

APPENDIX 12

DSGC – Geochemical Report, Rock Island #4-H



GEOCHEMICAL ANALYSIS OF
BLACK MATERIAL ON CORE FRACTURE
ROCK ISLAND 4H WELL

Prepared For

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INTRODUCTION

Black material on a fracture face of a conventional core from 15,424.55 MD in the Rock-Island 4H well was analyzed to determine its affinity and significance. A scraping of the black material was analyzed for organic carbon content and with Rock-Eval pyrolysis. Some free hydrocarbons were present and the sample was then analyzed with S_1 pyrolysis gc (thermal extraction) to determine their composition. Finally, a whole rock polished section of the core at the fracture location was analyzed with reflected light microscopy to determine the distribution of the black material in the sample.

DISCUSSION

The sample scraping yielded 0.69 wt. % organic carbon, showing that it is organic. Rock-Eval pyrolysis showed some free hydrocarbons (S_1) and hydrocarbon generating potential (hydrogen index [HI] of 32) as shown in Figure 1. The T_{max} of 490°C is equivalent to about 1.5% R_o or a maturity beyond the oil preservation limit. These data proved encouraging and the sample was analyzed with S_1 pyrolysis gas chromatography to determine the composition of the free hydrocarbons.

The S_1 pyrolysis gas chromatogram shows hydrocarbons mostly between nC_{10} and nC_{20} with a "tail" of normal paraffins (spikes) up to nC_{30} . This is characteristic of a very mature crude oil or condensate. Light hydrocarbons (less than nC_{10}) have been mostly lost to evaporation since sample collection. The free hydrocarbons indicated by the S_1 gas chromatogram could be, in part, diesel oil from the drilling fluid, as diesel typically falls in the same molecular weight range. The "tail" of heavier material, however, is very typical of a mature, naturally occurring oil or condensate (e.g. $\pm 50^\circ$ API) and is not found in refined products. The position of the sample on Figure 2 indicates very high thermal maturity.

A polished section of the core including the exposed black material on the fracture surface was made and examined with reflected light microscopy. A second, unexposed fracture containing black material and traces of black material filling very small pores in the reservoir sandstone were observed on the polished rock section. The black material gave no fluorescence and was identified as solid pyrobitumen. The black material was rough textured due to natural coking and filled open spaces along the fractures and coated mineral grains away from fractures. This distribution is characteristic of solid bitumen derived from thermal destruction of a previous oil accumulation. The reflectance of three particles of solid bitumen that were smooth enough for measurement, average 2.0% R_o , which equates to a vitrinite reflectance maturity of 2.25% R_o (Appendix). This maturity level is in the dry gas-only preservation free hydrocarbon range (2.0 to 3.2% R_o). Produced hydrocarbons from reservoirs represented by the subject cores should be only dry gas, possibly with some non hydrocarbon gases, such as carbon dioxide. The S_1 pyrolysis gas chromatogram previously described was derived from very small amounts of adsorbed hydrocarbons that have not yet been converted to gas.

APPLICATIONS

The black pyrobitumen found on fracture surfaces and in matrix porosity of the subject sample represents a paleo-oil accumulation that has been converted to gas by continued burial and maturation. Because hydrocarbon gas, especially methane, contains more hydrogen than crude oil, the maturation of oil into gas in a closed or semi-closed system results in precipitation of the excess carbon as pyrobitumen. This occurs near the "oil maturity floor" of between 1.2 and 1.4% R_o . The pyrobitumen distribution will approximate the distribution of the original oil pool, which may or may not be the same as the current gas pool. Changes in structural closure, gas production within closure of oil accumulation that was not filled to spill point, or down dip gas accumulation held in place by a pyrobitumen seal, all could extend current gas production beyond the limits of the pyrobitumen occurrence. This would be favorable because it would add to matrix porosity and trapped gas volumes. Current production is probably controlled by post oil destruction in fracture systems, which commonly are focused in faulted, flexured, or uplifted and eroded areas. The latter could result in overpressured gas accumulations if good seals are present.

RECOMMENDATIONS

We suggest that samples be collected at about 500 foot intervals from surface casing to reservoir depth from one well and analyzed with kerogen microscopy (vitrinite reflectance). This will establish a maturation profile for the field and from this we can determine the amount of overburden removal and the depth of original oil conversion to gas. This information will be useful to reconstruct the original crude oil pool, and hence the present solid bitumen distribution in the reservoir. Samples from the reservoir everywhere it is encountered should be examined to see if pyrobitumen is present. If engineering data confirm that gas production improves away from pyrobitumen occurrences, then the foregoing exercise could be very useful in field development by concentrating development in pyrobitumen-free areas.

