

Coal vitrinite analysis of Copper Valley well samples as follows:

Union Oil Company of California Tazlina No. 1 (well no. 1) cuttings (90'-200'),  
Mobil Oil Corporation Salmonberry Lake Unit No. 1 (well no. 2) cuttings (250'-1,890'),  
Atlantic Refining Co. Rainbow Federal No. 1 (well no. 3) cuttings (1,065'-2,780'), and  
Atlantic Refining Co. Rainbow Federal No. 2 (well no. 4) cuttings (1,122'-2,601').



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**SAMPLING FROM GMC COLLECTIONS BY BHP BILLITON**Brock Riedell & Terry Massoth, 14 April 2006

<u>Sample No.</u>	<u>Well</u>	<u>GMC collection</u>	<u>Footage</u>	<u>Comments</u>
CRB-01	Tazlina #1	USGS	90-200	composite of 4 samples
CRB-02	Salmonberry Lake Unit #1	USGS	250-270	composite of 2 samples
CRB-03	Salmonberry Lake Unit #1	USGS	530-540	
CRB-04	Salmonberry Lake Unit #1	USGS	1800-1810	
CRB-05	Salmonberry Lake Unit #1	USGS	1880-1890	
CRB-06	Rainbow Federal #1	State of Alaska	1065-1153	composite of 3 samples
CRB-07	Rainbow Federal #1	State of Alaska	2770-2780	
CRB-08	Rainbow Federal #2	State of Alaska	1122-1152	
CRB-09	Rainbow Federal #2	State of Alaska	2452-2482	
CRB-10	Rainbow Federal #2	State of Alaska	2572-2601	

<b>OIL WELL CUTTINGS SAMPLING BY BHP BILLITON</b>						
Brock Riedell & Terry Massoth, 14 April 2006						
Note: All samples were collected as "whole rock" samples, i.e., coals not separated out, not able to collect separately.						
<b>Sample No.</b>	<b>Footage</b>	<b>Weight (g)</b>	<b>Components</b>	<b>Comments</b>	<b>National Petrographic Service IDs</b>	
					<b>Sample</b>	<b>Well</b>
CRB-01	90-200	30	glacials, sand, shale, some coal grains	composite of 4 samples	Sample 1	WELL No. 1
CRB-02	250-270	7	dominantly coal, some carbonaceous shales	composite of 2 samples	Sample 2	WELL No. 2
CRB-03	530-540	8	dominantly coal		Sample 3	WELL No. 2
CRB-04	1800-1810	7	coal, sand, shale, carb shale		Sample 4	WELL No. 2
CRB-05	1880-1890	6	coal, sand, shale, carb shale		Sample 5	WELL No. 2
CRB-06	1065-1153	6	shale, coal, carb shale	composite of 3 samples	Sample 6	WELL No. 3
CRB-07	2770-2780	10	shale, siltstone, coal, carb shale		Sample 7	WELL No. 3
CRB-08	1122-1152	14	carb shale, coal		Sample 8	WELL No. 4
CRB-09	2452-2482	14	carb shale, coal		Sample 9	WELL No. 4
CRB-10	2572-2601	10	carb shale, coal		Sample 10	WELL No. 4

## **COAL VITRINITE ANALYSIS**

**Houston, Texas  
April 26, 2006**

**James H. Ruffin**

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THIN & POLISHED SECTIONS  
BIOSTRATIGRAPHIC STUDIES  
SOURCE - ROCK STUDIES

5933 BELLAIRE BLVD. SUITE 108 HOUSTON, TEXAS 77061 (713) 661-1884

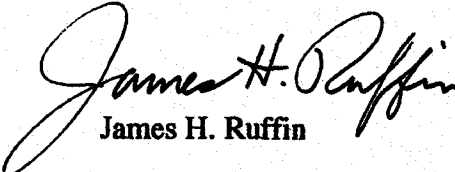
DATE: 04-26-06

TO: Terry W. Massoth BHP Billiton World Exploration  
FOR: Mr. Terry W. Massoth Brock Riedell  
FROM: Mr. James H. Ruffin  
RE: Coal Vitrinite Analysis

Ten coal/shale samples from four wells were analyzed for vitrinite to determine maturity/coal rank. The histograms show the in situ values in solid black bars, with clear bars to the left representing caving vitrinite and clear bars to the right reworked vitrinite. A set of standards is included.

