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SUMMARY/ SAMMENDRAG

Four cores and seven cuttings samples containing migrated hydrocarbon were supplied for correlation of the hydrocarbons found in well 30/6-11 with two oil samples from well 30/6-4. Chromatographic separation and GC, GC-MS and $\delta^{13}C$ isotope analyses were performed. The highest abundance of hydrocarbons was seen in three of the cores. The shallowest cores are thought to contain hydrocarbons that have originated from a source rock different to the one that has sourced the two oils. The hydrocarbons in the cuttings and possibly one of the cores show characteristics similar to the oils.

KEY WORDS/ STIKKORD

Correlation | North Sea | Oils | Migrated hydrocarbons

CONTENTS

1. INTRODUCTION

Four cores and seven cuttings samples from well 30/6-11 were supplied for correlation purposes together with two oil samples from well 30/6-4. The aim of the study is to compare the characteristics of the migrated hydrocarbons in the 30/6-11 samples with those of the two oils. A list of the sample codes and depth intervals is given in Table 1.

Chromatographic separation, GC and GC-MS analyses were performed. Six of the cuttings samples arrived in cans, and the samples did all contain water with a relatively dark colour. For these samples both the water and the cuttings were extracted separately to compare amounts and distribution of hydrocarbons.

Some of the samples gave too low concentrations of extractable organic matter for us to be able to perform all the suggested analyses. It was decided to do $\delta^{13}C$ isotope analyses rather than further HPLC separation of the aromatic hydrocarbons for these samples. Some samples contained even too small amounts for the isotope analysis, and only GC and GC-MS results were obtained for these samples.

This final report includes the $\delta^{13}C$ isotope analyses.

For all the other data that was reported previously we refer to the preliminary report (05.0147/1/83).

2. EXPERIMENTAL

2.1 Extractable Organic Matter

The extraction of the cores was performed on the inner part of the cores, thus omitting contamination from the waxed surfaces.

Approximately 50gm of powdered rock was extracted by a ultrasonic probe for 3 minutes using dichloromethane (DCM) as solvent. The DCM used was of organic geochemical grade and blank analyses showed the occurrence of negligible amounts of contaminating hydrocarbons.

Activated copper fillings were used to remove any free sulphur from the samples.

The cuttings samples were extracted by careful washing with DCM, instead of using the ultrasonic probe on crushed samples. Prior to the washing the coaly part of the cuttings was removed by heavy liquid separation. In addition the water that filled the cans of 6 of the samples were extracted by shaking with DCM.

After extraction the solvent was removed on a Buchi Rotavapor and the amount of extractable organic matter (EOM) was determined.

2.2 Chromatographic Separation

The extractable organic matter (EOM) was separated into saturated fraction, aromatic fraction and non hydrocarbon fraction using a MPLC system with hexane as eluant (Radke et al., Anal. Chem., 1980). The various fractions were evaporated on a Buchi Rotavapor and transferred to glass vials and dried in stream of nitrogen. The two oils were separated using the same system.

Further separation of some of the aromatic fractions was performed by HPLC, into subfractions according to ring size.

2.3 Gas Chromatographic Analysis

The hydrocarbon fractions were each diluted with n-hexane and analysed on a HP 5730A gas chromatograph, fitted with a 25m OV-101 fused silica

capillary column. Hydrogen (0.7ml/min) was used as carrier gas.

The aromatic AF2 fractions (aromatic compounds with 3 rings) were also analysed on a Varian Model 3700 GC especially designed for separation of aromatic components, fitted with a 100m glass capillary column and a back-flushing system. Hydrogen was used as carrier gas.

Injections on both systems were performed in the split mode (1:20). The temperature program applied was 80°C (2 min) to 260°C at 4°C/min.

The data processing for all the GC analyses was performed on a VG Multichrom System.

2.4 Thermal Extraction GC

20-30mg of fine ground whole rock sample was placed in a boat shaped sample probe and heated in a stream of helium at 300°C for five minutes. The extract was flushed directly into a capillary column via a laboratory built interface/splitter.

A 25m OV-1 fused silica column was fitted in the Varian 3700 gas chromatograph, and a temperature program of 40°C/min to 270°C/min at 4°C/min was employed. Nitrogen (1.5ml/min) was used as carrier gas and injections were performed in split mode (1:30).

