

CRUDE OIL TO PARENT SOURCE ROCK CORRELATION STUDY, NORSK HYDRO'S 33/5-1 WELL

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COMPANY PROPRIETARY

GEOCHEMICAL SERVICE REPORT

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CRUDE OIL TO PARENT SOURCE ROCK CORRELATION STUDY,

NORSK HYDRO'S 33/5-1 WELL

SUMMARY

The geochemical evaluation of 33/5-1 indicated shows of migrated crude oil within the gross interval 1640-2560[±] metres. As the better source rocks occur within the same part of the section, the possibility of oil generation within the lateral, off-structure equivalents of the associated shales was suggested.

However the present study, which was designed to test this hypothesis, indicates a lack of correlation between the crude oils and the shales penetrated in this well. Hence, unless there is a lateral facies change, a different source interval must be postulated for the migrated crude oil hydrocarbons.

It is recommended that the time-equivalent section should be examined in other wells in order to determine whether it does exhibit lateral facies changes and hence, whether it could have sourced the 33/5-1 crudes, or whether different migrational paths must be hypothesised.

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INTRODUCTION

This report presents the results of a correlation study involving the shows of migrated crude oil detected in Norsk Hydro's 33/5-1 well (Geochem report, December 1979) and the better source intervals.

This study was authorised by Mr. S.I. Leivestad, Norsk Hydro.

A. ANALYTICAL

Kerogens were isolated from a suite of eight extracted sediment samples selected to represent the better source intervals detected in the original study (December 1979) of 33/5-1. All of the samples were medium grey to medium light grey shales and their depths and organic carbon contents are presented below:

Geochem Sample Number	Depth (Metres)	Organic Carbon (१)	
377-023A	1840-1860	0.76	
377-025A	1880-1900	0.78	
377-028A	1940-1960	0.63	
377-033A	2040-2060	0.66	
377-036A	2100-2120	0.70	
377-040A	2180-2200	0.70	
377-045A	2280-2300	0.96	
377-048A	2340-2360	0.78	

The carbon isotopic composition of these kerogens was determined and compared to the carbon isotope values for the paraffin-naphthene and aromatic crude oil hydrocarbons from 1840-1860 metres, 1940-1960 metres, 2180-2200 metres and 2380-2400 metres. Hydrocarbons could not be used in the case of the potential source rocks due to the prevalence of migrated species.

A total of sixteen carbon isotope analyses were run in this study. The data are presented in table 1 and graphically in figure 1.

B. GENERAL INFORMATION

Ten (10) copies of this report have been forwarded to Mr. Svein I. Leivestad, Norsk Hydro. A copy of the data has been retained by Geochem for future consultation with authorised Norsk Hydro personnel.

The results of this study are proprietary to Norsk Hydro.

RESULTS AND INTERPRETATION

In the main study on 33/5-1 (Geochem report, December 1979), shows of crude oil were recognised within the gross interval 1640-2560[±] metres (Zones B, C and D). No rich source units were detected but Zones B through D, which are potentially fair source rocks, are the best sources within the analysed section.

This correlation between the occurrence of migrated crude oil hydrocarbons and the better source intervals suggested the possibility of oil generation from the more mature off-structure equivalents of the associated shales, followed by lateral migration into the structure. The present correlation study was authorised to test this possibility.

Source-indigenous hydrocarbons are masked by the migrated, out of place species and hence, it was not possible to use analyses involving the source rock hydrocarbons for the correlation. Instead, a correlation was sought using the carbon isotope compositions of the crude oil hydrocarbons and of the kerogen (organic matter) of the source rocks.