ORGANIC CARBON AND PYROLYSIS DATA

Total Organic Carbon (TOC) and Rock-Eval pyrolysis data provide basic geochemical information and are frequently used to select samples for more detailed studies, particularly kerogen microscopy, extract chromatography and biomarker analyses. Well data can be plotted to make geochemical logs. Unless otherwise specified by a client, DGSI uses LECO TOC then Rock-Eval II pyrolysis as the standard analytical sequence and Rock-Eval is recommended for samples with greater than 0.4% TOC. Samples for LECO TOC and Rock-Eval pyrolysis are ground to pass through a 60 mesh sieve to assure homogeneity.

LECO Organic Carbon and Total Sulfur

Total Organic Carbon is best determined by direct combustion. Approximately 0.15 grams of sample are carefully weighed, treated with concentrated HCl to remove carbonates, and vacuum filtered on glass fiber paper. The residue and paper are placed in a ceramic crucible, dried, and combusted with pure oxygen in a LECO EC-12 or LECO CS-444 carbon analyzer at about 1,000°C. A laboratory standard is run every five samples. Total, insoluble, mineral plus organic sulfur can be determined by the CS-444 analyzer during the carbon analysis. Total carbonate can be determined from sample and acid residue weight differences or by LECO combustion TOC differences before and after acid digestion.

Rock-Eval II Pyrolysis

Rock-Eval II pyrolysis is used to determine kerogen type, kerogen maturity and the amount of free hydrocarbons. About 0.1 grams of the same ground sample used for LECO TOC are carefully weighed in a pyrolysis crucible and then heated to 300°C to determine the amount of free hydrocarbons, S_1 , that is thermally distilled. Next, the amount of pyrolyzable hydrocarbons, S_2 , is measured when the sample is heated in an inert environment which rises from 300° to 550°C at a heating rate of 25°C/minute. S_1 and S_2 are reported in mg HC/g sample. T_{max} , a maturity indicator, is the temperature of maximum S_2 generation. When S_2 values are less than 0.2 mg HC/g sample, the S_2 maximum typically has poor definition and thus, T_{max} cannot be reliably determined (Peters, 1986). T_{max} values are reported as N.A. on samples with 0.00 S_2 . Carbon dioxide generated during the S_2 pyrolysis, an indicator of kerogen oxidation, is collected up to a temperature of 390°C and reported as S_3 in units of mg CO₂/g sample. A laboratory standard is run every 10 samples. Hydrogen Index (HI = $S_2 * 100/TOC$) and Oxygen Index (OI = $S_3 * 100/TOC$) are used as kerogen type indicators when plotted on a van Krevelen type diagram.

Rock-Eval II Pyrolysis with TOC

Rock-Eval II Plus TOC is used to determine both Rock-Eval data (S_1 , S_2 , S_3 , T_{max}) and TOC of a 0.1 gram ground sample. With this instrument, the pyrolysis stage (S_2) ramps to 600°C at which point the sample is switched to an oxidation oven where the sample is oxidized at 600°C for 5 minutes in air to measure the residual organic matter (S_4). A laboratory standard is run every 10 samples. S_1 , S_2 , S_3 , and S_4 are summed appropriately to calculate TOC. True TOC will be greater than this calculated sum for samples with maturity greater than about 1.0% R_o because the Rock-Eval final temperature is inadequate for complete combustion (Peters, 1986). This instrument is preferred when there is insufficient sample to run TOC and pyrolysis separately, or when all samples in a study are to be analyzed for both TOC and Rock-Eval data without prior TOC screening.

ORGANIC CARBON AND ROCK-EVAL PYROLYSIS DATA

Rock Island 4H Core

DGSI Project: 99/4522

SAMPLE IDENTIFICATION			TOC	S1	S2	S3	Tmax	S1/	HI	OI	S2/	PI
DGSI ID			Wt%	mg/g	mg/g	mg/g	degC	TOC			S3	
1	Black Material	15424 6	0 69	0 29	0 91	0 07	490	42	132	10	13 00	0 24

