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TWO CONTRACT REPORTS ON THE INFLUENCE OF OIL BASED DRILLING MUD ON GEOCHEMISTRY AND PETROGRAPHY ANALYSIS OF DRILL CUTTINGS.

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Calgary, Alberta

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INFLUENCE OF OIL-BASE MUD ON ORGANIC GEOCHEMICAL PARAMETERS

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ABSTRACT

This research project was initiated by ISPG, Calgary to evaluate the influence of oil-base drilling muds on cutting samples. One shale and one limestone source rock, and one oil-stained sandstone were subjected to simulation experiments with two base oils (Shell Sol DMS and Exxsol D80) similar to drilling with oil-base muds.

Both oil-base muds (especially Shell Sol DMS) showed a considerable impact on the organic geochemical parameters used in Petroleum Geochemistry Program such as: fluorescence to detect oil stain; R_o and TAI for maturity determination; Rock-Eval pyrolysis to evaluate source-rock potential/detect stains to determine maturity; bitumen extraction for detecting matured source rocks or migration; and gas chromatographic fingerprinting to detect oil type. The abrupt increase of some geochemical parameters indicate impregnation of the base oils which could not be removed by cleaning. The decrease in bitumen (or S_1 in Rock-Eval pyrolysis) in oil-stained sandstone or limestone source rock indicates that base oil was cracked to low molecular weight hydrocarbons, which eventually act as solvent to release the free hydrocarbons present in limestone or sandstone.

These experiments indicate that organic geochemical data should be used with extreme caution and more research is needed to determine a proper cleaning agent to recover the base line data.

INTRODUCTION

Administrative Aspect

This research proposal which was entitled 'Oil-base Drilling Mud Management', was requested by Department of Supply and Services of Canada, Ottawa at the initiation and formulation by the Institute of Sedimentary and Petroleum Geology, Geological Survey of Canada, Calgary, Alberta. Accordingly we submitted the research proposal in July 6, 1988. The proposal was accepted by DSS, Ottawa on August 19, 1988 (File no. 23294-7-1067/01-SG). The work was started from September 1, 1988. Canada-Newfoundland Offshore Petroleum Board, and Nova Scotia Department of Mines and Energy, Halifax on our request permitted us to collect five source rocks and one oil-stained sandstone from the COGLA Repository at Dartmouth. On our request, Steve Creaney of Esso Resources Canada Ltd, Calgary, Alberta sent four base oils which are generally used as oil-base drilling muds for this research.

Scientific Aspect

Oil base drilling mud which was first introduced in 1980 in the N. Sea boreholes, is designated as mud used in drilling operations with a continuous liquid phase of oil. Since its introduction, these low toxicity oil-base drilling fluids have become increasingly popular in N. Sea, Offshore Canada, W. Africa, Middle East, Malaysia and Thailand (Hodder, 1986). This is because they reduced drilling time, are easy for coring, have

much less cost (save about $2,240,000 per offshore well), and prevent cavings. Cuttings from the boreholes drilled with oil-base muds are geologically more representative of the drilled formation than those drilled by water-base muds because oil prevents sloughing and dispersion of shales and clays (Brown, 1988). Oil-base muds are very useful in special drilling conditions: formations such as rock salt, anhydrite, gypsum; prevention and relief of struck pipes: and drilling at high temperature and geopressured wells (Vorabutr and Chilingarian, 1983; Brown, 1988).

In spite of all these advantages of oil-base muds over water-base mud, oil-base muds coat the cuttings with oil (Swanson, 1981) and therefore are a potential contaminant. These organic drilling fluids (diesel oil, crude oil, etc.,) can be damaging to the environment (especially for biota) within 500m of the rig or platform (Simpson, 1979; Caenn and Chilingarian, 1981; Hodder, 1986). Like other organic contaminants (Snowdon and Powell, 1978), cuttings samples recovered from oil-base drilling mud could create a major threat to an organic geochemical program and the detection of oil shows, if not properly cleaned.

In addition to the disadvantages cited above, the base oils can be cracked to low molecular hydrocarbon compounds under the influence of elevated temperatures during drilling. These newly formed hydrocarbons will have a different composition than the base oil originally present and it can cause serious problems in the chromatographic fingerprinting of the mud both in heavier and

lighter ends. Moreover, these cracked low-molecular weight hydrocarbons may act as solvents for the liquid hydrocarbons which are in a free state and thereby induce fractionation effect.

This research work was therefore conducted as a first stage evaluation of the influence of oil-base muds on organic geochemical parameters generally used for evaluating source-rock potential, maturation, and oil stain detection. This evaluation was done by conducting a high pressure bomb experiment taking source-rock/reservoir rock samples and base oils to simulate drilling conditions at two temperatures. As a first step to evaluate this effect, we measured organic geochemical parameters like total organic carbon, S_1, S_2, T_{max}, and hydrogen index in Rock-Eval pyrolysis, vitrinite reflectance, Thermal Alteration Index, bitumen extraction, and liquid and gas chromatography. These analyses were conducted with the source and reservoir rocks and before and after the bomb experiment (before and after cleaning the samples).

SAMPLES AND ANALYTICAL METHODS

Samples

Two source-rock (one shale and one limestone) samples were collected from the Cumberland basin, Nova Scotia (Carboniferous age). One oil-soaked sandstone was selected from the Jean d'Arc basin. All these samples are core samples. Two other source-rock cuttings samples (Jurassic, Jean d' Arc basin) were also chosen.

Core samples were crushed to less than 2 to 3 mm in size in order to simulate normal cuttings samples available from drilling. Four base oils, Shell Vista ODC 500 (a common oil), Shell Sol DMS (a common oil), OBM Exxsol D-80 (Sarnia oil), and Exxsol D-80 (Sarnia oil) were also collected.

Analytical Methods

Kerogens were isolated from -40 mesh samples using HCl, HF, and heavy liquids (Zinc bromide). One part of the kerogen was prepared for smear slide for TAI determination and another part was used to prepare a polished plug for vitrinite reflectance measurement.

Qualitative fluorescence of shale , limestone, and oil-stained sandstone before and after the bomb experiment was determined using a UV lamp (Mineralight lamp, model UVGL-48, 254-356nm) in a dark room.

Rock-Eval pyrolysis was performed using a Delsi Oil Show Analyzer (after Espitalie et al., 1985). TOC was determined by LECO Carbon Analyzer after acid treatment.

Bitumen was extracted by soxhlet extraction using dichloromethane. Saturate, aromatics, and NSO compounds were separated after deasphalting with pentane and using column chromatography with hexane, dichloromethane:hexane (1:1), and methanol/chloroform. Gas chromatography was done in a Hewlett-Packard GC equipped with 30m/.25mm i.d. fused silica capillary column (SPB 5) with 0.25 μm film thickness (slightly polar, bonded phase: 5%

dephenyl, 94% demethyl, and 1% vinyl polysioeane). The temperature program for gas chromatography was: initial temperature: 80°C, final temperature 300°C, rate 10°C/min.

The high pressure bomb experiment was done using one litre and 300ml Alloy Steel Parr Pressure Vessels fitted with a pressure gauge, heating mantle, and rapture disc without stirrer. The apparatus commonly used was similar to the apparatus used for hydrous pyrolysis of whole rocks. A measured amount of sample, base oil, and water (sample 100gm, base oil 50ml, water 12.5 ml) was first put inside the reactor vessel. Vessel was sealed and checked about leaks using helium pressure. The reaction vessel was subjected to pressure (500 to 1000 psi) by helium flow after sealing the vent. The pressured vessel was placed inside a heating mantle fitted with a controller and a temperature detector rod. The reaction vessel was slowly heated (approximately 1.5°C/minute) till the required temperature (100 or 150°C) was reached and kept under that condition for 10 minutes. The reaction vessel was then kept for 3 to 4 hours to cool down to room temperature after shutting down the heating. Before opening, pressure (between 1400 to 2000 psi) was slowly vented off and samples were removed.

Cleaning

All samples after the bomb experiment were washed with water through a 325 mesh screen with a sprayer to achieve a quality of washed cuttings (similar to the cuttings recovered by normal

drilling procedures). Most of these samples was then subjected to soaking in Sunlight detergent and water for 1/2 hour and were later washed with water through a 325 mesh screen with sprayer. A part of the shale source rock which was subjected to bomb experiment and cleaned with water, was then soaked with acetone for 1/2 hour and later acetone was decanted and evaporated. Similarly another part of the shale source rock was cleaned with dichloromethane and chloroform/methanol.

RESULTS AND DISCUSSION

Samples

Table 1 shows that after all experiments, we recovered three sets of samples:

a. **Baseline samples** - Three shale source rocks (C539, C623, and C624), one limestone source rock (C540), one oil-soaked sandstone (C626), and four base oils were selected for the base-line analysis as formulated by the Scientific Authority. These shale, limestone, and oil-stained sandstone samples were free from oil-base muds. Table 1a lists these samples.

b. **Samples after bomb experiment** - One shale (C539) and one limestone (C540) source rocks, one oil-stained sandstone (C626), and two base oils (Shell Sol DMS - a common oil; Exxsol D-80 - Sarnia oil) were selected. Eight bomb experiments were carried out with three shale/limestone/sandstone samples with two base oils at two temperatures (100^{o}C and

150°C). We obtained eight samples as listed in Table 1b.

c. **Samples after bomb experiments and cleaning** - According to the schedule of work formulated by the Scientific Authority, we recovered ten samples after cleaning with water/detergent, acetone, dichloromethane, and chloroform, as listed in Figure 1c.

Fluorescence

Table 1a shows the fluorescence data of the baseline samples; table 1b is the fluorescence data after the bomb experiment; table 1c is the fluorescence data after cleaning the samples recovered after bomb experiments. All base line oils (common oil and Sarnia oil) showed very weak dull blue fluorescence. Both shale (C539) and (C540) source rock samples, after the bomb experiment with Shell Sol DMS oil-base mud, showed slight increase in fluorescence intensity. Not much change was observed when both these two samples (C539 and C540) are used with Exxsol D80 oil base mud. Similarly, a strong increase in fluorescence intensity was observed when oil-stained sandstone is associated with Shell Sol DMS during bomb experiment. After cleaning with detergent and water (also cleaning with acetone, DCM, and chloroform/methanol for the shale source rock), both shale and limestone source rocks came back to their normal base line fluorescence. However, oil-stained sandstone even after cleaning with water and detergent show increased fluorescence intensity.

Vitrinite Reflectance

Table 2 shows mean (R_o) and standard deviation of vitrinite reflectance data points for six samples. We selected three base line samples (C539, C540, C626), one sample after bomb experiment (C717: shale + Shell Sol DMS), and three samples after bomb experiment and cleaning (C724: sandstone + Shell Sol DMS + cleaning; C730: shale + Shell Sol DMS + cleaning; limestone + Shell Sol DMS + cleaning). However, no vitrinite grains could be encountered in sample C624 because of low amount of isolated kerogen. Table 2 indicates lowering (0.13%) of vitrinite reflectance (mean), when base line shale sample is compared with the shale samples associated with Shell Sol DMS (sample no. 717). Figure 1 clearly demonstrates the change in vitrinite reflectance histogram pattern. Cleaning of the oil-base mud (C730) however, partially increased the vitrinite reflectance relative to its base line data. Limestone samples show a similar effect.

Thermal Alteration Index

Table 3 shows the data on Thermal Alteration Index of the same seven samples discussed in vitrinite reflectance measurement. Shale source rock shows a wide variation in TAI values (2^- to 2^+ instead of 2) when affected by Shell Sol DMS base oils with or without cleaning. We did not see any change in TAI values for the limestone source rock before or after the addition/cleaning of Shell Sol DMS. However, oil-stained sandstone shows a wide

variation in TAI values (1^- to 1^+) instead of TAI of 1^+ in the base line sample.

Rock-Eval Pyrolysis

Rock-Eval pyrolysis data of the shale source rock (C539) showed a different type of data sets than the limestone source rock and oil-stained sandstone which were affected by oil-base muds (with or without cleaning with detergent or other chemicals) (Table 4).

Shale source rock showed a remarkable increase in S_1 (free hydrocarbons originally present in the rock which were released during pyrolysis up to 300°C, measured in mg HC/g of rock): 3.92/4.82 for the samples affected by Exxsol D80 and 9.44/7.88 for the samples affected by Shell Sol DMS compared to the base-line data of same shale source rock of 2.03. S_2 (residual petroleum potential from the cracking of kerogen during pyrolysis between 300° and 550°C) was not much affected by any of these two oil-base muds (Shell Sol DMS and Exxsol D80). Similarly, T_{max} (oven temperature measured in °C at the apex of S_2 peak) values were not affected (446 to 448 compared to 444°C of the base-line shale source rock). Production index (S_1/S_1+S_2) increased from 0.06 to 0.11/0.23 for the shale, 0.06 to 0.20/0.25 for limestone and decreased from 0.67 to 0.52/0.53. Total organic carbon was increased for the shale samples which were affected by Shell Sol DMS (9.02/8.77% compared to 8.22% for the base line sample) and decreased for oil-stained sandstone affected by both oil-base

muds (0.48/0.73% compared to 1.74% for the base-line samples. Hydrogen Index which is controlled by the data of TOC and S_2, has been changed according to the change in TOC values because there was not much change in S_2 values.

Not much improvement was noticed for the change in S_1 values after cleaning all the samples with water + detergent, and other chemicals. S_1 and production index remained much higher in amount than the base-line data for both shale and limestone source rocks. S_1 of sandstone was increased after cleaning. Cleaning with acetone, dichloromethane, chloroform/methanol decreased S_2 values and thereby reduced hydrogen index values. T_{max} values however, were also not affected by cleaning. Total organic carbon values were decreased relative to the base line shale samples when cleaned with three organic solvents and increased when cleaned by water/detergent.

The above data suggest that drilling with an oil-base mud affects differently the Rock-Eval data for shale source rocks and sandstone reservoir rocks. The increase in S_1 or production index values for the shale source rock clearly indicate an addition of bitumen/oil because of oil-base muds (specially Shell Sol DMS). This was not changed by normal cleaning of the sample even by organic solvents used in soxhlet extraction; these solvents even caused an adverse effect on S_2 and TOC which controls the hydrogen index (generally used to determine the hydrocarbon potential of a source rock). The decrease in S_1 and production index in oil-stained sandstone after the bomb experiment with the oil-base

muds and washing with water, may indicate that the cracked low-molecular weight compounds generated during the experiment may act as solvents for the oil-stained fraction which was released during washing with water. The increase in S_1 and production indices after cleaning with water + detergent may indicate that part of the detergent was reacted with the residual oil which was not washed with water and therefore remained with the oil fraction.

Bitumen Extraction and Liquid Chromatography

Table 5 illustrates the variability of fifteen bitumen extraction data from shale and limestone source rocks and oil-stained sandstone with or without oil-base muds and after cleaning. In most cases, these data resemble the variability of the TOC and S_1 (Rock-Eval pyrolysis) data. Shale samples associated with both oil base muds in both four experiments show very strong increase in bitumen content relative to the original base line sample. Shale samples when treated with Shell Sol DMS showed maximum increase (sample C717 increased four times) in bitumen content. It is interesting to note that after cleaning the shale sample + Shell Sol DMS + 150°C by detergent and water, the bitumen content increased to almost eight times the original base line sample. This might have the same explanation as given for the Rock-Eval data part for the sandstone sample. The Limestone sample showed a decrease in bitumen content relative to the base line sample. This data support the explanation that cracked low

molecular weight compounds generated during the experiment act as a solvent which washed away the bitumen during cleaning with water. On the other hand, the sandstone sample treated with Exxsol D80 (C714) decreased in bitumen content, whereas the sandstone sample treated with Shell Sol DMS increased in bitumen content. However, after cleaning, the same sample showed a decreased bitumen content even compared to the base line data.

Only one set of comparable data were analyzed by liquid chromatography (Table 6); sandstone with Shell Sol DMS was compared to their base line counterpart. These data however, suggest no drastic changes between those two samples.

Gas Chromatography

Figure 2 illustrates all the gas chromatograms of base oils and shale/limestone source rock, and oil-stained sandstone with or without base oils and before and after cleaning; Fig. 2a contains two gas chromatograms of two base oils; Fig. 2b contains six gas chromatograms from shale source rock with or without the two base oils and before and after cleaning with detergent; Fig. 2c contains four gas chromatograms of limestone source rock with or without the influence of two base oils before and after cleaning; Fig. 2d has four gas chromatograms of oil-stained sandstone with or without the influence of base oils and before/after cleaning.

The gas chromatograms of the two base oils indicate that Exxsol D80 base oil contains compounds between C_{10} & C_{14}, whereas Shell Sol DMS contains compounds between C_9 & C_{21} (Fig. 2a).

The gas chromatogram of whole extract from the base line shale sample (C539) has compounds between C_{14} and C_{34} (mainly n-alkanes) with a broad peak between C_{15} and C_{25} and with prominent pristane and phytane. C_{24} is the broadest of all compounds. The whole extract gas chromatograms of shale source rock with Shell Sol DMS at 100°C and 150°C show a dramatic change: compounds between C_9 and C_{16} fingerprint the base oil and the sample contains very high C_{24} compound at 150°C. After cleaning with detergent and water (sample C730), the chromatogram although lost most of the base oil fingerprints and did not match quite exactly with the base line sample. It lose some of the compounds at the heavier end possibly due to solvent effect of the cracked base oil. The gas chromatograms of the shale source rock affected by Exxsol D80 were not so dramatic like that of Shell Sol DMS. However, there is clear indication of addition of low molecular weight compounds at 100°C whereas there is loss of high molecular weight compounds at 150°C (possibly due to solvent effect of the base oil at an elevated temperature).

The gas chromatogram of the limestone baseline sample indicates the presence of mostly n-alkanes between C_{14} and C_{32} with dominance of odd numbered high molecular weight compounds (like nC_{27}). On the other hand, both limestone samples affected by Shell Sol DMS and Exxsol D80 increased low molecular weight

compounds between C_{14} and C_{16}. The gas chromatogram of the sample cleaned with detergent and water of limestone sample affected with Shell Sol DMS at 100°C clearly indicates loss of several high molecular weight compounds and increase of low molecular weight compounds.

The whole extract gas chromatogram of the oil-stained sandstone indicates a high-molecular weight biased n-alkane (dominant compounds) distribution pattern having a broad peak between C_{19} and C_{25}; n-alkanes between C_{15} and C_{34} are present. Similar to the shale sample, the gas chromatogram from the sandstone samples affected by Shell Sol DMS show dominantly low molecular weight (C_{13} and C_{16}) compounds; high molecular weight compounds up to C_{34} are present in minor amounts. After cleaning with detergent and water, a bimodal n-alkane distribution was noticed which was different from the base line sample. Oil-stained sandstone affected by Exxsol D80 showed a bimodal distribution of n-alkane which has fingerprints of both original base line sample and the base sarnia oil.

The above gas chromatographic data clearly indicate a strong influence of base oils in gas chromatographic fingerprinting. Cleaning with detergent and water did not improve the quality.

CONCLUSION

1. Two source rocks (one shale and one limestone) and one oil-stained sandstone were selected to undergo a pressure-vessel experiment with a mixture of base oil and water to simulate

conditions similar to drilling with oil-base muds under elevated temperature and pressure. Two temperatures (100° and 150°C) and two base oils (Shell Sol DMS - a common oil; Exxsol D80 - a Sarnia oil) were selected for these experiments. Base line data on those three samples for fluorescence, Rock-Eval pyrolysis, vitrinite reflectance and TAI, bitumen extract, and gas chromatography were done before the experiments.

2. The following effects on organic geochemical properties were observed after the bomb experiment and before and after cleaning with detergent/water and other chemicals:

   a. Increased fluorescence on all samples (especially the oil- stained sandstone). Cleaning did not improve the data.

   b. Decrease in mean vitrinite reflectance which is partially improved by cleaning.

   c. Sharp increase in S_1 and production index in Rock-Eval pyrolysis and TOC for the shale source rock and decrease of those parameters for oil-stained sandstone, which was not improved by cleaning. These data suggest that oil-base mud affect differently for shale source rock and oil-stained sandstone (reservoir rock). In shale source rock, addition of oil-base mud was noticed. In the sandstone, the bitumen fraction was from the oil-base muds, which act as solvents for the stained oil in sandstone and therefore removed during

washing.

d. Extracted bitumen was increased for the shale source rock, whereas it decreased in the limestone and stained sandstone. This abnormality was not improved by cleaning.

e. Addition of oil-base muds (especially Shell Sol DMS) totally change the gas chromatographic fingerprinting. Gas chromatograms of all three samples after cleaning were not comparable with the original base line samples.

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Table 1a. Fluorescence data, baseline samples

Sample no.	Sample type	Fluorescence Characteristics	Remarks
C539	Shale Source-rock (Type II) Carboniferous, Cumberland basin, Nova Scotia	Greenish brown	Dark fluorescence intensity
C540	Limestone source-rock location same as C539	Greenish yellow fluorescence specs within greenish brown	Dark fluorescence
C623	Type II source rock Kimmeridge Shale, Jean d'Arc Basin	Dark brown	Very dark fluorescence
C624	Type II source rock Kimmeridge shale, Jean d'Arc Basin	Dark brown	Very dark fluorescence
C626	Oil-soaked sandstone Jean d'Arc Basin	Yellowish brown	Strong fluorescence
C541	Oil-base mud,Vista ODC 500 (Shell),	Blue	Dark fluorescence
C542	Oil-base mud, OBM Exxsol D-80 (Sarnia oil)	Blue	Dark fluorescence
C543	Oil-base mud, Shell Sol DMS (a common oil)	Blue	Dark fluorescence
C544	Oil-base mud, Exxsol D-60, (Sarnia oil)	Blue	dark fluorescence

Table 1b . Fluorescence data, after bomb experiment, samples with oil-base mud

Sample No.	Sample type	Fluorescence Characteristics	Remarks
C717	Shale(C539) + Shell Sol DMS + 100°C + 1500 psi	Yellowish brown	Fluorescence increased compared to C539
C720	Shale(C539) + Shell Sol DMS + 150°C + 2000 psi.	Yellowish brown	Fluorescence increased compared to C539
C716	Shale (C539) + Exxsol D80 + 100°C + 1800 psi	Greenish brown	Not much change in fluorescence intensity
C721	Shale (C539) + Exxsol D80 + 150°C + 2000psi	Brown	No change in fluorescence than C539
C719	Limestone (C540) + Shell Sol DMS + 100°C + 1500 psi	Yellowish brown	Slight increase in fluorescence intensity
C715	Limestone (C540) + Exxsol D-80 + 100°C + 1500 psi	Greenish yellow fl. specs within greenish brown	No change than C540
C718	sandstone (C626) + Shell Sol 100°C + 1500 psi	Intense golden yellow	Strong increase in fluorescence intensity
C714	Sandstone (C626) + Exxsol D80 +100°C + 1400 psi	Yellowish brown	Fluorescence intensity similar to C626

Table 1c . Fluorescence data, after bomb experiment, samples with oil-base mud after cleaning

Sample No.	Sample type	Fluorescence Characteristics	Remarks
C726	Shale (C539) + Shell Sol DMS +100°C + Clean with detergent	yellowish brown	Fluorescence decreased compared to C717
C727	Shale (C539) + Shell Sol DMS +100°C + clean with acetone	greenish dark brown	Fluorescence decreased compared to C717
C728	Shale (C539) + Shell Sol DMS +100°C + clean with DCM	greenish dark brown	same as above
C729	Shale (C539) + Shell Sol DMS +100°C + clean with Chloroform and methanol	greenish dark brown	same as above
C730	Shale + Shell Sol DMS + 150°C + clean with detergent	Brown with some yellow specs	Fluorescence intensity increased compared to C720.
C731	Shale (C539) + Exxsol D80 + 100°C + clean with detergent	Brown	No change in fluorescence intensity compared to C716
C732	Shale (C539) + Exxsol D80 + 150°C + clean with detergent	Brown	No change in fluorescence compared to C721
C724	Sandstone (C626) + Shell Sol DMS + 100°C + clean with detergent	Golden yellow to yellowish brown	Fluorescence increased compared to C626 but decreased than C718
C725	Sandstone (C626) + Exxsol D80 + 100°c + clean with detergent	Yellowish brown	Fluorescence decreased compared to C714
C733	Limestone (C540) + Shell Sol DMS + 100°C +clean with detergent	Yellowish brown	Fluorescence decreased compared to C719

Table. 2. Vitrinite Reflectance Data Points

C539

0.39	0.40	0.43	0.43	0.44	0.45	0.46	0.48	0.48	0.50	0.50
0.50	0.51	0.51	0.51	0.53	0.53	0.53	0.53	0.53	0.55	0.56
0.56	0.57	0.57	0.57	0.58	0.58	0.59	0.60	0.60	0.60	0.63
0.64	0.65	0.67	0.68	0.72	0.78	0.78	0.88	0.88	0.91	0.93
0.98	1.00	1.16	1.23	1.35	1.46	1.66				

POPULATION 1 RANGES FROM .45 TO .749
MEAN = .56
STANDARD DEVIATION = .065
NUMBER OF POINTS = 33

C717

0.32	0.33	0.34	0.34	0.35	0.35	0.35	0.36	0.36	0.36	0.36
0.36	0.37	0.37	0.37	0.37	0.38	0.38	0.39	0.39	0.39	0.40
0.40	0.40	0.40	0.40	0.40	0.40	0.41	0.41	0.41	0.41	0.42
0.42	0.42	0.42	0.42	0.42	0.42	0.42	0.43	0.44	0.44	0.45
0.45	0.50	0.50	0.51	0.51	0.53	0.53	0.54	0.54	0.75	0.76
0.99										

POPULATION 1 RANGES FROM .35 TO .549
MEAN = .42
STANDARD DEVIATION = .053
NUMBER OF POINTS = 49

C730

0.20	0.36	0.41	0.43	0.43	0.44	0.44	0.45	0.45	0.46	0.46
0.47	0.47	0.47	0.48	0.48	0.49	0.49	0.49	0.49	0.50	0.50
0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.51	0.53	0.53	0.53
0.53	0.53	0.54	0.56	0.56	0.56	0.64	0.64	0.79	0.80	0.90
0.96	1.03	1.06	1.07	1.38	1.51					

POPULATION 1 RANGES FROM .45 TO .649
MEAN = .51
STANDARD DEVIATION = .045
NUMBER OF POINTS = 34

Table 2 . Vitrinite reflectance data points

C540

0.33	0.41	0.53	0.54	0.56	0.56	0.56	0.56	0.60	0.61	0.62
0.62	0.63	0.71	0.72	0.73	0.73	0.74	0.75	0.77	0.77	0.80
0.80	0.81	0.82	0.93	0.94	0.94	0.95	0.96	0.96	0.99	1.08
1.09	1.09	1.18	1.20	1.24	1.34	1.36	1.50	1.57	1.57	1.57
1.59	1.68	1.78	1.79	1.99	2.13					

POPULATION 1 RANGES FROM .5 TO .649
MEAN = .58
STANDARD DEVIATION = .036
NUMBER OF POINTS = 11

C733

0.37	0.39	0.40	0.40	0.41	0.44	0.45	0.50	0.53	0.56	0.62
0.62	0.63	0.66	0.70	0.72	0.80	0.84	0.84	0.90	0.91	0.95
1.02	1.08	1.16	1.19	1.23	1.32	1.51	1.79	1.94		

POPULATION 1 RANGES FROM .4 TO .749
MEAN = .55
STANDARD DEVIATION = .114
NUMBER OF POINTS = 14

C626

0.31	0.32	0.39	0.42	0.42	0.47	0.48	0.49	0.51	0.53	0.61
0.65	0.68	0.77	0.91	0.93	0.99	1.09	1.11	1.13	1.20	2.07

POPULATION 1 RANGES FROM .3 TO .549
MEAN = .43
STANDARD DEVIATION = .076
NUMBER OF POINTS = 10

Table 3 . Thermal Alteration Index data

Sample no.	Sample Type	Thermal Alteration Index (TAI)
C 539	Shale Source-rock (Type II) Carboniferous, Cumberland basin, Nova Scotia	2
C 717	Shale source rock (C539) + Shell Sol DMS + 100°C + 1500 psi	2^- to 2^+
C 730	Shale source rock (C539) + Shell Sol DMS + 150°C + clean with detergent	2^- to 2^+
C 540	Limestone (C540)source rock(Type II-III) Carboniferous, Cumberland basin, Nova Scotia	2^-
C 733	Limestone (C540) + Shell Sol DMS + 100°C + clean with detergent	2^-
C 626	Sandstone (C626) oil-soaked, Jean d'Arc basin	1^+
C 724	Sandstone(C 626) oil-soaked + Shell Sol DMS + 100°C + clean with detergent	1^- to 1^+

Table 4. Rock-Eval pyrolysis data

SAMPLE ID	S0 (mg/g) PRESENT HYDROCARBONS	S1 (mg/g) PRESENT HYDROCARBONS	S2 (mg/g) POTENTIAL HYDROCARBONS	T MAX °C	T.O.C. (WT%) LECO CARBON ANALYZER	O.P.I. S1/(S0+S1+S2)	H.I. 100*S2/TOC
CONTROL SAMPLE							
Cumberland shale (C539)	0.02	2.03	33.44	444	8.22	0.06	407
Cumberland Limestone (C540)	0.00	0.16	2.72	444	1.21	0.06	225
Hibernia I-46 oil-soaked sandstone 2506m (C626)	0.01	12.51	6.06	419	1.74	0.67	348
Hibernia K-18; shale 4835-4845m	0.02	6.77	12.02	439	6.30	0.36	191
South Tempest G-88; shale 3780-3790m	0.00	4.12	7.13	435	3.03	0.37	235
AFTER BOMB EXPERIMENTATION (washed with water)							
Shale(C539) + Exxsol D80 at 100°C and 1800 psi (C716)	0.00	3.92	31.95	447	7.87	0.11	406
Shale(C539) + Exxsol D80 at 150°C and 2000 psi (C721)	0.00	4.82	32.83	448	8.39	0.13	391
Shale(C539) + Shell sol DMS at 100°C and 1500 psi (C717)	0.00	9.44	31.90	446	8.77	0.23	364
Shale(C539) + Shell sol DMS at 150°C and 2000 psi (C720)	0.00	7.98	33.71	447	9.02	0.19	374
Limestone(C540) + Exxsol D80 at 100°C and 1500 psi (C715)	0.00	0.87	2.64	446	1.24	0.25	213
Limestone(C540) + Shell sol DMS at 100°C and 1500 psi (C719)	0.00	0.62	2.46	445	1.17	0.20	210
Sandstone(C626) + Exxsol D80 at 100°C and 1400 psi (C725)	0.00	1.48	1.40	422	0.48	0.51	292
Sandstone(C626) + Shell sol DMS at 100°C and 1500 psi (C724)	0.00	3.12	2.81	424	0.73	0.53	385