Four samples were selected to represent the migrated crude oils (two from Zone B, one each from Zones C and D). These gave carbon isotope values within the narrow range of -28.49% oo to 28.90% on the aromatics but, whereas two of the samples were comparable on the paraffin-naphthenes (-29.340/00, -29.440/00) the other two were much heavier and indeed, were heavier than the It is believed that the latter samples probably reflect aromatics. the presence of a contaminant and do not indicate variations within the oils. There are two reasons for this statement: firstly, the two similar samples are the shallowest and deepest and are separated by over five hundred metres of section; secondly, the paraffin-naphthenes are usually lighter (more negative) than the aromatics in crude oils. Hence, it is believed that the crudes belong to one family (as suggested by their chromatograms) with values approximating -29.40/00 for the paraffin-naphthenes and -28.7% of for the aromatics.

Zones B and C are each represented by three source rock kerogens and Zone D by two kerogens. They vary in composition from -(25.11) 25.76%/00 to -26.40%/00 and are apparently unrelated to richness or organic matter type, although there is a trend of increasing lightness down to 2150^{\pm} metres followed by a reversal. Nevertheless, the general range of values is relatively narrow, with a mean at approximately -26.1%/00. In order to establish a correlation, the kerogens should be not more than 10/00 heavier than the crude oil hydrocarbons. However in this study, they are approximately 30/00 heavier. Hence, it must be concluded that the crude oils do not correlate either with the sediments present in this well section or, unless there is a lateral facies change, with their off-structure equivalents. Unless there is a facies change, a different and probably deeper source must be postulated.

TABLE 1

CARBON ISOTOPES (%)00 PDB)

DEPTH	PARAFFIN- NAPHTHENE	AROMATICS	KEROGENS
1840-860m	- 29.341	- 28.487	
1940-960m	- 27.046	- 28.655	
2180-200m	- 28.016	- 28.899	
2380-400m	- 29.442	- 28.593	
•			
1840-860m		•	- 25.107
1880-900m			- 25.892
1940-960m			- 26.215
2040-060m			- 26.381
2100-120m			- 26.400
2180-200m			- 26.083
2280-300m			- 26.145
2340-360m			- 25,756
	DEPTH 1840-860m 1940-960m 2180-200m 2380-400m 1840-860m 1840-960m 2040-960m 2040-060m 2100-120m 2180-200m 2280-300m 2340-360m	DEPTH PARAFFIN- NAPHTHENE 1840-860m - 29.341 1940-960m - 27.046 2180-200m - 28.016 2380-400m - 29.442 1840-860m 1880-900m 1940-960m 2040-060m 2180-200m 2180-200m 2180-200m 2180-300m 2340-360m	DEPTHNAPHTHENEAROMATICS1840-860m- 29.341- 28.4871940-960m- 27.046- 28.6552180-200m- 28.016- 28.8992380-400m- 29.442- 28.5931840-860m1840-900m1840-900m2040-060m2180-200m2180-200m2180-200m2180-200m2340-360m

BRIEF DESCRIPTION OF THE ANALYSES PERFORMED BY GEOCHEM

"Screen Analyses" are described in sections A, C and D, "Sample Preparation" in section B, "Follow-up Analyses" in sections E through K and "Correlation Studies" in section L. The analyses can be run on either core or cuttings material with the proviso that samples must be canned for the C_1 - C_7 analysis and should be canned (or at least wet) for the C_4 - C_7 analysis. The other analyses can be run on both canned and bagged samples.

A) C1-C7 LIGHT HYDROCARBON ANALYSIS

The abundance and composition of the C_1-C_7 hydrocarbons in sediments reflects their source richness, maturity and the character of the hydrocarbons they can yield. Most importantly, it is extremely sensitive to the presence of migrated hydrocarbons and is an excellent method for their detection. As it provides the information on most of the critical parameters and is also economical, this analysis is excellent for screening samples to decide which of them merit further analysis.

During the time which elapses betwwen the collection of the sample at the wellsite and its analysis in the laboratory, a fraction of the total gas passes from the rock to the air space at the top of the can. For this reason, both the air space and the cuttings are analysed.

The analysis involves the gas chromatographic separation of the individual C_1-C4 gaseous hydrocarbons (methane, ethane, propane, isobutane and normal butane) and a partial resolution of the C5-C7 gasoline-range hydrocarbons (for their complete resolution see Section E). The ppm abundance of the five gases and of the total C_5-C_7 hydrocarbons are calculated from their electronically integrated peak areas (not from peak height) by comparison with a standard.