Rock Island 4H Core

DGSI Project: 99/4522

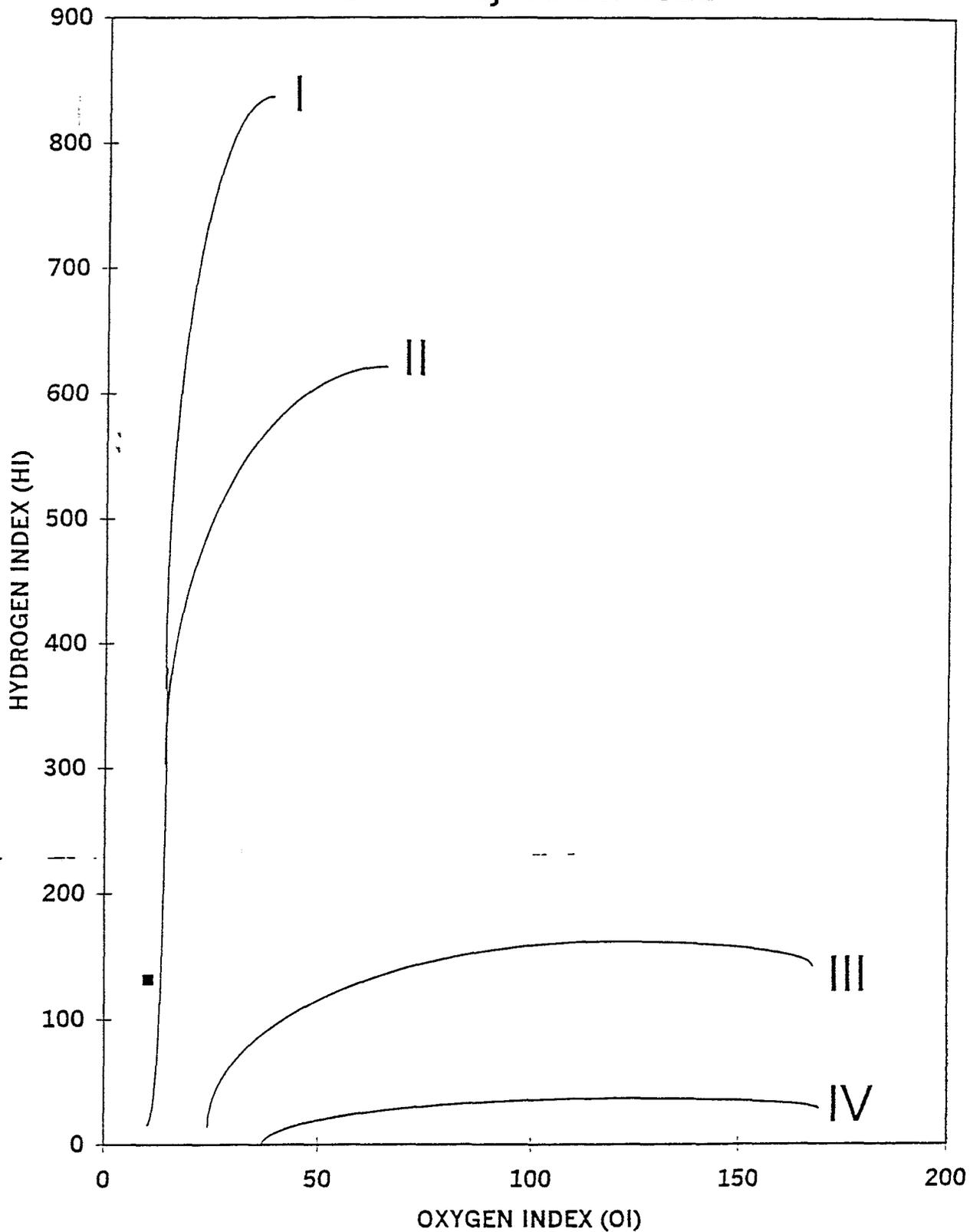


FIGURE - 1 Kerogen type determination from TOC and Rock-Eval pyrolysis data. Types I and II will generate oil, type III gas, and type IV little or no hydrocarbons.

SPECIALITY GAS CHROMATOGRAPHY

Pyrolysis-Gas Chromatography

A small quantity of isolated kerogen or whole rock is heated in a Ruska Laboratories, ThermEx pyrolyzer. Free hydrocarbons (S_1) are obtained by heating the sample up to 315°C and kerogen degradation products (S_2) by heating a second time up to 610°C. Pyrolysis products are trapped with liquid nitrogen at the head of a 50m X 0.25mm QUADREX fused silica capillary column and analyzed with a Varian 3400 gas chromatograph. Analytical data are processed with Genie Software System and HP Chemstation on a PC. Gas chromatograms of S_1 and S_2 are provided and standard calculations including pristane/phytane, pristane/ nC_{17} , and phytane/ nC_{18} and carbon preference index are made from the S_1 chromatogram. Chromatography data can also be supplied on computer diskette for client processing.

Pyrolysis S_1 gas chromatography data is used and interpreted in much the same way as solvent extract – whole oil gas chromatography, but with the advantage of requiring only very small samples. It provides information on source type and maturity of source rock samples as well as the type of oil in reservoir samples. Pyrolysis S_2 chromatography provides information on whether an organic rich source rock or isolated kerogen will yield oil or gas at maturities up to about 1.30 R_o . Both S_1 and S_2 analysis are recommended on rocks and kerogens but S_1 alone is advised in the case of reservoir rocks. Pyrolysis S_1 gas chromatography is a standard technique to identify diesel oil contamination in cuttings and cores.