RESULTS

	<u>Depth (ft.)</u>	<u>Vitrinite R<sub>v</sub></u>	<u>Maturity</u>	<u>Coal Rank</u>
WELL NUMBER 1				
Sample 1	90-200	Insufficient Vitrinite		
WELL NUMBER 2				
Sample 2	250-270	0.33	Immature	Lignite
Sample 3	530-540	0.34	Immature	Lignite
Sample 4	1800-1810	0.38	Immature	Sub Bituminous C
Sample 5	1880-1890	0.39	Immature	Sub Bituminous C
WELL NUMBER 3				
Sample 6	1065-1153	0.36	Immature	Lignite
Sample 7	2770-2780	0.45	Immature	Sub Bituminous B
WELL NUMBER 4				
Sample 8	1122-1152	0.36	Immature	Lignite
Sample 9	2452-2482	0.49	Immature	Sub Bituminous B
Sample 10	2572-2601	0.50	Immature	Sub Bituminous B

  
James H. Ruffin

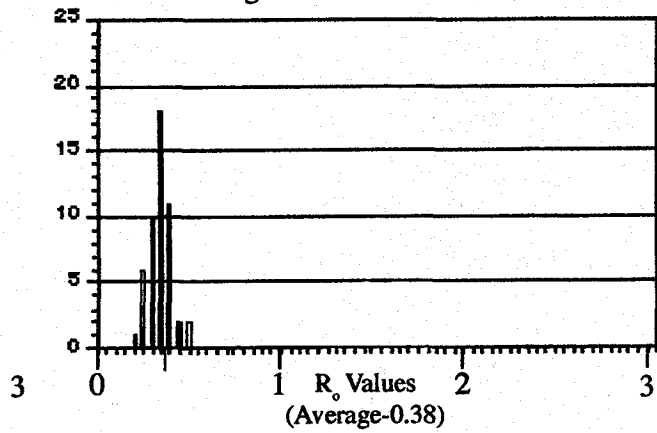
**HISTOGRAMS**

1. CRB-01 90'-200'

Insufficient Material

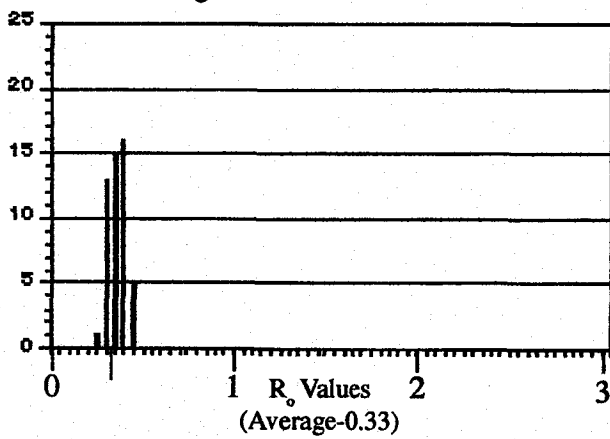
4. CRB-04 1800-1810

Reading



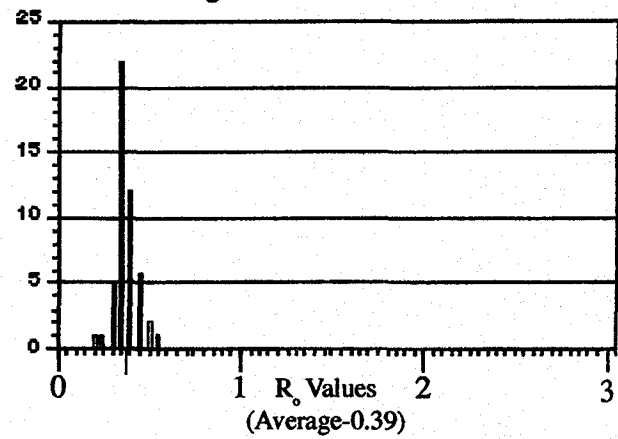
2. CRB-2 200'-270'

