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OIL and GAS DIVISION

1 6 MAY 1984

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PETROLEUM GEOCHEMISTRY

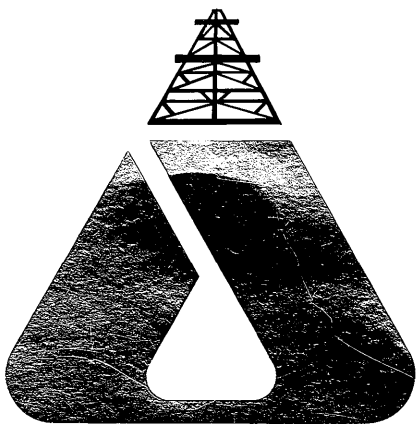HYDROCARBON SOURCE ROCK

EVALUATION STUDY

SOUTH BASKER NO. 1

Prepared for

SHELL DEVELOPMENT (AUST.) PTY. LTD.   January, 1984.

ANALABS
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SOUTH BASKER NO. 1

SUMMARY

Organic geochemical analyses performed on seven (7) side wall
core samples from 2554m to 3194m in the South Basker No. 1
well, drilled offshore Victoria, Australia have indicated the
following:

   The sediments are thermally immature and pre-oil
   generative.

   The rocks are very organic-rich, with potential very
   good to excellent oil and gas source rock characteristics,
   at more mature levels of thermal alteration.

INTRODUCTION

% total organic carbon determination and Rock Eval pyrolysis
analyses have been performed on seven (7) side wall core
samples from 2554m to 3194m in the South Basker No. 1 well.

The purpose of this study has been to evaluate the source
quality, richness and state of thermal maturity of the sediments
analysed from this well.

Upon arrival at Analabs the samples were assigned the Analabs
Job Number 31194. The results of the analyses are located
in the following:

Type of Analysis	Figure	Table
% total organic carbon determination	1	1
Pyrolysis	1	1

A description of these analyses are provided in the Theory and
Methods section located at the back of this report.

Copies of this report have been sent to Mr. John Stainforth
of the Shell Development (Aust.) Pty. Ltd., located in Perth,
Western Australia. Any questions related to this study should
be directed to either Mr. Paul Tybor or Dr. Garry Woodhouse of
Analabs in Perth, Western Australia.

All data and interpretations given herein are proprietary to
the Shell Development (Aust.) Pty. Ltd., and are treated as
highly confidential material by all Analabs personnel.

RESULTS AND INTERPRETATIONS

A.   Thermal Maturity of Sediments

Based on the Tmax temperatures and Production Index values,
obtained from the pyrolysis analyses, the sediments analysed
between 2554m to 3194m are interpreted to be thermally
immature, pre-oil generative.

The Tmax temperatures are all below 435°C and the Production
Index values are all below 0.05, which indicates an immature
level of thermal maturation for these rocks.