Table 4. Rock-Eval pyrolysis data

SAMPLE ID	S0 (mg/g) PRESENT HYDROCARBONS	S1 (mg/g) PRESENT HYDROCARBONS	S2 (mg/g) POTENTIAL HYDROCARBONS	T MAX °C	T.O.C. (WT%) LECO CARBON ANALYZER	O.P.I. S1/(S0+S1+S2)	H.I. 100*S2/TOC
AFTER CLEANING							
Shale(C539) + Exxsol D80(100°C) cleaned with detergent(Sunlight)(C731)	0.01	2.97	33.50	449	8.31	0.08	403
Shale(C539) + Exxsol D80(150°C) cleaned with detergent(Sunlight)(C732)	0.01	5.66	35.92	448	8.84	0.14	406
Shale(C539) + Shell sol DMS(100°C) cleaned with detergent(Sunlight)(C726)	0.07	9.70	31.16	445	8.07	0.24	386
Shale(C539) + Shell sol DMS(150°C) cleaned with detergent(Sunlight)(C730)	0.00	6.95	33.02	447	8.49	0.17	389
Shale(C539) + Shell sol DMS(100°C) cleaned with acetone (C727)	0.03	7.85	29.00	447	7.78	0.21	373
Shale(C539) + Shell sol DMS(100°C) cleaned with DCM (C728)	0.04	6.87	25.96	444	7.42	0.21	350
Shale(C539) + Shell sol DMS(100°C) cleaned with DCM and methanol(C729)	0.05	7.98	29.19	446	8.13	0.21	359
Limestone(C540) + Shell sol DMS(100°C) cleaned with detergent(Sunlight)(C733)	0.00	0.67	2.62	446	1.13	0.20	232
Sandstone(C626) + Shell sol DMS(100°C) cleaned with detergent(Sunlight)(C724)	0.00	4.55	3.01	420	0.89	0.60	338
Sandstone(C626) + Exxsol D80(100°C) cleaned with detergent(Sunlight)(C725)	0.00	1.87	1.58	420	0.59	0.54	268

TABLE 5. SOXHLET EXTRACTION DATA

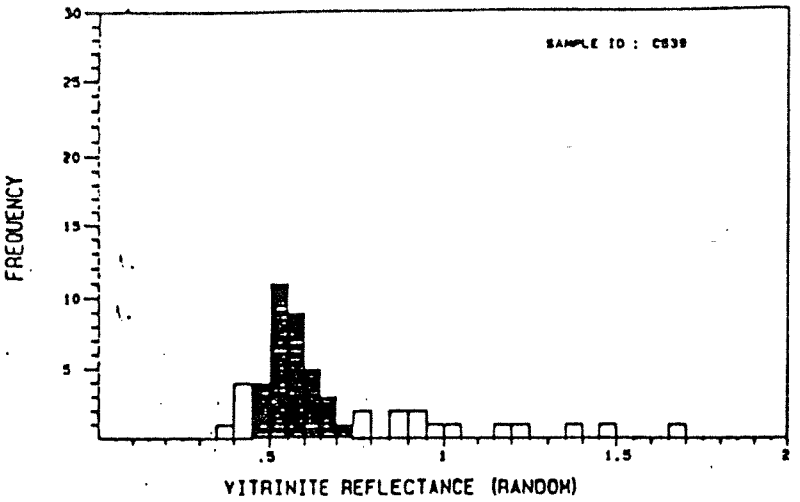
GEOFUEL SAMPLE I.D.	SAMPLE I.D.	T.O.C. WT %	Extract (ppm)	mg extract/ g rock	S1 mg/g
88G-031-C539	Shale, Cumberland Basin, Nova Scotia	8.22	2927	2.927	2.03
88G-031-C716	Shale (C539) + Exxsol D80 : 100° C & 1800 PSI	7.87	4088	4.088	3.92
88G-031-C721	Shale (C539) + Exxsol D80 : 150° C & 2000 PSI	8.39	9420	9.420	4.82
88G-031-C717	Shale (C539) + Shell Sol DMS : 100° C & 1500 PSI	8.77	12200	12.20	9.44
88G-031-C720	Shale (C539) + Shell Sol DMS : 150° C & 2000 PSI	9.02	4973	4.973	7.98
88G-031-C730	Shale (C539) + Shell Sol DMS : 150° C, detergent clean	8.49	23800	23.80	6.95
88G-031-C540	Limestone, Cumberland Basin, Nova Scotia	1.21	17740	17.74	0.16
88G-031-C715	Limestone (C540) + Exxsol D80 : 100° C & 1500 PSI	1.24	3074	3.074	0.87
88G-031-C719	Limestone (C540) + Shell Sol DMS : 100° C & 1500 PSI	1.17	862.2	0.862	0.62
88G-031-C733	Limestone (C540) + Shell Sol DMS : 100° C, detergent clean	1.13	1545	1.545	0.67
88G-031-C626	Hibernia I-46 Oil-soaked sandstone	1.74	16550	16.55	12.92
88G-031-C714	Sandstone (C626) + Exxsol D80 : 100° C & 1400 PSI	0.48	6500	6.500	1.48
88G-031-C718	Sandstone (C626) + Shell Sol DMS : 100° C & 1500 PSI	0.73	25820	25.82	3.12
88G-031-C724	Sandstone (C626) + Shell Sol DMS : 100° C, detergent clean	0.89	9071	9.071	4.55
88G-031-C623	Hibernia K-18 shale 4835-4845m	6.30	14330	14.33	6.77

TABLE 6. LIQUID CHROMAROGRAPHIC DATA

GEOFUEL SAMPLE I.D.	SAMPLE I.D.	P/N WT %	AROMATICS WT %	NSO's WT %	Wt% HC
B8G-031-C539	Shale, Cumberland Basin, Nova Scotia	46.86	32.67	15.18	79.53
B8G-031-C540	Limestone, Cumberland Basin, Nova Scotia	1.32	0.85	*	-
B8G-031-C733	Limestone (C540) + Shell Sol DMS : 100° C, detergent clean	0.00	0.00	0.00	
B8G-031-C626	Hibernia I-46 Oil-soaked sandstone	34.59	14.70	6.79	49.29
B8G-031-C724	Sandstone (C626) + Shell Sol DMS : 100° C, detergent clean	35.68	19.10	3.02	54.78

* inaccurate weight due to salts from column

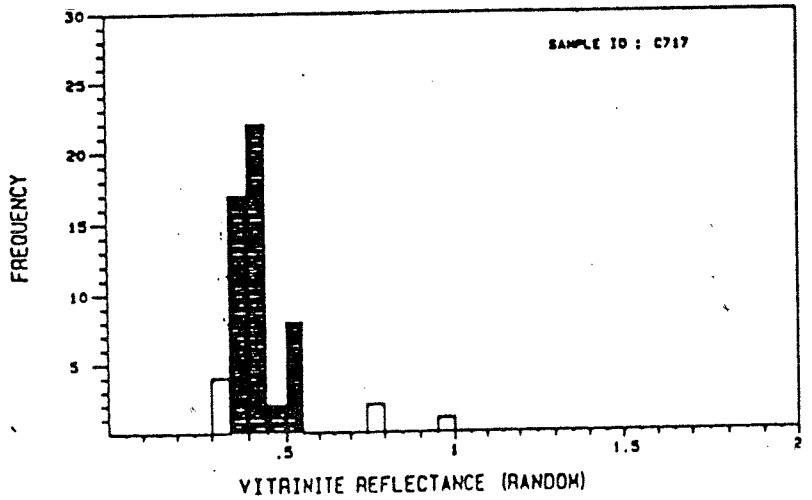
Type II shale source rock (without oil-mud)



R_o (mean) = 0.56

Std Dev. = 0.07

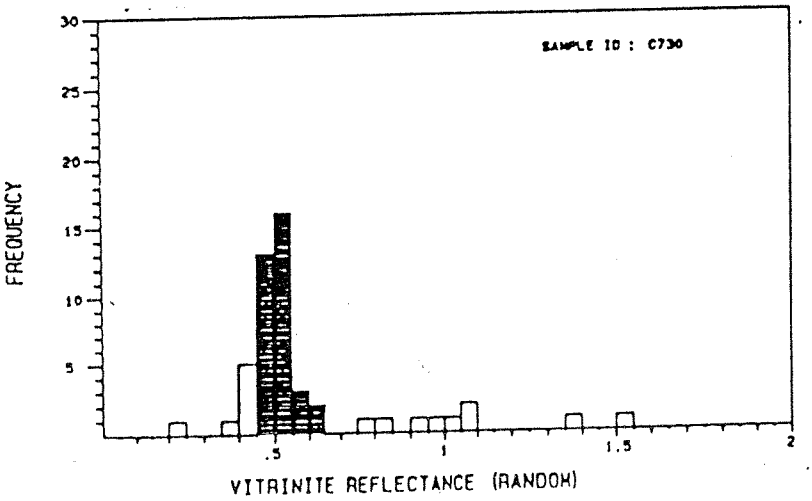
Shale SR (C539) + Shell Sol DMS after bomb experiment



R_o (mean) = 0.42

Std. Dev. = 0.05

Shale SR (C539) + Shell Sol DMS + clean with detergent

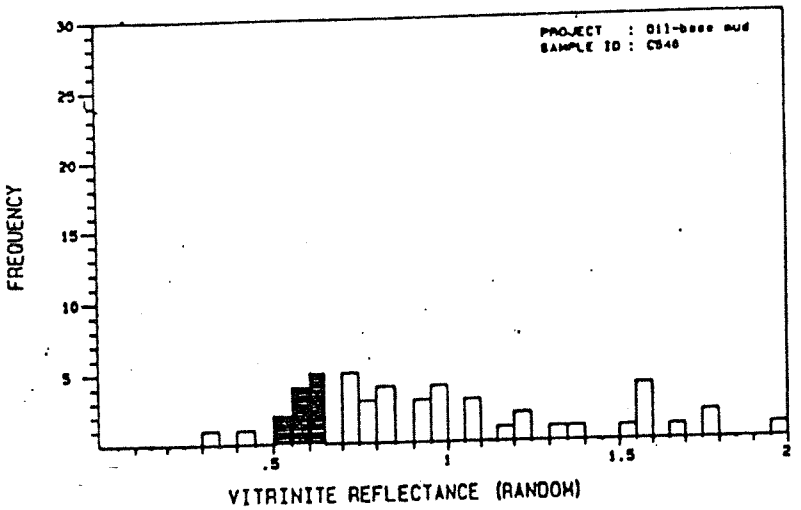


R_o (mean) = 0.51

Std. Dev. = 0.05

Fig. 1.

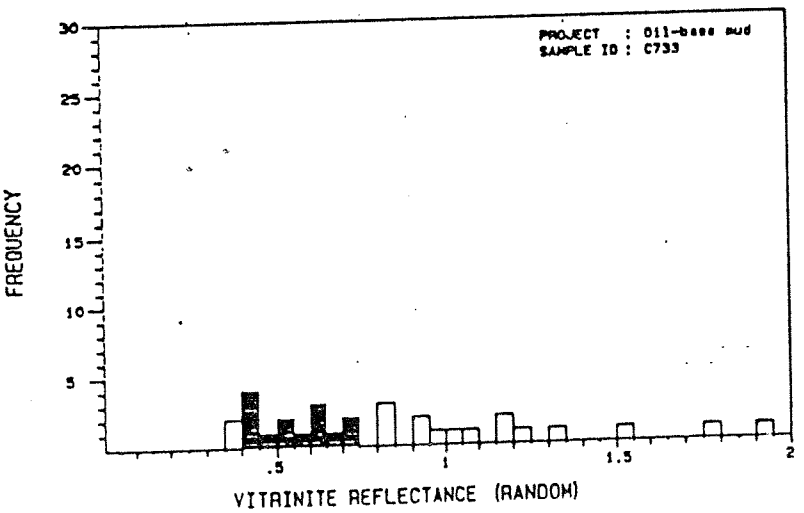
Type II-III Limestone source rock without oil-mud



R_o (mean) = 0.58

Std. Dev. = 0.04

Limestone (C540) + Shell sol DMS + clean with detergent

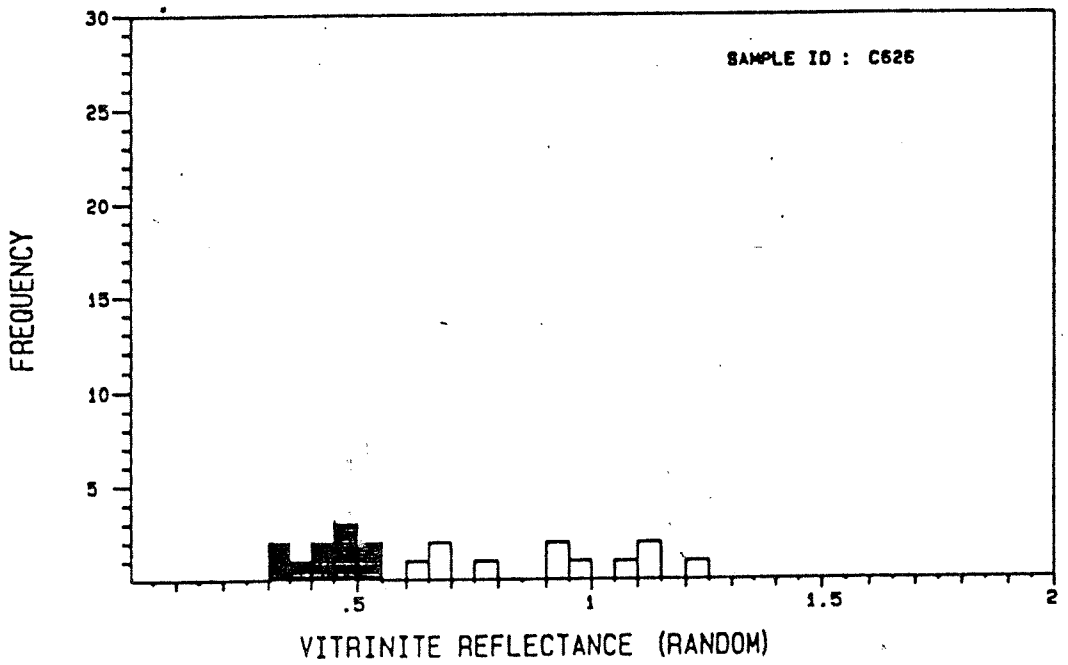


R_o (mean) = 0.55

Std. Dev. = 0.11

Fig. 1

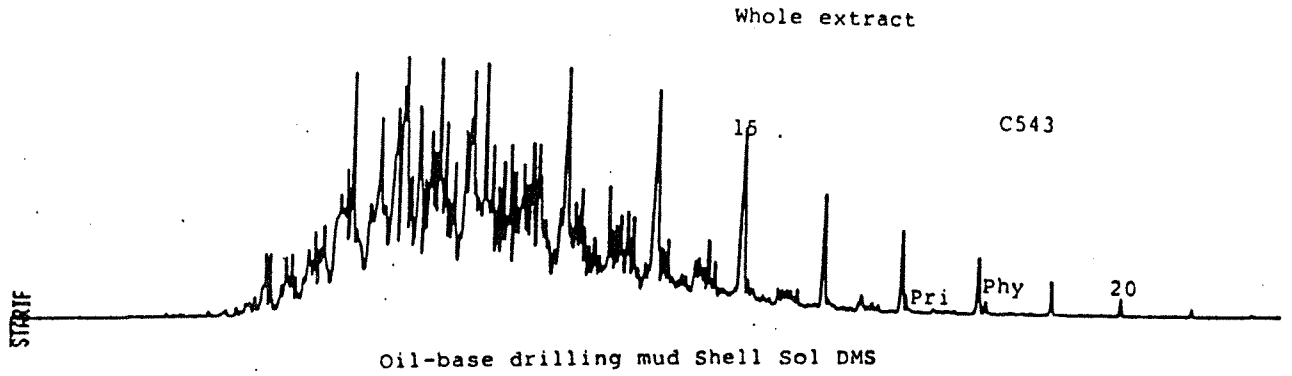
Oil-stained sandstone without oil-base mud



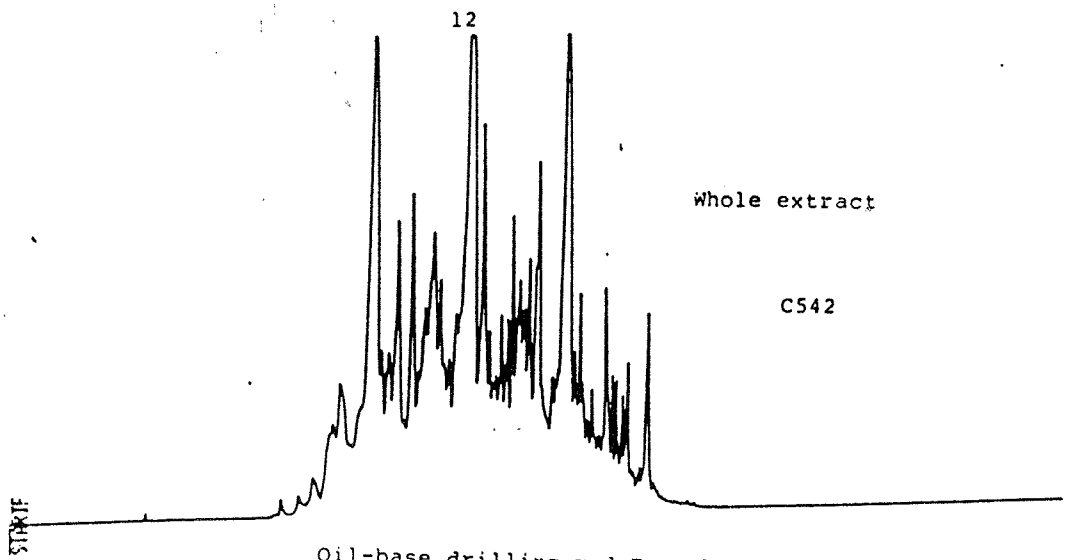
R_o = 0.43

Std.Dev.=0.08

Fig. 1.

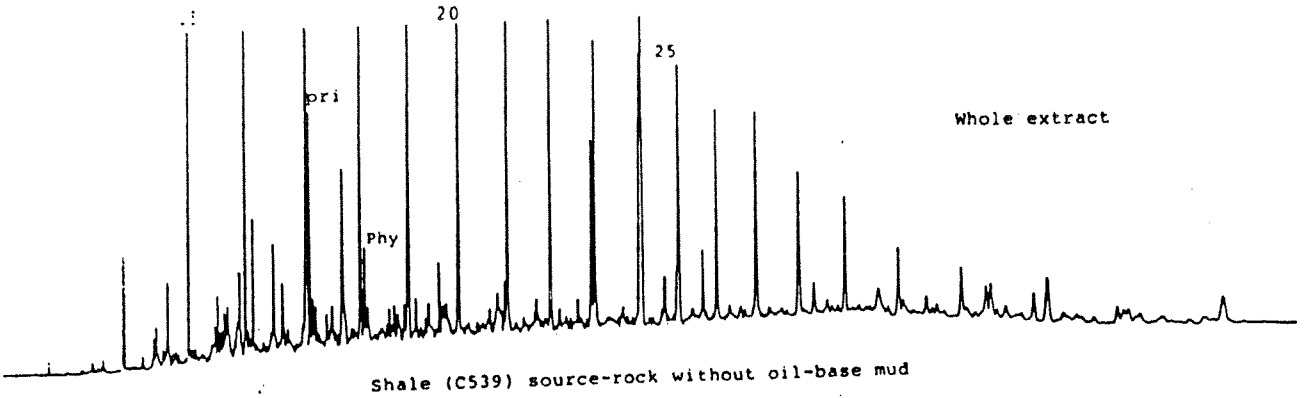


Oil-base drilling mud Shell Sol DMS

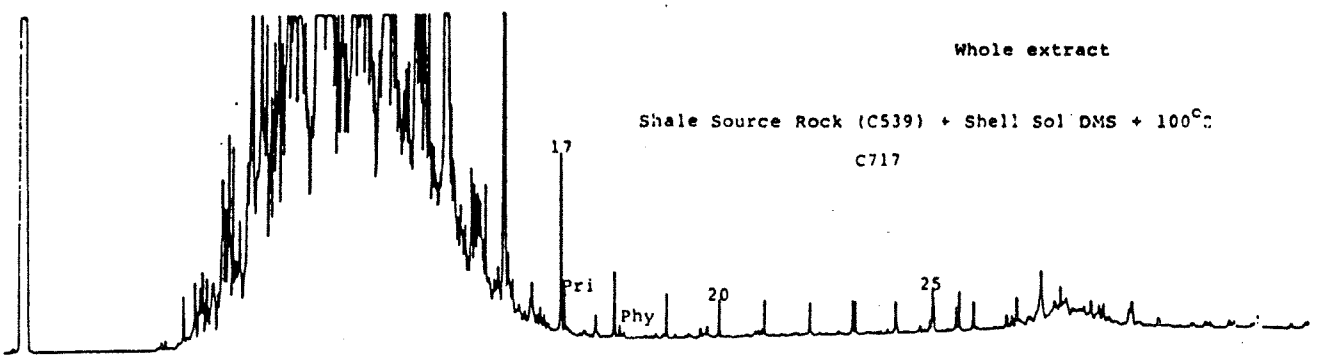


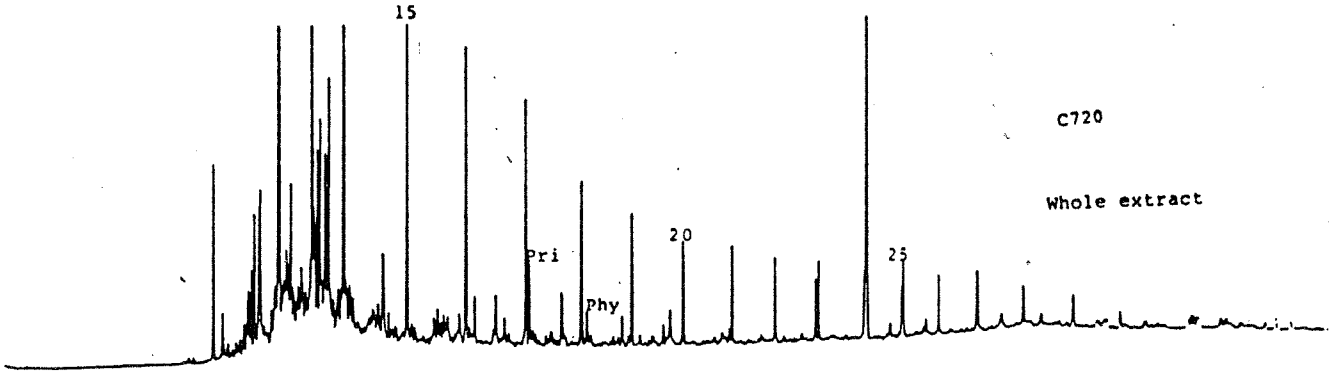
Oil-base drilling mud Exxsol D80

Fig. 2a.

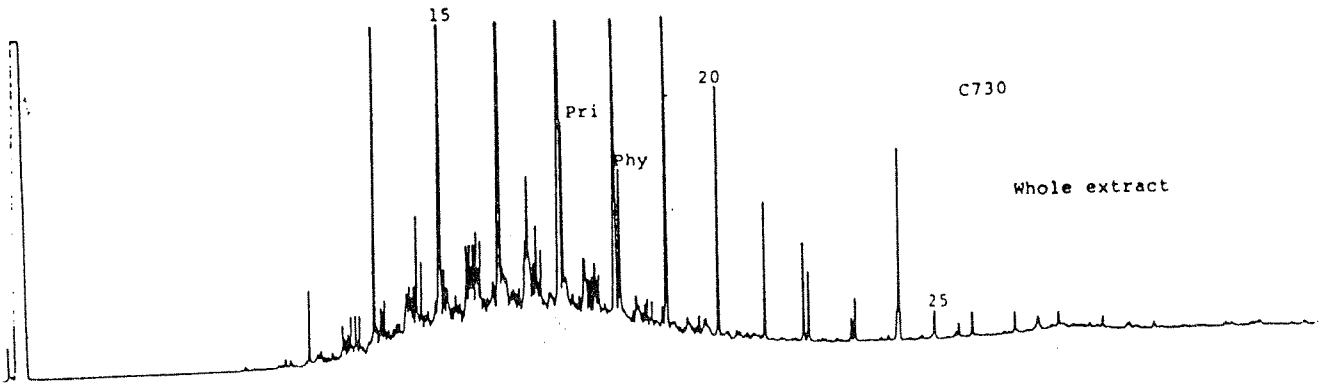


Shale (C539) source-rock without oil-base mud



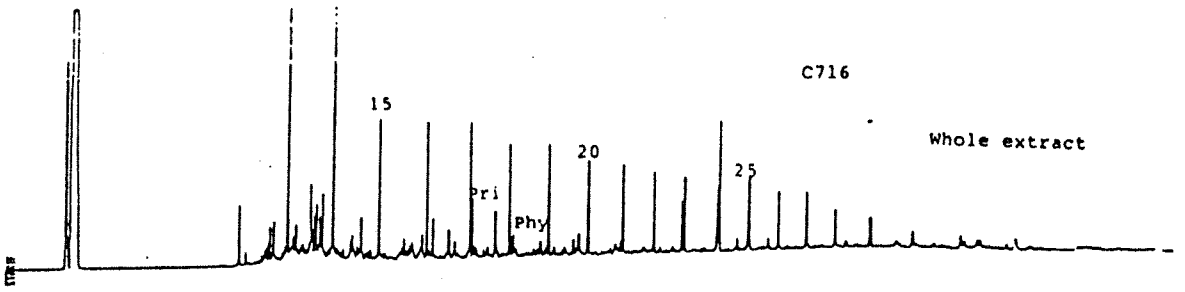


Shale Source Rock (C539) + Shell Sol DMS + 150°C

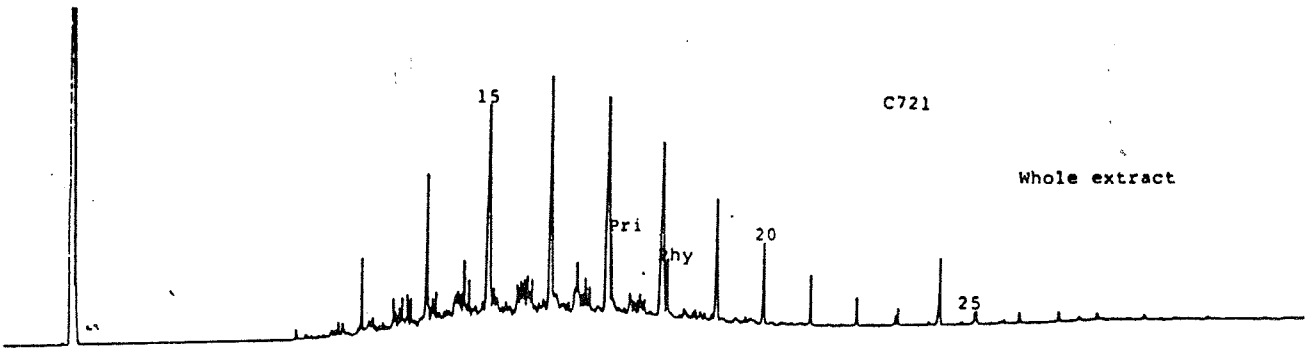


Shale Source Rock (C539) + Shell Sol DMS + 150°C + Cleaned with detergent

Fig. 2b.

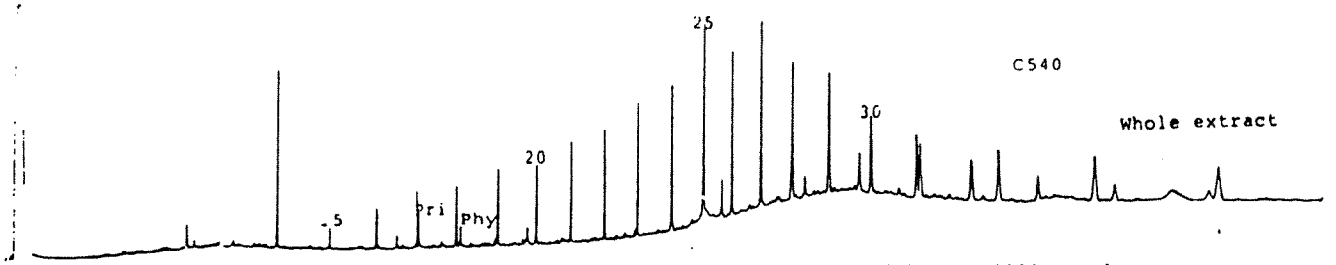


Shale (C539) source rock + Exxsol D80 + 100°C

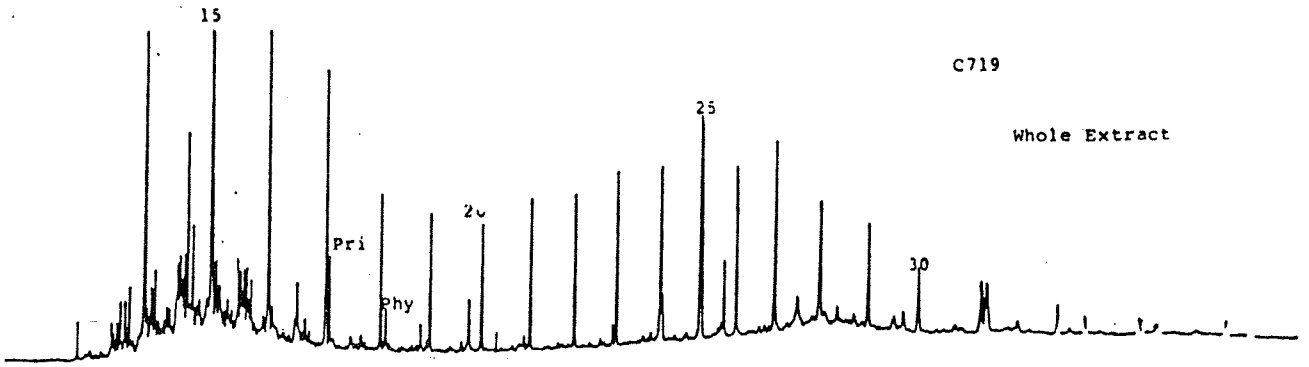


Shale Source Rock (C539) + Exxsol D80 + 150°C

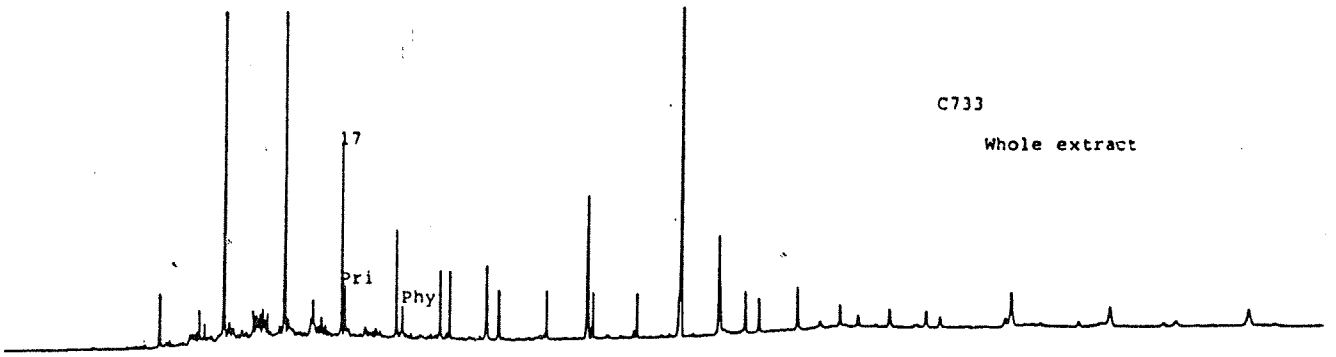
Fig. 2b.