Reading



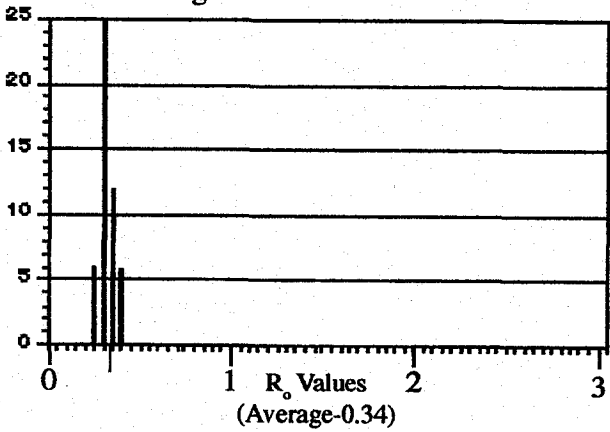
5. CRB-05 1800-1890

Reading



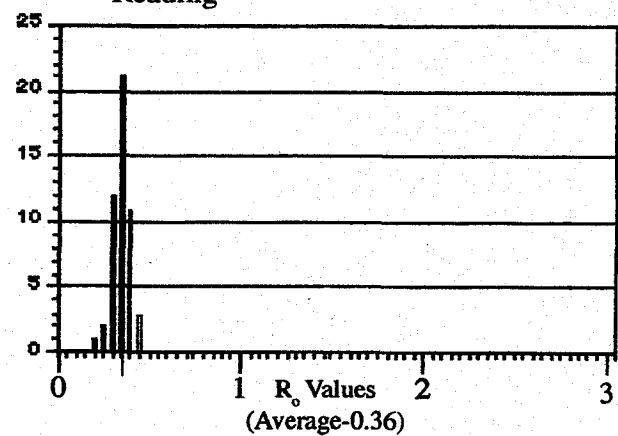
3. CRB-03 530'-540'