2.5 GC-MS Analysis

The GC-MS analysis were performed on a VG 70-70H mass spectrometer coupled to a Varian 3700 gas chromatograph. A 20m OV-1 fused silica column was fitted in the chromatograph and helium was used as carrier gas. Injections were performed in split mode.

The saturated hydrocarbons were analysed by Multiple Ion Detection (MID) with a scan cycle time of approcimately 2 seconds. Full data collection was applied for the aromatic fractions with a scan time of 2 sec/decade. Data acquisition was done by a VG data system.

2.6 Isotope analysis

The isotope analyses ($\delta^{13}C$) were performed at the Institute of Energy Technology (IFE) according to their method.

All data is reported in the usual delta notation, where

$$\delta\ C^{13} = \frac{^{13}C/^{12}C \text{ sample} - {}^{13}C/^{12}C \text{ standard}}{^{13}C/^{12}C \text{ standard}} \times 1000\ (\%)$$

The values are reported against PDB, and the $\delta^{13}C$ value for the international standard NBS 22 lubricating oil is 29.77 $\pm$ 0.06.

3. RESULTS AND DISCUSSION

Prior to extraction and chemical analyses various characteristics were noted for the cores and cuttings samples. Of the cores two (A-6664 and A-6665) were found to give bright yellow-white fluorescence and blue-white cut in UV. The shallowest core (A-6663) showed a very slight dull orange-brown fluorescence and no cut in UV. A dull brown fluorescence with a blue-white cut in UV was seen for the deepest core (A-6666). This indicates that there might be differences between the core samples, the samples that showed bright fluorescence might be expected to contain more abundant hydrocarbons.

A lithological description of the cuttings samples is given in Table 2. Among the cuttings samples, one (A-6671) gave a very strong smell of sulfur when the can was opened.

3.1 Gross Composition

The distribution of the various chromatographic fractions are given in Table 3.1-3.4.

Oil Samples

The oil samples were seen to be very similar, containing approximately twice as much saturated as aromatic hydrocarbons and equal amounts of hydrocarbons and non-hydrocarbons.

Core Samples

The three deepest cores were found to contain very high amounts of extractable organic matter, while the shallowest core (A-6663) was poorer by a factor of ten. There seem to be increased amounts of saturated hydrocarbons relative to aromatic compared to what was found for the oils. Particularly the ratio for sample A-6664 is high (6.6). These increased ratios might indicate either that the hydrocarbons in the cores are from a different source than the oils, or that different migration pathways have caused the variation.

The amount of hydrocarbons relative to non-hydrocarbons is also increased in the cores.

Cuttings Samples

The cuttings samples are seen to contain significantly lower amounts of hydrocarbons than the three richest cores, two of the cuttings (A-6668 and A-6673) being richer than the rest of the cuttings. The ratios between saturated and aromatic hydrocarbons are reduced compared to those for cores and oils.

Approximately equal amounts of hydrocarbons and non-hydrocarbons are seen for most of the samples.

Results from the extraction of the water above the cuttings are presented in Table 4. Due to the very low hydrocarbon concentrations these data will not be discussed in any detail.

3.2 GC analysis of saturated hydrocarbons

Gas chromatograms of the saturated hydrocarbons are presented in Figure 1, and ratios calculated from the chromatograms are given in Table 5.

Oil Samples

The two oil samples (M-3143 and M-6647) were seen to exhibit very similar alkane profiles, both being front end biased with maxima at nC_{15} and abundant n-alkanes above nC_{30}. Pristane/nC_{17} equals 0.5 and pristane/phytane equals 1.6 for both samples. The oils were found to be well mature from a CPI-value of 1.0 and 0.9, for M-3143 and M-6647, respectively.

Core samples

Among the four core samples there seem to be two different alkane patterns. Two of the cores (A-6663 and A-6666) showed distributions similar to those seen for the oil samples, as discussed above. The pristane/-phytane ratios are slightly higher in the cores, while pristane/nC_{17} and CPI give similar values to those for the oils. From the relative intensity of the internal standard peak (S) the shallowest sample (A-6663) is seen to contain lower amount of alkanes than A-6666. This is in good agreement with what was found from the extraction data.

The other two cores (A-6664 and A-6665) exhibit top end biased n-alkane distributions, A-6664 being weakly bimodal. Maximum intensities are seen at approximately nC_{26}, the weak bimodality represented by a shoulder around nC_{15}. This kind of profile may indicate that the two samples are mixture of two different type of hydrocarbons, one being similar to the oils and the other type consisting of the high molecular weight range components. The abundance of isoprenoids relative to n-alkanes is lower in these two cores, and the maturity of the high molecular weight compounds seem to be slightly lower from CPI-values of 1.1.