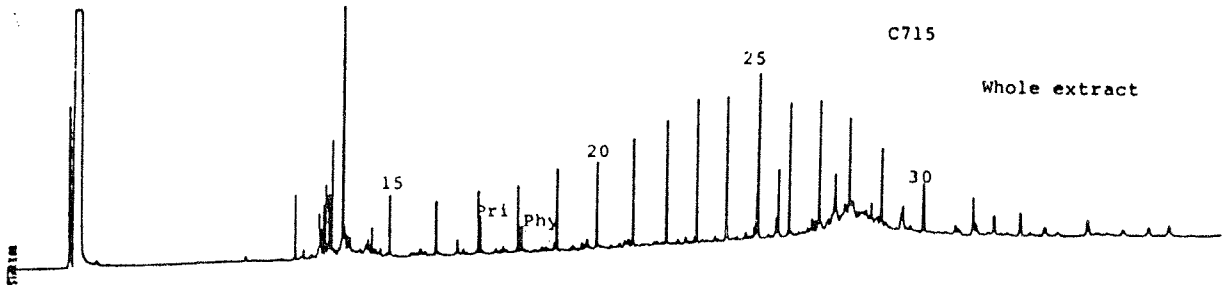
Limestone source rock (C540) without Oil-base drilling mud



Limestone source rock (C540) + Shell Sol DMS + 100°C

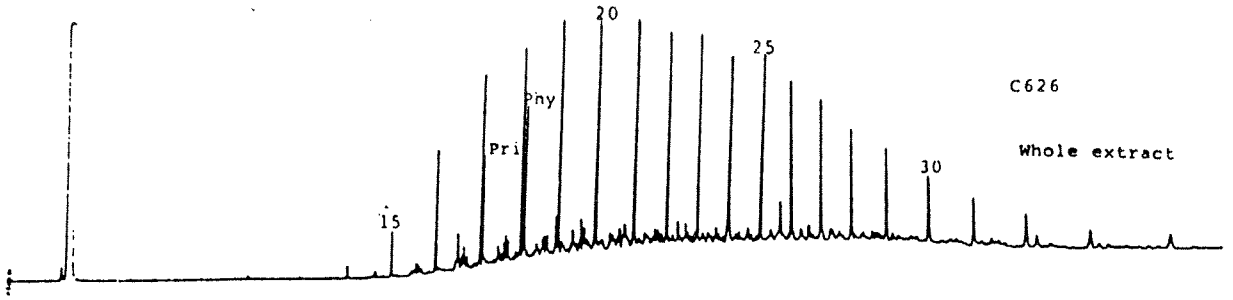


Limestone source rock (C540) + Shell Sol DMS + 100°C + cleaned with detergent

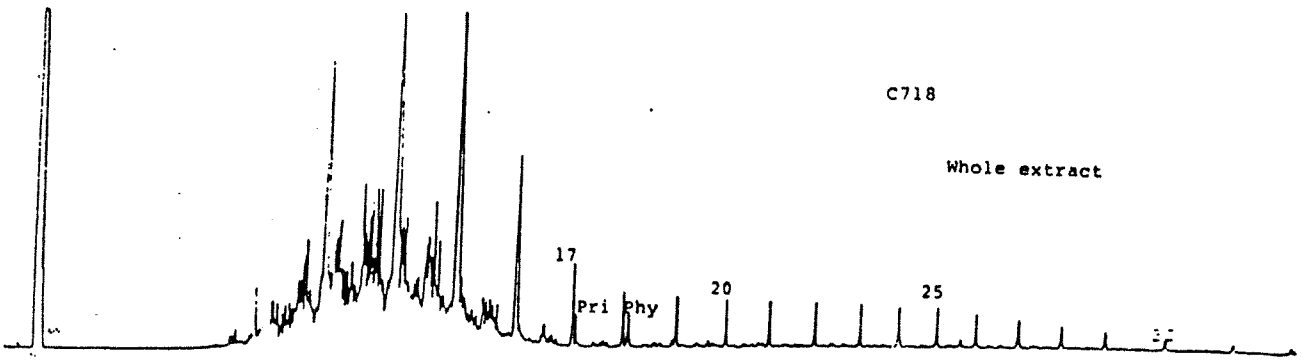


Limestone source rock (C540) + Exxol D80 + 100°C

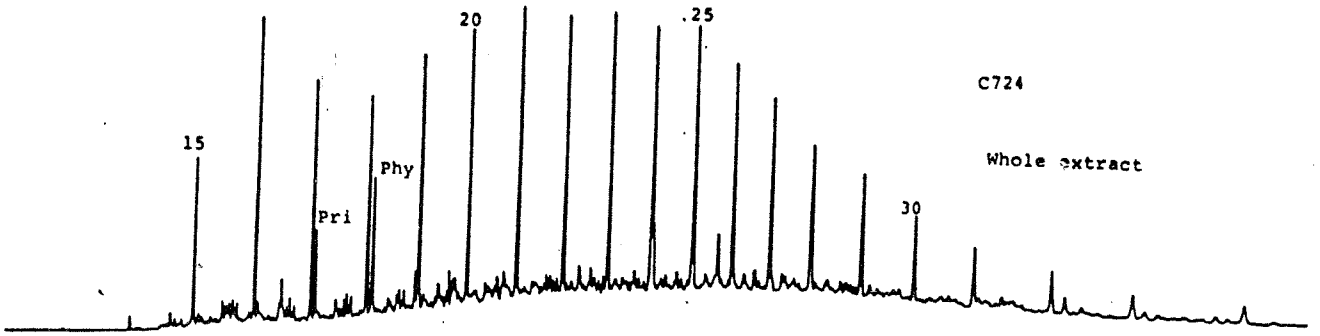
Fig. 2c.



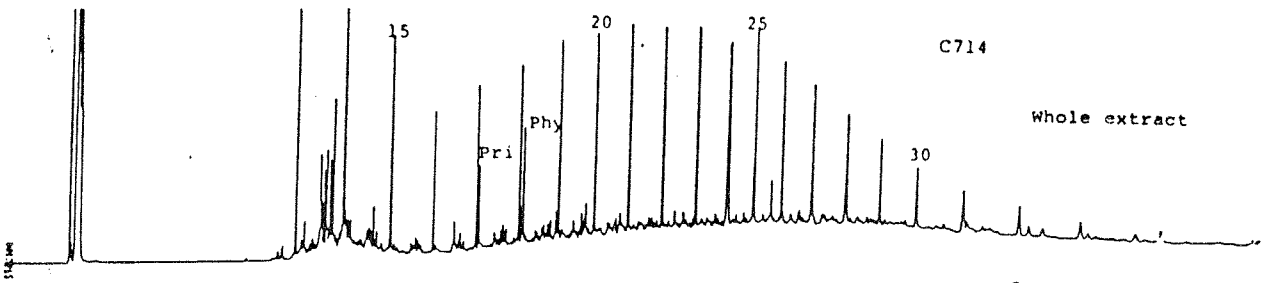
Sandstone (oil-soaked)(C626) without any Oil-base drilling mud



Sandstone (oil-soaked)(C626) + Shell Sol DMS + 100°C



Sandstone (oil-soaked)(C626) + Shell Sol DMS + 100°C + Cleaned with detergent



Sandstone (oil-soaked)(C626)+ Exxsol D80 + 100°C

Fig. 2d

OIL-BASE DRILLING MUD RESEARCH - PHASE II

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For

Scientific Authority, L. R. Snowdon
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March 30, 1990

LIST OF TABLES & FIGURES

Tables

Figures

ABSTRACT

The phase II research project initiated by ISPG (GSC), Calgary, Alberta in order to (a) further investigate the problems documented by Phase I research of this project, (b) evaluate the effect on natural sample and compare these effects with that of the experimental samples. For this purpose, original shale, limestone, and oil-stained sandstone and two base oils (Shell Sol DMS and Exxsol D80) from Phase I research, a different kerogen type shale source rock (cuttings sample from Terra Nova K-08), and eighteen samples (nine each) from two different wells were selected for both bomb experiment and normal analysis. All these samples are analyzed by organic geochemical analytical techniques like TOC determination, Rock-Eval pyrolysis, vitrinite reflectance, bitumen extraction, liquid chromatography, and gas chromatography.

Phase II research further corroborated the findings of Phase I study, which showed a considerable impact on the organic geochemical properties used in Petroleum Geochemistry Program such as: fluorescence to detect oil stain, vitrinite reflectance and Tmax (Rock-Eval pyrolysis) for maturity determination, total organic carbon/ hydrogen index-oxygen index to evaluate source potential, detect stains for maturity or migration or oil shows, gas chromatographic fingerprinting to detect oil type. The present analytical data suggest suppression of vitrinite reflectance and Tmax values, decrease or increase in total organic carbon content, increase or decrease in oil-stain detection and migration parameters, and complete or partial obliteration of gas chromatographic fingerprinting. Neither of the cleaning methods can regain original values of the baseline samples.

Phase II research indicates samples recovered from oil-base drilled wells should be viewed with extreme caution before geochemical evaluation and interpretation and oil shows in the exploratory well can be missed or over emphasized. Future research on various organic geochemical parameters taking actual samples was recommended.

INTRODUCTION

Administrative Aspect

This research project is the Phase II study of earlier work (Phase I - Oil-base Drilling Mud Management) conducted by Geofuel Research Inc. of Sydney, Nova Scotia during financial year of 1988-1989. Phase I research project was initiated in 1988 by Dr. L. R. Snowdon, Geochemistry Group, Institute of Sedimentary and Petroleum Geology (GSC), Calgary, Alberta. This project was initiated to determine the influence of some specific base oils (commonly used in drilling with oil-base mud) on various organic geochemical parameters used for source rock evaluation, maturation, fingerprinting for characterizing crude oils. During that time, as a scientist of Geofuel Research Inc., I used a high-pressure bomb experiment for the research project, to simulate drilling conditions and complete various organic geochemical analysis, and finally submitted a report containing all these data (Mukhopadhyay and Birk, 1989: DSS file no. 03AF.12193-8-1067, serial no. 23294-7-1067/01-SG). Based on results of Phase I, Scientific Authority of the project and GEEBOB Committee decided to study further on these aspects in more detail in Phase II. Accordingly, Global Geoenergy Research Ltd. was requested to submit a proposal on November 3, 1989 (DSS file XSG 89-00208- 605-A) by the Department of Supply and Services Canada from Edmonton at the initiation and formulation by the Institute of Sedimentary & Petroleum Geology (GSC), Calgary, Alberta. Accordingly, Global Geoenergy Research Ltd. submitted the research proposal in November 4, 1989. The proposal was accepted by DSS, Edmonton, Alberta on November 23, 1989. The work started from December 1, 1989. Ian Sinclair of CNOPB and Bill Smith of NSDME, on request sent oil-stained sandstone and shale/limestone source rocks from Newfoundland and Nova Scotia. S. Creaney of ESSO Canada, Williamson of Technifluid, and P. Nederlof of Shell Canada provided base oil samples for this research.

Scientific Aspect

Oil-base mud, a low toxic drilling fluid, operated in a continuous liquid phase of oil, is becoming increasingly popular as a drilling fluid throughout the world, especially in the offshore areas of Canada, Norway, England, Middle East etc. Oil-base drilling muds provide less borehole cost, increased drilling rate, better quality cores, and prevent caving. Oil-base drilling muds are useful in drilling overpressured and high temperature formations especially associated with Rock-Salt, anhydrite, and gypsum (Voratuhr and Chilingarian, 1983; Brown, 1988).

However, like other organic contaminants (Snowdon and Powell, 1978) oil-base muds coat the cuttings with oil (Swanson, 1981). Moreover, the base oils can be cracked to low molecular weight hydrocarbons due to elevated temperatures during drilling. These newly-formed hydrocarbons can penetrate the in situ reservoir hydrocarbons or source rock bitumens and change their characteristic composition. It is therefore, anticipated that cuttings samples from a drilled borehole using oil-base mud could cause a serious threat to an organic geochemical program and the detection of oil shows, if proper measures are not taken.

During the Phase I experiments using two specific base-oils (Shell Sol DMS and Exxsol D80 - commonly used in oil-base drilling mud) indicated possible changes in vitrinite reflectance, oil-stain fluorescence fingerprinting, change in source-rock characterization, migration parameters, and gas chromatographic fingerprinting. These changes could not be improved by cleaning with commonly used liquids (water and detergent as suggested by Brown, 1988) or various organic solvents. Normal short time cleaning by water or detergent do not improve the quality. On the contrary, in limestone and sandstone, the cleaning agent released the in-situ bitumen, which is possibly dissolved by the oil-base mud.

Phase II of this research was therefore conducted as a second stage to re-examine and repeat the original high-pressure bomb experiments and to establish a statistically significant data set. Moreover, some blank high pressure bomb

experiments with the original shale samples and water at two temperatures (100 and 150°C) were planned to check the analytical error. As proposed in the Phase I final report, several samples of two comparable nearby wells, which have similar geological horizons at the approximately similar depths but one drilled with oil-base mud and the other drilled with water-base mud, were geochemically fingerprinted (eg. maturation profiles based on vitrinite reflectance and source-rock and migration characteristics by Rock-Eval pyrolysis. In addition, cleaning methods were planned to be improved or some new cleaning method was adopted. The Phase II research was therefore, conducted to evaluate the influence of these two base-oils on the source-rock characterization, maturation, and oil-stain detection. Most of the bomb experiment samples were analyzed before and after cleaning with water, detergent or heavy liquid ($ZnBr_2$ in this case).

SAMPLES AND ANALYTICAL METHODS

Samples

Shale source rock was once again collected from borehole AP 84 (depth: 101.84-121.80m) of Stellarton Basin (printing mistake in Phase I where it was cited as Cumberland Basin), Nova Scotia. Limestone source rock (same as that of Phase I) was collected from borehole SH-94 (depth: 154.15 to 156.38m) of Cumberland Basin. Oil-stained sandstone (same as that Phase I) was collected from borehole Hibernia I-46 (depth: 2506-2508m) of Jeanne d'Arc Basin, Newfoundland. All three are core samples. One cuttings sample (Tithonian shale) from borehole Terra Nova K-08 from the Jeanne d'Arc Basin (depth: 3105 to 3165m) was selected for new bomb experiment. Nine samples each (up to a depth 3715m) from borehole Terra Nova K-08 (drilled with water-base mud) and Terra Nova C-09 (drilled with oil-base mud) were collected for study of comparable maturation profile and Rock-Eval pyrolysis. All these samples from these two boreholes were selected in consultation with the Scientific Authority (Dr. L. R. Snowdon), K. D. McAlpine of AGC, Dartmouth, Nova Scotia, Giles Morrell of COGLA, Ottawa, F. Altebaeumer of Petro-Canada, Calgary, Alberta, S. Creaney

of ESSO Canada, Calgary, Alberta. Core samples were crushed to less than 2 to 3 mm in size in order to simulate normal cuttings sample available during drilling.

Analytical Methods

Qualitative fluorescence of shale, limestone, and sandstone samples before and after the bomb experiments was determined using a Fluoroscope of Spectroline Model No. BLF6.

Rock-Eval pyrolysis of all bomb experiment samples was done using a Delsi Rock-Eval II with a TOC module (Espitalie et al., 1985). Rock-Eval pyrolysis data of eighteen samples from Terra Nova K-08 and C-09 wells were done using a Oil Show Analyzer at Esso Resources, Calgary, Alberta. The data from these 18 samples were received from S. Creaney of Esso Canada.

Kerogen isolation was done using 4N HCl and 48% HF. However, most of the vitrinite reflectance was measured using whole rock polished pellets. Vitrinite reflectance was measured using Zeiss Universal Microscope and Zeiss six-in one standard (0.3 to 1.68% Ro). The microscope was fitted with a computer program to recover the vitrinite reflectance histogram.

Bitumen was soxhlet extracted using dichloromethane. Saturate, aromatic, and NSO compounds were separated after deasphalting with hexane and using column chromatography with hexane, benzene, benzene:methanol (50:50) in silica:alumina column (1:1). Gas chromatography was done using a Varian 3400 GC equipped with 50m X 0.25 mm i.d. methyl silicone fused silica capillary column from Quadrix (007 series, bonded phase with 0.5 micron film thickness). The temperature program for gas chromatography was as follows: initial temperature 40°C (for 2 minutes), heating rate of 10°C/minute to a final temperature of 350°C (for 20 minutes).

The high pressure bomb experiment was done using a 300ml Alloy Steel Parr Pressure vessel fitted with pressure gauge, heating mantle, and rupture disc without stirrer. A measured amount of sample, base oil, and water (generally in the

proportion of 100gm sample: 50ml base oil: 12.5ml water) was first put inside the reactor vessel. The vessel was sealed and checked for leaks using helium pressure. The reactor vessel was subjected to pressure of 1500 psi with helium. The pressure vessel was placed inside a heating mantle fitted with a controller and a thermocouple. The reactor vessel was slowly heated (approximately 1.5°C/min) till the required temperature (100 or 150°C) was reached. However, in most cases, the temperature could not kept exactly at 100 or 150°C: it exceeded the required temperature by several degrees. The reaction vessel was then kept for 3 to 4 hours to cool down to room temperature after shutting down the heating. Before opening, pressure (between 1500 to 2000 psi) was slowly vented off and samples were removed. Bomb experiments were done at two temperatures 100 and 150°C using shale source rocks from Stellarton Basin and Jeanne d'Arc Basin, limestone source rock from Cumberland Basin, oil-stained reservoir sandstone from the Jeanne d'Arc Basin, and two base oils. A total of twelve experiments were performed using three source rocks and one reservoir rock. The small bomb restricted sample size and thus in order to obtain sufficient material for the various cleaning and analytical tests, six repetitive experiments were performed using the same sample temperature and pressure conditions.

Cleaning

As in Phase I, all samples after the bomb experiment, were washed with water on a 325 mesh screen with a sprayer to achieve a quality of washed cuttings recovered from normal drilling procedures. These samples were then soaked in Sunlight detergent solution for 1/2 hour and were later washed with water through a 325 mesh screen with sprayer. Some of the samples were mixed with heavy liquid ($ZnBr_2$: density 2.00 gm/cm^3), which were centrifuged. The supernatant was taken out and the residue (samples) were cleaned with water.

RESULTS AND DISCUSSION

Experimental

Table 1 illustrates the details of baseline samples and bomb experiment samples before and after cleaning with water, detergent, and Zinc Bromide. The right column of Table 1 indicates the exact temperatures and pressures achieved during the experiments for various samples. Maximum temperature recorded is 108°C (for the 100°C experiment) and 160°C (for the 150°C experiment). The maximum pressure recorded for 100°C is 1896 psi (129 bar) and 2080 psi (142 bar) for 150°C. The initial temperature and pressure was 25°C and 1500 psi for all experiments. The variation in temperature and pressure during and after the bomb experiment was possibly related to leaks and generation of different compounds during heating.

Fluorescence

Table 2 shows the fluorescence data of baseline and experimental samples. The results are comparable to Phase I analysis. Similar to Phase I, shale source rock from Stellarton Basin (marked as Cumberland Basin in Phase I) and limestone source rock from Cumberland Basin showed a slight increase in fluorescence intensity. Samples L333-2 and L333-3 (blank experiment) showed some increase in fluorescence intensity. This is possibly due to change in the intensity of the fluorophores in response to low temperature catagenesis. Oil-stained sandstone, in general, showed increase in fluorescence intensity. However, some parts of the samples (L339-2 and L339-4) showed blue to violet fluorescence instead of yellow-brown fluorescence. This is possibly because of the change in chemical composition during the bomb experiment and cleaning. The shale source rock of the Jeanne d'Arc Basin showed similar low fluorescence intensity and little change like the shale and limestone source rock from Nova Scotia.

Rock-Eval pyrolysis

Table 3 shows the Rock-Eval pyrolysis data of experimental and natural samples. In natural samples, no S3 fraction is reported because these samples were analyzed by an oil-show analyzer. Similar to the Phase I study, shale source rock samples (L333-1 to L333-12) are least affected by oil base mud experiments compared to limestone and sandstone. Total organic carbon, in contrast to Phase I study , is partially reduced (from 5.21 to 4.61%). However, in most cases, these data are within the experimental error. S2, S3, and Tmax data did not show any remarkable changes for the L333 samples. Anomalous S3 results for sample L333-6 (L333-1 + Shell Sol DMS + 100°C + clean with $ZnBr_2$) suggests partial oxidation during cleaning with $ZnBr_2$. Similar to the Phase I study, the S1 fraction and Production Index (PI = S1/[S1+S2]) increased in L333 samples. Shale samples of K-08 after the bomb experiment show remarkable changes in S1 and PI values without much change in Tmax, S2 and S3 values. Cleaning did not improve the results. Blank bomb experiment samples (L333-2 and L333-3), however, also show slight decrease in S1 fraction. Both limestone and oil-stained sandstone samples show a moderate to dramatic decrease in TOC content and S1 fraction. Oil-stained sandstone also showed a dramatic decrease in S2 content. Limestone samples show an abrupt increase in PI values. The abnormal Tmax and S2 values in bomb experiment samples cleaned with $ZnBr_2$ suggest partial cleaning of the salt and production of a double S2 peak. Compared to these artificial experimental samples, the natural samples (drilled with oil-base mud) of C-09 well show anomalously high S0, S1, PI and a suppression of Tmax values (below 2335 m) compared to K-08 samples (drilled with water base mud).

Vitrinite Reflectance

Vitrinite reflectance of the baseline shale/limestone samples from the Stellarton/Cumberland Basin before and after the bomb experiments are shown in Table 2 along with the fluorescence data. Table 2 indicates a suppression of vitrinite reflectance in the shale samples (especially L333-4 to L333-6) between 0.12 and 0.06 % Ro. Compared to baseline samples (L333-1), cleaning does not reverse the lowering of

vitrinite reflectance. On the other hand, the limestone source rock after bomb experiments with Shell Sol DMS did not show any suppression of vitrinite reflectance with respect to the baseline sample (L336-1). Figure 1a shows the reflectance histogram of all these samples. However, the pattern of the histogram L336-1 and L336-3 showed some changes. Table 4 shows the influence of the oil-base mud on vitrinite reflectance by comparing a cuttings sample (of borehole K-08) using artificial bomb experiments and cleaning and a natural suite of samples from two boreholes (Terra Nova K-08 and C-09). In the artificial bomb experiment, suppression of vitrinite was observed to those samples, which are associated with Shell Sol DMS oil. Exxsol D80, as in the Phase I experiment did not show much effect. The suppression of vitrinite reflectance could not be reversed by cleaning with water or detergent. However, cleaning with $ZnBr_2$ definitely improved the data. Natural samples from K-08 and C-09 (Table 4) show that between 945 and 1305m, there is no difference in vitrinite reflectance in the two wells. Between 1555 and 2335m, samples from C-09 well (oil-base mud) show higher reflectance than K-08 samples, possibly because of partial oxidation in samples, which did not show any visible microscopic oxidation features. Beyond 2745m, suppression of vitrinite reflectance was observed in all samples from C-09 well. The suppression of vitrinite reflectance in these depths corroborate the artificial bomb experiment samples from 3105 to 3165m depth. The reflectance histograms for all the artificial (Figure 1b) and natural samples show a similar effect. A plot of vitrinite reflectance versus depth (m) for samples from both K-08 and C-09 wells (Figure 2) show the corresponding values of reflectance from various depths.

These data on vitrinite reflectance when compared with the Tmax values, it showed that there is no effect of oil-base mud on Tmax values for the artificial samples. The abnormal Tmax value for K-08-7 indicate incomplete cleaning of $ZnBr_2$ which formed two S2 peaks affecting both Tmax and Hydrogen Index values. Compared to artificial samples, natural samples, surprisingly, show a suppression of Tmax values and thereby correspond to vitrinite reflectance data. Similar to vitrinite

reflectance data, higher Tmax values are observed in C-09 well up to a depth of 2335m. Below 2335m, most of the samples (except C-09-9) show lower Tmax values compared to K-08 samples of corresponding depths. Therefore, unlike the Phase I study (which evaluated only bomb experiment samples), Tmax values can be affected by oil-base mud for natural samples possibly because natural samples stay within the plastic container with oil-base mud for a longer period of time than the experimental samples.

Bitumen Extraction and Liquid Chromatography

Tables 5 and 6 illustrate the variability of twenty two bitumen extraction (in ppm and extract/TOC) and liquid chromatography data. In contrast to the Phase I study, the shale source rock (L333-1 to L333-12) did not show any marked changes in bitumen extract or liquid chromatography data. Similar to Phase I experiments, oil-stained sandstone samples show a remarkable decrease in bitumen extract. However, liquid chromatographic fractions did not show any marked variations. These data support the explanation that cracked low molecular weight compounds generated during the experiment, act as a solvent to wash away the bitumen during cleaning with water or detergent. In contrast to the Phase I study, limestone source rock (samples L336-2 to L336-3) and cuttings shale samples (K-08-2 to K-08-7) after the bomb experiment with oil-base muds, show an anomalous increase in bitumen content (in ppm) and saturate fraction compared to the baseline samples (L336-1 and K-08-1).

Gas Chromatography

Figure 2 shows twenty-four gas chromatograms of base oils (taken from phase I experiment), shale/limestone source/limestone source rocks, and oil-stained sandstones with or without the experiment with base-oils and before/after cleaning with water, detergent, and $ZnBr_2$. Table 6 shows pristane/phytane, CPI, pristane/nC_{17}, and ph/nC_{18}. Table 7 shows the relative percentages of isoprenoid hydrocarbons determined from gas chromatography. Figure 2a shows the

distribution of the hydrocarbons of the two base oils. As discussed in the Phase I study, the gas chromatograms of the two base oils indicate that Exxsol D80 base oil contains compounds between C_{10} and C_{14}, and Shell Sol DMS contains compounds between C_9 and C_{21} (Figure 2a).

Figure 2a shows the seven gas chromatograms of the shale source rock (before and after the bomb experiment) from the Stellarton Basin. These gas chromatograms. In contrast to the whole oil chromatograms of the Phase I study, the saturate fraction of the extract did not show any dramatic changes between baseline sample (L333-1) and bomb experiment samples (after cleaning with water, detergent, and $ZnBr_2$). However, the peak of the chromatograms changed from C_{13} to C_{15} or C_{16}. Pristane/phytane and pristane/nC_{17} are reduced in the experimental samples compared to baseline (L333-1) or blank (L333-2 and L333-3) samples which suggest preferential loss of pristane over phytane or nC_{17} during the experiment.

Figure 2c shows three gas chromatograms of the limestone source rock (before and after the bomb experiment) from the Cumberland Basin. The gas chromatogram of the limestone baseline sample indicates the presence of mostly n-alkanes between C_{13} to C_{32}. On the other hand, both samples after the bomb experiment (L336-2 and L336-3) show definite loss of part of the high molecular weight compounds compared to the baseline samples (L336-1); a similar effect was observed in Phase I analysis. This indicates that the base oil acted as a solvent during the experiment. The heavier compounds are extracted out during cleaning.

Figure 2d shows five gas chromatograms from the oil-stained sandstone (before and after the experiment) from the Jeanne d'Arc Basin. Compared to the chromatograms in Figures 2b and 2c, samples L339-2 to L339-5 showed the most significant effect of these two base oils. Compared to the baseline sample (L339-1), Shell Sol DMS yielded a larger affect than that of Exxsol D80. The stained sandstone plus Shell Sol DMS showed a complete change in chromatographic fingerprints in samples L339-2 and L339-3. Exxsol D80, on the other hand, showed a distinct fingerprint (within a narrow

range between C_{10} and C_{15}) of itself but preserved much of the chromatographic fingerprint of the oil stain. This shows that Exxsol D80 did not interact much with the saturate fraction of the oil-stained sandstone.

Figure 2e shows the seven chromatograms (K-08-1 to K-08-7) of the Tithonian shale (before and after the experiment) from the Jeanne d'Arc Basin. Similar to limestone in the Phase I study, some of the high molecular compounds were lost with Shell Sol DMS (K-08-2 to K-08-4). However, the most significant change was observed when the shale was mixed with Exxsol D80. Most of the chromatographic fingerprints of the shale were removed leaving only the compounds related to the base oil (Exxsol D80); most of the high molecular compounds cannot be observed in the chromatograms (K-08-5 and K-08-6). Cleaning with $ZnBr_2$, however, recovered some of the high molecular weight compounds. The high peak around C_{25} is a contaminant, possibly a plasticizer.

SUMMARY AND CONCLUSIONS

Similar to Phase I research, same two source rocks (one shale and one limestone) and oil-stained sandstone were selected to undergo pressure-vessel experiments with a mixture of base oil and water to simulate conditions similar to drilling with oil-base muds under elevated temperatures (100 and 150°C) and two base oils (Shell Sol DMS and Exxsol D80) were selected for these experiments. Baseline data on these three samples for fluorescence, Rock-Eval pyrolysis, vitrinite reflectance, bitumen extraction, and gas chromatography were done before the experiments. As in Phase I research, samples were cleaned with water and detergent after the bomb experiment and cleaned samples were analyzed by similar organic geochemical and petrolgraphic techniques.

As an extension of Phase I study, the following new experiments were made:

a. Two blank experiments were performed with water and shale source rock to check the instrument error.

b. $ZnBr_2$ (a heavy liquid with s.g.=2) was used as a cleaning agent to clean the bomb experiment shale samples.

c. A cuttings sample of Tithonian shale from Jeanne d'Arc Basin was selected to perform several bomb experiments with base oils at 100°C. Samples after the experiments were cleaned with water, detergent, and $ZnBr_2$.

d. Nine samples each of various depths between 945 to 3715m from two boreholes (Terra Nova K-08, drilled with water base and Terra Nova C-09, drilled with oil-base mud) of Jeanne d'Arc Basin were selected to evaluate the influence of oil base muds on vitrinite reflectance and Rock-Eval pyrolysis data. The influence of oil base mud on vitrinite reflectance was further compared with the artificial experimental shale samples selected from one of these two wells and the natural suite of samples drilled with oil-base mud.

Based on Phase II research, the following effects on organic geochemical properties were observed after the bomb experiment on shale, limestone, stained sandstone samples before and after cleaning with water, detergent, and $ZnBr_2$. Some of these data were compared with direct determination of organic geochemical properties of two suite of samples from two wells as defined earlier.

1. The Rock-Eval, Ro, bitumen extraction, liquid chromatography, and gas chromatography data of the blank experiments at 100 and 150°C with the shale source rock from Stellarton Basin did not show any marked changes compared to the baseline sample. This suggest that the effect of instrument and experimental errors are minimal.

2. There is no marked change in fluorescence of the shale and limestone source rocks before and after the bomb experiment and cleaning. The oil-stained sandstone showed a general increase and change in fluorescence properties after the experiment compared to the baseline sample.

3. Rock-Eval pyrolysis yielded different results for the experimental and natural suite of samples. S1 and PI increased in both type of samples. Natural suite of samples from C-09 well (oil base) show lower Tmax values, whereas the experimental samples do not show any effect. On the contrary, oil-stained sandstone and limestone samples show a decrease in S1 and PI values, suggesting release (extraction) of hydrocarbons due to solvent action of the base oils. Cleaning with $ZnBr_2$ sometimes created problem, if not properly cleaned. However, proper cleaning with $ZnBr_2$ may revive some of the original character of the baseline samples.