Pyrolysis-GC of Asphaltenes

A small quantity of asphaltenes from an oil or rock extract is heated in a Ruska Laboratories, ThermEx pyrolyzer. Free hydrocarbons are generated by heating the sample up to 550° C. Pyrolysis products are trapped with liquid nitrogen at the head of a 50 m. X 0.25 mm QUADREX fused silica capillary column and analyzed with a Varian 3400 gas chromatograph. Analytical data are processed with a Genie Software System and HP Chemstation on a PC. A gas chromatogram is provided and standard calculations are made. Chromatography data can also be supplied on computer diskette for client processing.

PYROLYSIS S1 GAS CHROMATOGRAPHY

Rock Island 4H Core

DGSI Project: 99/4522

Sample Identification			GAS CHROMATOGRAPHY RATIOS						
DGSI ID			TOC Wt%	PPM	Ext/TOC	Pr/Ph	Pr/C17	Ph/C18	OEP
1	: Black Material	15424 55	0.69	N.A.	N.A.	1.1	0.06	0.10	0.78
DGSI ID	Sample Weight	Extract Weight	C17	Pr	C18	AREA DATA			
						Ph	C28	C29	C30
1	: nd	nd	241144	13813	127243	12297	6383	3213	1857

Sample Identification			NORMALIZED ISOPRENOID PERCENT						
DGSI ID			iC13	iC14	iC15	iC16	iC18	iC19	iC20
1	: Black Material	15424 55	6.3	54.4	12.0	21.3	2.9	1.6	1.4
DGSI ID	Sample Identification		AREA DATA						
			iC13	iC14	iC15	iC16	iC18	iC19	iC20
1	: Black Material	15424 55	53763	462171	101577	180431	24871	13813	12297