The concentrations of alkanes relative to the amount of rock extracted is quite similar to that in sample A-6666.

Cuttings samples

Only minor differences were revealed in the GC traces of the seven cuttings samples. Two of the shallowest samples, A-6667 and A-6669, seem to contain more light components than the rest of the cuttings. Maximum intensities occur at approximately nC_{15} for all the samples, but the two samples mentioned above show a steeper decrease in intensity with increasing carbon number. The overall profiles seem to be fairly similar to the oils.

The isoprenoid ratios seem to be relatively consistent throughout the whole suite of samples, the pristane/nC_{17} varying from 0.3 to 0.6 and pristane/phytane from 1.3 to 2.3. Slightly lower maturity was seen for the high molecular weight compounds in the two shallowest and the deepest sample.

The water above the cuttings in the cans was extracted by DCM to compare the content of hydrocarbons here to that in the other samples. In an attempt to relate the abundance of hydrocarbons to the water volume, squalane (S) was added to the samples prior to extraction as an internal standard. The dark colour of the water was, however, misleading and too much squalane was added. The total weight of the saturated and aromatic hydrocarbon fractions was less than 2mg for the majority of the samples. Of the two samples analysed for saturated hydrocarbons, only one gave a chromatogram worth presenting. The profile in this looks quite similar to that seen in the cuttings extract, as would be expected. The very low concentration makes the sample very liable to contamination, which is probably the reason for the intense pristane peak.

3.3 GC analysis of aromatic hydrocarbons

3.3.1 Total aromatic fractions

Gas chromatograms of the total aromatic fractions are presented in Figure 2.

The main components seen to be methylated naphtalene and phenanthrene homologs, the naphtalenes being most abundant in the majority of the samples. The four methyl phenanthrenes (peaks mark D) are relatively

poorly resolved in these chromatograms, but the ratio of the two first eluting isomers to the two eluting last is tentatively assigned for all samples (Table 6). For the samples that were further separated by HPLC and then analysed by GC more accurate ratios were calculated (3.3.2).

Oil Samples

The two oil samples look very similar, the methylated naphtalene homologs predominating over the phenanthrenes. The methyl phenanthrene ratio equals 0.7 for both samples.

Core samples

The variations seen from the saturated GC traces of the cores, do not seem to be so obvious in the aromatic traces. At least the three deepest cores show the same general pattern of abundant naphtalenes as did the oils. Sample A-6663 look different in that almost equal abundance of naphtalenes and phenanthrenes is seen. This sample gave a relatively low amount of aromatic hydrocarbons, and is thus more liable to variations due to the work-up procedure. Apart from sample A-6663 being somewhat intermediate, there seem to be variations in the methyl phenanthrenes consistent with what was found from the saturated hydrocarbons. The deepest core (A-6666) gave a ratio similar to the oils, while the two cores with intermediate depths had ratios above 1.4.

Cuttings samples

There seems to be slightly higher abundance of the methylated phenanthrenes as compared to the naphtalenes in the cuttings samples than in the oils and cores. This is true in particular for samples A-6667 and A-6672. The variations do not seem to be systematically, and may be due to the work-up procedure and the relatively low absolute amounts. The methyl phenanthrene ratio varies from 0.8 to 1.1. This fits reasonably well in with the ratios for the oils and two of the cores, and is significantly lower than the two cores at intermediate depth.

3.3.2 AF2 fractions

After further HPLC separation of the total aromatic fractions, the sub-fraction containing components with 3 aromatic rings (AF2 fraction) were analysed gas chromatographically with dual FID/FPD detection. Chromatograms of oils, cores and one cuttings sample are presented in Figure 3.

Oil Samples

Apart from minor changes in the relative peak intensities the two oils look similar, both in the distribution of the total AF2 fractions and of the sulfur components. The methylphenanthrene ratios were seen to be nearly identical, both being similar to what was tentatively assigned previously (Table 6).

Core Samples

The core samples seem to be different from the oils based on the distribution in the AF2 fractions. This is in particular true for the two samples of intermediate depths, these two cores giving high methylphenanthrene ratios (Table 6). The high methylphenanthrene ratios are mainly caused by the increased intensity of the 2-methylphenanthrene. The shallowest core, A-6663, gives an intermediate value, while the deepest sample is more similar to the oils. This deepest core has, however, lost the low molecular weight sulfur components, making it difficult to directly compare this to the oils. The other 3 cores seem to give a dibenzothiophene distribution different to the oils, especially the realtive intensity of the four methyldibenzothiophenes.