Reading



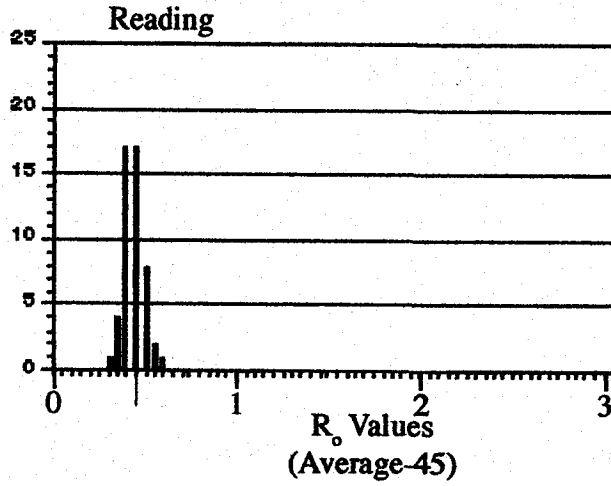
6. CRB-06 1065-1153

Reading

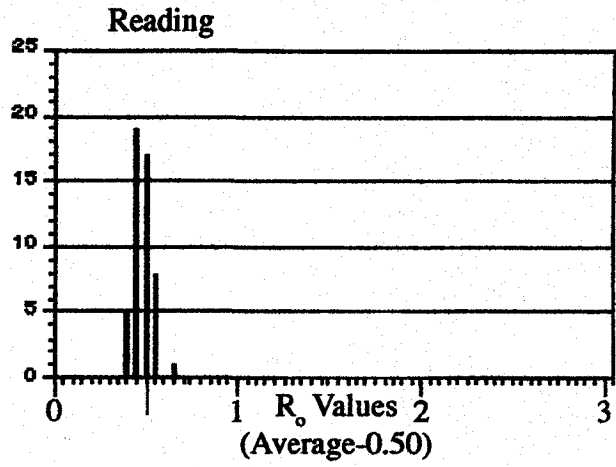


HISTOGRAMS

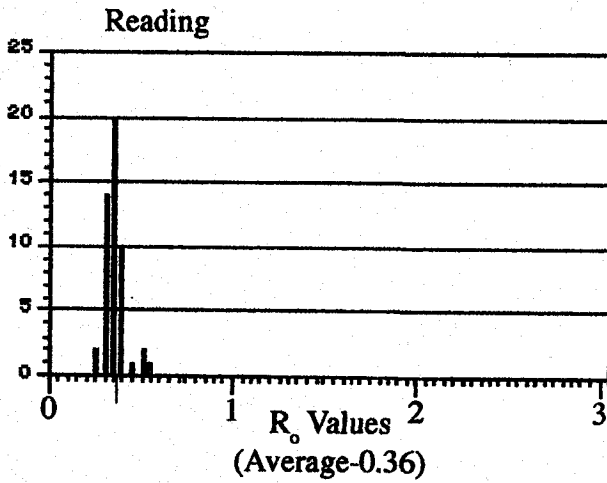
7. CRB-07 2770-2780



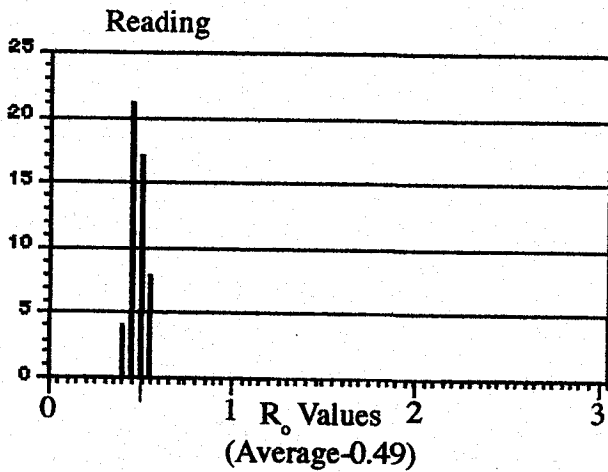
10. CRB-10 2572-2601



8. CRB-08 1122-1152



9. CRB-09 2452-2482



VITRINITE VALUES

1. CRB-01 90-200'      2. CRB-2 200'-270'      3. BHP-03 530'-540'      4. CRB-04 1800-1810

Insufficient Material

.24	1	.27	1	.22	1
.26	1	.28	2	.25	1
.27	5	.29	3	.26	1
.28	5	.30	6	.27	1
.29	2	.31	4	.28	2
.30	5	.32	9	.29	1
.31	1	.33	5	.31	1
.32	2	.34	2	.32	2
.33	2	.35	3	.33	4
.34	5	.36	5	.34	3
.35	3	.37	1	.35	5
.36	3	.38	1	.36	3
.37	4	.39	2	.37	1
.38	4	.40	2	.38	7
.39	2	.41	2	.39	2
.40	2	.42	1	.40	5
.41	1	.43	1	.41	3
.42	2	Avg-0.34		.42	2
Avg-0.33		Avg Range-0.27-0.43		.44	1
Avg. Range-0.24-0.42		Avg. Count-50		.46	1
Avg Count-50		Total Count-50		.48	1
Total Count-50				.52	1
				.54	1

Avg-0.38  
 Avg Range-0.32-0.48  
 Avg Count-41  
 Total Count-50



VITRINITE VALUES

5. CRB-05 1880-1890	6. CRB-06 1065-1153	7. CRB-07 2770-2780	8. CRB-08 1122-1152
.24 1	.24 1	.34 1	.29 2
.26 1	.28 1	.35 1	.30 3
.31 1	.29 1	.36 1	.31 1
.32 1	.30 1	.38 1	.32 5
.33 2	.31 1	.39 1	.33 2
.34 1	.32 3	.40 3	.34 3
.35 3	.33 4	.41 3	.35 4
.36 4	.34 3	.42 4	.36 3
.37 5	.35 5	.43 3	.37 8
.38 3	.36 7	.44 4	.38 3
.39 7	.37 5	.45 3	.39 2
.40 6	.38 2	.46 6	.40 4
.41 3	.39 2	.47 5	.41 2
.42 2	.40 2	.48 1	.42 3
.43 1	.41 3	.49 2	.43 1
.45 2	.42 4	.50 2	.46 1
.46 2	.43 1	.52 2	.50 1
.48 2	.44 1	.53 2	.51 1
.51 1	.48 1	.54 2	.56 1
.52 1	.49 2	.55 2	Avg-0.36
.55 1	Avg-0.36	.61 1	Avg Range-0.29-0.43
Avg-0.39	Avg Range-0.28-0.44	Avg-0.45	Avg Count-46
Avg Range-0.31-0.48	Avg Count-46	Avg Range-0.34-0.55	Total Count-50
Avg Count-45	Total Count-50	Avg Count-49	
Total Count-50		Total Count-50	