B.   Hydrocarbon Source Characterisation

The rocks between 2554m to 3194m have organic richness that
vary from very good amounts (3.68% TOC at 2627m) to excellent
amounts (73.16% TOC at 3064m) of organic matter (Figure 1;
Table 1).   The potential yields (S_1 + S_2, Figure 1; Table 1)
are also very good (11.76 mg/g at 2627m) to excellent
(404.77 mg/g at 2742m), and indicate that at a higher level
of maturation, these sediments would be capable of generating
significant amounts of hydrocarbon.   All of the samples have
high hydrogen Index values, which reflects the good hydrocarbon
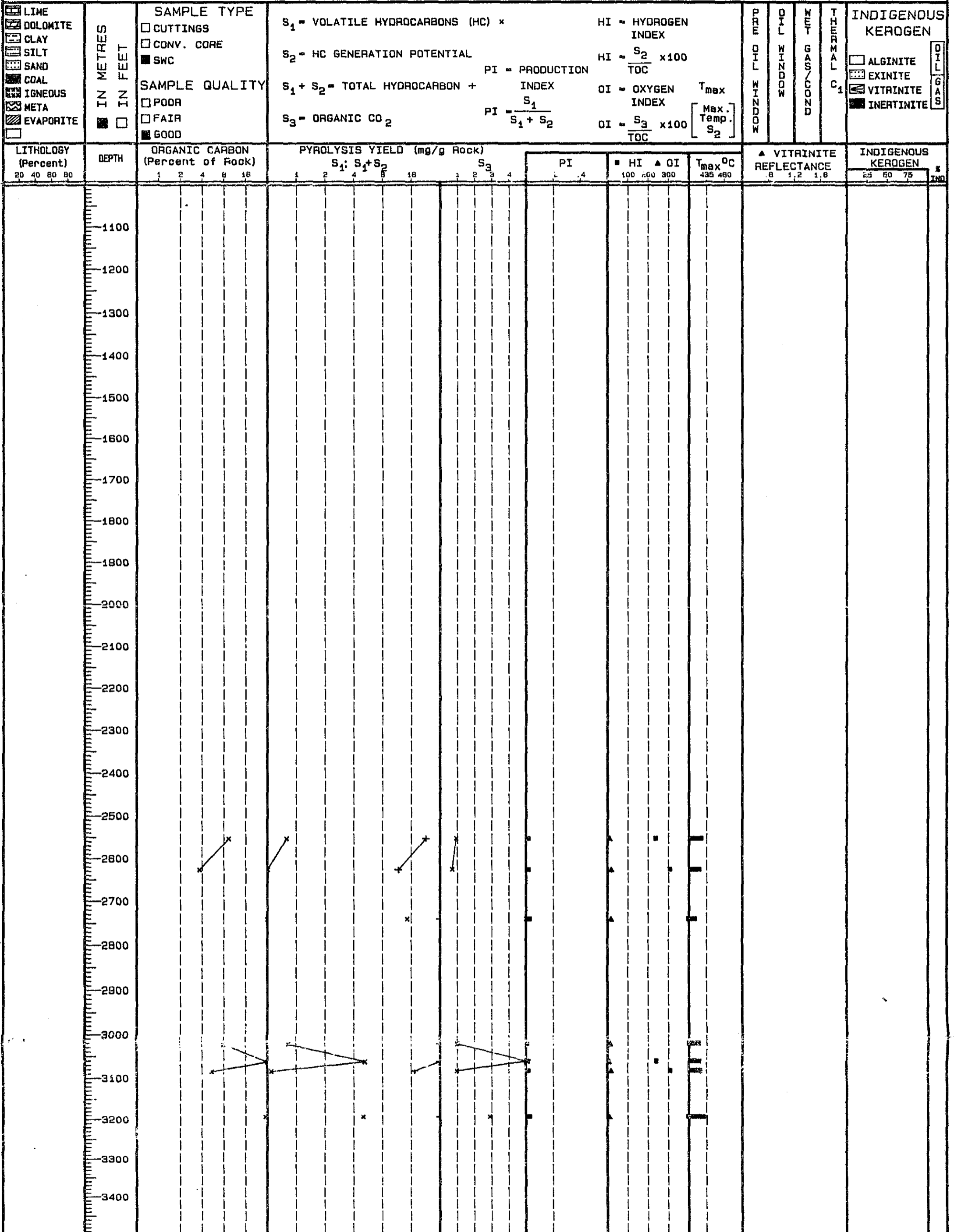generating potential of these sediments.

In summation, the sediments analysed from the South Basker
No. 1 well are potential very good to excellent oil and gas source
rocks, at more mature levels of thermal maturity.

ANA-LOG
HYDROCARBON SOURCE ROCK EVALUATION

FIGURE 1

JANUARY 1984

SHELL DEVELOPMENT (AUSTRALIA) PTY LTD

BASKER SOUTH #1

LITHOLOGY
- LIME
- DOLOMITE
- CLAY
- SILT
- SAND
- COAL
- IGNEOUS
- META
- EVAPORITE

IN METRES
IN FEET

SAMPLE TYPE
- CUTTINGS
- CONV. CORE
- SWC

SAMPLE QUALITY
- POOR
- FAIR
- GOOD

S_1 = VOLATILE HYDROCARBONS (HC) ×

S_2 = HC GENERATION POTENTIAL

$S_1 + S_2$ = TOTAL HYDROCARBON +

S_3 = ORGANIC CO_2

PI = PRODUCTION INDEX

$PI = \dfrac{S_1}{S_1 + S_2}$

HI = HYDROGEN INDEX

$HI = \dfrac{S_2}{TOC} \times 100$

OI = OXYGEN INDEX

$OI = \dfrac{S_3}{TOC} \times 100$

T_{max}

$\begin{bmatrix} \text{Max.} \\ \text{Temp.} \\ S_2 \end{bmatrix}$

PRE OIL WINDOW

OIL WINDOW

WET GAS/COND

THERMAL C_1

INDIGENOUS KEROGEN
- ALGINITE
- EXINITE
- VITRINITE
- INERTINITE

OIL GAS

| LITHOLOGY (Percent) 20 40 60 80 | DEPTH | ORGANIC CARBON (Percent of Rock) 1 2 4 8 16 | PYROLYSIS YIELD (mg/g Rock) S_1; $S_1 + S_2$ 1 2 4 8 16 | S_3 1 2 3 4 | PI .4 | ■ HI ▲ OI 100 200 300 | T_{max} °C 435 460 | ▲ VITRINITE REFLECTANCE .8 1.2 1.6 | INDIGENOUS KEROGEN 25 50 75 % IND |

ANALABS OIL AND GAS DIVISION. 52 Murray Road. Welshpool. W.A. 6106.
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TABLE 1

ROCK-EVAL PYROLYSIS DATA (one run)