Cutting samples

Only one of the cuttings samples gave enough extractable material to be able to perform the HPLC separation. Sample A-6670 gave distributions fairly similar to the oils, both of the phenanthrenes and of the sulfur components.

3.4 Thermal extraction GC

Gas chromatograms representing thermally extracted hydrocarbons are given in Figure 4.

Oil Samples

The two samples were seen to exhibit similar n-alkane profiles, both front end biased with maximum at nC_{10} and only low amounts of the components above nC_{25}. This front end biased profile was also seen from the GC-analysis of the saturated hydrocarbons (Figure 1).

Core Samples

Again the two intermediate cores give a distribution different to the other cores and to the oils. The weak bimodal patterns with abundant n-alkanes above nC_{30}, also seen from the saturated hydrocarbon traces, make these two samples different to the oils. Sample A-6666, the deepest core, shows a distribution more similar to the oils, while the shallowest sample seems to contain only relatively low total concentrations. None of the samples contain significant abundances of components in the C_8-C_{10} carbon number range.

Cutting Samples

The cuttings samples were found to give some variations in the distribution, probably mainly due to differences in the amount of hydrocarbons in the samples. All samples seem to be more or less similar in the content of hydrocarbons with less than ten C-atoms. The amount of higher molecular weight components varies, but the overall profile seems to be very similar for all the samples.

3.5 GC-MS analysis of saturated hydrocarbons

Mass chromatograms representing terpanes (m/e 191) and steranes (m/e 217) are given in Figure 5, and molecular ratios calculated from peak intensities are reported in Table 7.

Oil Samples

The two oil samples contain the ubiquitous 17α(H),21β(H)-hopanes as the major components in the m/e 191 mass chromatograms. In addition to the commonly found hopane members, the bisnorhopane (Z) is seen in significant amount. This compound has been seen in samples from certain horizons in the North Sea, but it is not known if this is a true marker of the depositional environments, or if the compound might be "picked up" during migration processes. Two other unidentified components (X and Y) and a certain amount of tricyclic terpanes (*) are also detected in both samples.

The sterane distribution is also seen to be nearly identical for the two oils, the isomerisation ratios (%20S and %ββ in Table 7) implying well mature hydrocarbons.

Core Samples

There seems to be considerably lower amount of terpanes relative to n-alkanes in the cores than in the oils. This is in particular true for the two cores of intermediate depth, while the shallowest core contains generally low abundance of hydrocarbons. The overall distribution of terpanes was seen to be quite similar for all the cores, the unidentified component Y being of relatively high intensity. The bisnorhopane (Z) was not detected in any of the cores, and only the deepest sample contained tricyclic terpanes (*).

In the sterane mass chromatograms (m/e 217) less variations were seen, the rearranged steranes being very abundant in all the cores. This was also the case for the oils, making it difficult to draw conclusions based on the steranes. The somewhat different pattern in A-6663 is probably due to the low total concentration in this sample.

Cuttings Samples

The cuttings samples were found to be more similar to the oils than the cores, based on the terpane chromatograms. This conclusion is drawn on the basis of the amount of tricyclic terpanes in the cuttings samples and the varying intensities of unidentified components X and Y. The bisnorhopane (Z) was tentatively detected in some of the samples, but

the concentration was seen to be significantly lower than in the oils. These differences are either due to two different source rocks having produced the hydrocarbons in the oils and the cuttings, or different migration pathways have caused the dissimilarities.

Only minor variations were seen in the sterane traces (m/e 217).

The odd pattern seen for sample A-6669 is probably due to low overall concentration rather than significantly different type of hydrocarbons in this sample.

3.6 GC-MS analysis of aromatic hydrocarbons

Mass chromatograms of the aromatic hydrocarbons are presented in Figure 6. The total ion chromatograms are similar to the GC traces of the total aromatic fractions (Figure 2) and are therefore not presented.

Oil samples

All the presented mass chromatograms show the two oil samples to be very similar.

Core samples

As was seen from previously discussed data variations occur among the four cores. Two ions representing monoaromatic components, m/e 92 and 106 show homologous series as seen for the oils. However, some early eluting peaks (*) are more prominent in the cores than in the oils. This is true in particular for A-6664 and A-6665, while the other two cores are somewhat intermediate.