4. Vitrinite reflectance is seen to be affected by oil-base mud in both experimental and natural samples for shale source rocks. In general, a suppression of vitrinite reflectance and a change in histogram pattern were observed. Cleaning with $ZnBr_2$ definitely improved this suppression effect. It is therefore suggested to use both whole rock and isolated kerogen (uses $ZnBr_2$ for isolation) pellets for vitrinite reflectance of samples drilled with oil base mud.

5. Bitumen extraction of shale source rock from Stellarton Basin (core sample) is not affected by oil-base mud. However, cuttings samples of the shale source rock (K-08-1) or limestone source rock show an increase in bitumen extraction after the bomb experiment. This suggests that base oil is added to these source rocks. On the other hand, stained sandstone show significant decrease in bitumen extraction during bomb experiment and cleaning. This suggests base oil acts as an solvent to release part of the stain during cleaning.

6. Similar to bitumen extraction, gas chromatograms of two shale source rock (core sample, L333-1 - Kerogen Type II; cuttings sample, K-08-1 - Kerogen Type III) show different effect. The L333-1 sample after the bomb experiment and cleaning did not show much variation in gas chromatograms. On the other hand, the Type III cuttings sample is significantly affected by both base oils during the experiment and cleaning (especially by Exxsol D80). The chromatographic fingerprinting

is totally changed. The limestone source rock after the bomb experiment and cleaning lost a minor part of the high molecular weight hydrocarbons. The chromatographic fingerprints of oil-stained sandstone is mainly affected by Shell Sol DMS. Bomb experiments with Exxsol D80 clearly separate the original oil-stain fraction and the base oil.

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RECOMMENDATION

Based on this Phase II research it is recommended that more research on the influence of these base oils on various organic geochemical properties is needed. Samples should be taken from the actual wells drilled with oil base and water base muds.

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Table A: Description of base-line samples and experimental data

Sample No.	Sample Type	Location	Experimental Data	
			Final Temperature	Final Pressure
L333-10	L333-1+Exxsol D80+100°C+clean with detergent	Experiment	106°C	1793 psi (122 bar)
L333-11	L333-1+Exxsol D80+150°C+clean with water	Experiment	156°C	1838 psi (125 bar)
L333-12	L333-1+Exxsol D80+150°C+clean with detergent	Experiment	156°C	1838 psi (125 bar)
L336-1	Baseline limestone Source Rock (SR)	Cumberland Basin, N. S.	-	-
L336-2	L336-1+Shell Sol DMS+100°C+clean with water	Experiment	106°C	1749 psi (119 bar)
L336-3	L336-1+Shell Sol DMS+100°C+clean with detergent	Experiment	106°C	1749 psi (119 bar)
L336-4	L336-1+Exxsol D80+100°C+clean with water	Experiment	106°C	1661 psi (113 bar)
L336-5	L336-1+Exxsol D80+100°C+clean with detergent	Experiment	106°C	1661 psi (113 bar)

Table A: Description of base-line samples and experimental data

Sample No.	Sample Type	Location	Experimental Data	
			Final Temperature	Final Pressure
L333-1	Baseline shale Source Roc (SR)	Stellarton Basin Nova Scotia	-	-
L333-2	L333-1+water+ 100°C	Experiment	101°C	1800 psi(123 bar)
L333-3	L333-1+water+ 150°C	Experiment	160°C	2080 psi(142 bar)
L333-4	L333-1+Shell Sol DMS+100°C+clean with water	Experiment	106°C	1880 psi (128 bar)
L333-5	L333-1+Shell Sol DMS+100°C+clean with detergent	Experiment	106°C	1880 psi (128 bar)
L333-6	L333-1+Shell Sol DMS+100°C+clean with $ZnBr_2$	Experiment	106°C	1880 psi (128 bar)
L333-7	L333-1+Shell Sol DMS+150°C+clean with water	Experiment	154°C	2014 psi (137 bar)
L333-8	L333-1+Shell Sol DMS+150°C+clean with detergent	Experiment	154°C	2014 psi (122 bar)
L333-9	L333-1+Exxsol D80+100°C+clean water	Experiment	106°C	1793 psi (122 bar)

Table A: Description of base-line samples and experimental data

Sample No.	Sample Type	Location	Experimental Data	
			Final Temperature	Final Pressure
L339-1	Baseline oil-stained sandstone	Borehole Hibernia I-46 2506-2508m, Jean d'Arc basin Newfoundland	-	-
L339-2	L339-1+Shell Sol DMS+100°C+clean with water	Experiment	106°C	1793 psi (122 bar)
L339-3	L339-1+Shell Sol DMS+100°C+clean with detergent	Experiment	106°C	1793 psi (122 bar)
L339-4	L339-1+Exxsol D80 +100°C+clean with water	Experiment	106°C	1793 psi (122 bar)
L339-5	L339-1+Exxsol D80 +100°C+clean with detergent	Experiment	106°C	1793 psi (122 bar)
K-08-1	Baseline shale Source Rock	Borehole Terra Nova K-08,depth, 3115-3165m, Jean d'Arc basin, Newfoundland	-	-
K-08-2	K-08-1+Shell Sol DMS+100°C+clean with water	Experiment	108°C	1779 psi (121 bar)

Table A: Description of base-line samples and experimental data

Sample No.	Sample Type	Location	Experimental Data	
			Final Temperature	Final Pressure
K-08-3	K-08-1+Shell Sol DMS+100°C+clean with detergent	Experiment	108°C	1779 psi (121 bar)
K-08-4	K-08-1+Shell Sol DMS+100°C+clean with $ZnBr_2$	Experiment	108°C	1779 psi (121 bar)
K-08-5	K-08-1+Exxsol D80 +100°C+clean with water	Experiment	105°C	1838 psi (125 bar)
K-08-6	K-08-1+Exxsol D80 +100°C+clean with detergent	Experiment	105°C	1838 psi (125 bar)
K-08-7	K-08-1+Exxsol D80 +100°C+clean with $ZnBr_2$	Experiment	105°C	1838 psi (125 bar)
K-08-8	Basline shale source rock (SR)	Borehole Terra Nova - K-08, 3115-3165m, Jean d'Arc Basin Newfoundland		-
K-08-9	K-08-8+Shell Sol DMS+100°C+clean with water	Experiment	101°C	1838 psi (125 bar)
K-08-10	K-08-8+Shell Sol DMS+100°C+clean with detergent	Experiment	101°C	1838 psi (125 bar)

Table A: Description of base-line samples and experimental data

Sample No.	Sample Type	Location	Experimental Data	
			Final Temperature	Final Pressure
K-08-11	K-08-8+Shell Sol DMS+100°C+clean with $ZnBr_2$	Experiment	101°C	1838 psi (125 bar)
K-08-12	K-08-8+Exxsol D80 +100°C+clean with water	Experiment	103°C	1896 psi (129 bar)
K-08-13	K-08-8+Exxsol D80 +100°C+clean with with detergent	Experiment	103°C	1896 psi (129 bar)
K-08-14	K-08-8+Exxsol D80 +100°C+clean with $ZnBr_2$	Experiment	103°C	1896 psi (129 bar)

Table 1: Fluorescence and vitrinite reflectance data

Sample No.	Sample type	Fluorescence Characteristics	Remarks	Vitrinite Refl. R_o	Std. Dev.
L333-1	Shale Source Rock Stellarton Basin, N. S.	Greenish brown	Dark intensity	0.50	0.09
L333-2	Shale (L333-1)+Water+ 100°C	Yellowish brown	Slight increase in fluorescence	0.49	0.09
L333-3	Shale(L333-1)+water+ 150°C	Same as in L333-2		0.47	0.07
L333-4	Shale (L333-1)+Shell Sol DMS + 100°C +clean with water	Yellow brown	Slight increase	0.38	0.08
L333-5	Shale (333-1)+Shell Sol DMS + 100°C+ clean with deterg.	Same as L333-4		0.44	0.08
L333-6	Shale (L333-1)+Shell Sol DMS + 100°C + clean w/$ZnBr_2$	Similar to L333-1	No change	0.44	0.07
L333-7	Shale (L333-1)+Shell Sol DMS+150°C+clean w/water	Greenish brown with yellow specs	slight increase		
L333-8	Shale (L333-1)+Shell Sol DMS + 150°C + clean w/detergent	Greenish Brown	No change		
L333-9	Shale (L333-1)+Exxsol D-80+100°C+clean with water	Greenish brown	No change		

Table 1: Fluorescence and vitrinite reflectance data

Sample No.	Sample type	Fluorescence Characteristics	Remarks	Vitrinite Refl. R_o	Std. Dev.
L333-10	Shale (L333-1)+Exxsol D80+100°C+clean with detergent	Greenish brown	No change		
L333-11	Shale (L333-1)+Exxsol D80+150°C+clean with water	Greenish brown with yellow stain	slight increase		
L333-12	Shale (L333-1)+Exxsol D80+clean with deterg.	Same as L333-11			
L336-1	Limestone Source Rock Cumberland Basin, N. S.	Greenish brown with yellow brown specs	Dark intensity	0.58	0.05
L336-2	Limestone(L336-1)+Shell Sol DMS+100°C+clean with water	Greenish brown with yellow specs	Slight increase in fl.	0.58	0.06
L336-3	Limestone (L336-1)+ Shell Sol DMS+100°C+ clean with detergent	Same as L336-2		0.58	0.08
L336-4	Limestone(L336-1)+Exxsol D80+100°C+clean with water	Greenish brown with yellow specs	slight increase in fl.		
L336-5	Limestone(L336-1)+Exxsol D80+100°C+clean with detergent	Greenish brown with yellow specs	same as L336-4		

Table 1: Fluorescence and vitrinite reflectance data

Sample No.	Sample type	Fluorescence characteristics	Remarks	Vitrinite Refl. R_o	Std. Dev.
L339-1	Stained sandstone, Jean d'Arc Basin, Newfoundland	Yellowish brown	Strong Fluor.		
L339-2	Sandstone (L339-1)+Shell Sol DMS+100°C+clean with with water	Yellow brown to blue brown	Increased partially		
L339-3	Sandstone(L339-1)+Shell Sol DMS+100°C+clean with detergent	Same as L339-2			
L339-4	Sandstone(L339-1)+Exxsol D80+100°C+clean with water	Partly ywllow Br. to violet brown	Partially increased and partially decreased		
L339-5	Sandstone(L339-1)+Exxsol D80+100°C+clean with detergent	Same as L339-4			

Table 1: Fluorescence and vitrinite reflectance data

Sample No.	Sample type	Fluorescence Characteristics	Remarks	Vitrinite Refl. R_o Std. Dev.
K-08-1	Shale, Tithonian, Jean d'Arc Basin, Newfound-land	Dark Bluish Brown with minor yellow specs	Dark Fl.	
K-08-2	Shale(K-08-1)+Shell Sol DMS+100°C+clean with water	Same as K-08-1	No change	
K-08-3	Shale(K-08-1)+Shell Sol DMS+100°C+clean with detergent	Dark bluish Brown with lots of yellow specs	Dark Fl. increased than K-08-1	
K-08-4	Shale(K-08-1)+Shell Sol DMS+100°C+clean with $ZnBr_2$	Same as K-08-1	No change	
K-08-5	Shale(k-08-1)+Exxsol D80+100°C+clean with water	Same as K-08-1	No change	
K-08-6	Shale(K-08-1)+Exxsol D80+100°C+clean with with detergent	Same as K-08-3	Dark fl. increased than K-08-1	
K-08-7	Shale(K-08-1)+Exxsol D80+100°C+clean with $ZnBr_2$	Same as K-08-1	No change	

Table 2: Rock-Eval pyrolysis data from bomb experiment samples

SAMPLE IDENTIFICATION DEPTH (Feet)	TOC Wt%	S1 mg/g	S2 mg/g	S3 mg/g	T-max degC	S1/TOC	S2/TOC HI	S3/TOC OI	S2/S3	S1/S1+S2 PI
L333- 1 : -	5.12	1.34	21.07	0.76	440	26	412	15	27.72	0.06
L333- 2 : -	4.59	1.24	18.58	0.89	439	27	405	19	20.88	0.06
L333- 3 : -	4.59	1.09	17.24	0.65	439	24	376	14	26.52	0.06
L333- 4 : -	4.41	1.53	17.60	0.74	440	35	399	17	23.78	0.08
L333- 5 : -	5.05	1.46	19.47	0.79	440	29	386	16	24.65	0.07
L333- 6 : -	4.60	1.42	23.43	3.01	435	31	509	65	7.78	0.06
L333- 7 : -	4.85	1.81	19.58	0.71	441	37	404	15	27.58	0.08
L333- 8 : -	4.77	1.94	20.35	0.73	439	41	427	15	27.88	0.09
L333- 9 : -	4.61	1.83	18.16	0.76	438	40	394	16	23.89	0.09
L333-10 : -	5.21	1.75	19.54	0.74	441	34	375	14	26.41	0.08
L333-11 : -	4.87	2.17	19.27	0.76	441	45	396	16	25.36	0.10
L333-12 : -	4.71	1.86	18.19	0.90	439	39	386	19	20.21	0.09
L336- 1 : -	1.90	0.13	1.39	0.51	440	7	73	27	2.73	0.09
L336- 2 : -	1.67	2.00	1.36	0.41	438	120	81	25	3.32	0.60
L336- 3 : -	1.57	0.74	1.27	0.37	441	47	81	24	3.43	0.37
L336- 4 : -	1.51	0.90	1.27	0.42	439	60	84	28	3.02	0.41
L336- 5 : -	1.74	0.69	1.38	0.41	439	40	79	24	3.37	0.33
L339- 1 : -	1.36	11.00	5.31	0.41	418	809	390	30	12.95	0.67
L339- 2 : -	0.63	8.13	2.47	0.50	419	1290	392	79	4.94	0.77
L339- 3 : -	0.51	7.11	1.79	0.46	419	1394	351	90	3.89	0.80
L339- 4 : -	0.61	4.92	2.47	0.42	419	807	405	69	5.88	0.67
L339- 5 : -	0.64	3.03	1.58	0.41	416	473	247	64	3.85	0.66
K-08- 1 : -	1.07	0.23	0.82	1.60	433	21	77	150	0.51	0.22
K-08- 2 : -	1.22	3.35	0.79	1.83	431	275	65	150	0.43	0.81
K-08- 3 : -	1.25	2.60	0.83	1.87	431	208	66	150	0.44	0.76
K-08- 4 : -	1.12	1.98	1.87	3.46	431	177	167	309	0.54	0.51
K-08- 5 : -	1.16	2.65	0.56	1.75	431	228	48	151	0.32	0.83
K-08- 6 : -	1.11	1.91	0.69	1.81	431	172	62	163	0.38	0.73
K-08- 7 : -	1.08	0.98	7.95	2.62	537	91	736	243	3.03	0.11

Table 2: Rock-Eval pyrolysis data of natural samples from borehole Terra Nova K-08 and Terra Nova C-09, Jean d'Arc Basin, Newfoundland

Sample No.	Depth(m)	Sample Type	S_o	S_1	S_2	TOC	T_{max}	S_1/S_1+S_2	$S_1/S_o+S_1+S_2$	$S_2/TOC*100$	S_o/S_o+S_1+S
K-08-15	945-965	Cuttings	.05	.69	4.15	3.24	428	.14	.14	128	.01
C-09-1	965	Cuttings	.00	.64	1.21	2.13	426	.35	.35	57	.00
K-08-16	1295	Cuttings	.00	.09	1.96	1.14	433	.04	.04	172	.00
C-09-2	1305	Cuttings	.01	2.44	2.19	1.51	432	.53	.53	145	.00
K-08-17	1555	Cuttings	.01	.54	.94	1.26	429	.36	.36	75	.01
C-09-3	1555	Cuttings	.19	9.78	6.15	3.32	438	.61	.61	185	.01
K-08-18	2045	Cuttings	.00	.11	1.08	1.52	428	.10	.10	64	.00
C-09-4	2045	Cuttings	.14	3.50	1.19	.79	391	.75	.72	150	.03
K-08-19	2335	Cuttings	.01	.44	.65	.61	432	.40	.40	107	.01
C-09-5	2335	Cuttings	.05	2.38	1.14	.66	415	.68	.67	173	.01
C-09-6	2745	Cuttings	.14	4.97	1.30	.91	411	.79	.78	143	.02
K-08-20	2835	Cuttings	.00	.07	1.03	1.38	435	.06	.06	75	.00
C-09-7	3115	Cuttings	.02	3.66	1.47	1.39	433	.71	.71	106	.00
K-08-21	3105-3175	Cuttings	.01	.22	.85	1.26	437	.21	.20	68	.01
K-08-22	3365	Cuttings	.01	.24	1.25	1.07	434	.16	.16	117	.01
C-09-8	3415	Cuttings	.12	4.46	1.10	1.28	426	.80	.79	86	.02
C-09-9	3635	Cuttings	.08	1.94	5.83	1.19	436	.25	.25	490	.01
K-08-23	3715	Cuttings	.02	1.06	12.26	2.51	434	.08	.08	488	.00

Table 3: Vitrinite reflectance data of experimental and natural samples

Experimental Samples

Sample No.	Sample type	R_o	Std, Dev
K-08-8	Shale, Tithonian 3115-3165m, Jean d'Arc Basin, Newfoundland	0.50	0.07
K-08-9	Shale(K-08-8)+Shell Sol DMS+100°C+clean with water	0.43	0.08
K-08-10	Shale(K-08-8)+Shell Sol DMS+100°C+clean with detergent	0.44	0.05
K-08-11	Shale(K-08-8)+Shell Sol DMS+100°C+clean with $ZnBr_2$	0.47	0.03
K-08-12	Shale(K-08-8)+Exxsol D80+100°C+clean with water	0.49	0.05
K-08-13	Shale(K-08-8)+Exxsol D80+100°C+clean with detergent	0.48	0.06
K-08-14	Shale(K-08-8)+Exxsol D80+100°C+clean with $ZnBr_2$	0.50	0.08

Natural Samples

Sample No.	Depth(m)	R_o	Std. Dev
K-08-15	945-965	0.26	0.04
C-09-1	965	0.24	0.03
K-08-16	1295	0.30	0.03
C-09-2	1305	0.29	0.04
K-08-17	1555	0.34	0.05
C-09-3	1555	0.38	0.10
K-08-18	2045	0.39	0.07
C-09-4	2045	0.44	0.08
K-08-19	2335	0.40	0.04
C-09-5	2335	0.45	0.08
K-08-20	2835	0.51	0.07
C-09-6	2745	0.43	0.06
K-08-21	3115	0.52	0.08
C-09-7	3115	0.45	0.06
K-08-22	3365	0.55	0.08
C-09-8	3415	0.56	0.05
K-08-23	3715	0.58	0.06
C-09-9	3635	0.51	0.05

K-08: Well drilled with water-base drilling mud

C-09: Well drilled with oil-base mud

Table 4.Liquid chromatography data

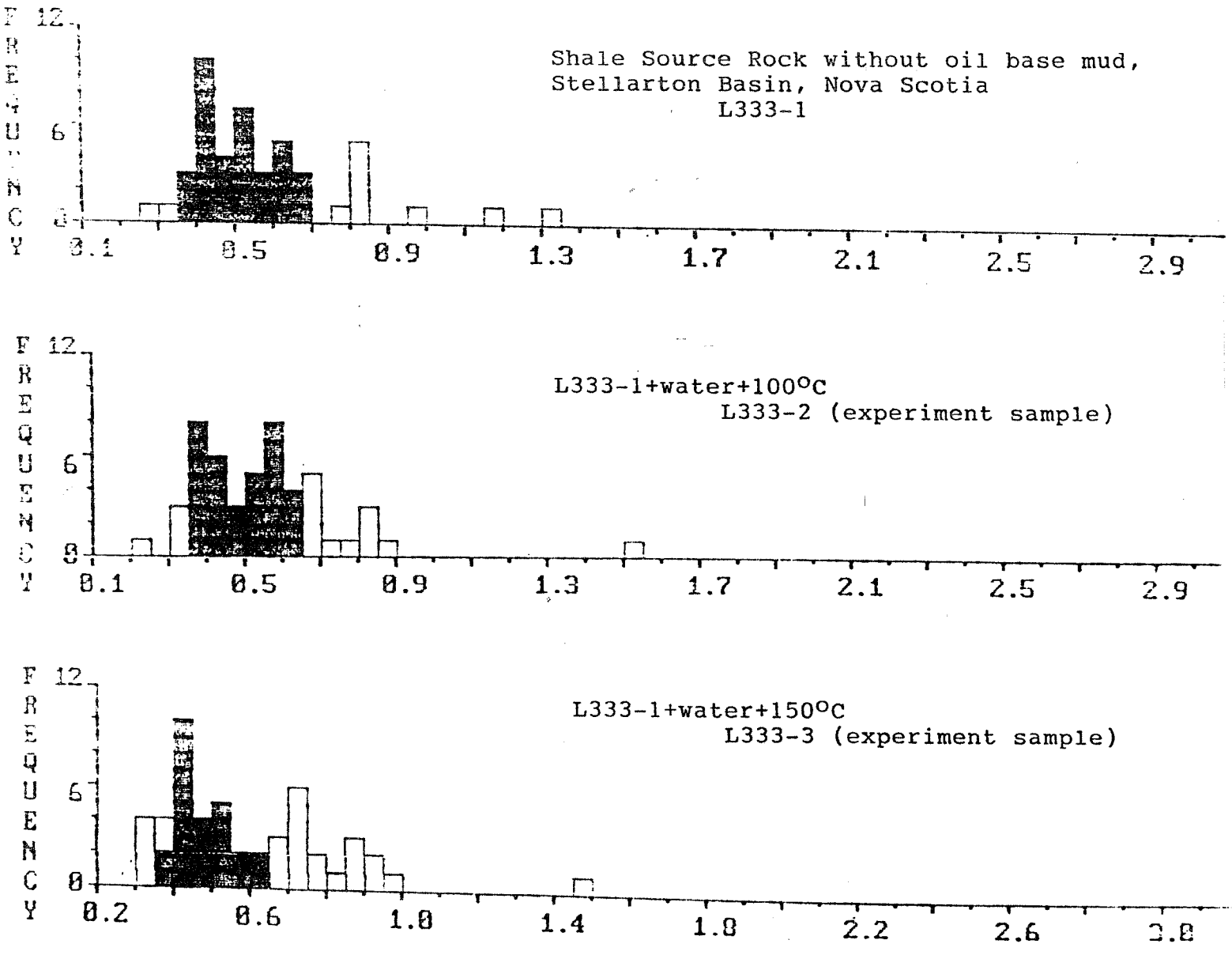
SAMPLE IDENTIFICATION	SAT (%)	AROM (%)	NSO (%)	ASPH (%)
L333- 1 : -	55.4	19.8	20.8	3.9
L333- 2 : -	57.0	21.6	14.6	6.7
L333- 3 : -	55.8	19.7	16.9	7.6
L333- 4 : -	56.6	18.8	20.4	4.1
L333- 5 : -	54.7	19.2	21.8	4.2
L333- 6 : -	61.6	14.0	19.5	4.9
L333- 7 : -	62.2	16.1	17.9	3.7
L336- 1 : -	33.3	21.0	28.6	17.1
L336- 2 : -	88.7	3.1	5.4	2.9
L336- 3 : -	61.9	13.3	17.1	7.6
L339- 1 : -	49.9	25.3	23.0	1.8
L339- 2 : -	57.1	21.4	19.1	2.4
L339- 3 : -	65.8	14.9	16.8	2.6
L339- 4 : -	51.5	21.2	24.3	3.1
L339- 5 : -	49.6	21.9	24.6	3.9
K-08- 1 : -	37.0	17.3	29.6	16.0
K-08- 2 : -	92.5	1.2	5.4	0.9
K-08- 3 : -	88.6	1.9	8.3	1.2
K-08- 4 : -	89.7	2.9	5.4	2.0
K-08- 5 : -	69.4	6.5	18.5	5.6
K-08- 6 : -	74.0	3.3	16.6	6.1
K-08- 7 : -	33.3	0.0	66.7	0.0

Table 5. Bitumen extract and gas chromatography data

SAMPLE IDENTIFICATION	SAMPLE NO.	PPM	EXTRACT /TOC	Pr/Ph	Pr/C17	Ph/C18	CPI
L333- 1 : -	1	2647.0	0.052	3.2	0.63	0.26	1.12
L333- 2 : -	2	2537.8	0.055	3.0	0.64	0.25	1.15
L333- 3 : -	3	2294.2	0.050	3.1	0.64	0.25	1.13
L333- 4 : -	4	2391.3	0.054	2.5	0.43	0.24	1.05
L333- 5 : -	5	2462.3	0.049	2.8	0.51	0.24	1.09
L333- 6 : -	6	2586.6	0.056	1.8	0.36	0.25	1.10
L333- 7 : -	7	2980.8	0.061	2.0	0.32	0.22	1.08
L336- 1 : -	13	373.8	0.020	2.9	0.89	0.35	0.64
L336- 2 : -	14	2660.2	0.159	1.3	0.17	0.20	0.54
L336- 3 : -	15	2104.3	0.134	1.7	0.29	0.26	1.12
L339- 1 : -	18	21385.0	1.572	0.9	0.58	0.71	1.01
L339- 2 : -	19	14331.5	2.275	1.2	0.32	0.59	0.97
L339- 3 : -	20	13152.5	2.579	1.2	0.33	0.61	0.95
L339- 4 : -	21	9582.7	1.571	0.8	0.53	0.69	1.00
L339- 5 : -	22	6831.2	1.067	0.8	0.53	0.68	0.99
K-08- 1 : -	23	608.4	0.057	1.9	0.98	0.95	2.09
K-08- 2 : -	24	4468.0	0.366	1.2	0.16	0.20	1.53
K-08- 3 : -	25	3866.3	0.309	1.2	0.16	0.20	2.07
K-08- 4 : -	26	2287.3	0.204	1.4	0.15	0.17	1.77
K-08- 5 : -	27	2475.3	0.213	2.4	0.66	0.51	2.03
K-08- 6 : -	28	569.5	0.051	4.5	1.39	0.27	1.58
K-08- 7 : -	29	1355.8	0.126	2.3	0.52	0.59	2.22

Table 6: Percentages of isoprenoid hydrocarbons from gas chromatography

SAMPLE IDENTIFICATION	SAMPLE NUMBER	i-C13 (%)	i-C14 (%)	i-C15 (%)	i-C16 (%)	i-C18 (%)	i-C19 (%)	i-C20 (%)
L333- 1 : -	1	9.9	9.0	10.9	23.1	11.5	27.0	8.5
L333- 2 : -	2	7.9	7.2	9.6	22.7	12.8	30.0	9.9
L333- 3 : -	3	6.2	6.4	9.7	23.4	13.5	30.9	9.8
L333- 4 : -	4	9.3	6.4	12.2	24.9	12.0	25.1	10.1
L333- 5 : -	5	11.9	6.5	13.0	24.7	10.9	24.2	8.7
L333- 6 : -	6	4.1	3.4	12.6	22.6	18.2	25.1	14.2
L333- 7 : -	7	10.5	3.9	11.7	23.3	11.4	26.0	13.2
L336- 1 : -	13	0.2	1.7	5.7	19.4	16.0	42.5	14.4
L336- 2 : -	14	9.1	8.0	16.6	28.0	12.4	14.5	11.5
L336- 3 : -	15	2.5	3.0	14.5	19.7	14.9	28.3	17.0
L339- 1 : -	18	0.0	0.3	2.9	10.9	14.2	34.5	37.2
L339- 2 : -	19	3.3	3.6	16.6	33.7	11.2	17.5	14.1
L339- 3 : -	20	8.5	4.6	20.2	32.0	9.1	14.1	11.6
L339- 4 : -	21	3.8	14.2	32.9	5.6	6.0	16.4	21.1
L339- 5 : -	22	4.7	9.9	33.9	6.0	6.1	17.5	22.0
K-08- 1 : -	23	0.7	2.1	6.9	23.1	13.5	35.2	18.6
K-08- 2 : -	24	22.6	9.5	16.4	22.7	9.6	10.7	8.6
K-08- 3 : -	25	25.7	6.5	16.7	21.3	9.4	11.2	9.2
K-08- 4 : -	26	13.7	8.7	17.9	26.7	11.2	12.6	9.2
K-08- 5 : -	27	24.9	23.8	38.7	5.1	0.6	1.4	5.5
K-08- 6 : -	28	29.1	26.5	36.7	3.7	1.2	2.3	0.5
K-08- 7 : -	29	0.0	0.4	18.7	18.3	14.4	33.4	14.7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0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale Source Rock without oil base mud,
Stellarton Basin, Nova Scotia
L333-1
L333-1+water+100°C
L333-2 (experiment sample)
L333-1+water+150°C
L333-3 (experiment sample)
0.2
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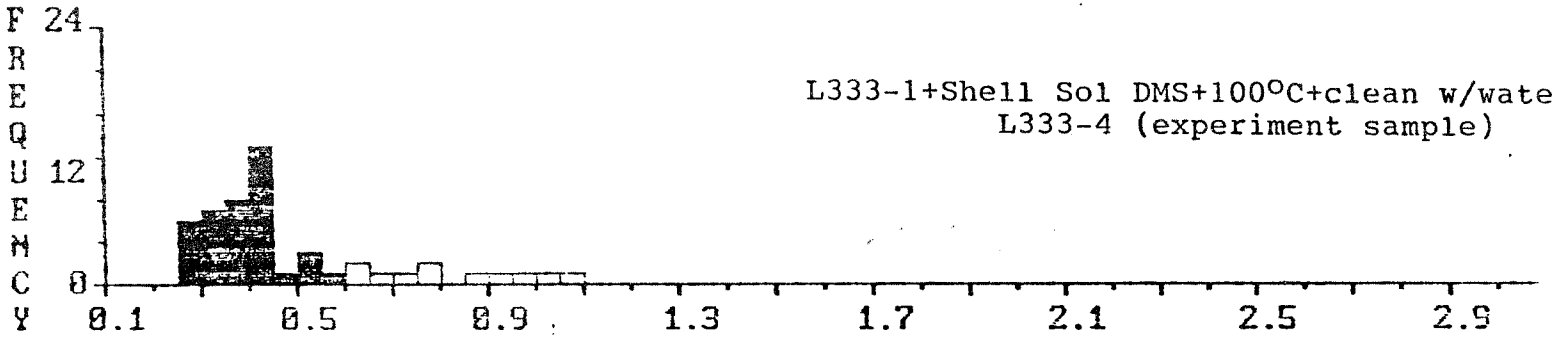
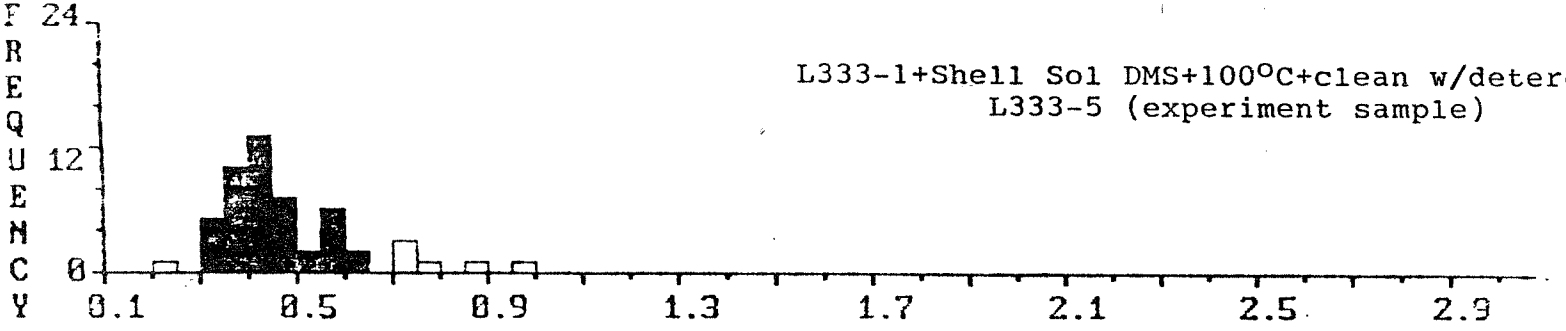
1.0
1.4
1.8
2.2
2.6
3.0
% VITRINITE REFLECTANCE