VITRINITE VALUES

9. CRB-09 2452-2482    10. CRB-10 2572-2601

.41	2	.42	1
.44	2	.43	2
.45	6	.44	2
.46	2	.45	4
.47	1	.46	4
.48	1	.47	2
.49	11	.48	4
.50	3	.49	5
.51	2	.50	4
.52	3	.51	7
.53	5	.52	2
.54	4	.53	2
.55	2	.54	2
.56	2	.55	3
.57	3	.56	3
.58	1	.57	2
Avg-0.49		.65	1
Avg Range-0.41-0.58		Avg-0.50	
Avg Count-50		Avg Range-0.42-0.57	
Total Count-50		Avg Count-49	
		Total Count-50	

**OIL WELL CUTTINGS SAMPLING BY BHP BILLITON****Brock Riedell & Terry Massoth, 14 April 2006**

Note: All samples were collected as "whole rock" samples, i.e., coals not separated out, not able to collect separately.

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2 CRB-02 Well 2	250-270	7	dominantly coal, some carbonaceous shales	composite of 2 samples
3 CRB-03	530-540	8	dominantly coal	
4 CRB-04	1800-1810	7	coal, sand, shale, carb shale	
5 CRB-05	1880-1890	6	coal, sand, shale, carb shale	
6 CRB-06 Well 3	1065-1153	6	shale, coal, carb shale	composite of 3 samples
7 CRB-07	2770-2780	10	shale, siltstone, coal, carb shale	
8 CRB-08 Well 4	1122-1152	14	carb shale, coal	
9 CRB-09	2452-2482	14	carb shale, coal	
10 CRB-10	2572-2601	10	carb shale, coal	

**STANDARD FOR  
HYDROCARBON SOURCE-ROCK EVALUATIONS  
by James H. Ruffin**

<b>Maturation Level</b>	<b>Thermal Alteration Index (T.A.I)</b>	<b>Vitrinite R<sub>v</sub></b>	<b>Probable Hydrocarbon</b>
Immature	1, 1+, 2-, 2 (Yellow)	<0.55	Gas
Transitional	2+ (Yellow Brown)	0.55 - 0.7	Gas & Minor Oil
Mature*	3-, 3 (Brown)	0.7 - 1.2	Gas & Oil
Very Mature	3, 3+, 4- (Dark Brown)	1.2 - 1.5	Wet Gas/Condensate
Advanced	4-, 4, 5 (Dark Brn.-Black)	>1.5	Gas

**Total Organic Carbon (T.O.C.) (% of Rock)**

	<b>Shales</b>	<b>Carbonates</b>
Poor	<0.5	<0.2
Fair	0.5-1.0	0.2-0.5
Rich	1.0-2.0	0.5-1.0
Very Rich	>2.0	>1.0

**Sapropel Quality (Oil Generation)**

1. Excellent - Globular (i.e. Botryococcus)
2. Good - Coarse granular (>2 μ)
3. Fair - Medium granular (±1 μ)
4. Poor - Fine granular-dispersed (<1 μ)

**Extractable Hydrocarbons (H.C.) (ppm. of Rock)**

	<b>Shales</b>	<b>Carbonates</b>
Poor	<500	<100
Fair	500-1000	100-500
Rich	1000-2000	500-1000
Very Rich	>2000	>1000

**Sapropel (% of T.O.C.)**

Poor Primary Oil - Migration Potential <30  
 Good Primary Oil - Migration Potential >30

**Kerogen Content of Rock (ppm. of Rock)**

	<b>Shales</b>	<b>Carbonates</b>
Poor	<5000	<2000
Fair	5000-10,000	2000-5000
Rich	10,000-20,000	5000-10,000
Very Rich	>20,000	>10,000

**Calculating Kerogen Content of Rock**

% Kerogen Type x T.O.C. x 10,000 = ppm.

**Inertinite (INR) (% of T.O.C.)**

GMC DATA REPORT 3 3 1

Generates no hydrocarbons. Analyzed due to inclusion in total organic carbon analysis.

\* Mature Threshold Varies - 0.65 for Paleozoic.