WELLNAME = BASKER SOUTH #1   DATE OF JOB = JANUARY 1984

DEPTH(m)	TMAX	S1	S2	S3	S1+S2	S2/S3	PI	PC	TOC	HI	OI
2554.0	430	0.79	22.12	0.93	22.91	23.78	0.03	1.90	9.28	238	10
2627.0	427	0.40	11.36	0.70	11.76	16.23	0.03	0.98	3.68	308	19
2742.0	421	14.56	390.21	11.30	404.77	34.53	0.04	33.60	62.53	624	18
3024.0	426	0.83	33.21	0.99	34.04	33.55	0.02	2.83	7.98	416	12
3064.0	427	5.26	176.84	6.05	182.10	29.23	0.03	15.11	73.16	241	8
3085.0	429	0.55	16.91	0.98	17.46	17.26	0.03	1.45	5.44	310	18
3194.0	433	5.03	125.79	2.89	130.82	43.53	0.04	10.86	30.23	416	9

TMAX	= Max. temperature S2	S1	= Volatile hydrocarbons (HC)	S2 = HC generating potential
S1+S2	= Potential yield	S3	= Organic carbon dioxide	PI = Production index
PC	= Pyrolysable carbon	TOC	= Total organic carbon	HI = Hydrogen index
OI	= Oxygen Index	nd	= no data	

This section details a series of geochemical methods which are commonly used in our laboratory, including those used to obtain the data presented in this report. Where applicable, the discussion is accompanied by a summary of the general theory used to interpret the data generated by each method.

1. SEDIMENTARY GAS ANALYSIS

a) Headspace Analysis

Headspace analysis is carried out using sealed containers (usually tinned cans) of wet cuttings. The containers are approximately three quarters filled with the cuttings and water to leave an appreciable headspace into which volatile hydrocarbons contained in the cuttings diffuse.

After covering about $1cm^2$ of the container lid with liquid silicone and allowing the silicone to dry, the procedure involves placing a small hole in the lid through the silicone, then sampling an aliquot of the headspace gas with a gas injection syringe, and finally gas chromatographing this sample of gas under the following conditions: instrument = Shimadzu GC-8APF; column = 6' x 1/8" Chromosorb 102; column temperature = 110°C; carrier gas = nitrogen at 23mls/min; injector temperature = 120°C; detector temperature = 120°C; analysis cycle = C_1-C_4 components are flushed from the column in the forward direction and then the C_5-C_7 compounds are removed from the column by backflushing.

The integrated areas of peaks representing each of the C_1-C_7 components of the headspace gas are compared to the areas of the corresponding components of a standard gas of known composition. The calculated amount of each component in the sample gas is adjusted for the total headspace volume and reported as ppm (parts of gas per million parts of sediment by volume).

Data from headspace analysis is commonly used to identify the zone of oil generation by plotting gas wetness (C_2-C_4/C_1-C_4) expressed as a % against sediment burial depth. Gas containing appreciable quantities of C_2-C_4 components, termed wet gas (Fuex, 1977), is generally considered to be gas associated with oil generation. In addition, the ratio of isomeric butanes can sometimes be used for assement of sediment maturity (Alexander et al., 1981). The amount of gas in sediments can be used to identify zones of significant gas generation and out-of-place gas (LeTran et al., 1975).

b) Cuttings Gas Analysis

This analysis is the same as Headspace Analysis with the exception that instead of analysing the gas in the container headspace, a known volume of the wet cuttings are transferred to the blender bowl of a Kenwood electronic blender with the lid modified to incorporate a septum, water at 75°C is added to leave a headspace of 160ml, and the mixture is blended at maximum speed for 2 minutes. Following a 2 minute settling period 1ml of the blending bowl headspace gas is analysed as described in section 1 a).

It is recommended that for the most meaningful gas data both headspace and cuttings gas analysis are carried out. In such cases we provide tabulations of the headspace, cuttings gas, and combined headspace/cuttings gas data. Normally, the combined data is used for plotting purposes.

2. SAMPLE PREPARATION

a) Cuttings

Cuttings samples are inspected by our qualified geological staff and then water washed according to the level of drilling mud and the lithology. In special cases (e.g. diesel contamination) it is necessary to lightly solvent wash samples. After washing, the samples are air dried, either sieved or picked free of cavings, and crushed to 0.1mm using a ring pulveriser.

b) Sidewall Cores

Sidewall samples are freed of mud cake and any other visible contaminants, and are also inspected for lithologic homogeneity. For homogeneous samples, the minumum amount of material required for the requested analyses is air dried and hand-crushed to 0.1mm. For non-homogeneous samples, the whole sample is air dried and handcrushed to 0.1mm.

c) Conventional Core and Outcrop Samples

These sample types are firstly inspected for visible contaminants, and where applicable, are freed of these contaminants to the best of our ability. Commonly, the surface of conventional core and outcrop samples are lightly solvent washed. The samples are then crushed to approximately 1/8" chips using a jaw crusher, air dried, and finally further crushed to 0.1mm using a ring pulveriser.

d) Petroleum/Aqueous Mixtures

The most common sample type in this catagory are RFT tests containing oil, water and mud. The mixture is placed in a separation funnel and allowed to stand for several hours which enables the petroleum and water/mud fractions to separate. The neat petroleum is isolated by removal of the lower layer (water/mud) from the funnel. To remove the last traces of water and mud, the neat petroleum is centrifuged at moderate speed.