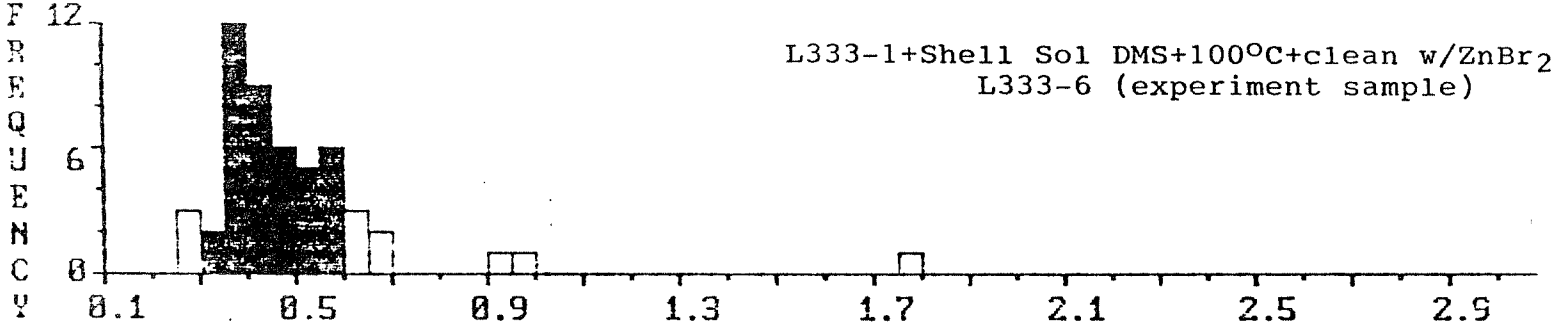
Fig. 1a



L333-1+Shell Sol DMS+100°C+clean w/water
L333-4 (experiment sample)



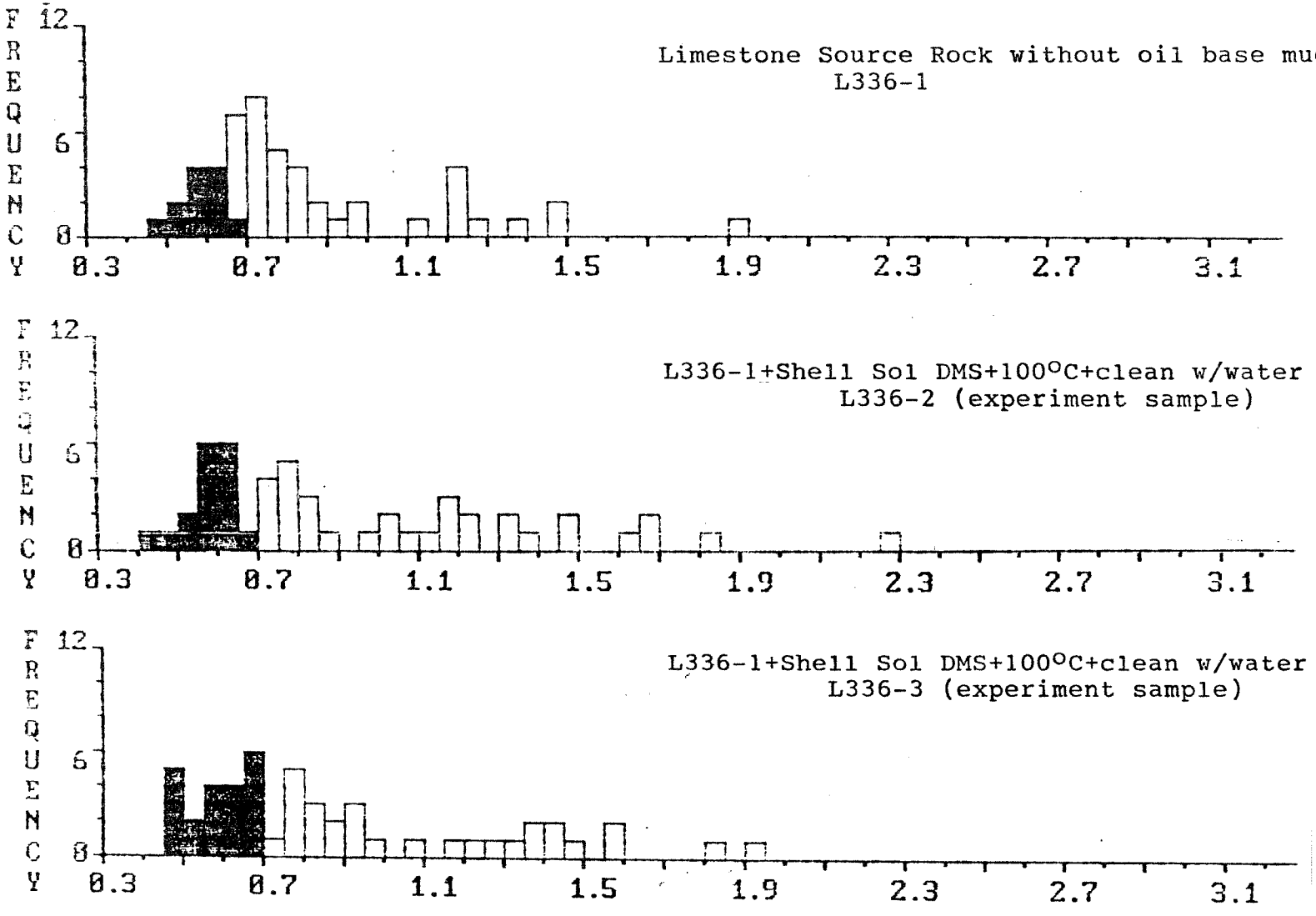
L333-1+Shell Sol DMS+100°C+clean w/detergent
L333-5 (experiment sample)



L333-1+Shell Sol DMS+100°C+clean w/$ZnBr_2$
L333-6 (experiment sample)

% VITRINITE REFLECTANCE

Fig. 1a


FREQUENCY
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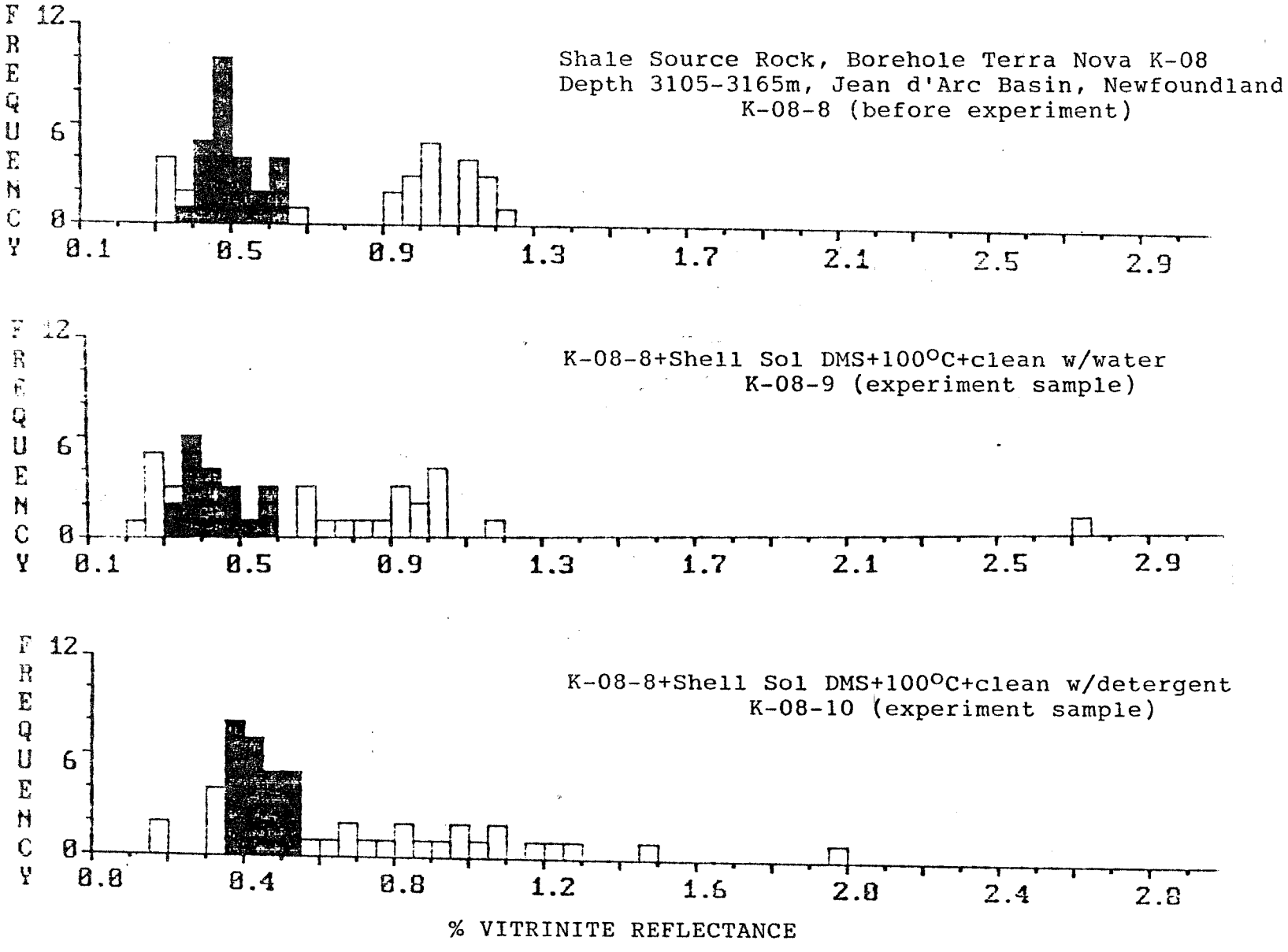
0.7
1.1
1.5
1.9
2.3
2.7
3.1
Limestone Source Rock without oil base mud
L336-1
L336-1+Shell Sol DMS+100°C+clean w/water
L336-2 (experiment sample)
L336-1+Shell Sol DMS+100°C+clean w/water
L336-3 (experiment sample)
% VITRINITE REFLECTANCE

Fig. 1a


FREQUENCY
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0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale Source Rock, Borehole Terra Nova K-08
Depth 3105-3165m, Jean d'Arc Basin, Newfoundland
K-08-8 (before experiment)
K-08-8+Shell Sol DMS+100°C+clean w/water
K-08-9 (experiment sample)
K-08-8+Shell Sol DMS+100°C+clean w/detergent
K-08-10 (experiment sample)
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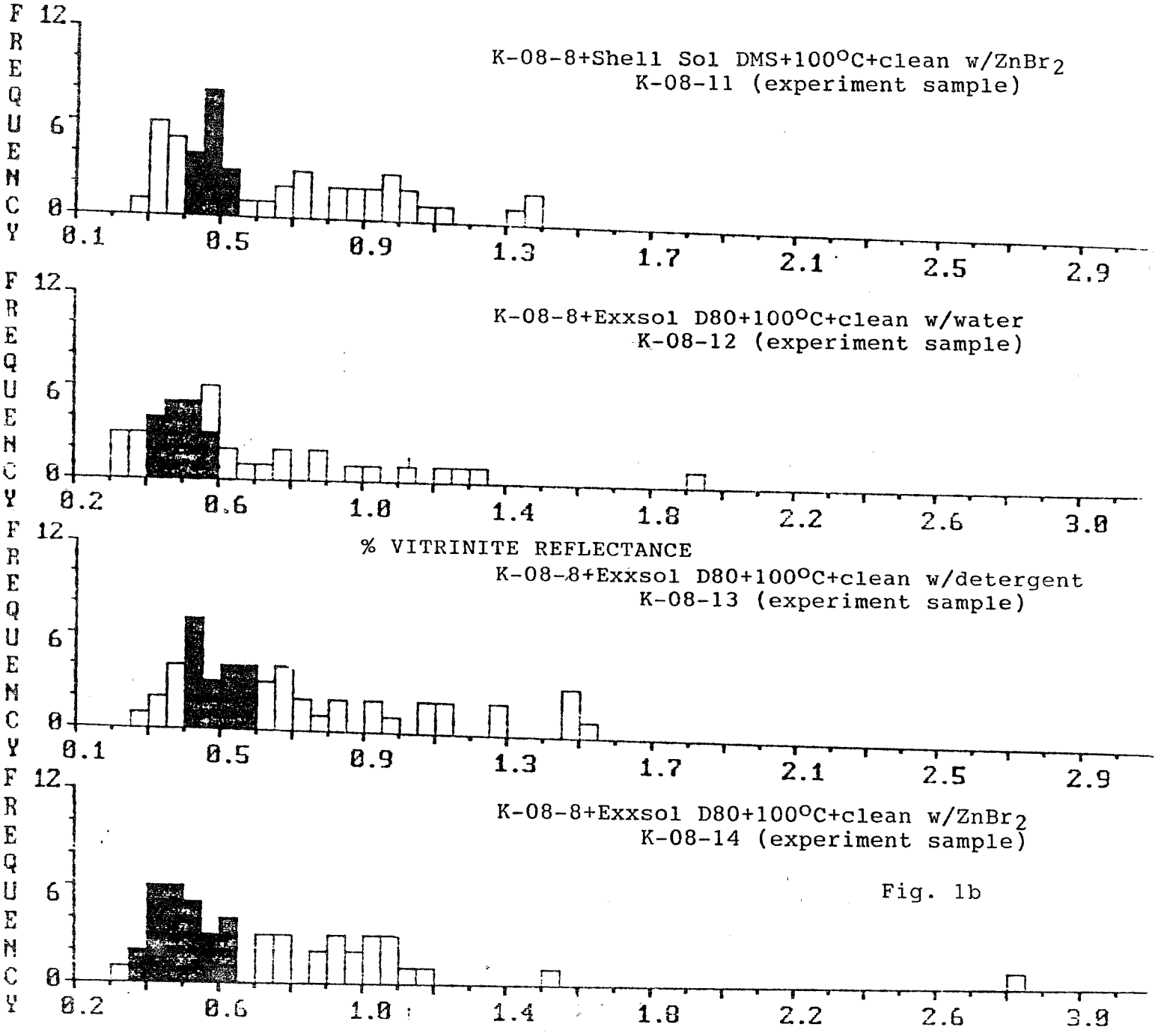
0.8
1.2
1.6
2.0
2.4
2.8
% VITRINITE REFLECTANCE

Fig. 1b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0.5
0.9
1.3
1.7
2.1
2.5
2.9
K-08-8+Shell Sol DMS+100°C+clean w/ZnBr2
K-08-11 (experiment sample)
FREQUENCY
12
6
0
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
K-08-8+Exxsol D80+100°C+clean w/water
K-08-12 (experiment sample)
% VITRINITE REFLECTANCE
FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
K-08-8+Exxsol D80+100°C+clean w/detergent
K-08-13 (experiment sample)
FREQUENCY
12
6
0
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
K-08-8+Exxsol D80+100°C+clean w/ZnBr2
K-08-14 (experiment sample)

Fig. 1b

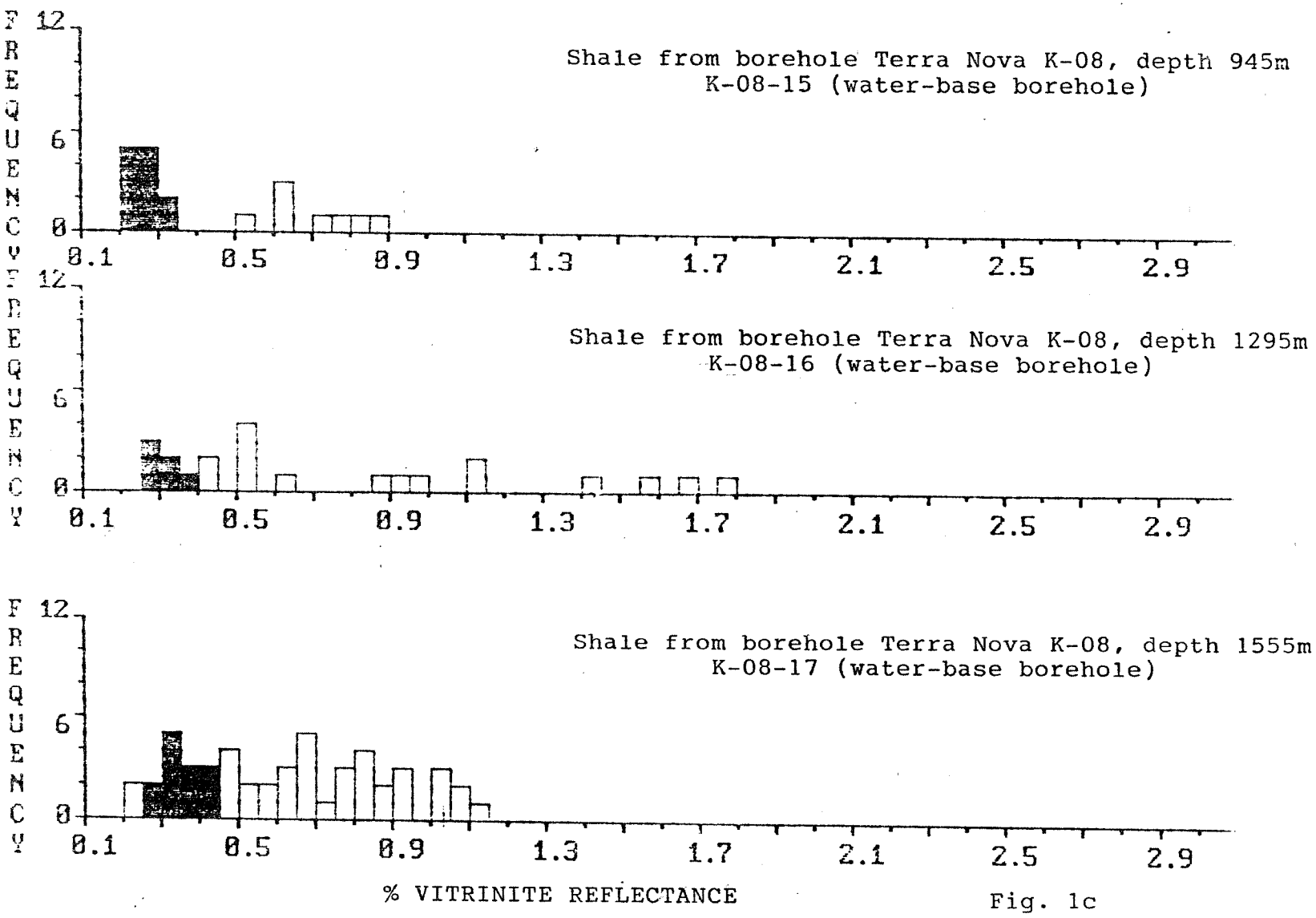

FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova K-08, depth 945m
K-08-15 (water-base borehole)
Shale from borehole Terra Nova K-08, depth 1295m
K-08-16 (water-base borehole)
Shale from borehole Terra Nova K-08, depth 1555m
K-08-17 (water-base borehole)
% VITRINITE REFLECTANCE

Fig. 1c

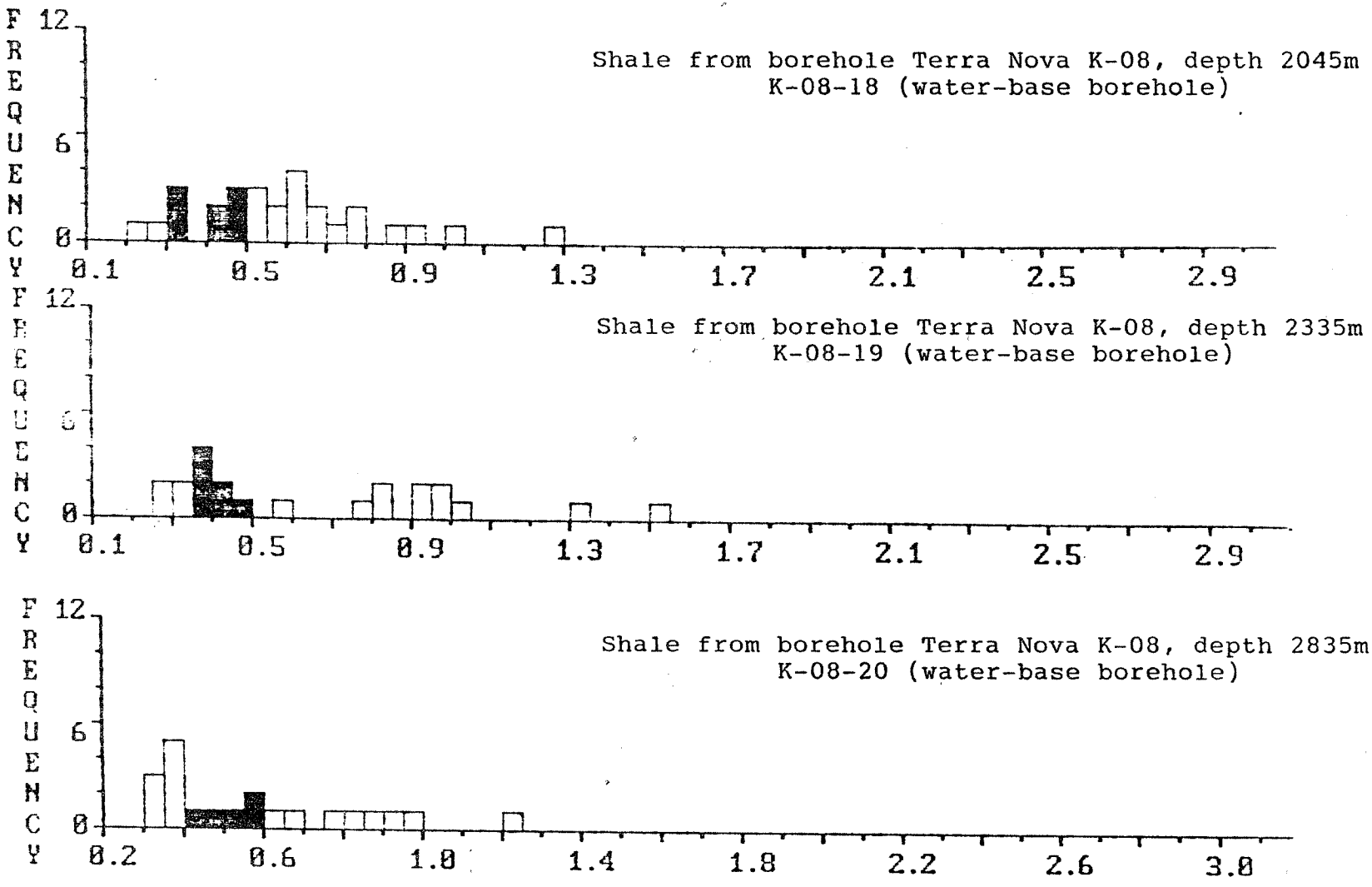

FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova K-08, depth 2045m
K-08-18 (water-base borehole)
Shale from borehole Terra Nova K-08, depth 2335m
K-08-19 (water-base borehole)
Shale from borehole Terra Nova K-08, depth 2835m
K-08-20 (water-base borehole)
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
% VITRINITE REFLECTANCE

Fig. 1c

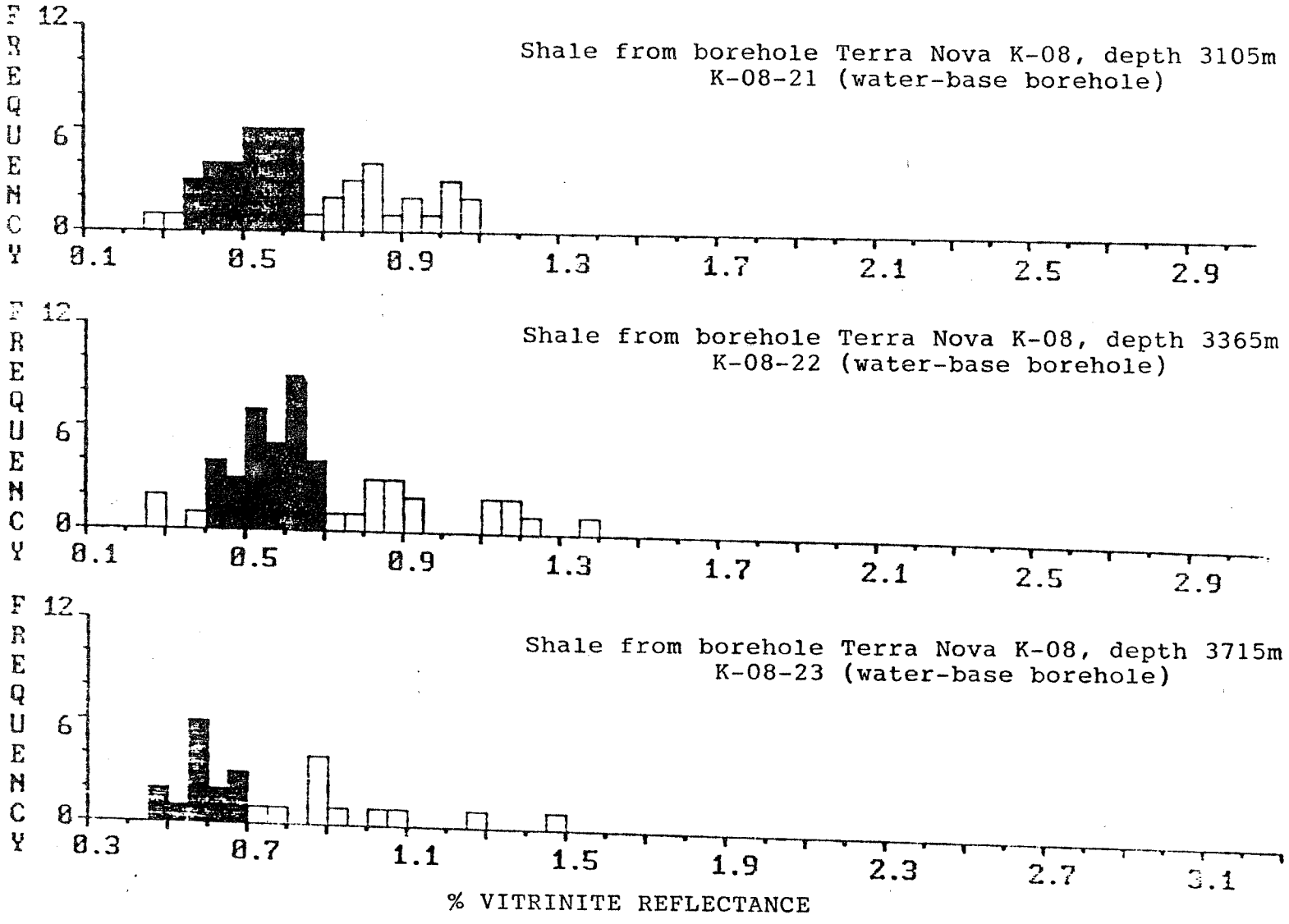

FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova K-08, depth 3105m
K-08-21 (water-base borehole)
FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova K-08, depth 3365m
K-08-22 (water-base borehole)
FREQUENCY
12
6
0
0.3
0.7
1.1
1.5
1.9
2.3
2.7
3.1
Shale from borehole Terra Nova K-08, depth 3715m
K-08-23 (water-base borehole)
% VITRINITE REFLECTANCE

Fig. 1c

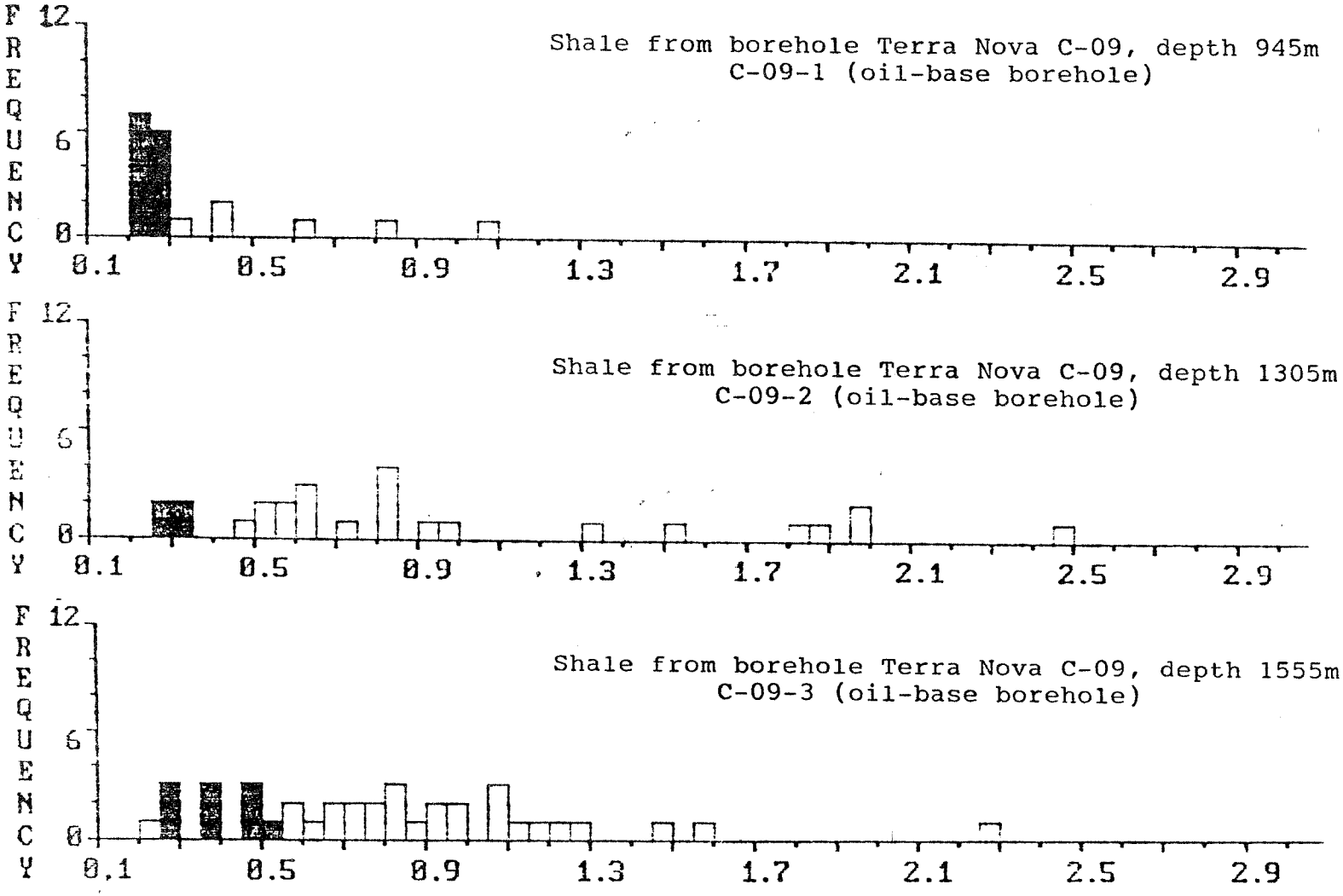

FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova C-09, depth 945m
C-09-1 (oil-base borehole)
Shale from borehole Terra Nova C-09, depth 1305m
C-09-2 (oil-base borehole)
Shale from borehole Terra Nova C-09, depth 1555m
C-09-3 (oil-base borehole)
% VITRINITE REFLECTANCE