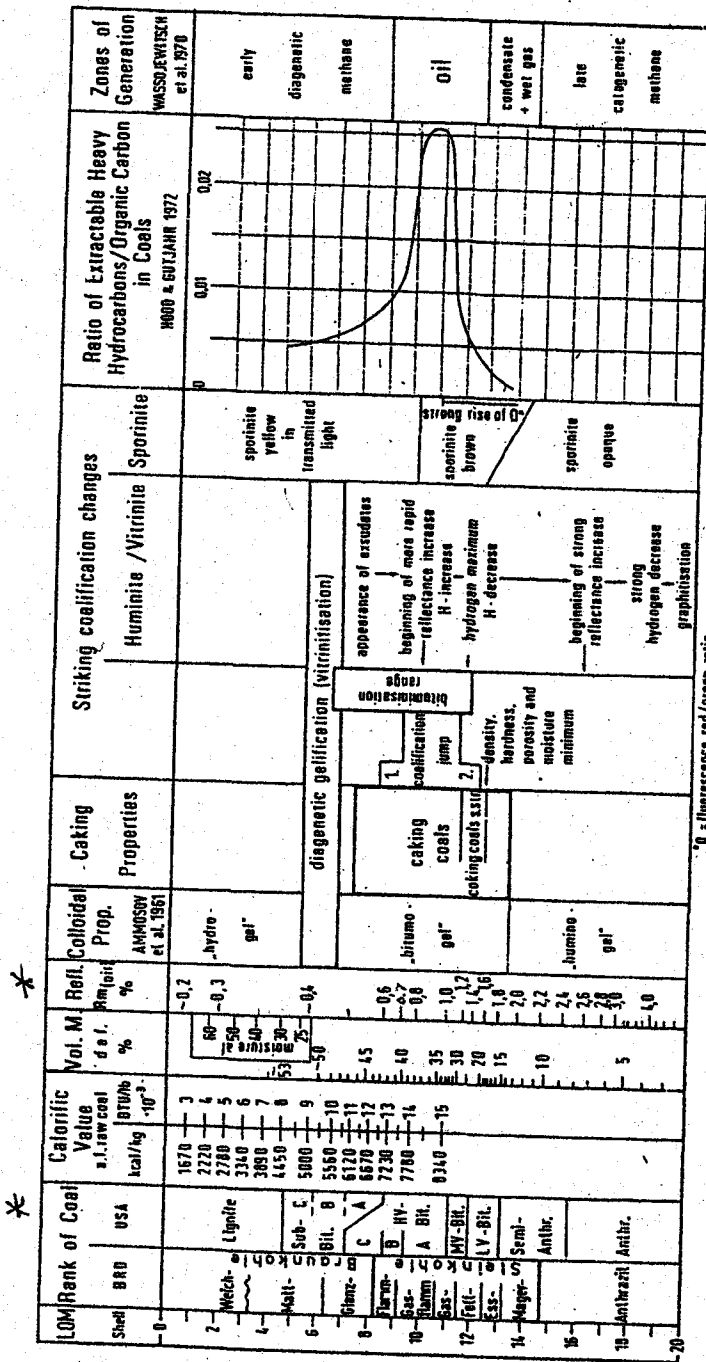


Fig. 25. Relationships between coal properties and oil generation (after M. TEICHMÜLLER, 1974 a).

during storage (o on certain coal pr as is demonstrat dark-brown 'hy 'bitumogel', bitun These relationship

2.142.4 Coalifica

Coalification sediments which, and permeability of Ch. 5.2 e. g. sh porosity of petrol lonite into mixed 0.4-0.5%) (HELI tions in clay rock rank (Fig. 26). C minerals.

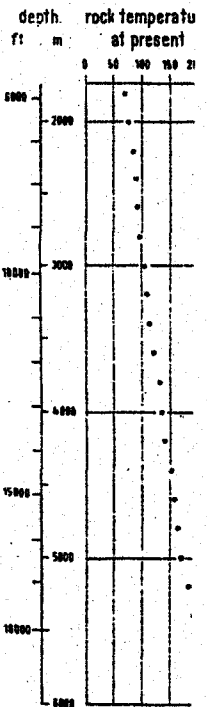


Fig. 26. Rock temperatures in the Münsi TEICHMÜLLER, 1966

# HYDROCARBON SOURCE-ROCK EVALUATION

James H. Ruffin

Revised 2003

## INTRODUCTION

The evaluation of hydrocarbon source-rocks is another fundamental tool in the successful search for oil and gas accumulations. The standard or routine analyses consist of kerogen content, thermal maturation, total organic carbon content, and extractable hydrocarbon content. These four parameters are checked against each other to effectively determine the oil/gas generation activity or potential.