The naphtalene homologs are seen in similar distribution as in the oils.

It is not known whether the extra peak in the m/e 166 mass chromatograms is a significant difference, but this peak is seen in the three shallowest cores. The peak is not detected in the deepest core sample (A-6666), making this core most similar to the oils.

The ion representing methyl phenanthrenes, m/e 192, gives different mass profiles for the four cores. As seen from the GC traces discussed pre-

viously, the two cores of intermediate depth, A-6664 and A-6665, contain higher concentrations of the last eluting isomers, resulting in methyl phenanthrene ratios of 1.4 and more. These two cores were thus seen to be different to the other two cores and the oils.

Only minor variations were seen in the naphtalene and dibenzothiophene mass chromatograms.

While the mono- and triaromatic steranes, m/e 253 and 231, respectively, gave distinct profiles for the oils, the components could hardly be detected in any of the cores. This might indicate either that the cores contain a different type of petroleum hydrocarbons, or that the hydrocarbons have migrated further from the source to the reservoir in the 30/6-11 cores, and that the heavy components have been lost by this process.

Cuttings samples

The majority of the presented mass chromatograms does not reveal much difference in the cuttings samples. They were seen to be fairly similar to the oils. Three of the samples contained the extra peak in the m/e 166 mass chromatograms. The aromatic steranes were more prominent than in the cores, but not as much as in the oils. This could again be explained by different migration pathways, and loss of heavy hydrocarbons in this way.

3.7 $\delta^{13}C$ isotope analysis

Isotope analyses have been performed on extracts from cores and cuttings and on the oils. Values for saturated and aromatic hydrocarbons and for non-hydrocarbons are given in Table 8. The results for the two hydrocarbon fractions are presented graphically in Figure 7.

The variations in the saturated and aromatic hydrocarbon fractions seem to be more consistent than those seen in the non-hydrocarbons. This might be due to the separation procedure, where the non-hydrocarbons can be difficult to recover, possibly creating further fractionation of the polar components.

When discussing the data one should bear in mind that the DCM-washing of the cuttings samples may have extracted some of the indigenous material from the cuttings. This may give results for the cuttings that represent mixtures of indigenous and migrated hydrocarbons.

Oil samples

The $\delta^{13}C$ values for the two oils give slightly more positive values for the deepest oil samples. This could imply that the oils have been generated at slightly different maturity stages of the source rock, and then migrated into the reservoirs at different times. The differences are, however, only minor, indicating that the same source rock has generated the two oils.

Core samples

As can be seen from Figure 7 and Table 8 the three shallowest core samples were found to give significantly higher $\delta^{13}C$ values than the two oils. This is true for all three chromatographic fractions and indicates a different source for the hydrocarbons in these cores as compared to the oils. The deepest core showed values intermediate between the oils and the other cores, possibly implying mixed inputs in this case.

Cuttings samples

With small variations all the cuttings samples were seen to give $\delta^{13}C$ values intermediate between the cores and the cuttings. The data indicate that the hydrocarbons in the cuttings are more similar to the oils than the hydrocarbons in at least three of the cores.

4. CONCLUSION

- The two oils from 30/6-4 were seen to be similar by all the analyses performed.

- The three deepest cores from 30/6-11 contain high concentration of migrated hydrocarbons. These hydrocarbons, especially in the richest cores, are seen to be different to those in the oils. Mixed input can not be excluded.

- The overall abundance of hydrocarbons in the cuttings from 30/6-11 was generally considerably lower than in the cores. The hydroarbon distribution in the cuttings was found to be more similar to that in the oils.

Table 1: Sample codes and depth intervals.

IKU no.	Core no.	Depth	Well	Comments
Oils				
M-3143		2630.5-38m	30/6-4	
A-6647		2655-65m	"	
Cores				
A-6663	2	3452.4-.7m	30/6-11	Waxed sample
A-6664	3	3465.2-.5m	"	"
A-6665	4	3469.5-.8m	"	"
A-6666	7	3756.0-.4m	"	"
Cuttings				
A-6667		3260-65m	30/6-11	Plastic bag
A-6668		3340-45m	"	Can
A-6669		3540-50m	"	"
A-6670		3560-65m	"	"
A-6671		3615-20m	"	"
A-6672		3630-40m	"	"
A-6673		3750-55m	"	"