Fig. 1c

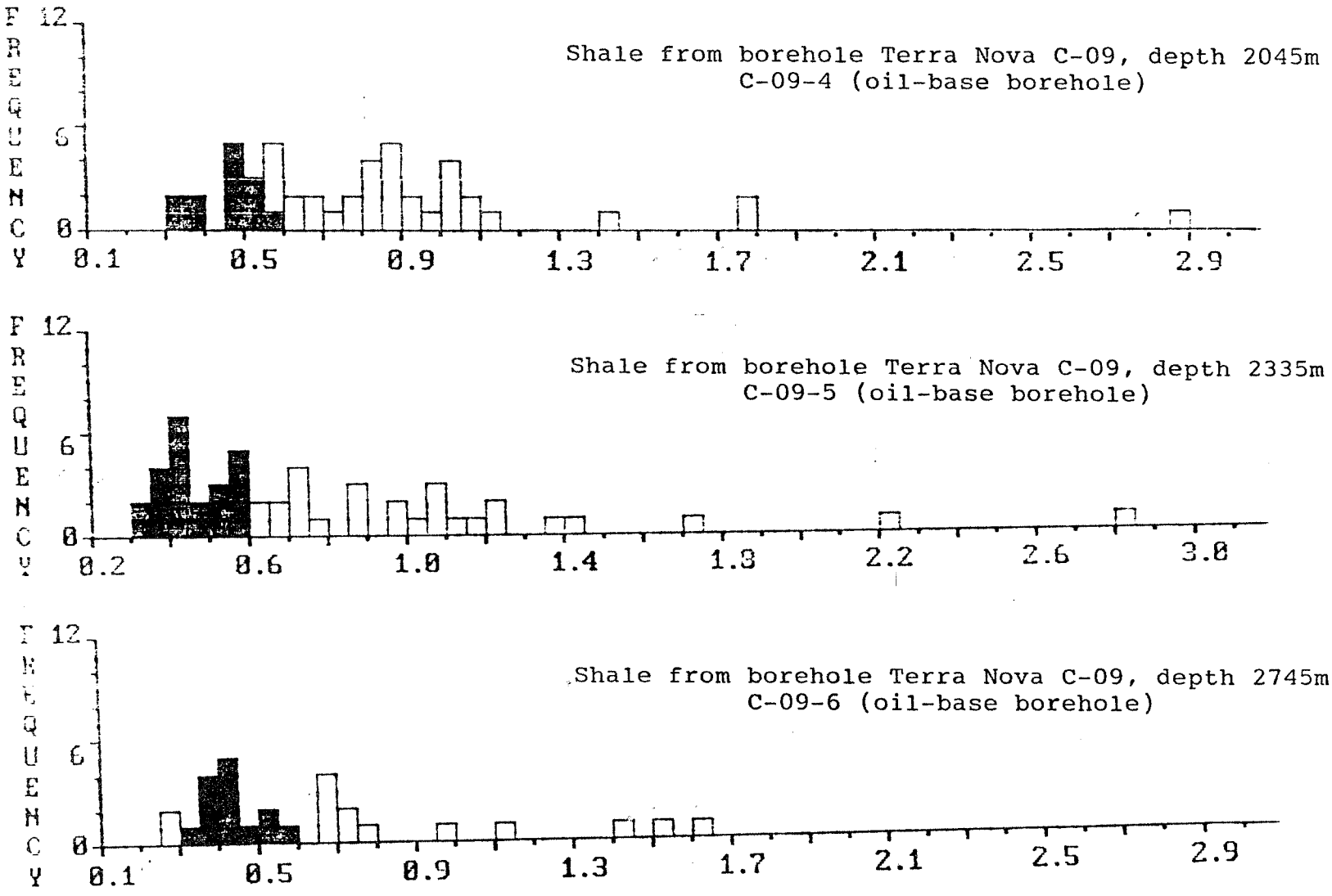

FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova C-09, depth 2045m
C-09-4 (oil-base borehole)
FREQUENCY
12
6
0
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
Shale from borehole Terra Nova C-09, depth 2335m
C-09-5 (oil-base borehole)
FREQUENCY
12
6
0
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
Shale from borehole Terra Nova C-09, depth 2745m
C-09-6 (oil-base borehole)
% VITRINITE REFLECTANCE

Fig. 1c

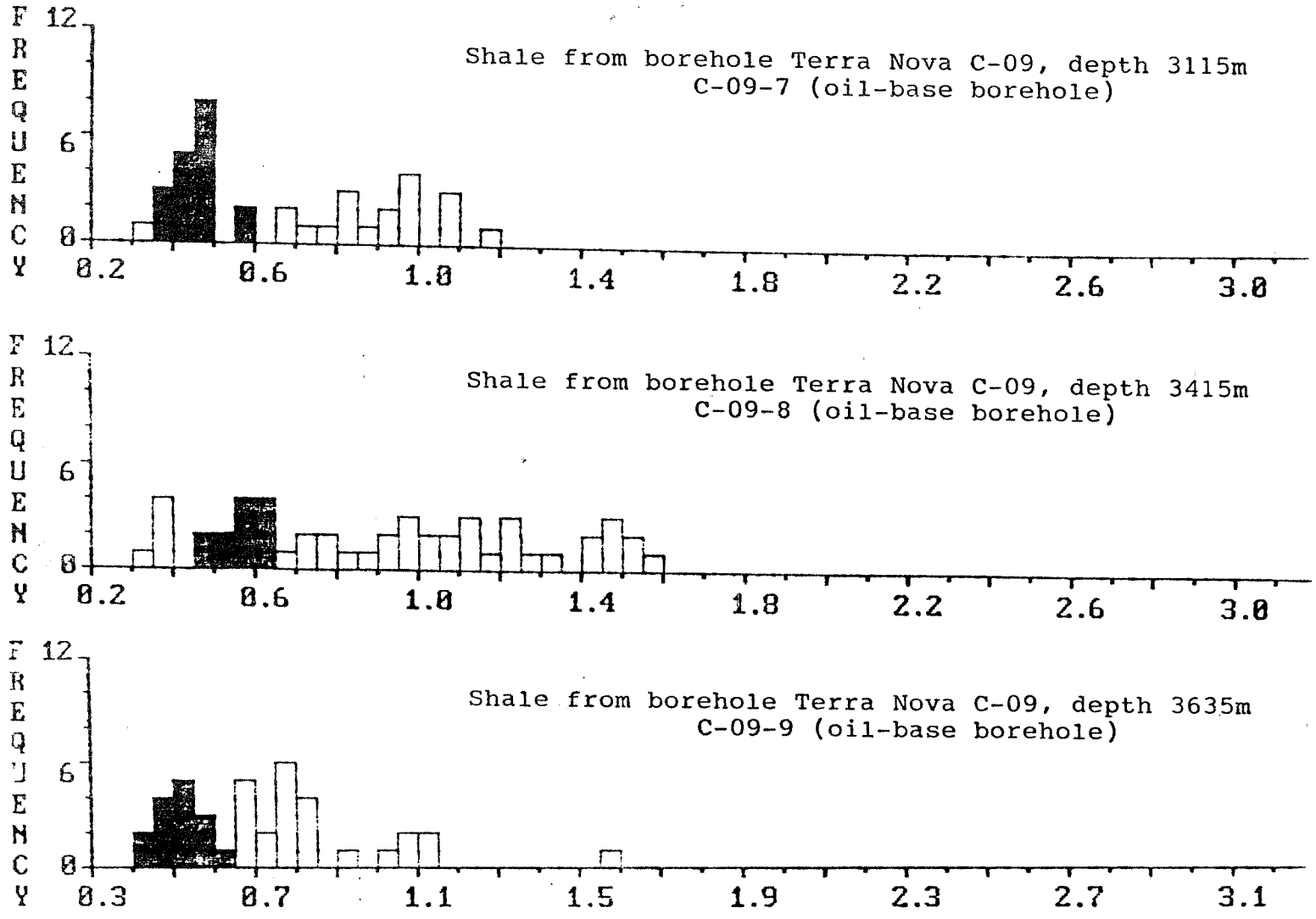

FREQUENCY
12
6
0
Shale from borehole Terra Nova C-09, depth 3115m
C-09-7 (oil-base borehole)
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
FREQUENCY
12
6
0
Shale from borehole Terra Nova C-09, depth 3415m
C-09-8 (oil-base borehole)
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
FREQUENCY
12
6
0
Shale from borehole Terra Nova C-09, depth 3635m
C-09-9 (oil-base borehole)
0.3
0.7
1.1
1.5
1.9
2.3
2.7
3.1
% VITRINITE REFLECTANCE

Fig. 1c

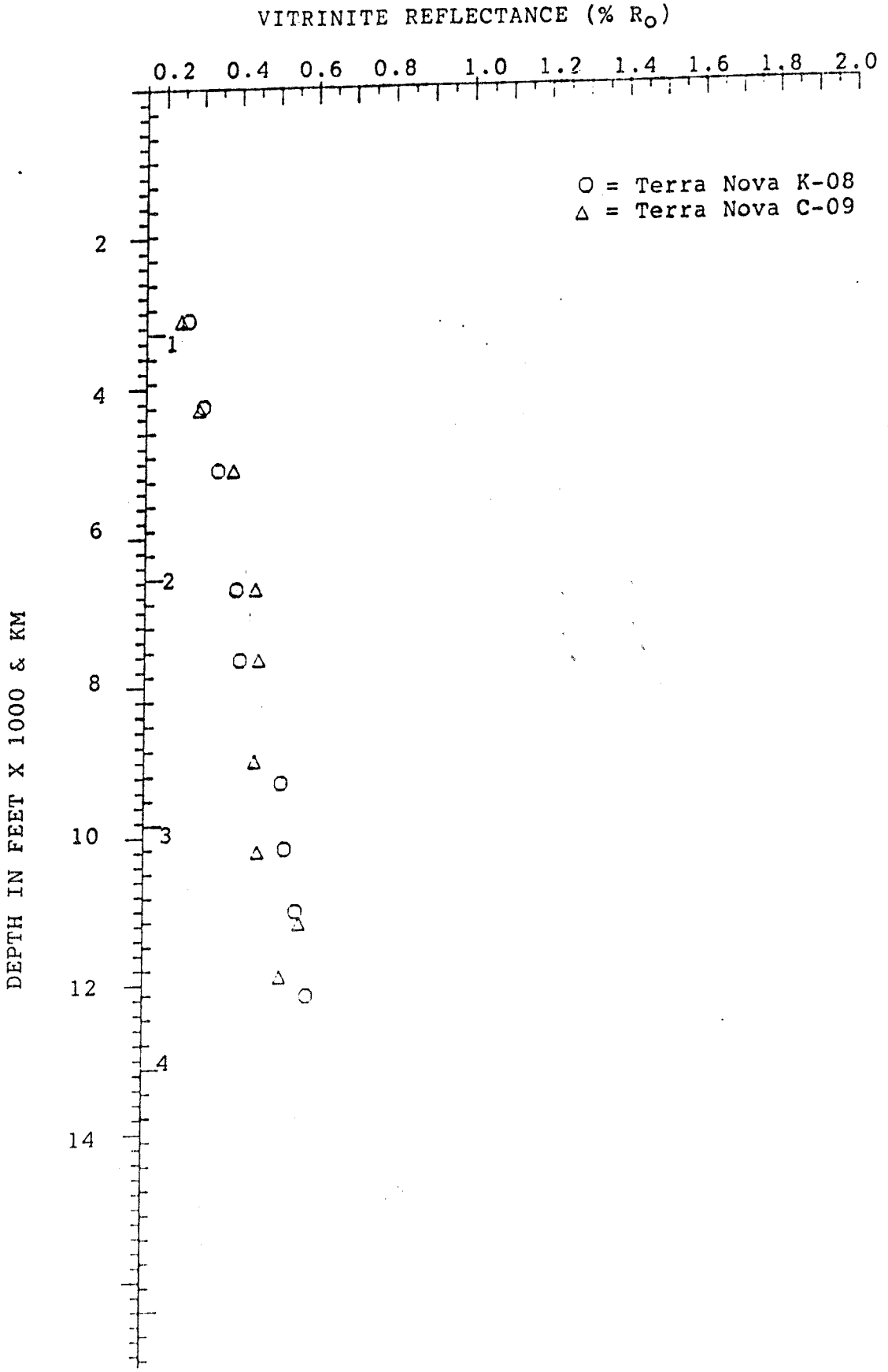
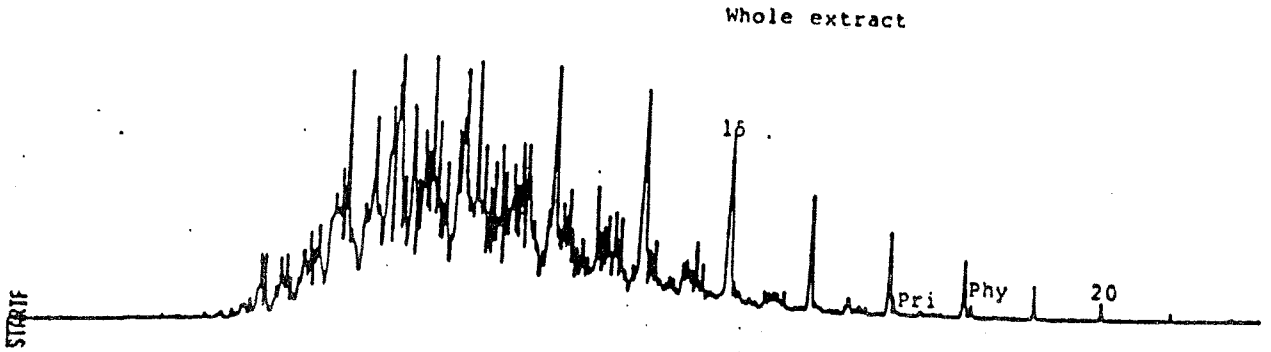
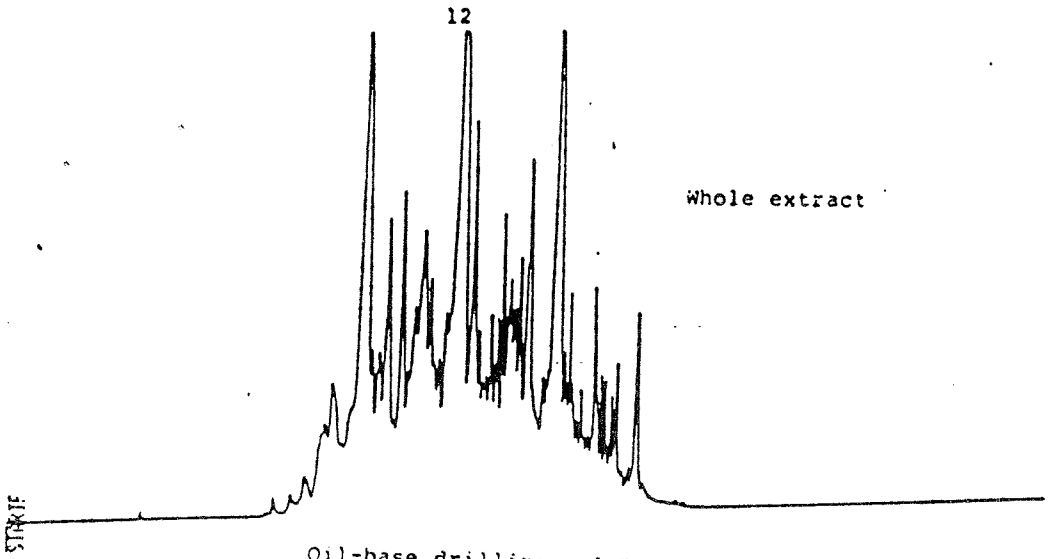

VITRINITE REFLECTANCE (% R_o)
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0
O = Terra Nova K-08
Δ = Terra Nova C-09
DEPTH IN FEET X 1000 & KM
2
4
6
8
10
12
14
1
2
3
4

Fig. 1d



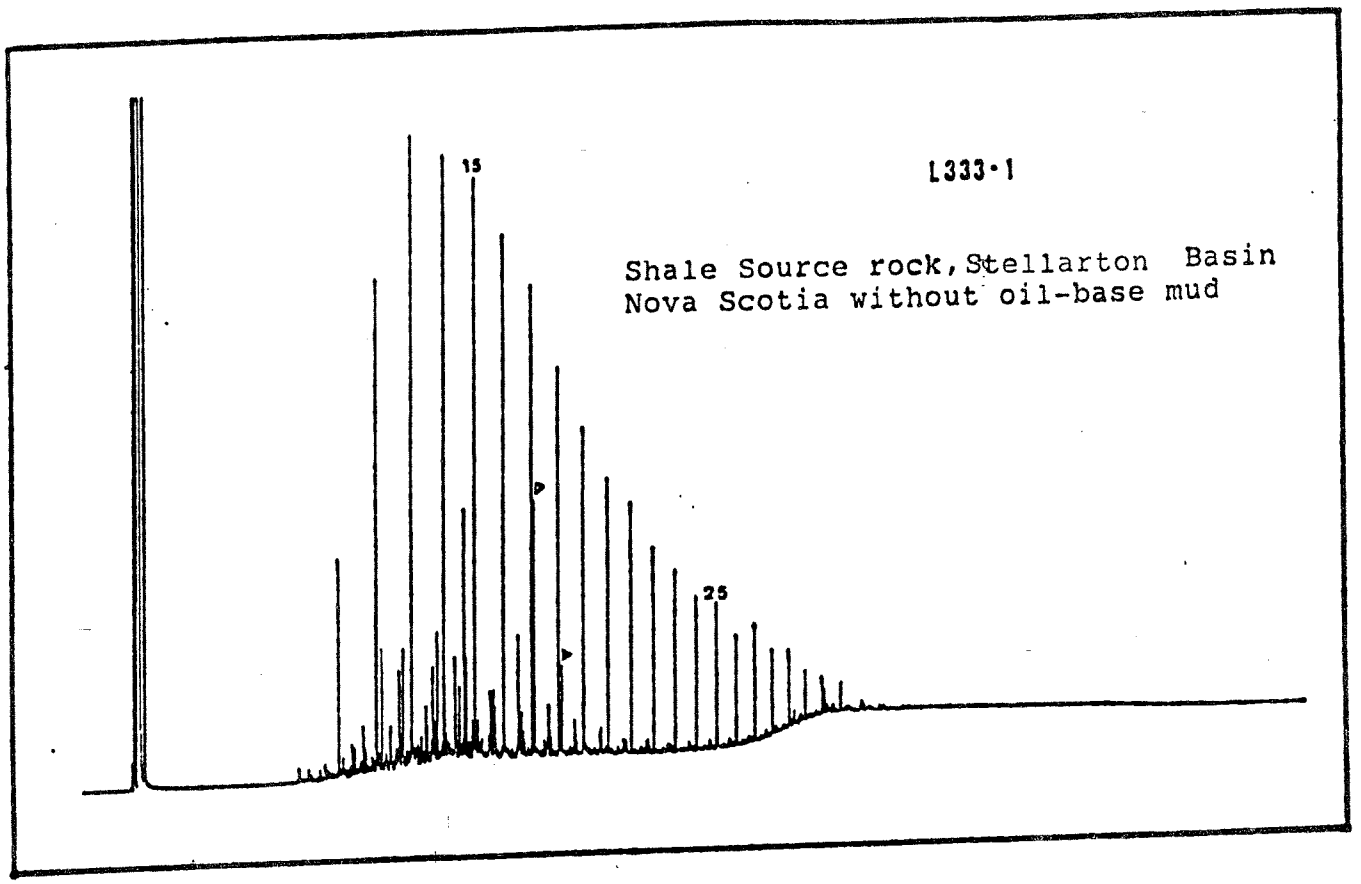
Oil-base drilling mud Shell Sol DMS



Oil-base drilling mud Exxsol D80

Fig. 2

Fig. 2a



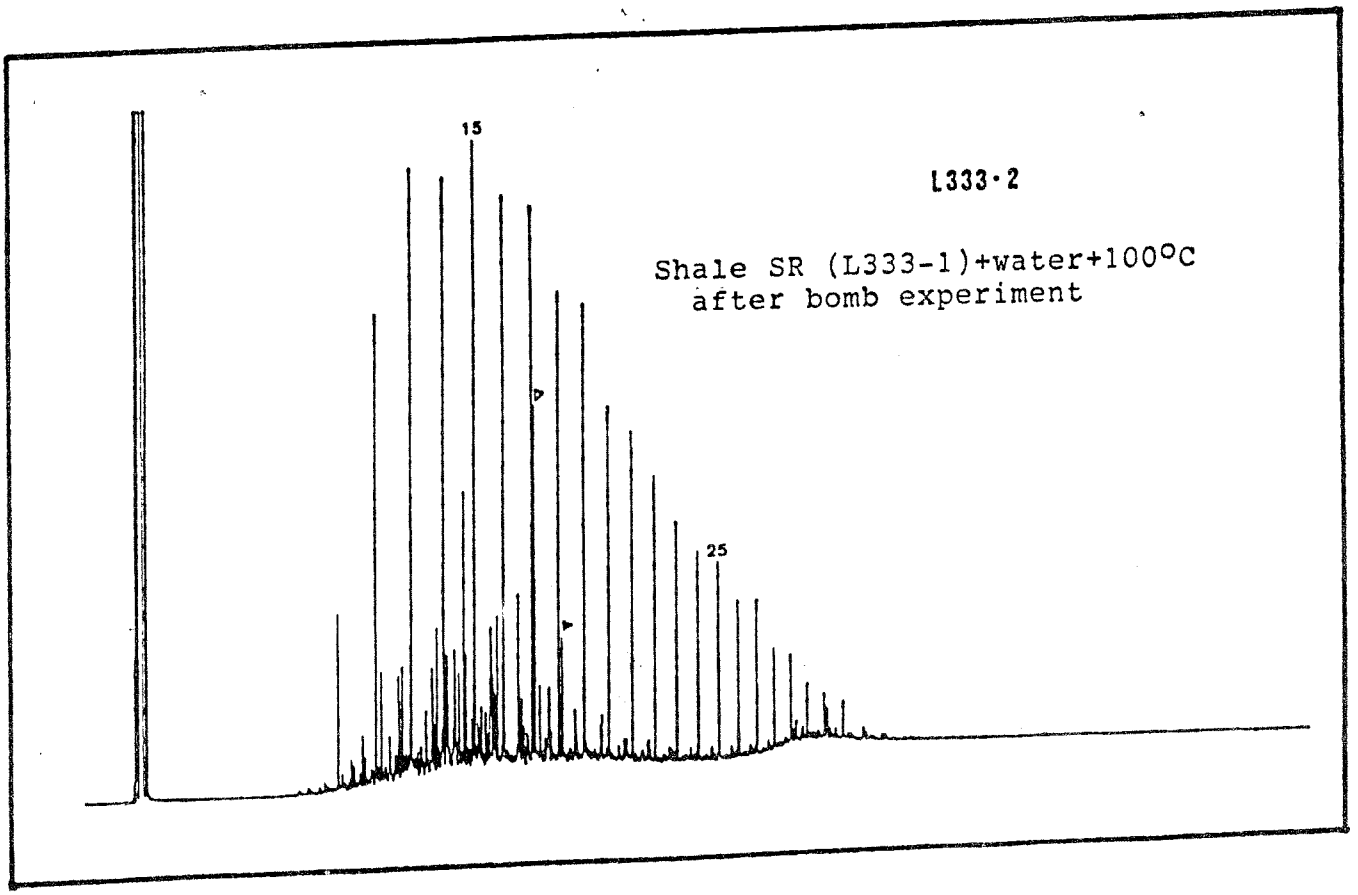
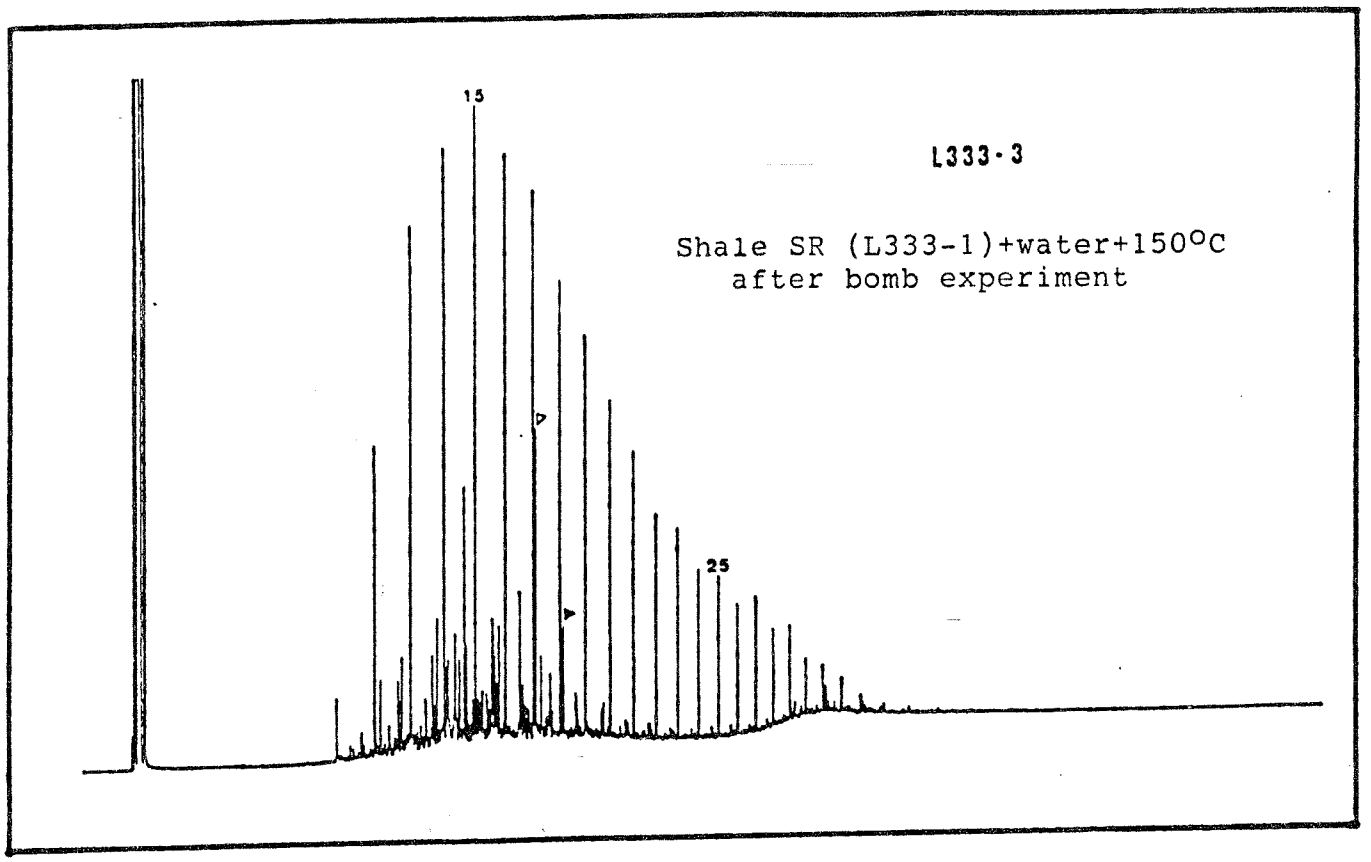


Fig.2b Capillary gas chromatograms of extract saturate fractions.