When the volume of petroleum accounts for only a very small part of the sample the method above is unsatisfactory and the petroleum is solvent extracted from the mixture with dichloromethane. The petroleum is recovered by careful evaporation of the solvent from the organic layer.

3. TOTAL ORGANIC CARBON DETERMINATION

The total organic carbon value (TOC) is determined on the unextracted sediment sample. The value is determined by treating a known weight of sediment with hot dilute HCl for 1 hour to remove carbonate minerals, and then heating the residue to 1700°C (Leco Induction Furnace CS-044) in a atmosphere of pure oxygen. The carbon dioxide produced is transferred to an infra-red detector which has been calibrated with a series of standards, and the microprocessor of the Leco unit then automatically calculates the % TOC in the sample. To ensure reliable data a standard is run after every 10 samples, regular sample repeats are carried out, and at least one blank determination is carried out for each batch of samples.

The following scales are normally used for source rock classification based on % TOC data:

Classification	Clastics	Carbonates
Poor	0.00 - 0.50	0.00 - 0.25
Fair	0.50 - 1.00	0.25 - 0.50
Good	1.00 - 2.00	0.50 - 1.00
Very Good	2.00 - 4.00	1.00 - 2.00
Excellent	> 4.00	> 2.00

4. ROCK-EVAL PYROLYSIS

Although a prelimenary source rock classification is made using TOC data a more accurate assessment accounting for organic source type and maturity is made by pyrolysis analysis. Two types of Rock-Eval pyrolysis services are offered: "one run" which involves pyrolysis of the crushed but otherwise untreated sediment and "two run" which involves pyrolysis of both the crushed, untreated sediment and sediment which has been rendered free of carbonate minerals by treatment with hot dilute HCl. The two run service offers considerably more reliable S_3 data.

The method involves accurately weighing approximately 100mg of the sample into a sintered steel crucible and subjecting it to the following pyrolysis cycle:

Stage (i)   - Sample purged with helium for 3.5 minutes in unheated part of pyrolysis furnace;

Stage (ii) - Sample heated at 300°C for 3 minutes to liberate free petroleum (S_1 peak);

Stage (iii) - Sample heated from 300°C to 550°C at 25°C/minute to produce petroleum from kerogen (S_2 peak). The furnace is maintained at 550°C for one minute. Carbon dioxide produced during this pyrolysis up to 390°C in the case of "one run" and 550°C for "two run" is absorbed on a molecular sieve trap;

Stage (iv) - During cool-down period the carbon dioxide produced during pyrolysis is measured (S_3 peak).

The units used for Rock-Eval data are as follows:

S_1, S_2, S_3 = kg/tonne or mg/g of rock

T_{max} = °C

Hydrogen Index = $\dfrac{S_2}{TOC} \times \dfrac{100}{1}$

Oxygen Index = $\dfrac{S_3}{TOC} \times \dfrac{100}{1}$

Rock-Eval data is most commonly used in the following manner:

(i) S_1 - indicates the level of oil and/or gas already generated by the sample according to the following scale:

S_1 (mg/g or kg/tonne)	Classification
0.00 - 0.20	Poor
0.20 - 0.40	Fair
0.40 - 0.80	Good
0.80 - 1.60	Very Good
> 1.60	Excellent

(ii) S_1+S_2 - referred to as the genetic potential this parameter is used for source rock classification according to the following criteria:

S_1+S_2 (mg/g or kg/tonne)	Classification
0.00 - 1.00	Poor
1.00 - 2.00	Marginal
2.00 - 6.00	Moderate
6.00 - 10.00	Good
10.00 - 20.00	Very Good
> 20.00	Excellent

(iii) $S_1/(S_1+S_2)$ - this parameter is the production index (PI) which is a measure of the level of maturity of the sample. For oil prone sediments, values less than 0.1 are indicative of immaturity, the values increase from 0.1 to 0.4 over the oil window and values greater than 0.4 represent overmaturity. For gas prone sediments, the PI data shows a relatively smaller change with increasing maturity.

(iv) T_{max} - the temperature corresponding to the S_2 maxima. This temperature increases with increasingly mature sediments. Values less than 430°C are indicative of immaturity while values from 430/435 to 460°C represent the maturity range of the oil window. T_{max} values greater than 460°C are indicative of overmaturity.

(v) HI, OI - the hydrogen ($[S_2 \times 100]$/TOC) and oxygen ($[S_3 \times 100]$/TOC) indices when plotted against one another provide information about the type of kerogen contained in the sample and the maturity of the sample. Both parameters decrease in value with increasing maturity. Samples with large HI and low OI are dominantly oil prone and conversely samples with low HI and large OI are at best gas prone.