In the report, the following data are tabulated: the abundance and composition of the air space gas, of the cuttings gas and of the combined air space and cuttings gases. The combined results are also presented graphically.

B) SAMPLE WASHING AND HAND PICKING

All of the analyses described in subsequent sections are run on washed and hand picked samples.

Cuttings are washed to remove the drilling mud, care being taken not to remove soft clays and fine sand during the washing procedure. Using the C_1-C_7 hydrocarbon data profile of the well, or the organic carbon profile (if this analysis is used for screening), electric logs (if supplied) and the appearance of the cuttings under the binocular microscope, samples are selected to represent the lithological and geochemical zones penetrated by the well. These samples are then carefully hand picked and the lithology of the uncaved material is described. It is these samples which are submitted for further analysis.

Sample material remaining after analysis is retained for six months. Unless instructions are received to the contrary, Geochem Laboratories may then destroy the samples.

Our reports incorporate a gross lithological description of <u>all</u> the samples which have been analysed and litho percentage logs. As screen analyses are recommended at narrow intervals, a complete lithological profile is obtained.

C) ORGANIC CARBON ANALYSIS

The organic carbon content of a rock is a measure of its total organic richness. Combined with the visual kerogen, C_1 - C_7 , C_4 - C_7 , pyrolysis and C_{15+} analyses, the organic carbon content is used to evaluate the potential (not necessarily actual) hydrocarbon source richness of the sediment. This analysis is an integral part of a total evaluation and it can also be used as an economical screen analysis for dry samples (when the C_1 - C_7 analysis cannot be used).

Hand picked samples are dried, crushed and then acidised to remove the inorganic calcium and magnesium carbonates. The actual analysis involves combustion in a Leco carbon analyser. Blanks, standards and duplicates are run routinely for purposes of quality control at no extra cost to the client.

The data are tabulated and presented diagramatically in our reports in a manner which facilitates comparison with the gross lithology (see Section B) of the samples.

D) MINI-PYROLYSIS

An ideal screen analysis which provides a definitive measure of potential source richness upon those samples whose organic carbon contents suggest fair or good source potential. This is described in detail in section K.

E) DETAILED C4-C7 HYDROCARBON ANALYSIS

The abundance and composition of the C_4-C_7 gasoline-range hydrocarbons in sediments reflects their source quality, level of thermal maturation and organic facies. In addition, the data also reveal the presence of migrated hydrocarbons and can be used for crude oil-parent source rock correlation studies.

This powerful analysis, performed upon hand picked lithologies, is employed as a follow-up to confirm the potential of samples which have been selected using the initial screen analysis. It is used in conjunction with the organic carbon, visual kerogen and C_{15+} analyses.

The individual normal paraffins, isoparaffins, naphthenes and aromatics with between four and seven carbon atoms in the molecule (but also including toluene) are resolved by capillary gas chromatography and their peak areas electronically integrated.

Normalised compositions, selected ratios and the ppm abundance of the total gasoline-range fraction are tabulated in the report and also presented graphically.

F) KEROGEN TYPE AND MATURATION

Kerogen is the insoluble organic matter in rocks. Visual examination of the kerogen gives a direct measure of thermal maturity and of the composition of the organic matter (organic facies) and indicates the source quality of the sediment - which is confirmed using the organic carbon, light hydrocarbon, pyrolysis and C_{15+} analyses.

The type of hydrocarbon (oil or gas) generated by a source rock is a function of the types and level of thermal maturation of the organic matter which are present. Both of these parameters are measured directly by this method.

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Kerogen is separated from the inorganic rock matrix by acid digestion and flotation methods which avoid oxidation of the organic matter. It is then mounted on a glass slide and examined at high and low magnifications with a Leitz microscope. Chemical methods measure the total kerogen population but, with this technique, individual particles can be selected for examination and spurious material identified. This is particularly valuable in reworked, contaminated and turbodrilled sediments.