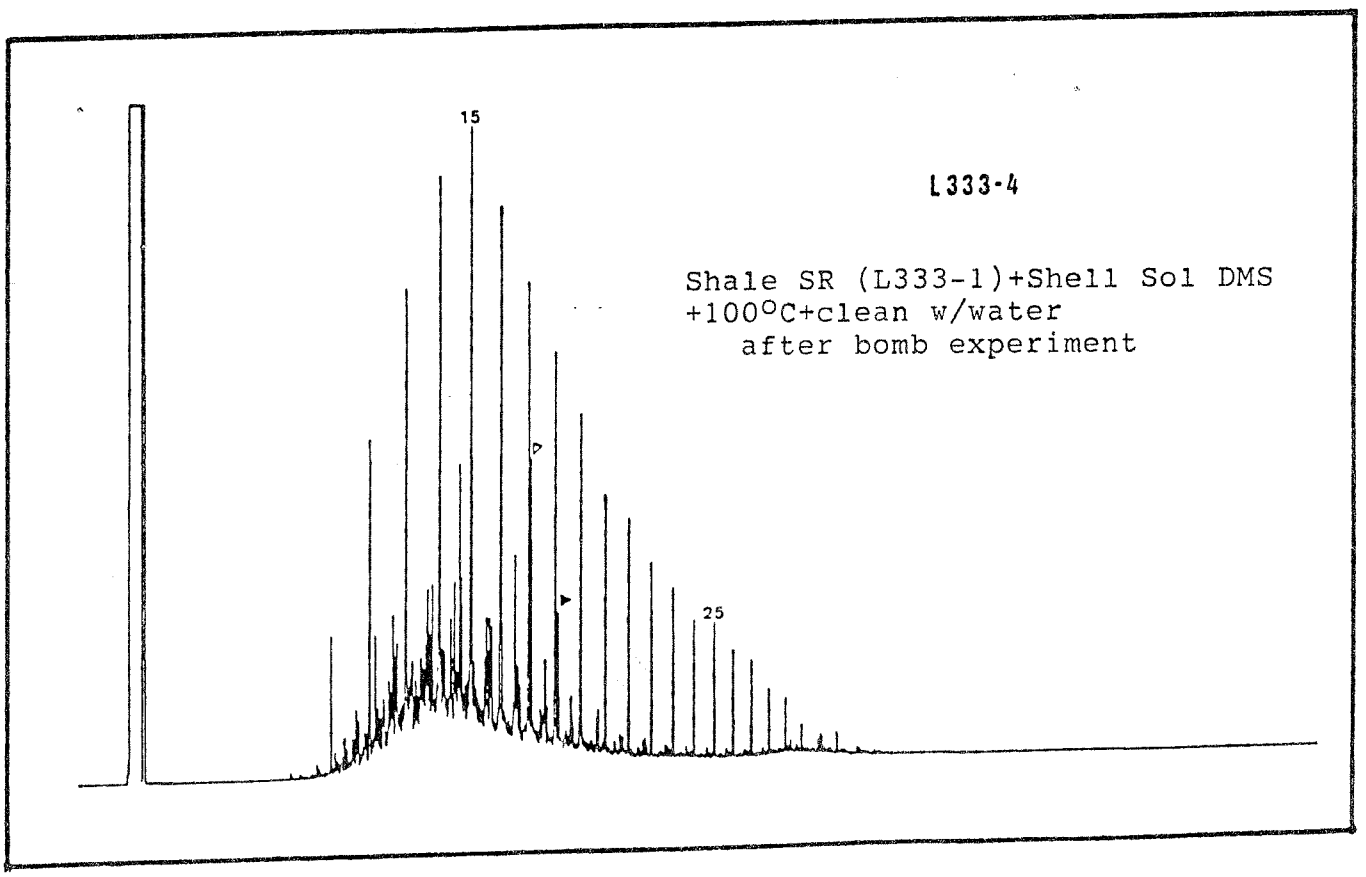
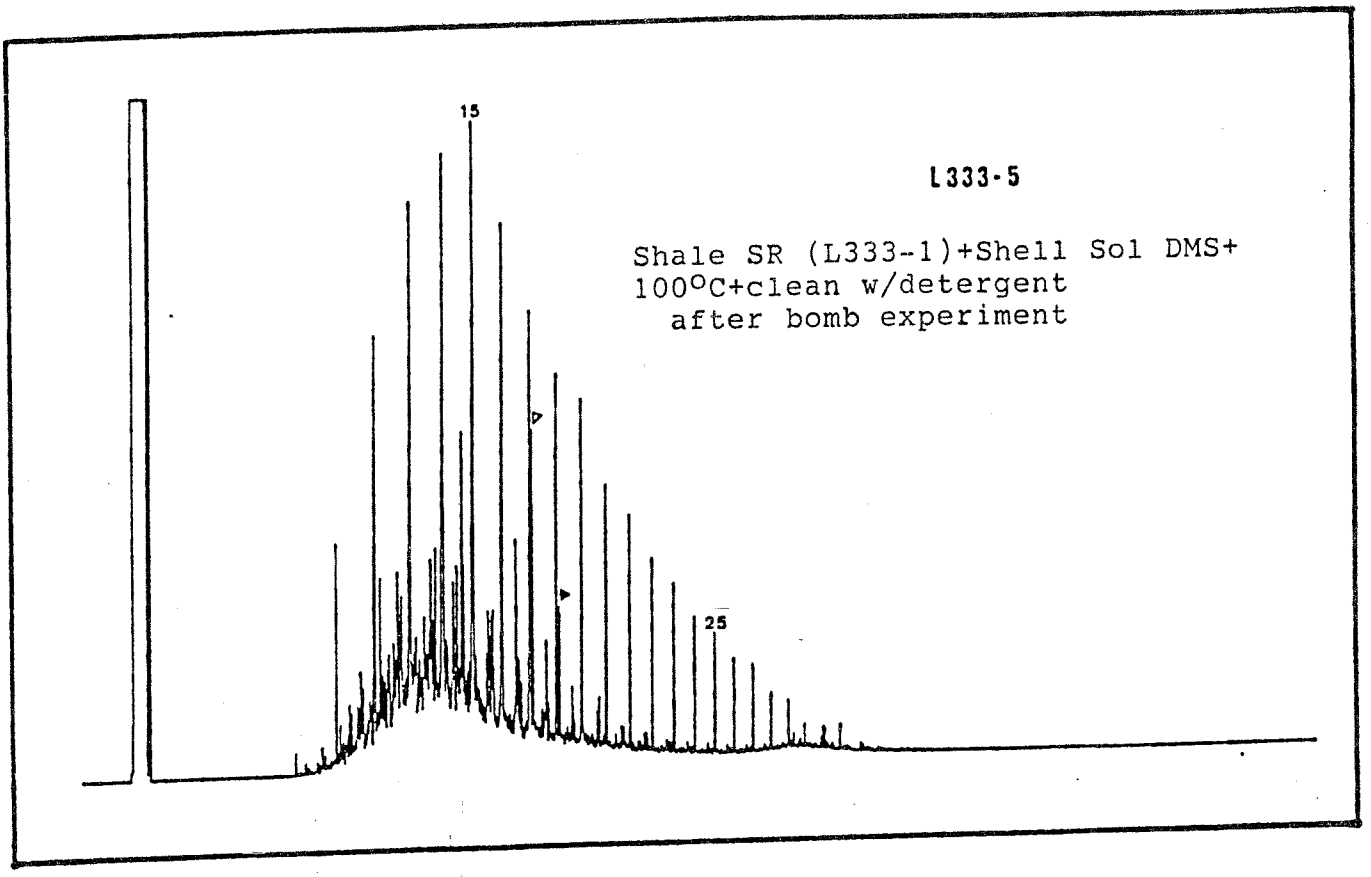


Fig.2b Capillary gas chromatograms of extract saturate fractions.



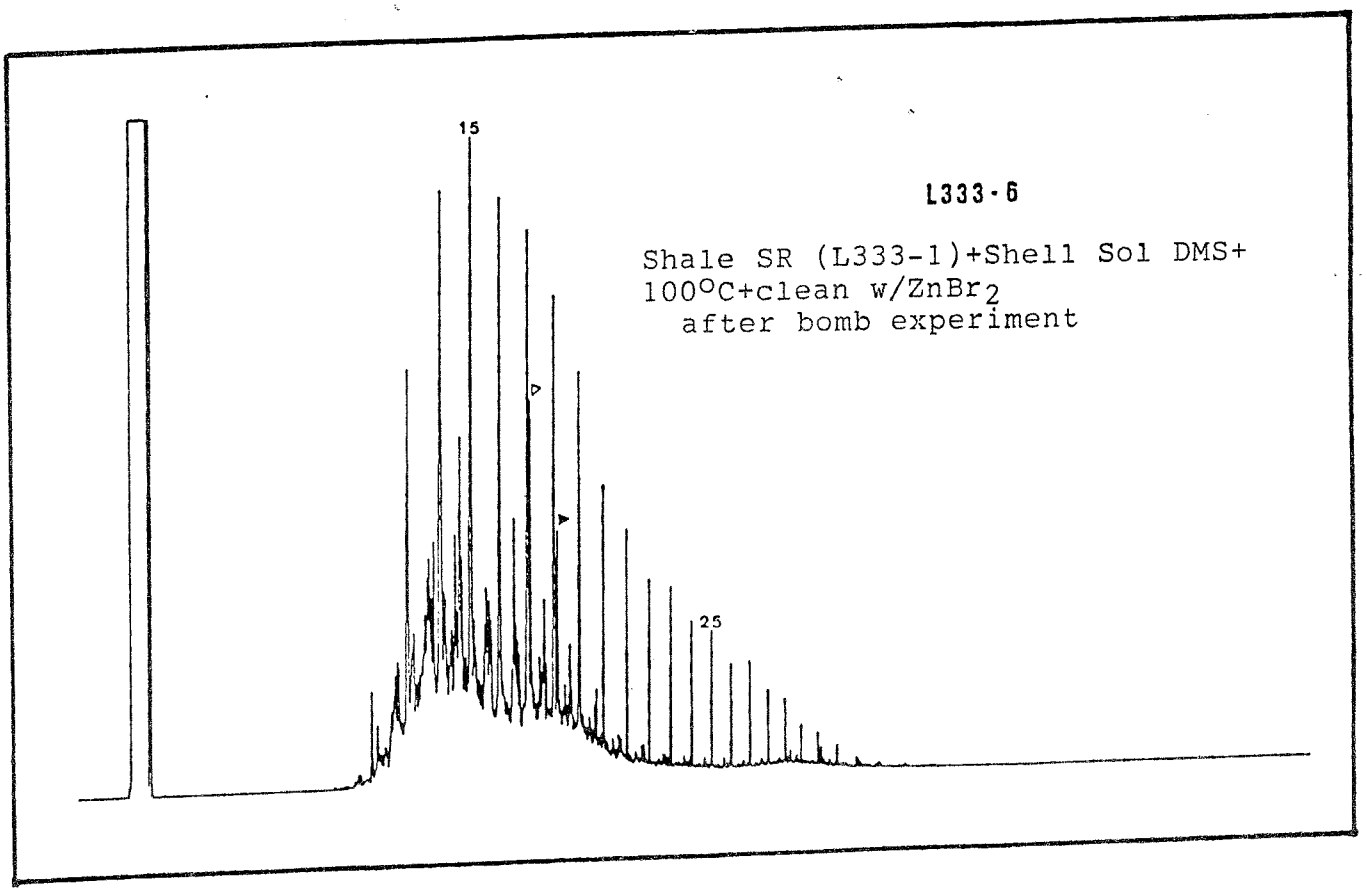


Fig 2b Capillary gas chromatograms of extract saturate fractions.

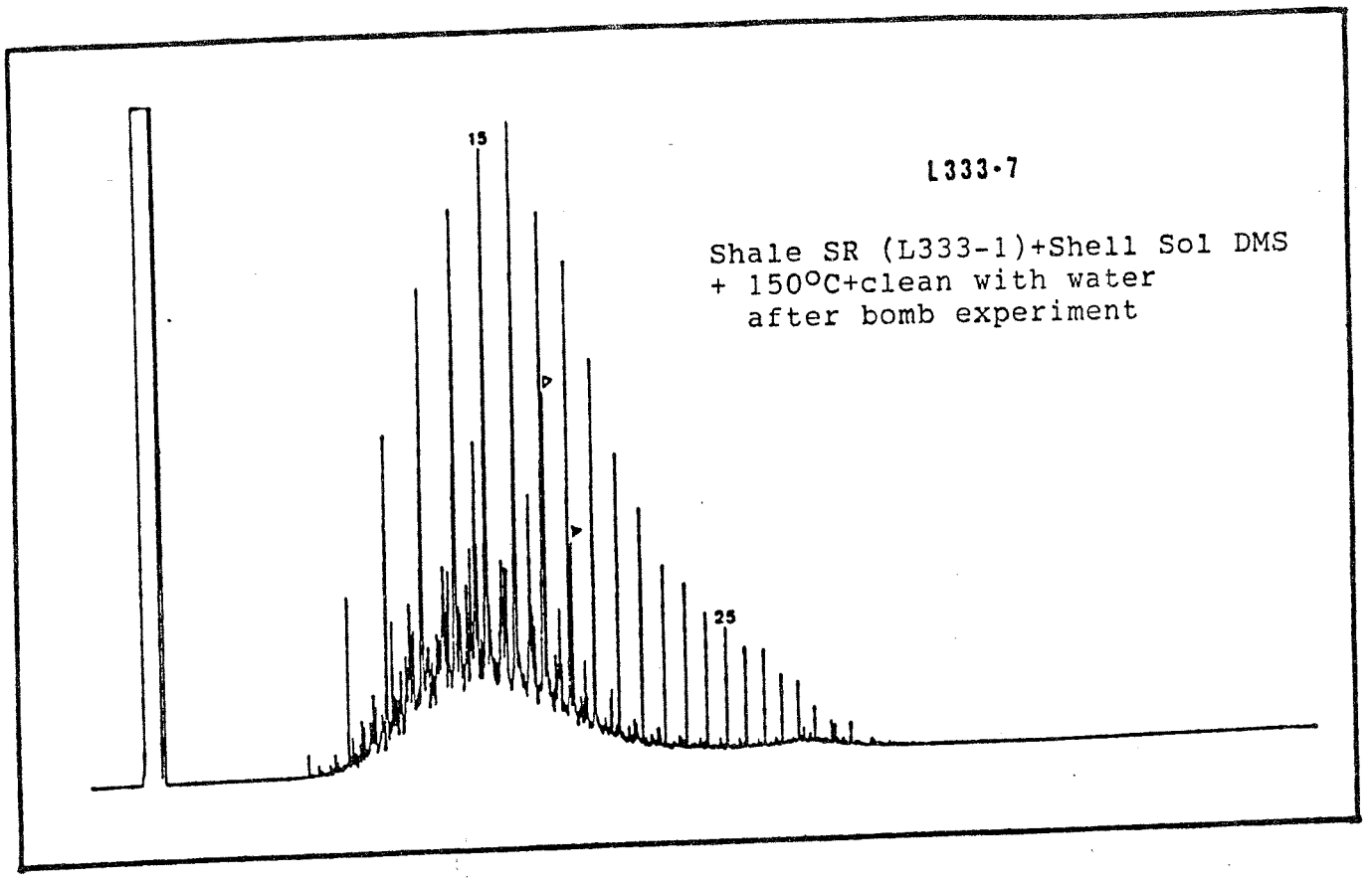
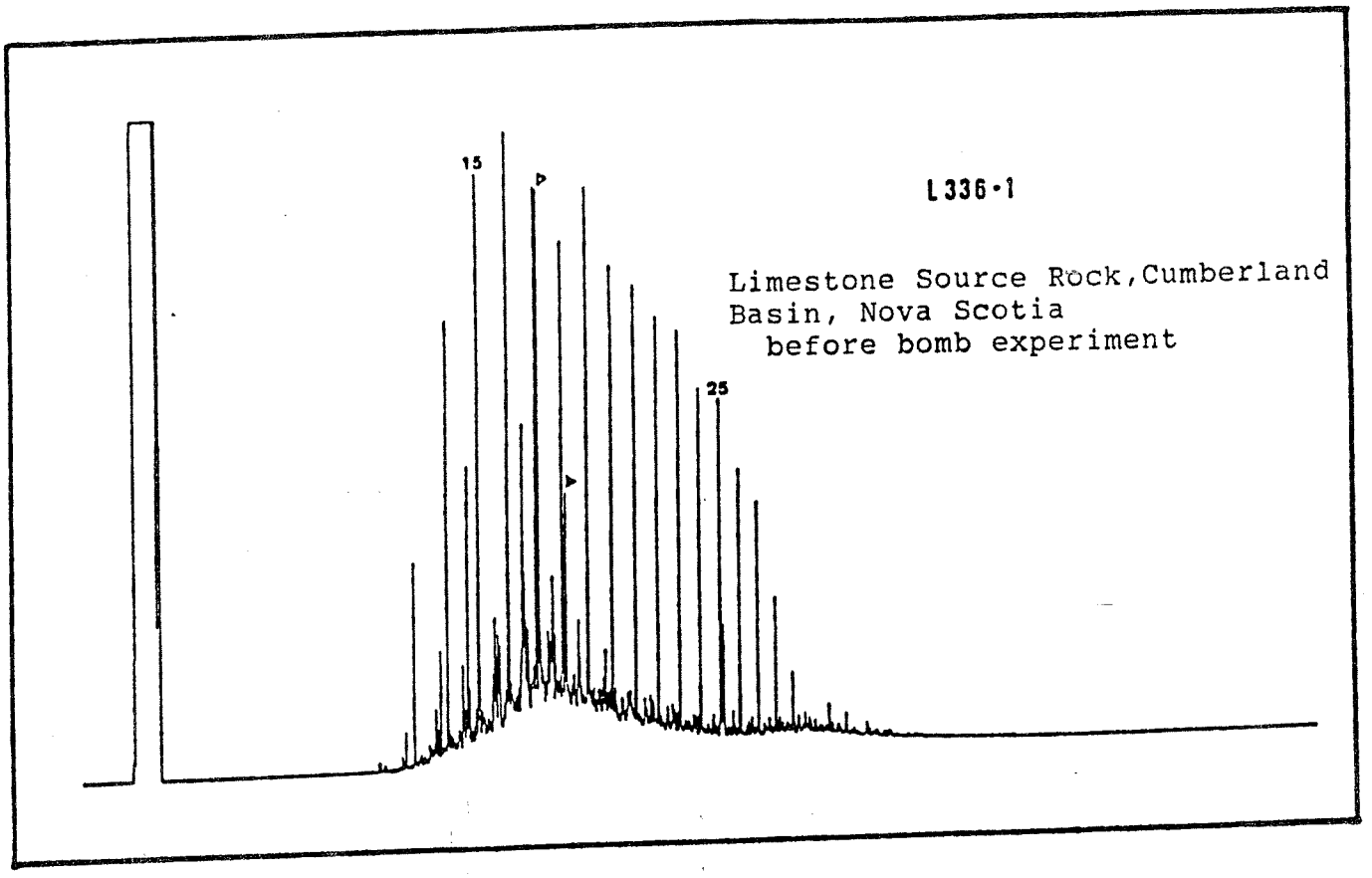


Fig. 2b. Capillary gas chromatograms of extract saturate fractions.



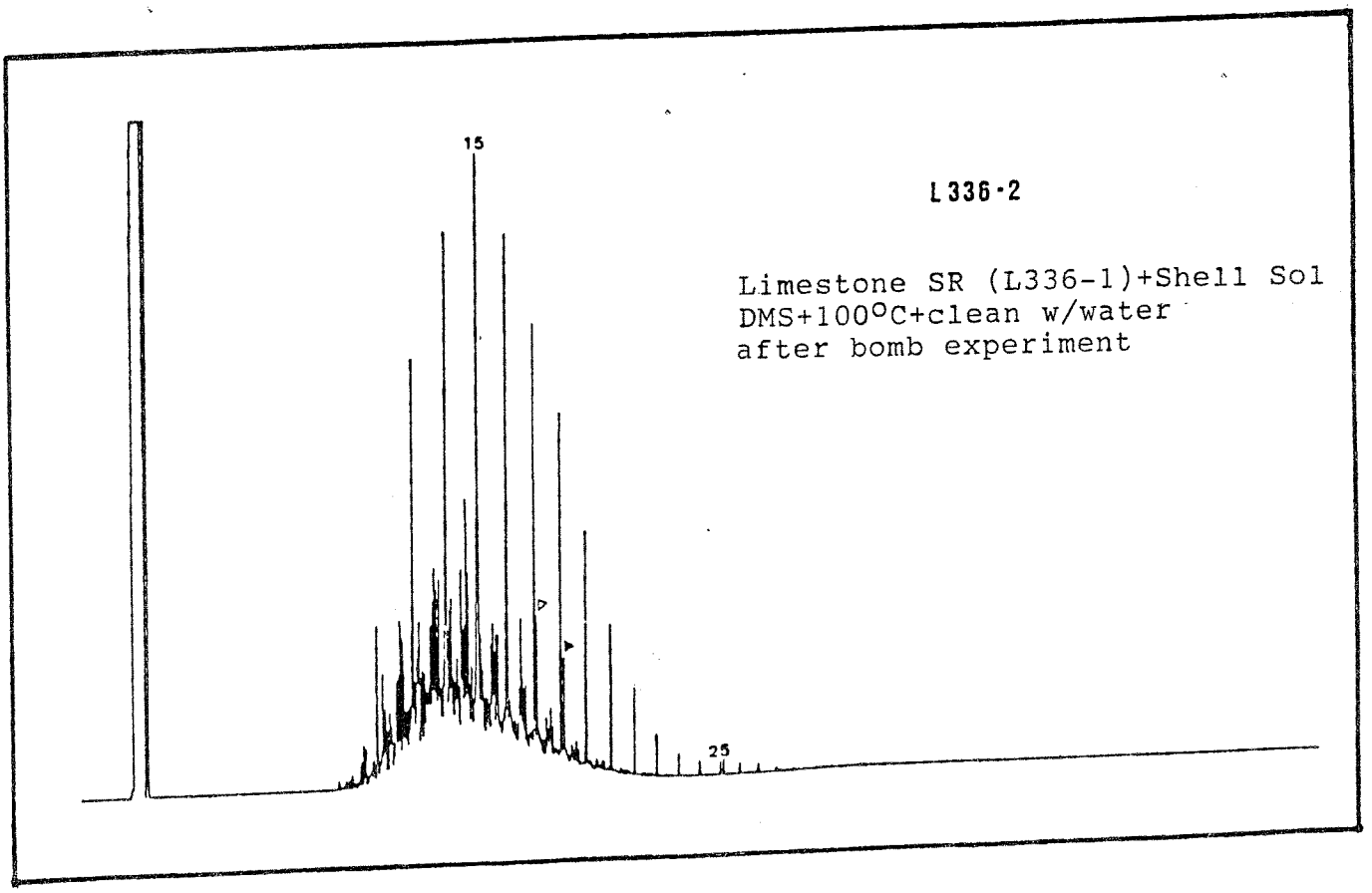


Fig.2c Capillary gas chromatograms of extract saturate fractions.

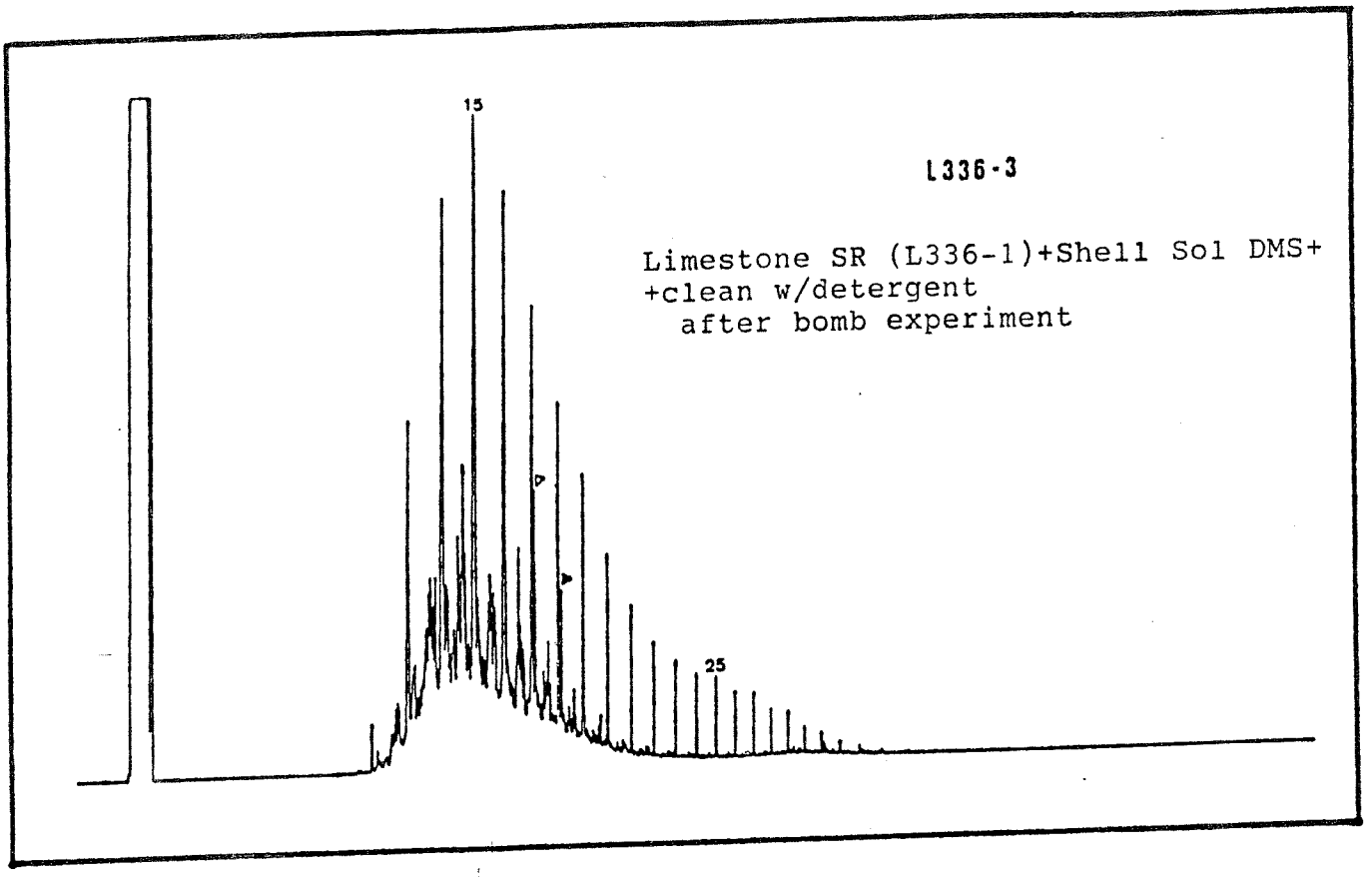
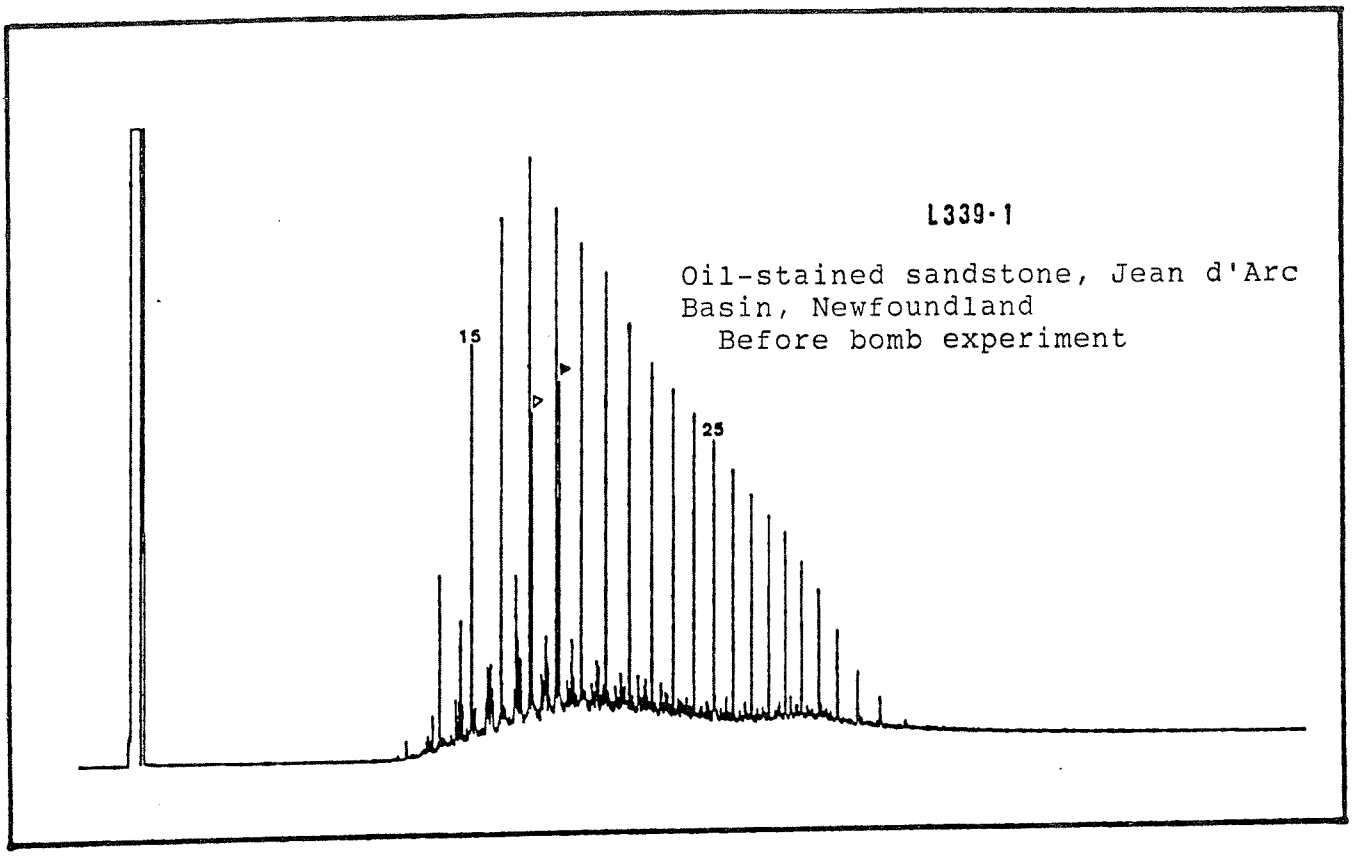


Fig. 2.Capillary gas chromatograms of extract saturate fractions.
Fig. 2c



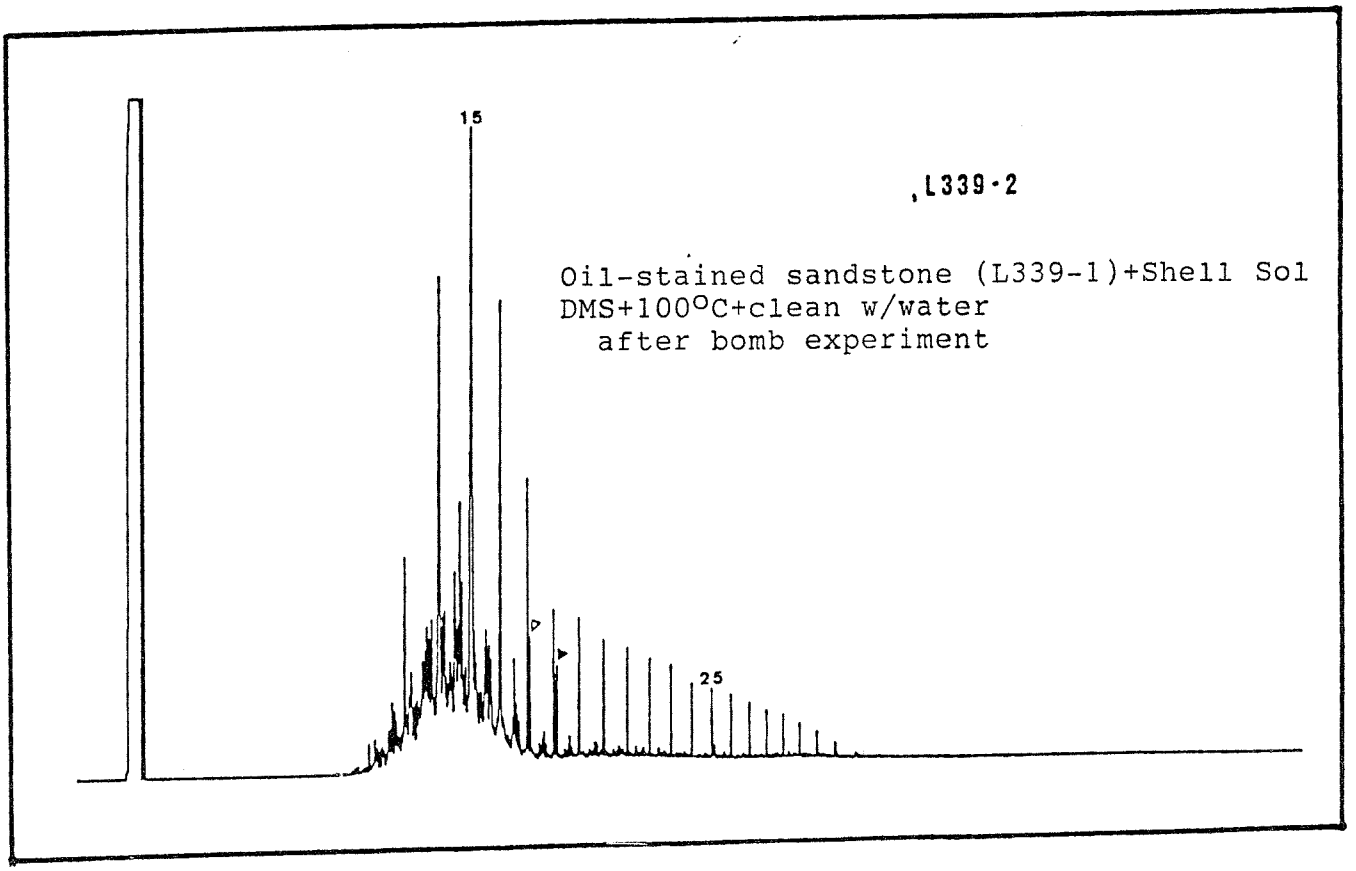
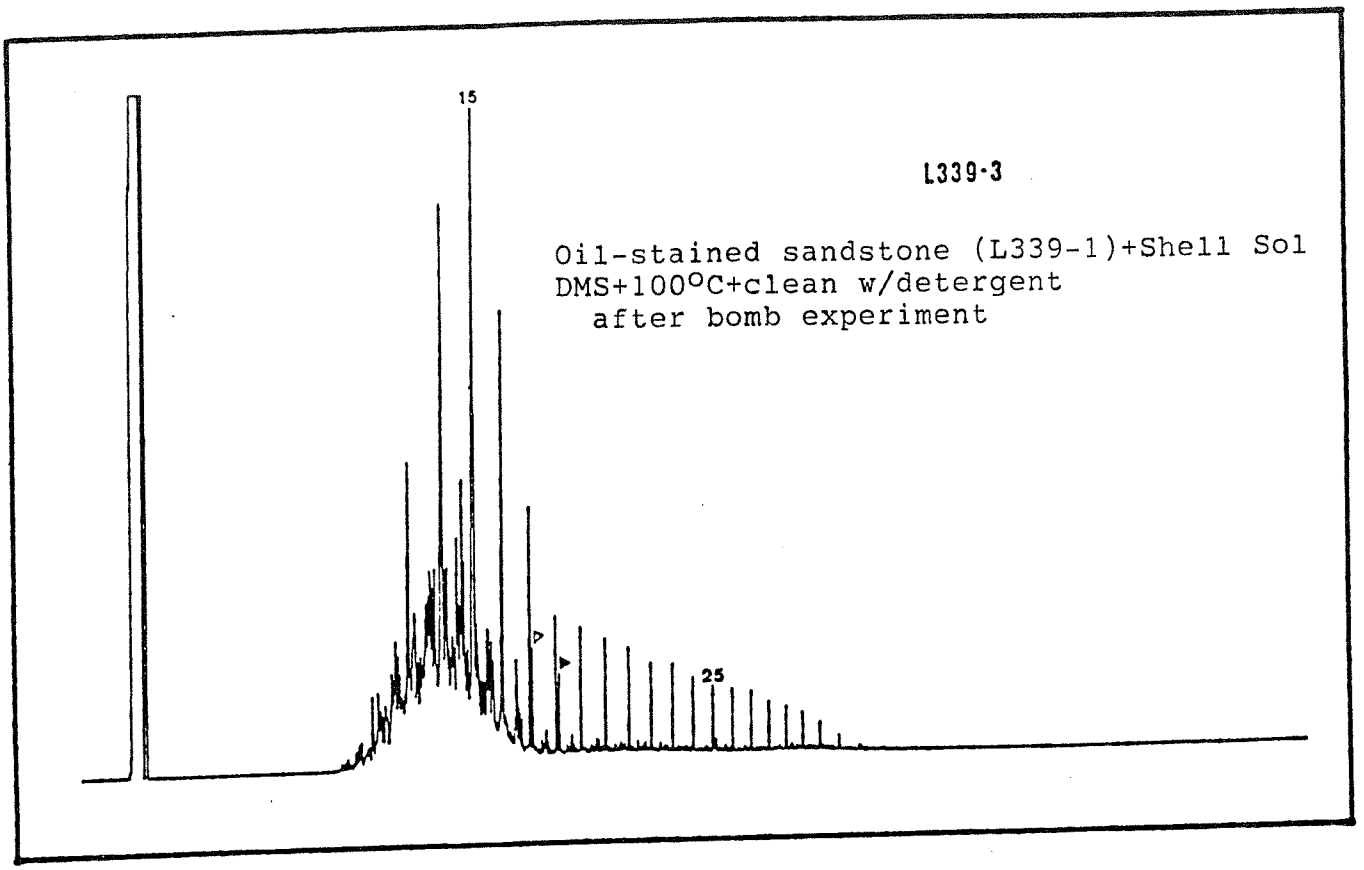


Fig.2. Capillary gas chromatograms of extract saturate fractions.
Fig. 2d.