5. EXTRACTION OF SEDIMENT SAMPLES

Crushed sediment (maximum of 250g) and 300mls of purified dichloromethane are placed in a 500ml conical flask and are then blended for ten minutes with a Janke and Kunkel Ultra-Turrax T45/2G high efficiency disperser. After a ten minute settling period the solvent is separated from the sediment using a large Buchner filtration system. The extract is recovered by careful evaporation of the solvent on a steam bath and weighed. The weight of extract is used to calculate % EOM and ppm EOM using the following formulas:

$$\% \text{ EOM } = \frac{\text{Wt EOM (g)}}{\text{Wt Sediment Extracted (g)}} \times \frac{100}{1}$$

$$\text{ppm EOM } = \frac{\text{Wt EOM (mg)}}{\text{Wt Sediment Extracted (kg)}}$$

The following scale is used to classify the source rock richness of samples based on C_{12}^+ extractables:

Classification	ppm Total Extract
Poor	0 - 500
Fair	500 - 1000
Good	1000 - 2000
Very Good	2000 - 4000
Excellent	> 4000

6. SEPARATION OF PETROLEUM INTO CONSTITUENT FRACTIONS

Sediment extracts and crude oil or condensate samples are separated into saturate, aromatic and NSO (asphaltenes plus resins) fractions by medium pressure liquid chromatography (MPLC). That part of the petroleum which is soluble in pentane is applied to the MPLC system via a sample loop and is then pumped using pentane to a partially activated silicic acid pre-column which prevents further movement of the non-hydrocarbon compounds. The hydrocarbon components are pumped further to a Merck Si60 column where the saturate fraction is obtained by forward flushing and the aromatic fraction is recovered by reverse flushing. This separation procedure is monitored using a refractive index detector. To complete the separation the pre-column is removed from the MPLC system and flushed with dichloromethane: methanol (1:10). This non-hydrocarbon fraction is combined with the pentane insoluble material which is not applied to the MPLC system, and is labelled as the NSO fraction. The neat fractions are recovered by careful removal of the solvent by distillation and are weighed.

The weight of each fraction is used to calculate the % of each fraction in the petroleum and the ppm of each fraction in the sediment according to the following formulas:

$$\% \text{ Fraction } = \frac{\text{Wt Fraction}}{\text{Wt All Fractions}} \times \frac{100}{1}$$

$$\text{ppm Fraction } = \frac{\text{Wt Fraction (mg)}}{\text{Wt Sediment Extracted (kg)}}$$

The ppm hydrocarbon (saturates + aromatics) and ppm saturate values can be used to classify source rock richness and oil source potential respectively according to the following criteria:

Classification	ppm Hydrocarbon	ppm Saturates
Poor	0 - 300	0 - 200
Fair	300 - 600	200 - 400
Good	600 - 1200	400 - 800
Very Good	1200 - 2400	800 - 1600
Excellent	> 2400	> 1600

The composition of the extracts can also provide information about their levels of maturity and/or source type (LeTran et. al., 1974; Philippi, 1974). Generally, marine extracts have relatively low concentrations of saturated and NSO compounds at low levels of maturity, but these concentrations increase with increased maturation. Terrestrially derived organic matter often has a low level of saturates and large amount of aromatic and NSO compounds irrespective of the level of maturity.

N.B. If requested by a client the NSO fraction is separated into asphalentenes and resins by conventional methods.

7. EXTRACTABLE/TOTAL ORGANIC CARBON RATIOS

The ratios of EOM(mg)/TOC(g) and SAT(mg)/TOC(g) are determined from the appropriate data. The EOM (mg)/TOC(g) ratio can be used as a maturation indicator, especially if the parameter is plotted against depth for a given sedimentary sequence. In an absolute sense it is less reliable as a maturation indicator, although previous work (Tissot et. al., 1971; LeTran et. al., 1974) suggests that the following criteria can be used to determine maturity with this parameter:

$$<50 \qquad \text{Low maturity}$$
$$50\text{-}100 \qquad \text{Moderate maturity}$$
$$>100 \qquad \text{High maturity}$$

The ratios of EOM(mg)/TOC(g) and SAT(mg)/TOC(g) can be used collectively to provide information about source type. For example, if SOM(mg)/TOC(g) is >100, suggesting a high level of maturity, but the SAT(mg)/TOC(g) <20 it is very likely that the organic matter is gas prone. Conversely, the same EOM (mg)/TOC(g) value with a SAT(mg)/TOC(g) value >40 suggests oil prone source type.

8. C_{12}^{+} GAS CHROMATOGRAPHY

C_{12}^{+} gas chromatography is commonly carried out on the saturate fraction but in certain instances is carried out on neat oil, condensate or extract. The analysis is carried out under the following conditions: instrument = Shimadzu GC-9A; column = 50m x 0.2mm ID OV101 vitreous silica; column temperature = programmed from 60°C to 280°C at 4°C/min; injection system = Grob splitless using a 30 sec. dump time and split ratio of 25:1; carrier gas = hydrogen at 2mls/min; injector temperature = 300°C; detector temperature = 310°C; recorder/integrator speed = 0.5cm/min; Sample = 1μl of 0.5% soln in pentane.

The following information is commonly obtained from C_{12}^{+} gas chromatographic analysis:

(a) n-Alkane Distribution - The C_{12}-C_{31} n-alkane distribution is determined from the area under peaks representing each of these n-alkanes. This distribution can yield information about both the level of maturity and the source type (LeTran et. al., 1974).