The following data are generated: the types of organic matter present and their relative abundances, an estimate of the proportion of reworked material, preservation state, the thermal maturity of the non-reworked organic matter using the spore colouration technique. A ten point maturation scale is employed (1 through 10 but also including intermediate points (e.g. 1, 1+, 2 etc., see below)). A total of fourteen types of organic matter are sought based upon the primary categories of algal, amorphous, herbaceous, inertinite, wood and resin. This detail is essential for a proper understanding of hydrocarbon source potential as the different sub-groups within each category have different properties.

Maturation levels are identical to those reported by Geochem prior to 1980 and correlate as follows (old scale in brackets): 1(1), 2(1+), 3(2-), 4(2), 4+(2 to 2+), 5(2+), 6(3-), 7(3), 8(3+), 9(4), 10(5). The new scale has intermediate points e.g. 3, 3+, 4, 4+, 5 etc.

Upon completion of the study, the glass slides are sent to the client.

G) VITRINITE REFLECTANCE

Vitrinite reflectance is an alternative/confirmatory method for evaluating thermal maturation which is used in conjection with the visual kerogen analysis. The reflectivity of vitrinite macerals increases in response to thermal alteration and is used to define maturation levels and, by projection, to predict maturity at depth or the thicknesses of section removed by erosion.

Measurements are made upon kerogen separations in conjunction with polished whole rock samples. In general, this analysis is performed upon the same samples as the visual kerogen analysis, thus facilitating a direct comparison of the two sets of results.

If possible, forty to fifty measurements are taken per sample - unless the sediments are organically lean, vitrinite is sparse or only a single uniform population is present. The data are plotted in a histogram which distinguishes the indigenous vitrinite from possible reworked or caved material. Averages are calculated for each population. Comments upon exinite fluorescence and upon the character of the phytoclasts are noted on the histograms. The reports contain the tabulated data, histograms and the reflectivities plotted against depth.

The vitrinite and visual kerogen techniques provide mutually complementary information upon maturity, organic matter type and diagenesis.

H) C15+ EXTRACTION, DEASPHALTENING AND CHROMATOGRAPHIC SEPARATION

Sections "A" and "E" dealt with analyses covering the light end of the hydrocarbon spectrum. This section is concerned with the solvent extractable organic material in the rock with more than fourteen carbon atoms in the molecule (i.e. the heavy end). The amount and composition of this extract indicates source richness and type, the level of thermal maturation and the possible presence of migrated hydrocarbons.

These results are integrated with those derived from the pyrolysis, visual kerogen, organic carbon and light hydrocarbon analyses.

The techniques involved in this analysis employ pure solvents and have been designed to give reproducible results. Hand picked samples are ground and then solvent extracted in a soxhlet apparatus, or by blending, with dichloromethane (the solvent system can be adapted to client's specifications). After asphaltene precipitation, the total extract is separated by column chromatography or high pressure liquid chromatography into the following fractions: paraffin-naphthene hydrocarbons, aromatic hydrocarbons, eluted NSO's (nitrogen-, sulphur-, and oxygen- containing non-hydrocarbons) and non-eluted NSO's. Note that the non-hydrocarbons are split into three fractions and not reported as a gross value. These fractions can be submitted for further analyses (carbon isotopes, gas chromatography, high mass spectroscopy) including correlation studies.

For convenience and thoroughness, the data are reported in three formats: the weights of the fractions, ppm abundances and normalised percentage compositions. The data are also presented diagramatically.

J) <u>GC ANALYSIS OF C15+ PARAFFIN-NAPHTHENE HYDROCARBONS</u>

The gas chromatographic configurations of the heavy C_{15+} paraffinnaphthene hydrocarbons reflect source type, the degree of thermal maturation and the presence and character of migrated hydrocarbons or contamination.

Not only is this analysis an integral part of any source rock study but it also provides a fingerprint for correlation purposes and helps to define the geochemical/palynological environmental character of the source rocks from which crude oils were derived.