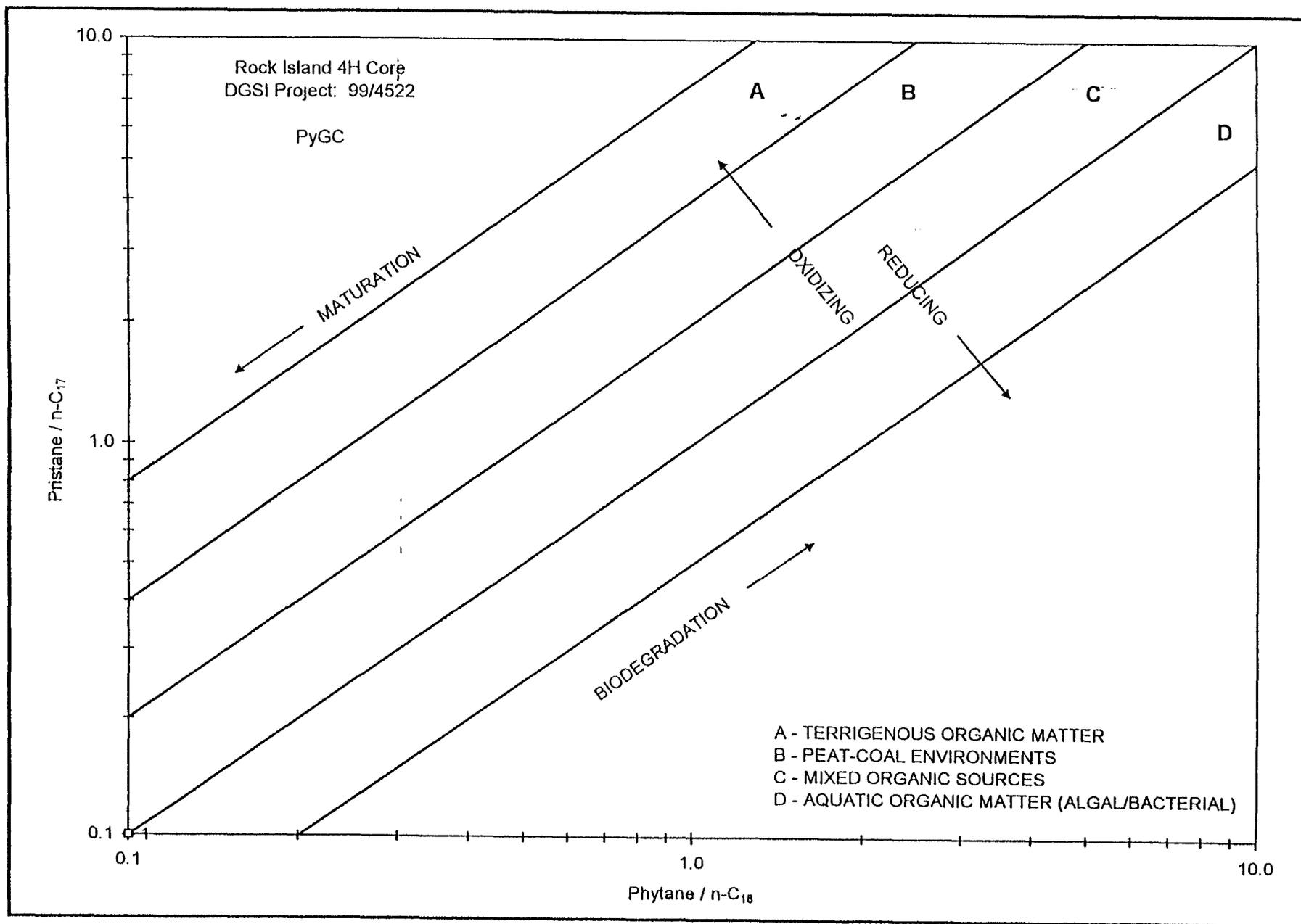


FIGURE 2 - Plot from chromatography data showing organic matter type, source rock depositional environment, and thermal maturity.

KEROGEN MICROSCOPY

Visual kerogen analysis employs a Zeiss Universal microscope system equipped with halogen, xenon, and tungsten light sources or a Jena Lumar microscope equipped with halogen and mercury light sources. Vitrinite reflectance and kerogen typing are performed on a polished epoxy plug of unfloated kerogen concentrate using reflected light from the halogen source. In certain situations, the whole rock is used for analysis. This approach is used for coals, where acid treatment is unnecessary in studies of solid bitumen and graptolites where preservation of rock structure is important, and in samples too small for acid treatment. The digital indicator is calibrated using a glass standard with a reflectance of 1.02% in oil. This calibration is linearly accurate for reflectance values ranging from peat (R_o 0.20%) through anthracite (R_o 4.0%)

Vitrinite Reflectance

Reflectance values are recorded only on good quality vitrinite, including obvious contamination and recycled material. The relative abundance of normal, altered, lipid-rich, oxidized, and coked vitrinite is recorded. When good quality, normal vitrinite is absent, notations are made indicating how the maturity is affected by weathering, oxidation, bitumen saturation, or coking. When normal vitrinite is absent or sparse, other macerals may be substituted. Solid bitumen, for example is present in many samples. Although solid bitumen has a different reflectance than vitrinite, Landis and Castaño's calibration chart is used to obtain an estimated vitrinite reflectance equivalent. Graptolites have a slightly higher reflectance than vitrinite and can often be used to obtain maturity data in Upper Cambrian-Silurian rocks that have no vitrinite.

Maturity calculations are made from the vitrinite reflectance histograms. Decisions as to which reflectance measurements indicate the maturity of the sample are based not only on the histogram but on all of the kerogen descriptive elements as well. Because it is not done at the time of measurement, alternate maturity calculations can be made if kerogen data and geological information dictate.

DGSI's vitrinite reflectance histograms contain much useful information. All reflectance measurements are graphically displayed and the individual readings are listed below the histogram in numeric order. In the reflectance table, each reading is coded with a letter corresponding to the measured maceral. Capital letters are used to designate reflectance values that are used in calculating the mean reflectance while reflectance values falling outside the selected range are shown with a lower case letter code. Reflectance readings lying inside the selected range are marked with a pattern on the histogram diagram and readings falling outside the selected range are left open. Each maceral has a different pattern.

Codes currently in use include. Solid bitumen - B, Granular solid bitumen - X, Coked solid bitumen - Y, Graptolites - G, Inertinite - I, Other1 - O, Other2 - W, Vitrinite - V, Lipid-rich vitrinite - L, and Coked Vitrinite - Z. The use of two 'other' categories allows us the flexibility of measuring unusual materials that do not fall into one of the other classes or contamination from mud additives or caving. Specific information regarding 'other' material is shown in the Comments section at the lower right corner of the Figure and in the Comments section of the VKA data sheet.

Statistics for selected macerals are listed adjacent to the histogram and the mean reflectance values are also listed below the TOC and Rock-Eval data at the upper right corner of the Figure. The measured reflectance values for solid bitumen and graptolites are recalculated in order to obtain a vitrinite reflectance equivalent (VRE). Therefore, for these two macerals we show both the measured reflectance and the VRE. For example, VRE-B signifies vitrinite reflectance equivalent for solid bitumen and VRE-G is the vitrinite reflectance equivalent for graptolites.