(b) Carbon Preference Index - Two values are determined:

$$CPI(1) = \frac{(C_{23} + C_{25} + C_{27} + C_{29})Wt\% + (C_{25} + C_{27} + C_{29} + C_{31})Wt\%}{2 \times (C_{24} + C_{26} + C_{28} + C_{30})Wt\%}$$

$$CPI(2) = \frac{(C_{23} + C_{25} + C_{27})Wt\% + (C_{25} + C_{27} + C_{29})Wt\%}{2 \times (C_{24} + C_{26} + C_{28})Wt\%}$$

The CPI is believed to be a function of both the level of maturity (Cooper and Bray, 1963; Scalan and Smith, 1970) and the source type (Tissot and Welte, 1978). Marine extracts tend to have values close to 1 irrespective of maturity whereas values for terrestrial extracts decrease with maturity from values as high as 20 but don't usually reach a value of 1.

(c) $C_{21}+C_{22}/C_{28}+C_{29}$ - This parameter provides information about the source of the organic matter (Philippi, 1974). Generally, a terrestrial source gives values <1.2 whereas a marine source results in values >1.5.

(d) Pristane/Phytane Ratio - This value was determined from the areas of peaks representing these compounds. The ratio renders information about the depositional environment according to the following scale (Powell and McKirdy, 1975):

<3.0   Relatively reducing depositional environment
3.0-4.5 Reducing/oxidizing depositional environment
>4.5   Relatively Oxidizing depositional environment

(e) Pristane/nC_{17} Ratio - This ratio was determined from the areas of peaks representing these compounds. The value can provide information about both the depositional environment and the level of maturation (Lijmbach, 1975). Very immature crude oil has a pristane/n-C_{17} ratio >1.0, irrespective of the depositional environment. However, the following classification can be applied to mature crude oil:

<0.5   Open water depositional environment
0.5-1.0 Mixed depositional environment
>1.0   Peat-swamp depositional environment

In the case of sediment extracts these values are significantly higher and the following classification is used:

<1.0   Open water depositional environment

1.0-1.5 Mixed depositional environment

>1.5   Peat-swamp depositional environment

(f) Phytane/$\underline{n}$-C_{18}Ratio - This ratio was determined from the areas of peaks representing these compounds. The value usually only provides information about the level of maturity of petroleum. The value decreases with increased maturation.

(g) Relative Amounts of $\underline{n}$-Alkanes and Naphthenes - Since $\underline{n}$-alkanes and naphthenes are the two dominant classes of compounds in the saturate fraction, a semi-quantitative estimate of the relative amounts of these compounds can be made from saturate GLC's. This information can be used to assess the degree of maturation and/or the source type of the petroleum (Philippi, 1974; Tissot and Welte, 1978). Very immature petroleum has only small proportions of $\underline{n}$-alkanes, but as maturity increases the relative amount of $\underline{n}$-alkanes increases. In addition, terrestrial petroleum has a greater proportion of high molecular weight naphthenes than marine petroleum.

9. API/SPECIFIC GRAVITY

A specific gravity (SG) bottle was accurately weighed, then filled with crude oil at 60°F and finally reweighed. The weight difference was divided by the weight of an equal volume of water at 60°F to obtain the specific gravity. The following formula was then used to calculate the API gravity:

$$\text{API Gravity} = \left(\frac{141.5}{SG\ (60°F)} \right) - 131.5$$

The reported gravity value is the average of duplicate determinations.

10. SULPHUR DETERMINATION

The % sulphur by weight is determined by dissolving 0.5g of the petroleum in 50mls kerosene and then analysing this mixture with an inductively coupled plasma (ICP) instrument which has been calibrated with a series of sulphur standards.

This parameter is influenced by the nature of the source material from which a crude is derived, the depositional environment of the source rocks, and reservoir alteration processed such as bacterial alteration.

11. C_1-C_{31} WHOLE SAMPLE GAS CHROMATOGRAPHY

This method of analysis is normally only applied to oil or condensate samples. The technique provides a "picture" of the sample which shows good resolution of the low, medium and high molecular weight components. Whole sample GC data is considered to be more useful than C_{12}+ saturate fraction GC data for oil or condensate samples.

The analysis is carried out under the same conditions as for the C_{12}+ GC analysis with the following exceptions: column temperature = programmed from -20°C to 280°C at 4°C/min (uses cryogenic mode); injection is carried out in split mode; sample = 0.1μl of neat petroleum.

C_1-C_{31} analysis data can be used to obtain the same information as that obtained from C_{12}+ GC but further provides detailed compositional data on the C_1-C_{11} fraction and enables calculation of the distillation range of the sample.

12. MOLECULAR SIEVE EXTRACTION

This technique is used to isolate the branched/cyclic alkanes from the saturate fraction for gas chromatography/mass spectrometry analysis. A mixture of saturates: 5A molecular sieves: purified benzene in the proportions 1:5:12 by weight is placed in a 100ml round bottom flask and refluxed for 24 hours. After cooling, the sieves are filtered from the liquid phase and are washed with 4 x 10ml aliquots of benzene. The liquid phase plus washings are freed of benzene by distillation yielding the branched/cycle compounds.