Table 8 $\delta^{13}C$ isotope values

IKU no	Depth (m)	SAT	ARO	NSO
Oils				
M-3143	2630.5-38	-29.2	-28.1	-27.8
M-6647	2655-65	-29.0	-27.8	-27.0
Cores				
A-6663	3452.4-.7	-27.6	-25.3	
A-6664	3465.2-.5	-27.7	-26.1	-25.9
A-6665	3469.5-.8	-27.3	-26.1	-25.9
A-6666	3756.0-.4	-28.0	-27.3	-27.2
Cuttings				
A-6667	3260-65		-28.0	-25.8
A-6668	3340-45	-28.9	-27.7	-26.6
A-6669	3540-50	-28.6	-27.2	-24.8
A-6670	3560-65	-28.2	-27.3	-26.8
A-6671	3615-20		-27.1	-26.6
A-6672	3630-40		-27.8	-27.9
A-6673	3750-55	-28.6	-26.6	-25.5

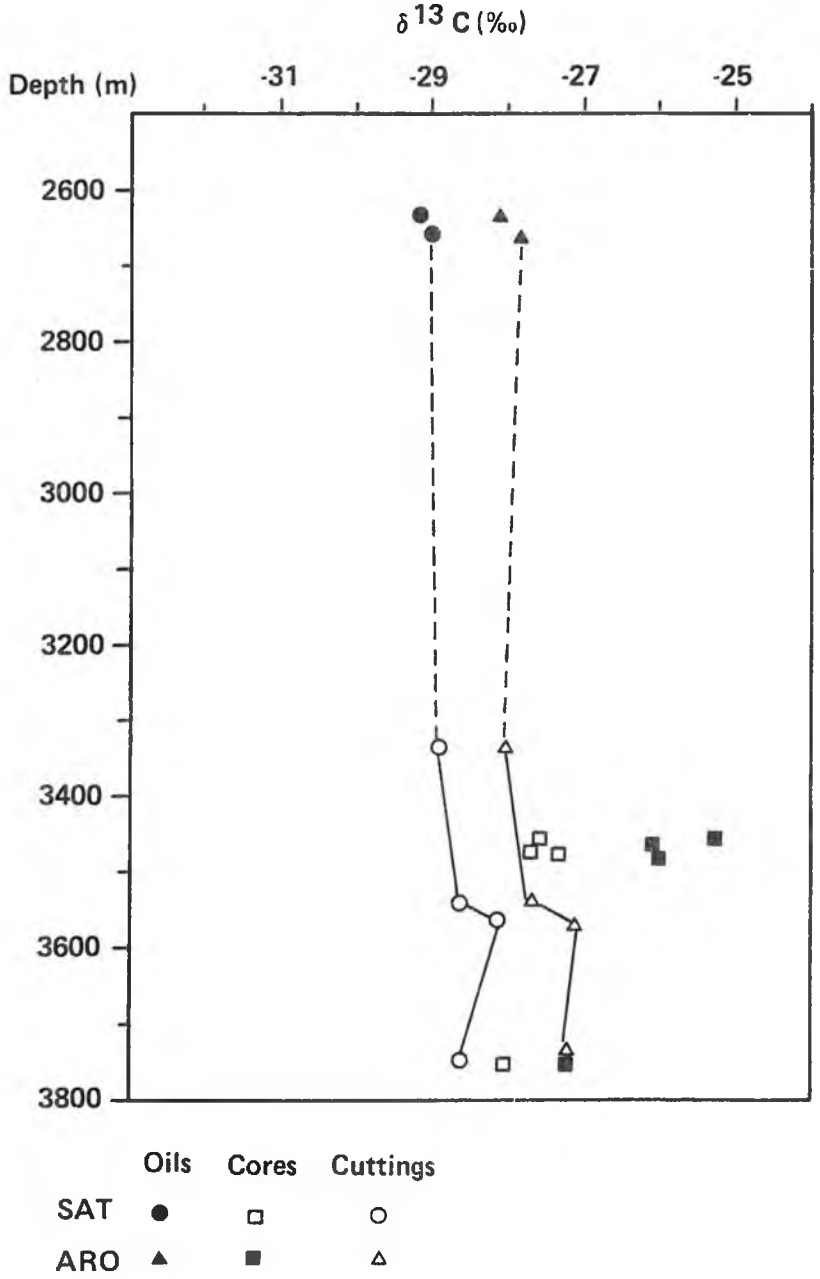

Figure 7. δ^{13} C isotope data