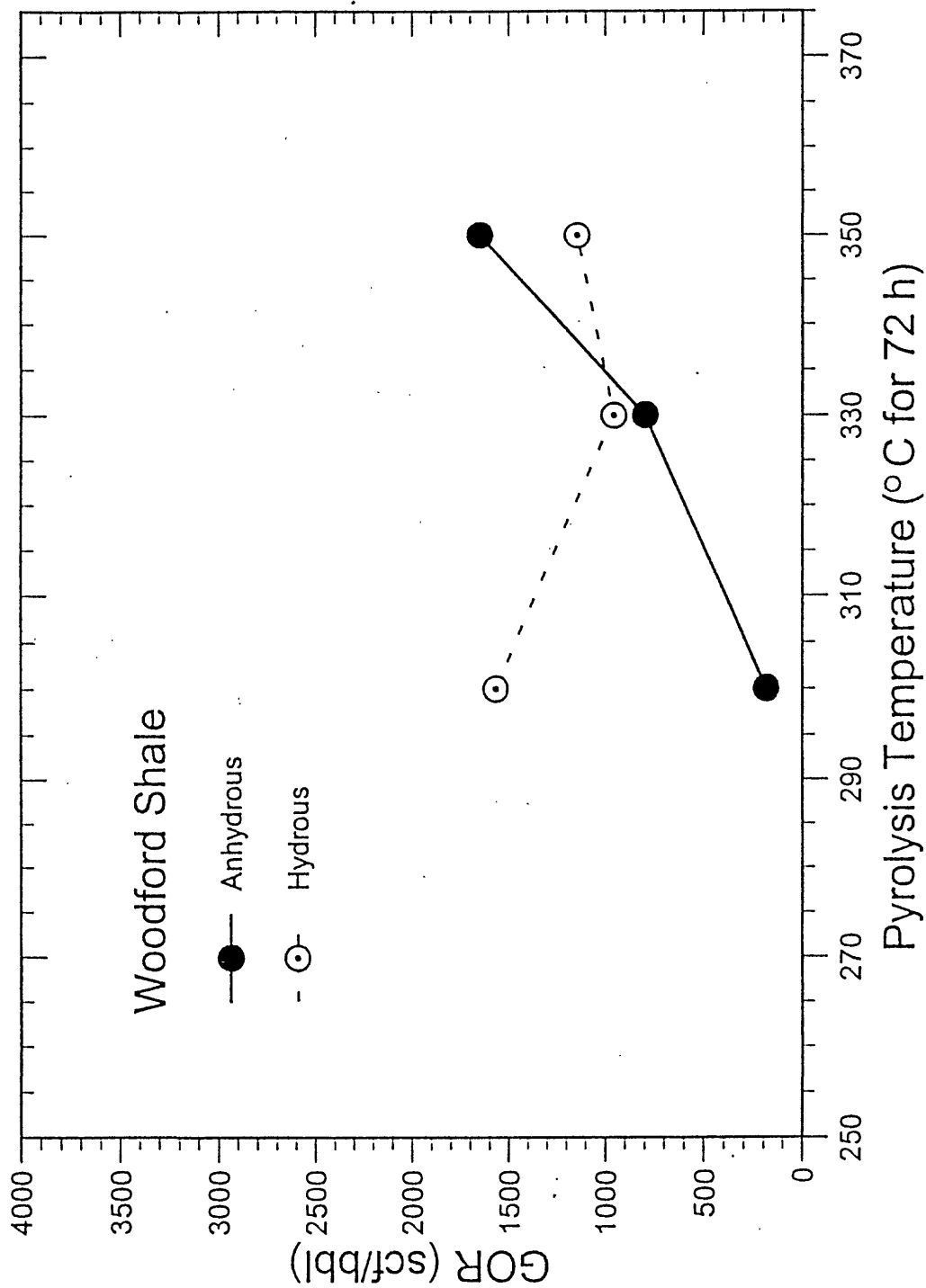
Figure 4: Comparison of gas:oil ratios (GOR) for aliquots of a sample of Woodford Shale (Type-II) subjected to hydrous- and anhydrous-pyrolysis at 300, 330, and 350°C for 72 hours. Original data reported by Lewan (1997; Tables 2 and 6).