13. COMPUTERIZED GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

Gas chromatography/mass spectrometry employs a capillary column gas chromatograph linked in series with a mass spectrometer and data system (GC/MS/DS). As molecules are eluted from the capillary column they are bled into the analyser tube of the mass spectrometer where they are bombarded with high energy electrons and consequently fragment to form several . each with molecular weights less than that of the parent molecule. The fragmentation pattern is characteristic of the particular molecular type. The spectrum of these ions (referred to as a mass spectrum) is recorded approximately once every second and all of the mass spectra recorded during a GC/MS/DS analysis are memorized by the data system. Since any given class of molecules will break down in the analyser tube to give one or more characteristic ion fragments of known molecular weight, after a GC/MS/DS analysis it is possible to examine the distribution of compounds within a given class by having the data system reproduce a mass fragmentogram (plot of ion concentration against gas chromatography retention time) representative of the particular class.

GC/MS/DS analyses can be carried out using one of the following two modes of operation:

(i) Acquire mode - in which all ions in each mass spectrum are memorized by the data system;

(ii) Selective ion monitoring (SIM) mode - in which only selected ions of interest are memorized by the data system.

At present the sterane/triterpane fraction of petroleum is considered most useful for GC/MS/DS analysis and therefore we commonly use the second of the above mentioned modes of operation and run the following twenty ions which are pertinent to the sterane/triterpane fraction.

Ion	Molecular Type
177	Demethylated triterpanes
191	Normal triterpanes
205	Methyl triterpanes
163	Specific dethylated triterpanes
356	Parent ion - C_{26} triterpanes
370	Parent ion - C_{27} triterpanes
384	Parent ion - C_{28} triterpanes
398	Parent ion - C_{29} triterpanes
412	Parent ion - C_{30} triterpanes
426	Parent ion - C_{31} triterpanes
183	Isoprenoids
217	Normal steranes
218	Normal steranes
231	4-methyl steranes
259	Diasteranes
358	Parent ion - C_{26} steranes
372	Parent ion - C_{27} steranes
386	Parent ion - C_{28} steranes
400	Parent ion - C_{29} steranes
414	Parent ion - C_{30} steranes

GC/MS/DS analysis of the sterane/triterpane fraction can often provide information about the maturity and source type of petroleum and whether it has been affected by microorganisms. This technique is also often useful for oil:oil and oil:source rock correlation. The following sections indicate which parameters are used to obtain this information and summarize the theory behind their use.

Maturity

(i) Based on Steranes

(a) The biologically produced $\alpha\alpha\alpha$(20R) sterioisomer is converted in sediments to a mixture of the $\alpha\alpha\alpha$(20R) and $\alpha\alpha\alpha$(20S) compounds. The ratio of $C_{29} \frac{\alpha\alpha\alpha(20S)}{\alpha\alpha\alpha(20R)+\alpha\alpha\alpha(20S)}$ expressed as a percentage is about 25% at the onset of oil generation and increases almost linearly to a value of about 50% at the peak of oil generation.

(b) The biologically produced $\alpha\alpha\alpha$ steranes are partially converted during catagenesis to the corresponding $\alpha\beta\beta$ series. The percentage of the C_{29} $\alpha\beta\beta$ component in the total C_{29} steranes is another measure of maturation. The value of this parameter is about 25% at the onset of oil generation and it increases exponentially to a value of about 70% at the peak of oil generation.

(ii) Based on Triterpanes

(a) The C_{31}, C_{32}, C_{33}, C_{34}, and C_{35} hopanes have the biological R configuration at C_{22}. On mild thermal maturation equilibration occurs to produce a 60/40 mixture of S/R. This equilibration occurs before the onset of oil generation.

(b) The conversion of the biological 17β,21β hopanes to the corresponding 17α,21β and 17β,21α compounds is also maturation dependent. For C_{30} triterpanes the ration of $\frac{17\beta,21\alpha}{17\alpha,21\beta}$ decreases steadily from a value of about 0.4 at the onset of oil generation to a value of about 0.1 at peak oil generation.

(c) Two of the C_{27} triterpanes can also be used as maturity indicators. The ratio of 18α(H) trisnorhopane to 17α(H) trisnorhopane increases exponentially with increasing maturity from a value of approximately 0.2 at the onset of oil generation to approximately 1.0 at peak oil generation.

(d) It is our experience that the ratio of the C_{27} 18α(H) + C_{27} 17α(H) triterpanes to the C_{30} 17α,21β triterpane is maturity dependent. The

ratio decreases from values around 1.0 at the onset of oil generation to a value of approximately 0.4 at peak oil generation. With increasing maturity at levels greater than that equivalent to peak oil generation the ratio increases steadily to values greater than 3.0.