The purpose of this paper is to present a brief description and discussion of the above mentioned routine analyses, characteristics of oil/gas source-rocks, and applications to exploration/exploitation.

## KEROGEN CONTENT ANALYSIS

A kerogen analysis preparation is made by dissolving the mineral matter via acids from a rock sample (dark shales preferred) leaving an insoluble organic residue (kerogen) to be stained, washed and mounted on glass slides for study with a biological microscope using transmitted light.

The kerogen content of a rock evaluation (see standards) was obtained by multiplying percent of type, from 100-grain counts, times percent total organic carbon times 10,000 to express in parts-per-million (ppm).

The kerogen material is conveniently organized into four chemically and/or genetically related fractions, as discussed below, with their hydrocarbon-generating significance.

**INERTINITE** - Organic derived, almost pure carbon, such as burned wood (fusinite). This fraction yields almost no hydrocarbons, but is necessary to count because it is included in the total organic content analysis.

**HUMIC** - Humic acid (biodegradation products of woody tissue) and vitrinite (thermally matured humic acids). This fraction is low in hydrogen (+ 5% weight) and subjected to thermal catagenesis will yield mainly gas.

**EXINITE** - Resins (Hardened tree sap) and wall structures (exines) of spores, pollen, cuticle (leaf tissue) and algae. This fraction is moderately high in hydrogen (+ 9% weight), and when initially subjected to thermal catagenesis will produce gases and liquid hydrocarbons.

**SAPROPEL** - Amorphous biodegradation product of rich lipid and protein residues from the exinite fraction, mainly algae. This fraction is high in hydrogen (+ 10% weight), and will tend to form mainly liquid hydrocarbons when initially subjected to thermal catagenesis.

## SAPROPEL QUALITY

Sapropelic kerogen is evaluated for oil-generating quality, based principally on its structure as follows:

Very Rich - Globular (i.e. Botryococcus)

Rich - Coarse Granular ( $> 2 \mu$ )

Fair - Medium Granular ( $\pm 1 \mu$ )

Poor - Fine Granular ( $< 1 \mu$ )

In addition, sapropel that tends to clump and have strong color is considered to have good characteristics for oil generation. This often occurred in the globular and coarse-grained sapropels. Conversely, the finer grained sapropels, which are considered poor oil-generators, tended to be dispersed and have pale, or no color.

## THERMAL MATURATION

It has been well established that it is necessary for the kerogen in source-rocks to undergo heating at sufficient temperatures for sufficient time to produce oil and/or gas. Thermal maturation, which is a measure of the temperature/time history of rocks, is determined by vitrinite reflectance in oil (Ro) and spore/pollen coloration (TAI).

Vitrinite on thermally maturing will yield volatiles and harden, thus increase in the ability to take a polish and reflect light. Samples are prepared similarly to the kerogen analysis, but the residues are mounted in plastic plugs for polishing and light reflectance measurements in oil.

Spore/pollen on thermally maturing will yield volatiles and their exines will darken as the fixed carbon content increases. The ability to take stain tends to be lost on increasing maturation beyond the immature rank. This method has an advantage over vitrinite reflectance, because reworked and contamination forms can be more readily detected. The two methods are used to cross-check each other for reliable determinations.

All of the above discussed topics are shown in their interrelationships by the attached standards for source-rock evaluations.

## TOTAL ORGANIC CARBON (TOC)

The TOC measures the enrichment of organic matter in sediments. However, it does not indicate the type of kerogen, thus whether the sample has gas or oil generating potential. The TOC indicates the general hydrocarbon potential. The minimum content for a source-rock is 0.5% for shales and 0.2% for carbonates. (See Standards)

The analysis involves using approximately one gram of dried, powdered sample. The carbonate material (non organic carbon source) is removed by HCL, leaving a residue which is analyzed with a thermal carbon determinator (burns material to completion measuring the CO<sub>2</sub> released) and reported as the TOC weight percent of rock. The value can also be obtained from a pyrolysis analysis (Rock-Eval).

## EXTRACTABLE HYDROCARBONS (HC)

This is the amount of liquid or free hydrocarbon naturally produced in a sediment, thus is a direct measure of oil-generating capabilities. The minimum for commercial consideration is 500 ppm for shales and 100 ppm for carbonates (see standards). If the samples have been forced dried, the HC content will be artificially low. The value can be obtained from a Rock-Eval pyrolysis analysis (S1 value).