In summary, vitrinite reflectance measurements are performed on a polished plug in reflected light, TAI is performed on a slide in transmitted light, and kerogen typing is estimated from both preparations using a combination of reflected, transmitted, and fluorescent light techniques. Fluorescence in blue light is used to enhance the identification of structured and unstructured lipid material, solid bitumens, and drilling mud contaminants. Fluorescence also correlates with the maturity and state of preservation of the sample. Maturity calculations from measured reflectance data are made from the histograms and are influenced by all of the kerogen data.

Visual Kerogen Analysis Techniques

Unstructured lipid kerogen changes in texture and color during the maturation process. Typically, unstructured kerogen at low maturity is reddish brown and amorphous. Somewhere between R_0 0.50 to 0.65%, the kerogen takes on a massive texture and is gray in color. At higher maturity, generally above R_0 1.30%, unstructured kerogen is light gray and micrinized.

Kerogen typing and maturity assessments from the polished plug are enhanced by utilizing fluorescence from blue light excitation. The xenon or mercury lamp is used with an excitation filter at 495 nm coupled with a barrier filter of 520 nm. With the Jena microscope we also have the option of observing fluorescence under ultraviolet excitation. The intensity of fluorescence in the epoxy mounting medium (background fluorescence) correlates well with the onset of oil generation and destruction. The identification of structured and unstructured liptinite is also enhanced with the use of fluorescence in those samples having a maturity less than R_0 1.3%. The relative abundance and type of pyrite is also recorded.

Thermal alteration index (TAI) is performed using tungsten or halogen light source that is transmitted through a glass slide made from the unfloatated kerogen concentrate. Ideally, TAI color is based on sporinite of terrestrial origin. When sporinite is absent, TAI is estimated from the unstructured lipid material. Weathering, bitumen admixed with the unstructured material and micrinization can darken the kerogen and raise the TAI value. The character of the organic matter in transmitted light is correlated with observations made in reflected light for kerogen typing.

Kerogen typing and maturity assessments from the slide preparation are also reinforced by using different light sources. The slide is first observed in transmitted light to obtain TAI color and organic matter structure or type. The light is then switched to reflected halogen light to observe structure and amount of pyrite and finally to reflected blue light excitation from the xenon or mercury source for fluorescence. The fluorescence of structured and unstructured liptinite is not masked by the epoxy fluorescence as it is in the reflected light mode because the mounting medium is non-fluorescent. Lipid structures (e.g. sporinite and alginite) within the unstructured kerogen can often be identified in blue light.

VISUAL KEROGEN ANALYSIS GLOSSARY

Several key definitions are included in this glossary in order to make our reports more self-explanatory. In our reports, we refer to organic substances as macerals. Macerals are akin to minerals in rock in that they are organic constituents that have microscopically recognizable characteristics. However, macerals vary widely in their chemical and physical properties and they are not crystalline.

1. UNSTRUCTURED KEROGEN is sometimes called structureless organic matter (SOM) or bituminite. It is widely held that unstructured kerogen represents the bacterial breakdown of lipid material. It also includes fecal pellets, minute particles of algae, organic gels, and may contain a humic component. As described on the first page of this section, unstructured lipid kerogen changes character during maturation. The three principal stages are amorphous, massive, and micrinized. Amorphous kerogen is simply without any structure. Massive kerogen has taken on a cohesive structure, as the result of polymerization during the process of oil generation. At high maturity, unstructured kerogen becomes micrinized. Micrinite is characterized optically by an aggregation of very small (less than one micron) round bodies that make up the kerogen.
2. STRUCTURED LIPID KEROGEN consists of a group of macerals which have a recognized structure, and can be related to the original living tissue from which they were derived. There are many different types, and the types can be group follows:
 - a. Alginite, derived from algae. It is sometimes very useful to distinguish the different algal types, for botryococcus and pediastrum are associated with lacustrine and non-marine source rocks, while algae such as tasmanites, gloecapsomorpha, and nostocopsis are typically marine. Acritarchs and dinoflagellates are marine organisms which are also included in the algal category
 - b. Cutinite, derived from plant cuticles, the remains of leaves.
 - c. Resinite, (including fluorinite) derived from plant resins, balsams, latexes, and waxes.
 - d. Sporinite, derived from spores and pollen from a wide variety of land plants.
 - e. Suberinite is derived from the corky tissue of land plants.

f Liptodetrinite is that structured lipid material that is too small to be specifically identified. Usually, it is derived from alginite or sporinite.

The algae are an important part of many oil source rocks, both marine and lacustrine. Alginite has a very high hydrogen index in Rock-Eval pyrolysis. Resins, cuticles, and suberinite contribute to the waxy, non-marine oils that are found in Africa and the Far East. At vitrinite reflectance levels above R_o 1.2 - 1.4%, structured lipid kerogen changes structure and it becomes very difficult to distinguish them from vitrinite.