Source Type

(i) Based on Steranes

Algal organic matter contains steranes in which the C_{27} compounds are more abundant than the C_{29} compounds. General marine organic matter has approximately equivalent amounts of the C_{27} and C_{29} compounds while organic matter rich in land-plants usually has more of the C_{29} steranes.

(ii) Based on Triterpanes

The triterpane components in petroleum can be derived from both bacteria and higher plants. The common bacterial products are the C_{27}-C_{35} hopanes and moretanes whereas the higher plant triterpanes are compounds other than hopanes or moretanes and are commonly C_{30} compounds.

(iii) Based on Diasteranes

The diasteranes are not produced biologically but are formed during early diagenesis from sterane precursors. The diasterane ratios $\frac{C_{27}(2OR)}{C_{29}(2OR)}$ and $\frac{C_{27}(2OR+2OS)}{C_{29}(2OR+2OS)}$ should reflect the nature of the organic matter in the same manner as that outlined above for the steranes.

Biodegradation

It has been observed that in severely biodegraded petroleum the series of normal hopanes are converted to a series of A ring demethylated hopanes and the C_{29} $\alpha\alpha\alpha(2OR)$ sterane is selectively removed. For altered crudes which have not been degraded to this extent the severity of biodegradation can often be gauged by studying the isoprenoid and aromatic fractions. However, this type of investigation extends beyond a standard GC/MS/DS analysis.

Correlation

Our present approach to oil:oil or oil:source rock correlation problems is as follows:

(i) Compare the distribution of compounds in the 177, 191, 217, 218, 259 and 400 mass fragmentograms for an oil or sediment extract to the distribution of compounds in the respective fragmentograms for the other oil(s) or sediment extract(s). It is necessary in this type of comparison to make allowance for small variations due to possible maturity differences.

(ii) Examine the fragmentograms for peaks or sets of peaks which may represent compounds that are specific to the geological system under investigation. Normal steranes, diasteranes and bacterial hopanes cannot be used for this purpose because they are present in virtually all crude oils and sediment extracts. However, compounds like higher plant triterpanes, 4-methyl steranes, bisnorhopane and botryococcane can often prove very useful for this purpose.

14. CARBON ISOTOPE ANALYSIS

The measurement is carried out on one or more of the following mixtures; topped oil; saturate fraction; aromatic fraction; NSO fraction. The organic matter is combusted at 860°C in oxygen and the carbon dioxide formed is purified and transferred to an isotope mass spectrometer. The carbon isotope ratio is measured relative to a standard gas of known isotopic composition. In our case the standard gas is prepared from the NBS No. 22 oil. However, since the isotopic relationship between NBS No. 22 oil and the international reference PDB limestone are known, the values are adjusted to be relative to PDB limestone.

Although carbon isotope data has been commonly used for oil to oil and oil to source rock correlation its most significant application is the identification of source of gas according to following criteria (Fuex, 1977):

$\delta^{13}C$ (PDB)	Gas Type
-85 → -58	Biogenic methane
-58 → -40	Wet gas/associated with oil
-40 → -25	Thermal methane

15. VITRINITE REFLECTANCE MEASUREMENT

Vitrinite is a coal maceral which responds to increasing levels of thermal maturity. This response can be measured by the percent of light reflected off a polished surface of a vitrinite particle emursed in oil. Reflectance measurements are made on a number (40 if possible) of vitrinite particles in each sample, in order to establish a range and mean for reflectance values. Immature rocks have low reflectance values (0.2% Ro to 0.6% Ro), with mature values ranging from 0.6% Ro to 1.6% Ro. Very mature values are between 1.6% Ro and 2.4% Ro, while severly altered rocks have reflectances above 2.5% Ro.

Vitrinite reflectance results are best obtained from coals or rocks deposited in environments receiving large influxes of terrestrially-derived organic matter. Unfortunately, these environments are not conducive to the accumulation of large quantities of oil-prone organic matter. Also vitrinite reflectance cannot be performed on rocks older than Devonian Age, due to the absence of land plants in the older geologic time periods.

16. VISUAL KEROGEN

Visual kerogen assessment is carried out by the coal petrologist and/or the palynologist. In the case of the petrologist the assessment is made in reflected light using the plug prepared for vitrinite reflectance measurement, and reports the relative amounts of alginite, exinite, vitrinite and inertinite particles.

Visual study of kerogen by the palynologist is carried out in transmitted light and can indicate the relative abundance, size, and state of preservation of the various recognizable kerogen types and hence indicates the source character of a sedimentary rock. In addition, the color of the kerogen is related to the thermal maturity of the sediments and is often used as a maturation indicator.

The preparation of slides for visual kerogen assessment by the palynologist firstly involves concentration of the organic matter by removal of the rock matrix using hydrochloric and hydrofluoric acid treatment and heavy liquid separation. The organic concentrate is then mounted on a glass slide using Petropoxy.

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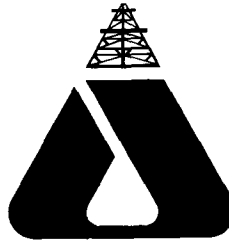
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