## CHARACTERISTICS OF OIL SOURCE-ROCKS

Philippi (1965, *Geochem, at Cosmochem.*) established that source-rocks have to generate oil in excess of the sorption capacity of organic matter (mainly humic from my studies) for primary migration to take place. This requirement was expressed by a HC/TOC ratio, where 3% to 12% is when oil can be released from the rocks. Since sapropelic matter is the main source of oil, Philippi's principle can also be expressed via sapropelic percent of TOC. My studies indicate that approximately 30-40% sapropel of TOC is when oil can be sufficiently generated to primarily migrate from the shales. In carbonate source-rocks, where there is little or no humic material, almost all of the oil generated can primarily migrate.

It is generally believed (Tissot & Welte, 1984, Petroleum Formation and Occurrence, Springer-Verlag, N. Y.) that the expulsion action takes place along the bedding planes of the shales where the organic matter is concentrated and the kerogen-to-oil conversion mainly occurs, locally over pressuring and ejecting the excess oil in a pulse. Afterward the pressure reduces, thus completing a cycle which can be repeated. In a carbonate the expulsion is more continuous due to the lack of inhibiting humic matter.

From the above assumptions and maturation data, the optimum conditions for producing liquid hydrocarbons is a mature maturation rank ( $R_o$  0.7 to 1.2), greater than 30% sapropelic matter of TOC for clastics, and a minimum organic matter enrichment of 0.5% of rock for shales and 0.2% for carbonates.

### CHARACTERISTICS OF GAS SOURCE-ROCKS

The maturation level for gas generation is not as critical as for oil. Gas can be generated in immature maturation environments via bacterial-fungal breakdown of organic matter and in mature to advanced environments via heat degradation (catagenesis); the latter being best for large accumulations. The optimum gas-generating parameters are: very mature to advanced maturation rank ( $R_o$  1.2-1.5), dominance of sapropel kerogen (>80%), and a TOC greater than 2%. Ironically, sapropel (oil prone kerogen) is better than humic kerogen (gas prone), because it has a higher H content, and all organic matter turns to gas at higher maturations.

### SOLID BITUMENS

There is relationship between vitrinite and solid bitumen reflectances in the range of 0.1 to 3.0%  $R_o$ , expressed by the equation:  $R_v = 0.618 R_b + 0.4$ , where  $R_v$  is vitrinite reflectance and  $R_b$  bitumen reflectance. (Gentzis and Goudarzi, 1990, Application of Thermal Maturity Studies to Energy Exploration, SEPM-Rocky Mt. Section, p. 23)

Solid Bitumen can be used in place of vitrinite for maturity analysis, if it is primary-formed from the insitu kerogen. It's presence indicates oil generation if primary, or oil migration if secondary.

### EXPLORATION APPLICATIONS

Overlay contour maps based on a given datum (source-rock or strata) for a basin or area should be made when there is sufficient well control, using the following data: maturation (vitrinite  $R_o$  and spore coloration rank), total organic carbon, hydrocarbon extracts, sapropelic percent (primary migration potential) and sapropelic content of rock (oil generation potential). This will localize the best source-rock areas.

The above information has to be coordinated with the geology to answer the following critical questions:

- At what time, depth and area are the source-rocks?
- At what time, depth and area are the source-rocks mature?
- What are the times and routes of primary migration?
- When/where did the reservoirs occur vs. the hydrocarbon generation?

### SECONDARY-MIGRATED OILS

Secondary-migrated oils (movement after the primary expulsion of migration) can often be detected by comparing the TOC contents to the HC contents. In a mature maturation facies for example, if the TOC content is poor, but the HC content is rich, then secondary oil migration has probably occurred. The poor TOC content is not sufficient to have generated a rich HC content. If no oil source-rocks are found in an area, the detection of secondary migration is vital, because it indicates that free oil is or was present for entrapment.



**EXPLOITATION APPLICATION**

Source-rock studies are primarily important for exploration; however they can also be applied to exploitation. Determining a source-rock and its areas of greatest generation within a known oil/gas field could help guide the locations of development or step-out wells. Such studies, of course, would be more significant in sparsely developed fields.

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