The paraffin-naphthene hydrocarbons obtained by column chromatography are separated by high resolution capillary chromatography. Excellent resolution of the individual normal paraffins, isoprenoids and significant individual isoparaffins and naphthenes is achieved. Runs are normally terminated at nC35. A powerful in-house microprocessor system is being introduced to correct for the change in response factor with chain length.

The normal paraffin carbon preference indices (C.P.I.) indicate if odd (values in excess of 1) or even (values less than 1) normal paraffins are dominant. Strong odd preferences (± strong pristane peaks) are characteristic of immature land plant organic matter whilst even preferences (± strong phytane peaks) suggest a reducing environment of deposition. With increasing maturity, values approach 1.0 and oils are typically close to 1.0. The indices are calculated using the following formulae:

$C.P.I_A =$	=	$C_{21} + C_{23} + C_{25} + C_{25}$	-27 +	$C_{21} + C_{23} + C_{25} + C_{27}$
		$\overline{C_{20} + C_{22} + C_{24} + C_{24}}$	26	$C_{22} + C_{24} + C_{26} + C_{28}$
		·	2	· · · · · · · · · · · · · · · · · · ·
$C.P.I_B$	=	$C_{25} + C_{27} + C_{29} + C_{29}$	31 +	$C_{25} + C_{27} + C_{29} + C_{31}$
		$C_{24} + C_{26} + C_{28} + C_{28}$	30	$C_{26} + C_{28} + C_{30} + C_{32}$
			2	

Chromatograms are reproduced in the report for use as visual fingerprints and in addition, the following data are tabulated: normalised normal paraffin distributions; proportions of paraffins, isoprenoids and naphthenes in the total paraffin-naphthene fraction; C.P.I_A and C.P.I_B; pristane to phytane ratio; pristane to nC_{17} ratio.

K) PYROLYSIS

The process of thermal maturation can be simulated in the laboratory by pyrolysis, which involves heating the sample under specified conditions and measuring the oil-like material which is freed/generated from the rock. With this analysis, the potential richness of immature sediments can be determined and, by coupling the pyrolysis unit to a gas chromatograph, the liberated material can be characterised. These results are correlated with those obtained from the organic carbon, kerogen and C_{15+} analyses.

Small amounts of powdered sample are heated in helium to release the thermal bitumen (up to 340°C) and pyrolysate (340-550°C). The thermal bitumen correlates with the solvent extractable material (see above) whilst the pyrolysate fraction does not exist in a "free" state bút is generated from the kerogen, thus simulating maturation in the subsurface. Abundances (weight ppm of rock) are measured with a flame ionisation detector against a standard. Thermal bitumen includes source indigenous, contaminant and migrated hydrocarbons but the pyrolysate abundance is a measure of ultimate source richness. The capillary gas chromatogram of the pyrolysate is used to evaluate the character of the parent organic matter and whether it is oil or gas prone. Peak temperature(s) of pyrolysate evolution is recorded and if necessary, methane yields are also measured. Carbon dioxide can be measured if requested but is normally ignored as the separation of the organic and inorganic species has been found to be artificial and unreliable.

Pyrolysate yields provide a definitive measure of potential source richness which avoids the ambiguities of the organic carbon data and the problem of contamination. This analysis is also used to evaluate the quality and character of the organic matter, whether it is oil or gas prone and the degree to which it has realised its ultimate hydrocarbon potential. Carbon dioxide yields are not used and Geochem does not employ the pyrolysis technique to evaluate maturation, preferring the more reliable kerogen and vitrinite reflectance analyses.

The data are tabulated and presented graphically. MINI-PYROLYSIS includes ppm thermal bitumen and ppm pyrolysate. PYROLYSIS-GC also provides the above together with the temperature of peak pyrolysate evolution and a capillary chromatogram of the pyrolysate. The Mini-Pyrolysis is recommended as a screening technique.