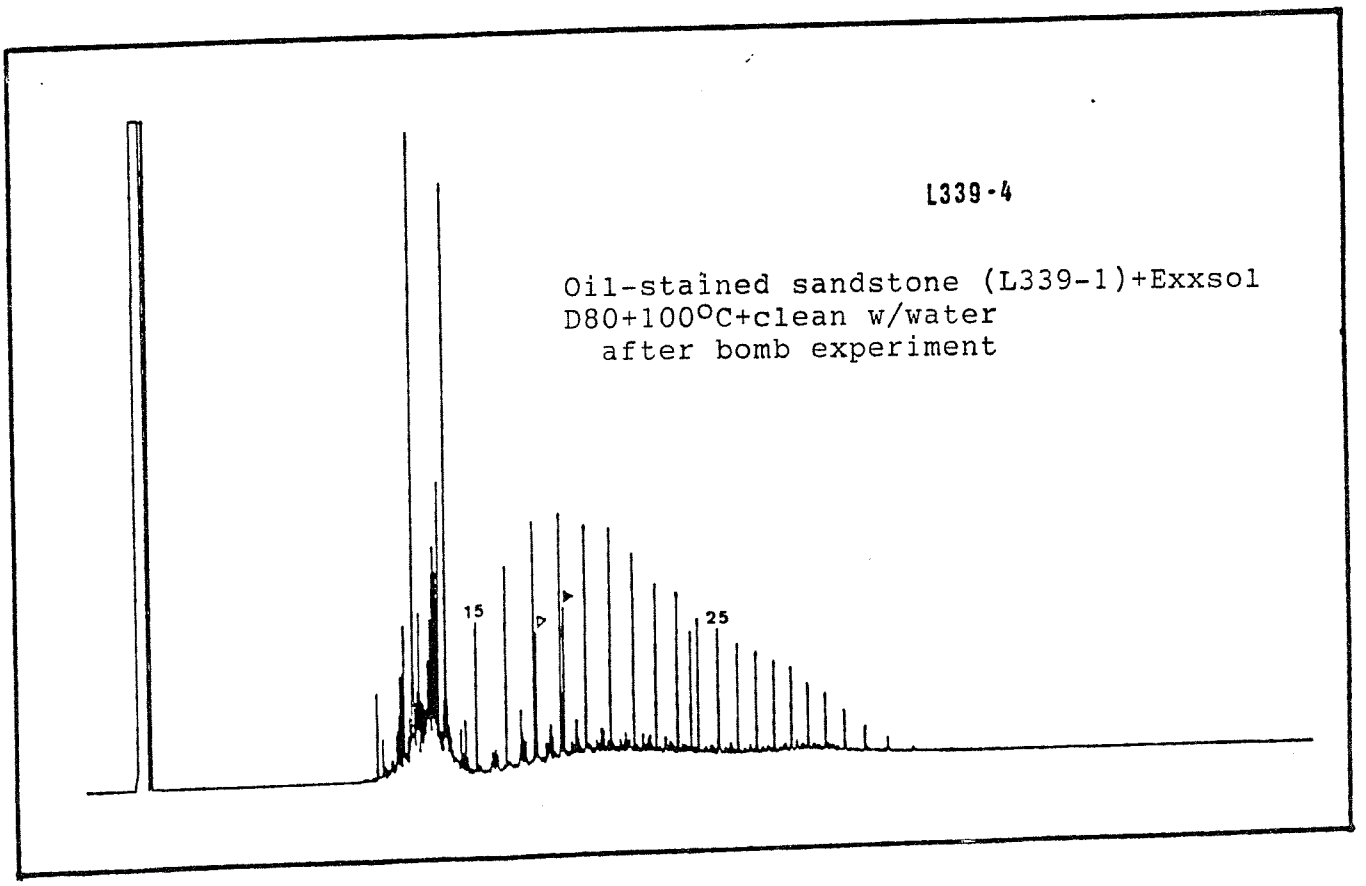


Fig.2 Capillary gas chromatograms of extract saturate fractions.

Fig. 2d

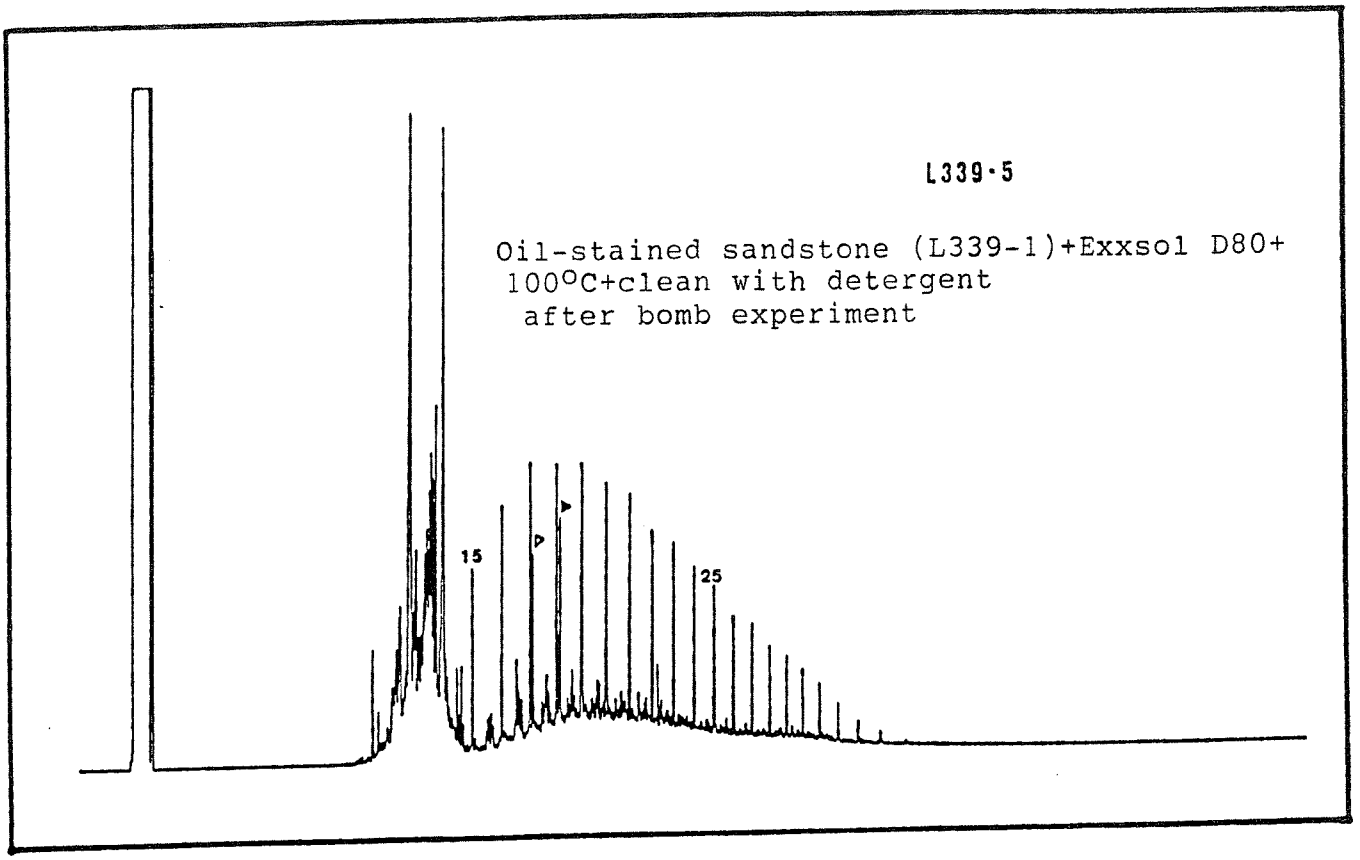
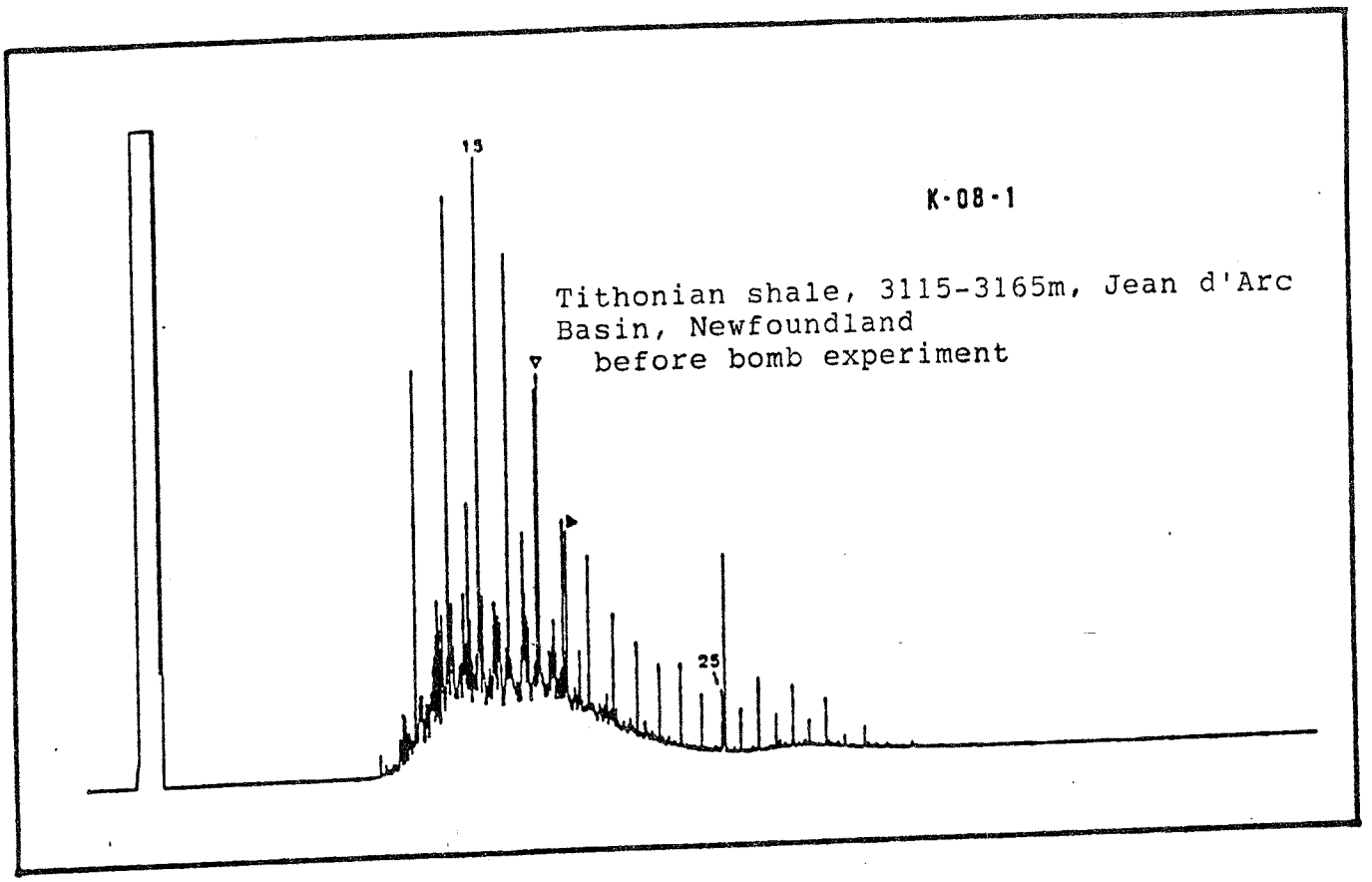


Fig.2 Capillary gas chromatograms of extract saturate fractions.

Fig. 2d



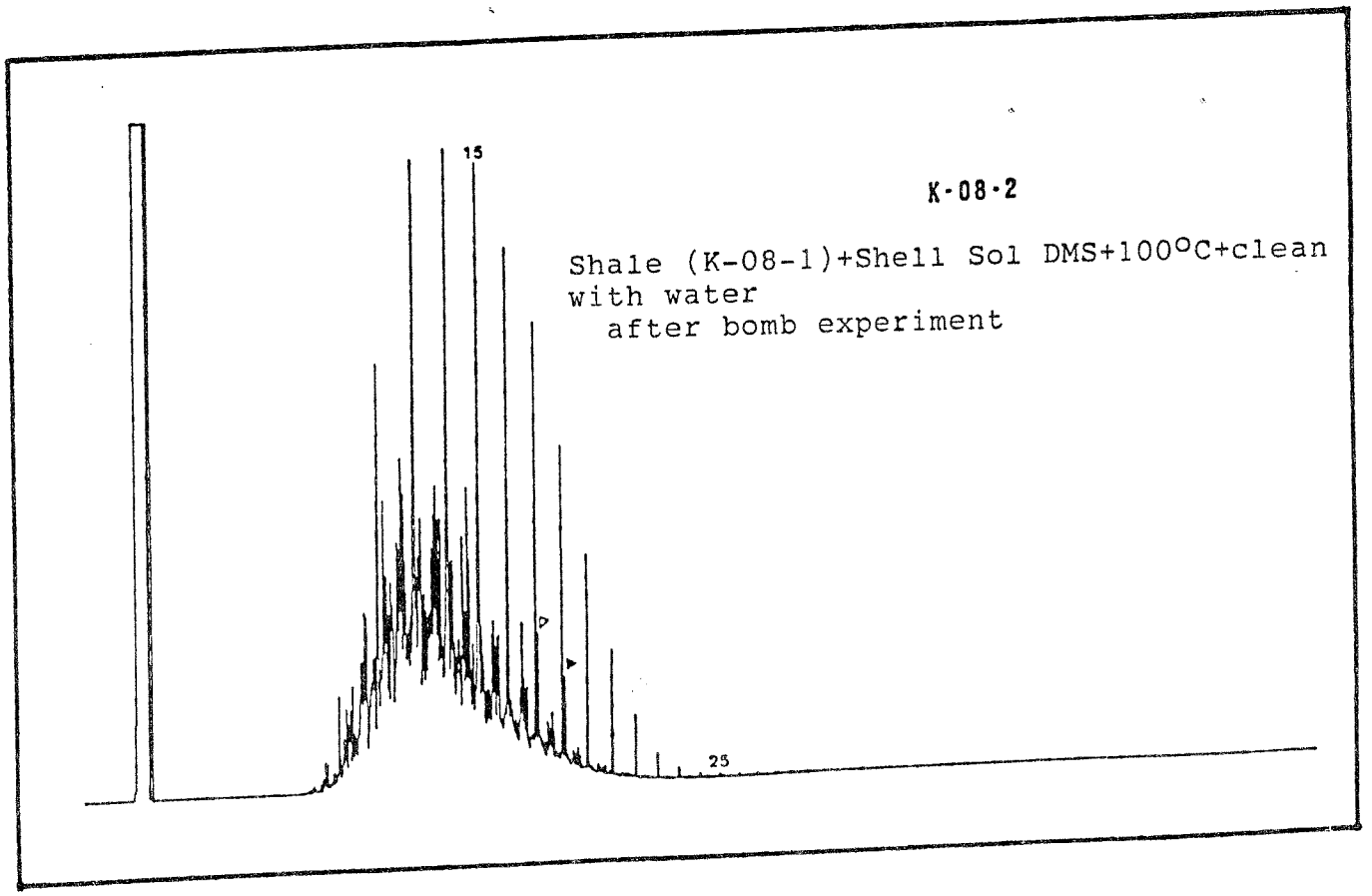
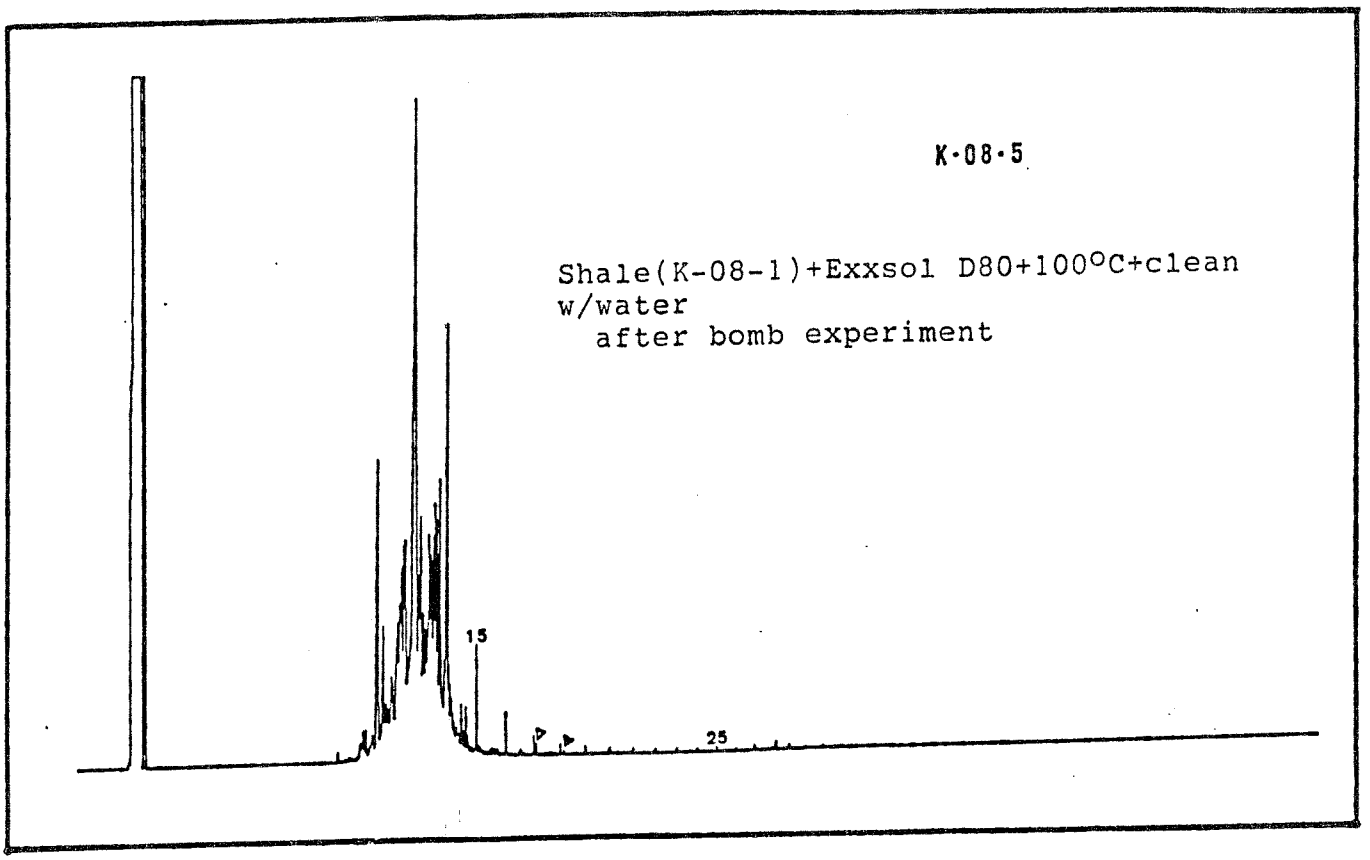


Fig.2. Capillary gas chromatograms of extract saturate fractions.



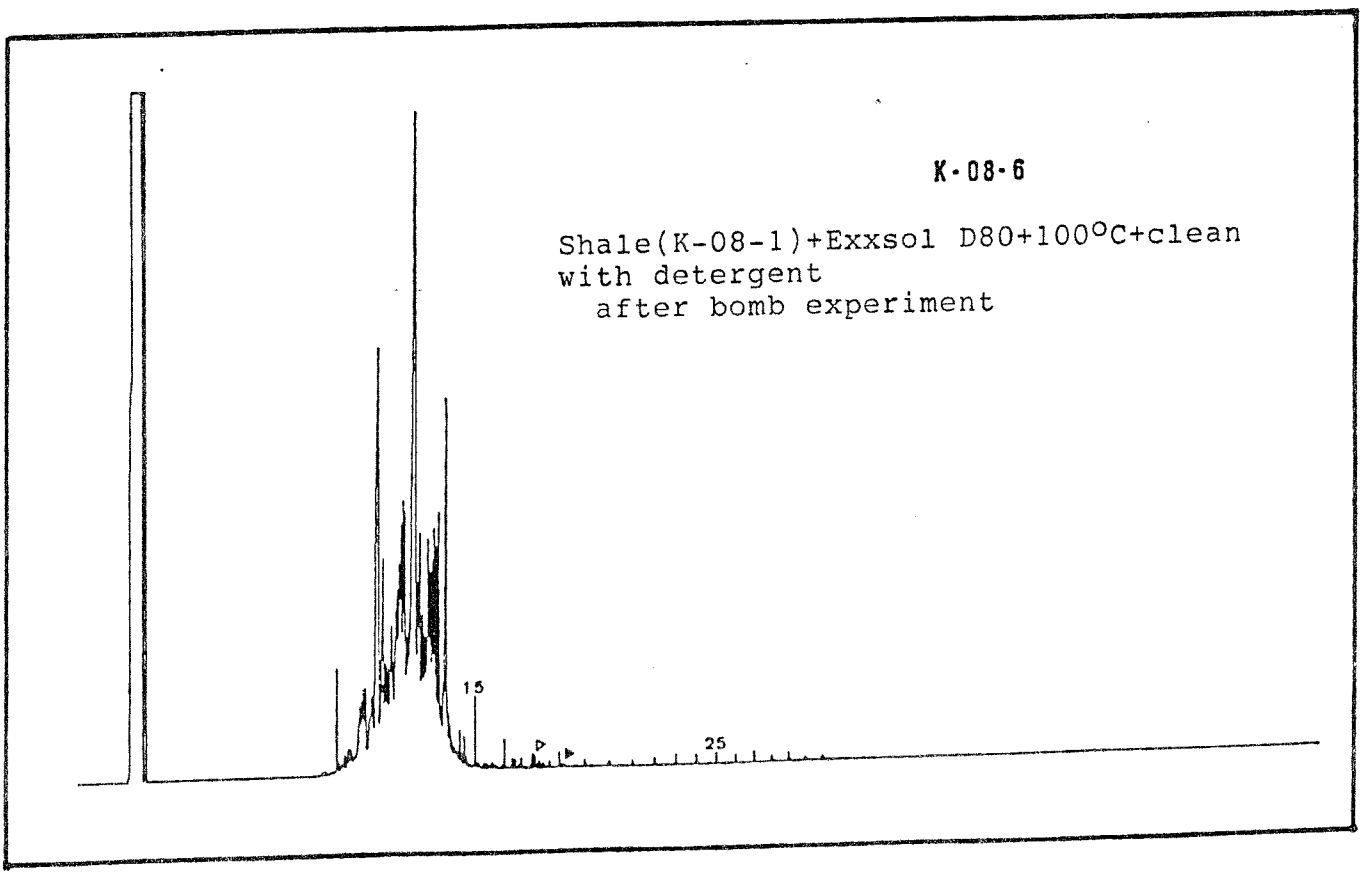


Fig.2. Capillary gas chromatograms of extract saturate fractions.

Fig. 2a

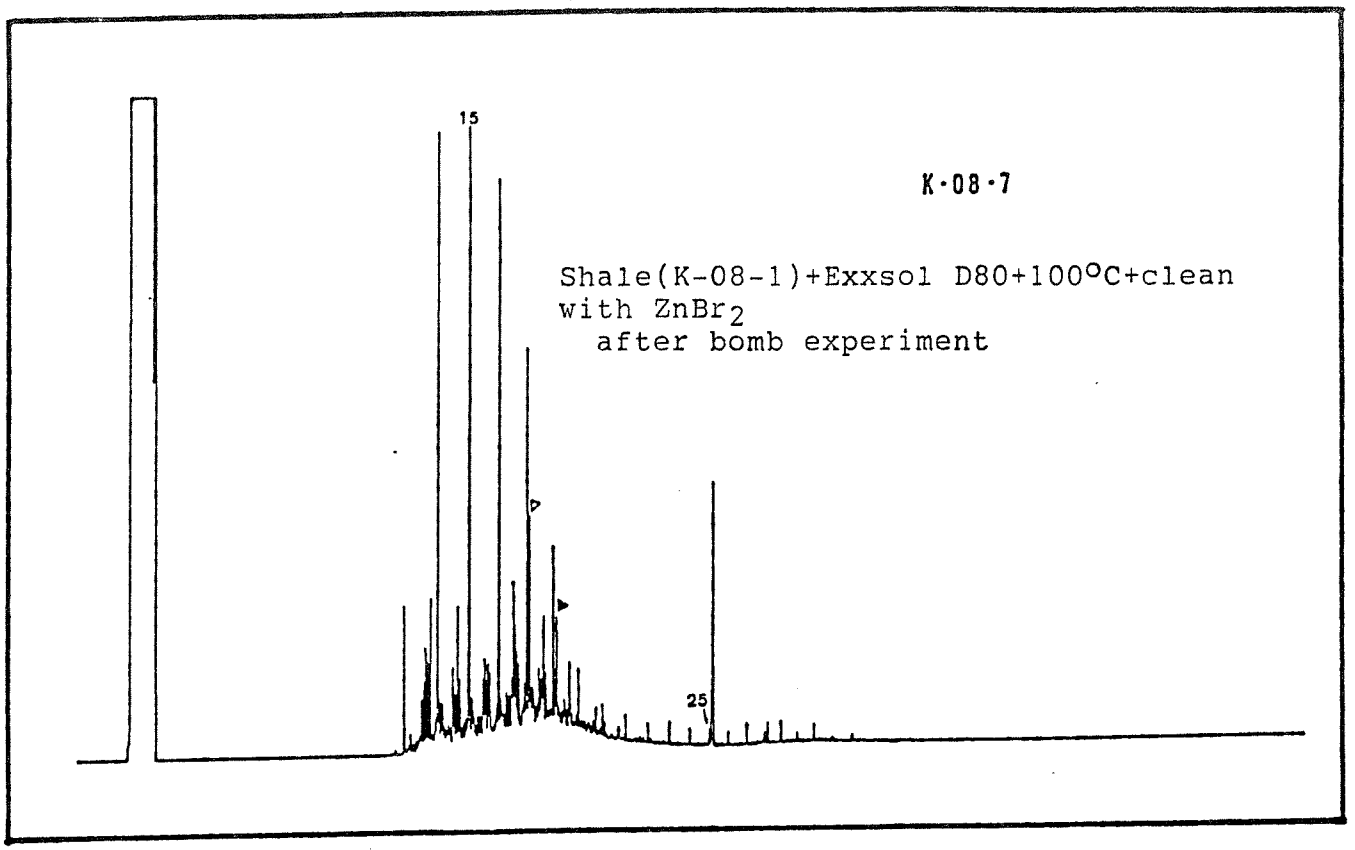


Fig.2. Capillary gas chromatograms of extract saturate fractions.

Fig. 2e