3. SOLID BITUMEN also is called migrabitumen and solid hydrocarbon. In 1992, the International Committee for Coal and Organic Petrology (ICCP) decided to include solid bitumen in the Exsudatinitite group. Solid bitumens are expelled hydrocarbon products which have particular morphology, reflectance and fluorescence properties which make it possible to identify them. They represent two classes of substances: one which is present at or near the place where it was generated, and second is a substance which is present in a reservoir rock and may have migrated a great distance from its point of origin. The solid bitumens have been given names, such as gilsonite, imposonite, grahamite, etc., but they represent generated heavy hydrocarbons which remain in place in the source rock or have migrated into a reservoir and mature along with the rock. Consequently, it is possible to use the reflectance of solid bitumens for maturation determinations when vitrinite is not present.

4. HUMIC TISSUE is organic material derived from the woody tissue of land plants. The most important of this group are vitrinite and inertinite:

a. Vitrinite is derived from woody tissue which has been subjected to a minimum amount of oxidation. Normally it is by far the most abundant maceral in humic coals and because the rate of change of vitrinite reflectance is at a more even pace than it is for other macerals, it offers the best means of obtaining thermal maturity data in coals and other types of sedimentary rocks.

Because the measurement of vitrinite is so important, care is taken to distinguish normal (fresh, unaltered) vitrinite from other kinds of vitrinite. Rough vitrinite does not take a good polish and therefore may not yield good data. Oxidized vitrinite may have a reflectance higher or lower than fresh vitrinite, this is a problem often encountered in outcrop samples. Lipid-rich vitrinite, or saprovitrinite, has a lower reflectance than normal vitrinite and will produce an abnormally low thermal maturity value. Coked vitrinite is vitrinite that has structures found in vitrinite heated in a coke oven. Naturally coked vitrinite is the product of very rapid heating, such as that found adjacent to intrusions. Where it is possible to do so, vitrinite derived from an uphole portion of a well will be identified as caved vitrinite. Recycled vitrinite is the vitrinite of higher maturity which clearly can be separated from the indigenous first-cycle vitrinite population. Often, the recycled vitrinite merges in with the inert group.

b. Inertinite is made up of woody tissue that has been matured by a different pathway. Early intense oxidation, usually involving charring, fungal attack or biochemical gelification, creates the much more highly reflecting fusinite and semi-fusinite. Sometimes the division between vitrinite and fusinite is transitional. Sclerotinite, fungal remains having a distinct morphology, are considered to be inert. An important consideration is that the inerts, as the name implies, are largely non-reactive "dead carbon" and they have an extremely low hydrogen index in Rock-Eval pyrolysis.