L) CORRELATION STUDY ANALYSES

Oil to oil and oil to parent source rock correlation studies require high resolution analytical techniques. This requirement is satisfied by some of the analyses discussed above but others have been selected specifically for correlation work. Many of these analyses also provide information upon the character of the environment of deposition of the parent source rocks.

- detailed C₄-C₇ hydrocarbon (gasoline range) analysis. See Section E. Although these hydrocarbons can be affected by migrational/alteration processes, they commonly provide a very useful correlation parameter.
- capillary gas chromatography of the C15+ paraffin-naphthenes.
 See section J. The branched[±]normal paraffin distributions are used to "fingerprint" the samples.
- capillary chromatograms of whole oils and of the C₈₊ fraction of source rocks.

- capillary gas chromatography of C₁₅₊ aromatic hydrocarbons.
 Separate chromatograms of the hydrocarbons and of the sulphurbearing species are reproduced.
- high pressure liquid chromatograms.
- mass spectrometric carbon isotope analyses of crude oil and rock extract fractions and of kerogen separations. A powerful tool for comparing hydrocarbons and correlating hydrocarbons to organic matter. With this technique the problem of source rock contamination can be avoided. The data are recorded on x-y or Galimov plots.
- mass fragmentograms (mass chromatograms) of fragment ions characteristic of selected hydrocarbon groups such as the steranes and terpanes. The fragmentograms provide a convenient and simple means of presenting detailed mass spectrometric data and are used as a sophisticated fingerprinting technique. This provides the ultimate resolution for correlating hydrocarbons and facilitates the examination of hydrocarbon classes.
- vanedium and nickel contents.

Suites of (rather than single) analyses are employed in correlation studies, the actual selection depending upon the complexity of the problem. See also section N.

M) ANALYSES FOR SPECIAL CASES

M-1) ELEMENTAL KEROGEN ANALYSIS

This analysis evaluates source quality, whether the sediments are oil or gas prone, the character of the organic matter and its level of thermal maturation. It is the chemical equivalent of the visual kerogen analysis. The pyrolysis analysis is generally preferred to this technique, both methods providing similar information.

M-2) SULPHUR ANALYSIS

The abundance of sulphur in source rocks.

M-3) CARBONATE CONTENT

The mineral carbonate content of sediments is determined by acid treatment. These data are particularly useful when used in conjunction with organic carbon contents as a screening technique.

M-4) NORMAL PARAFFIN ANALYSIS

Following the removal of the branched paraffins and naphthenes from the total paraffin-naphthene fraction, a chromatogram of the normal paraffins is obtained. The resulting less complicated chromatogram facilitates the examination of normal paraffin distributions.

M-5) SOLID BITUMEN EVALUATION

Residual solid bitumen after crude oil is generated by three prime processes: the action of waters, gas deasphalting, thermal alteration. Thus it provides a means of determing the reservoir history of a crude and of evaluating whether adjacent traps will or will not be prospective for oil. In carbonate sections, where organic matter is sometimes sparse, this technique is also used to evaluate thermal maturation levels. The analysis involves the determination of the solubility (in CS_2) of the solid bitumen and of the atomic hydrogen to carbon ratio of the insoluble fraction.

N) CRUDE OIL ANALYSIS

N-1) API GRAVITY

This can be performed upon large (hydrometer) and small (SG bottle, pycnometer) samples and even upon stains extracted from sediments (refractive index).

- N-2) SULPHUR CONTENTS (ASTM E30-47)
- N-3) POUR POINT (ASTM D97-66, IP15/67)

N-4) <u>VISCOSITY</u> (ASTM D445-72, IP71/75)

N-5) FRACTIONAL DISTILLATION

Graph of cumulative distillation yield against temperature. Five percent cuts taken for further analysis. Mass spectrometric studies of these fractions provide a detailed picture of the distribution of paraffins and of the various naphthene and aromatic groups within a crude, which is useful both for correlation and for refinery evaluation purposes.

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FIGURE 1

CARBON ISOTOPES

(‰, PDB)