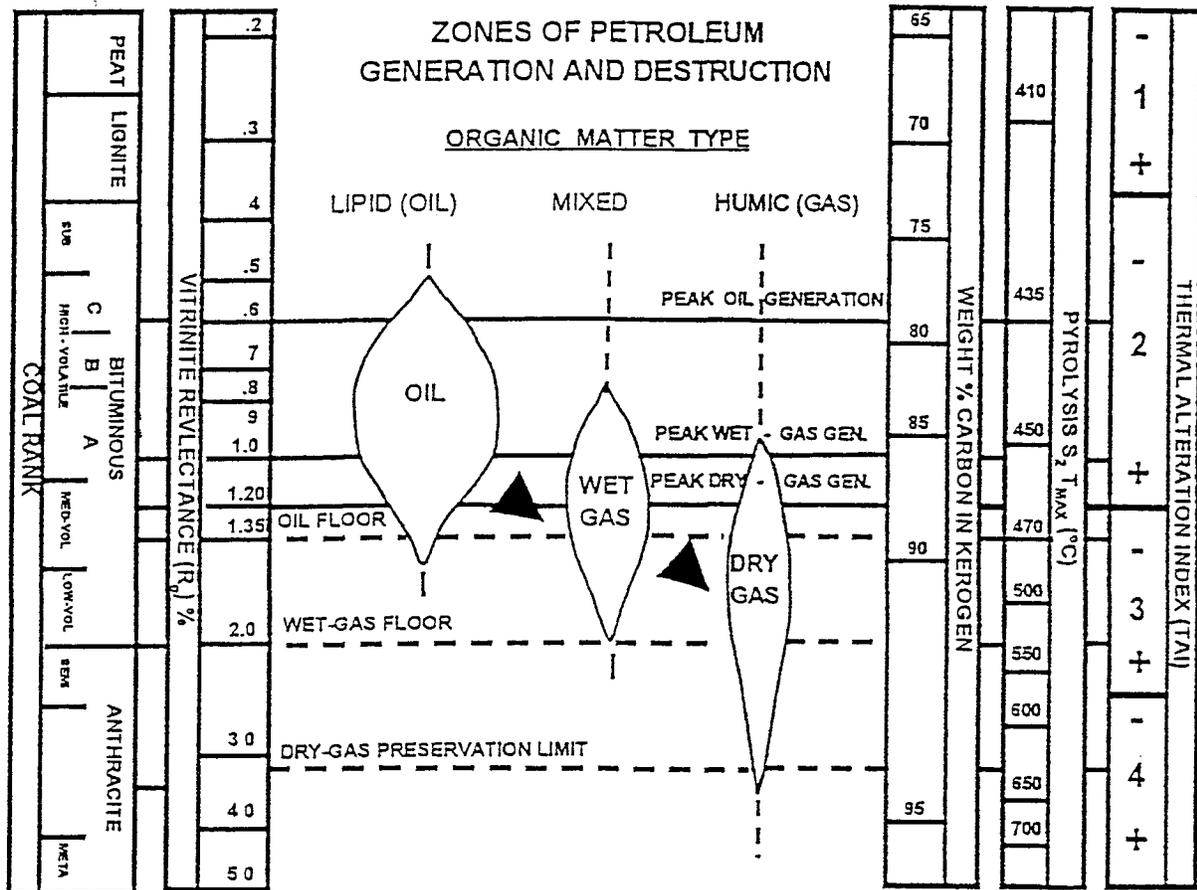
5. OTHER ORGANIC MATERIAL

a. Lipid-rich, caved and recycled vitrinite. These are put in this section so we can show the percentages of these macerals; they are described above.

b. Exsudatinitite. Oil and oily exudates fall in this group. Exsudatinitite differs from the solid bitumens on the basis of mobility and solubility. We prefer to maintain this distinction although the ICCP has now included the solid bitumens in with the Exsudatinitite group.

c. Graptolites are marine organisms that range from the Cambrian to the lower Mississippian; it has been found that they have a reflectance slightly higher than vitrinite. Because vitrinite is lacking in early Paleozoic rocks, the proper identification and measurement of graptolites is important in these sediments.

6. PYRITE. Various forms of pyrite can be readily identified under the microscope. Euhedral is pyrite with a definite crystalline habit. Framboidal is pyrite in the form of grape-like clusters which are made up of euhedral to subhedral crystals. Framboidal pyrite is normally found in sediments with a marine influence, for example, coals with a marine shale roof rock usually contain framboidal pyrite. Massive pyrite is pyrite with no particular external form. Often this is pyrite that forms rather late in the pore spaces of the sediment. Replacement/infilling is self-explanatory.



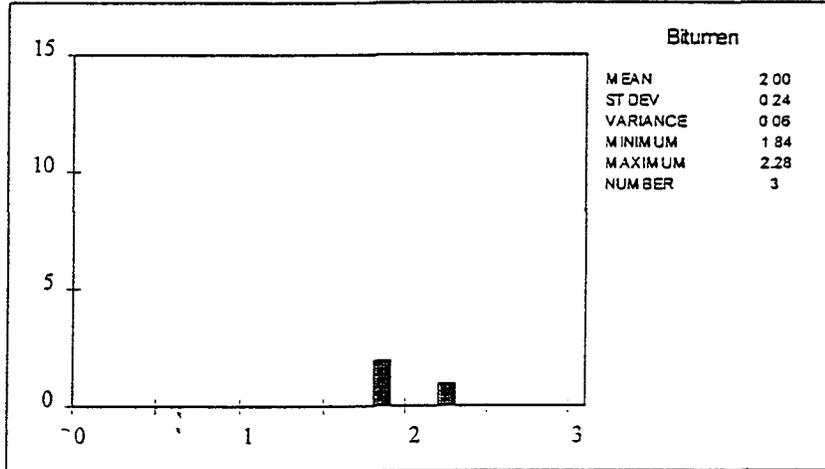
CORRELATION OF VARIOUS MATURATION INDICES AND ZONES OF PETROLEUM GENERATION AND DESTRUCTION

VITRINITE REFLECTANCE

Rock Island 4H Core

DGSI Project 99/4522 Sample No 1
 OTHER ID Black Material 15424 55 Ft.

TYPE	WR/CC
	TOC 0.69
	TMAX 490
	HI 132
	V Ro -
	B Ro 2.00
	VRE-B 2.25



Visual Kerogen Summary

Unstructured Lipids	-
Structured Lipids	-
Solid Bitumen	100
Inertinite	-
Vitrinite	-
Other	0
TOTAL	100

B 1 84
 B 1 89
 B 2 28

Background Fluorescence None
 TAI Unstructured
 TAI Structured

COMMENTS: