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REPORT TITLE/ TITTEL CORRELATION OF HYDROCARBON STAINING OF SANDSTONE CORES AND AN OIL 31/3-1 CLIENT/ OFFORAGEORYCER Statot1	

CORRELATIO	N OF HYDROCARE	BON STAINING 3-1	OF SANDSTONE
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One oil sample and six sandstone cores were analysed in an attempt to perform hydrocarbon correlation. All the applied methods suggest that the same type of source rock is responsible for the main part of the hydrocarbons extracted from the cores and for the oil.

Correlation	North Sea
GC-MS	δ ¹³ C isotopes

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1. JNTRODUCTION

An attempt to correlate hydrocarbon staining of six sandstone cores with an oil, and then further source rock correlation were performed. The oil was taken from the same depth interval as the cored section in this well, the Upper Jurassic sandstones from 1400-1600m.

A list of the samples analysed follows:

JKU no.	Sample type	Depth (m)
A-9617	oil (FMT 1)	1574.2
A-9620	<pre>sst. core (clst?)</pre>	1406.22
A-9621	sst. core	1567.86
A-9622	sst. core	1571.89
A-9623	sst. core	1573.03
A-9624	sst. core	1576.32
A-9625	sst. core	1578.59

Common organic geochemical methods were applied in the correlation. In addition to extraction and GC analyses, GC-MS and $\delta^{13}C$ isotope data were used.

1.1 <u>Molecular ratios from terpane and sterane mass chromatograms</u> <u>applied as maturity and source characteristic parameters</u>.

Geochemical fossils or biological marker components are characteristic of the type of organic matter present at the time the sediments were deposited. The biological isomers of these components undergo changes due to increased maturity in particular, but also to a certain degree caused by migration and weathering processes.

1.1.1 Source characteristics parameters

In the m/z 191 mass chromatograms, representing terpanes, the hopanes and moretanes are the major components in most extracts and oils. Of the hopanes the C_{27} and $C_{29}-C_{35}$ homologs are ubiquitous, while the C_{28} bisnorhopane is believed to be typical of certain types of source rocks. The amounts of tricyclic terpanes relative to the hopanes are also believed to a certain extent to be characteristic of the source rock. This

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is also the case for the component, probably gammacerane, sometimes seen to coelute with the 22S isomer of the C_{31} 17 α (H)-hopanes (H). In the sterane mass chromatograms, m/z 217 and m/z 218, the molecular weight distribution of the C_{27} - C_{29} regular steranes is believed to be representative of the original input of organic matter. The highest molecular weight compounds, the C_{29} steranes, represent organic matter of terrestrial origin, while the lower molecular weight analogs originate from more marine type environments.

1.1.2 Maturity parameters

The biological isomers of the hopanes, the $17\beta(H)$, $21\beta(H)$ -hopanes, undergo structural changes during the maturation process. The isomerisation reactions are thought to produced via the $17\beta(H)$, $21\alpha(H)$ -hopanes (moretanes) to the most stable $17\alpha(H)$, $21\beta(H)$ -hopanes. At equilibrium 100% of the $17\alpha(H)$ -hopanes are seen. The ratio $\alpha\beta/\alpha\beta+\beta\alpha$ is used to describe this reaction. In the extended hopanes $(\geq C_{31})$, the thermally stable S configurations at C-22 become increasingly more abundant as compared to the biological preferred R configurations at increased maturity level. The equilibrium ratio is approximately 60% of the 22S configuration. Another ratio that is known to change with maturity is the Tm/Ts (Seifert et al., 1978) of the C_{27} hopanes. The maturable $18\alpha(H)$ -trisnorneohopane (Tm) is reduced in intensity relative to the more stable $17\alpha(H)$ trisnorhopane (Ts), causing the Tm/Ts to decrease at increased maturity. This ratio is also believed to be source dependant, and this should be born in mind when applying the ratio for maturity comparison. The amount of tricyclic terpanes is also to a certain extent seen to be maturity dependant.

Two isomerisation reactions taking place in the steranes are most commonly applied for maturity assignments from the m/z 217 mass chromatograms. The biologically preferred $14\alpha(H)$, $17\alpha(H)$ -isomers of the regular steranes are transformed to the thermally stable $14\alpha(H)$, $17\beta(H)$ -steranes, the %BB approaching 75% at equilibrium. An equilibrium concentration of 50% is seen of the stable S configuration at C-20 as opposed to the 100% of the biological 20R epimer (Mackenzie et al., 1980). The abundance of rearranged steranes increases with increasing maturity.

One of the reactions taking place at an early stage of diagenesis is the aromatisation of steranes, leading to the formation of mono- and



triaromatic analogs. This process is measured as the abundance of triaromatic relative to mono-aromatic compounds (% tri/tri + mono) in the m/z 231 and 253 mass chromatograms, respectively. In addition the degree of side chain cracking, as $C_{20}/C_{26,.27}$ and $C_{21}/C_{28,29}$ respectively, is applied. These cracking processes are also taking place during early diagenesis, and are used for maturity assignment together with the previously mentioned ratios.

1.1.3 Migration and weathering

The effect on the geochemical fossils of migration and weathering is less apparent than the maturity induced changes. Migration is believed to cause an increase in the relative amounts of rearranged and $14\beta(H)$, $17\beta(H)$ regular steranes (Seifert and Moldowan, 1978, 1981). Severe biological alteration leads to the formation of desmethyl-hopanes (Seifert and Moldowan, 1979).



2. EXPERIMENTAL

2.1 Extractable Organic Matter

Approximately 50gm of powdered rock was extracted by flow blending 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.

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

Squalane was added prior to the extraction as an internal standard.

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 a stream of nitrogen. The oil was separated using the same system.

2.3 <u>Urea</u> adduction

Urea-adduction was performed on the same samples that were analysed on GC-MS. The sample containing 5 mg of n-alkanes was dissolved in 2 ml of n-hexane and 1 ml of acetone was added. A saturated solution of urea in methanol (1 ml) was then added dropwise. The solvent was removed (N_2) and the adduction step repeated twice. The white crystals were rinsed (3x5ml hexane) and the combined extract filtered (cotton wool plug covered with Al_2O_3), to afford a non-adduct. GC analyses were performed on the samples after the urea adduction, using the same conditions as for the other GC analyses.



2.4 Gas Chromatographic Analysis

The saturated and the branched/cyclic 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 total aromatic fractions were after dilution with n-hexane, analysed on a Carlo Erba Fractovap Series 2150 GC fitted with a 20mm SE-54 fused silica column.

Injections 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.

In addition the whole oil was analysed on the HP 5730 A GC, applying a temperature program of the GC oven from -50° C (2 min.) to 280° C at 4° C/min. The C₂-C₈ GC's were acquired by hydrogen stripping on a Carlo Erba Fractovap GC. The column used for this was a 30m capillary column coated with squalane.

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

2.5 Gas chromatography - mass spectrometry (GC-MS)

GC-MS analyses were performed on a VG Micromass 70-70H GC-MS-DS system. The Varian Series 3700 GC was fitted with a fused silica OV-1 capillary column (30m x 0.3mm i.d.). Helium (0.7kg/cm^2) was used as carrier gas and the injections were performed in split mode $(1.5\mu$ l, split ratio 1:15). The GC oven was programmed from 70^oC to 280^oC at 4^oC/min. after an initial isothermal period of 2 minutes.

The saturated hydrocarbons were analysed in multiple ion mode (MJD) at a scan cycle time of approximately 2 secs. Full data collection was applied for the aromatic hydrocarbons at a scan time of 1 sec/decade. The mass spectrometer operated at 70eV electron energy and an ion source temperature of 200° C. Data acquisition was done by VG data systems.

Peak identification was performed applying knowledge of elution patterns in certain mass chromatograms. Calculation of peak ratios was done from peak height in the appropriate mass chromatograms.



2.6 δ^{13} C istotope analyis

The δ^{13} C isotope analysis was performed by mass spectrometry at Institute for Energy Technology (IFE) in Oslo according to their method. Their reference value for the standard NBS-22 is -29.8.



3. RESULTS AND DISCUSSION

3.1 <u>APJ gravity</u>

The APJ gravity for the oil was determined to 24.3^OAPJ, (Table 1) indicating the oil to be relatively heavy.

3.2 GC of whole oil

The cryogenic gas chromatogram of the whole oil is presented in Figure 1. Hardly any n-alkanes below nC_{10} and only small amounts of higher n-alkanes are revealed in this chromatogram. The main components are branched and cyclic components of low molecular weight. This is probably an indication of microbial alteration of the oil.

3.3 GC of C_2-C_8 hydrocarbons

The hydrogen stripping gas chromatogram in Figure 2 and the quantitative data in Table 2 indicate the same as the whole oil GC above. Very low relative amounts of n-alkanes and highest abundance of mono-cyclic components.

3.4 Extraction and chromatographic separation

Six sandstone cores were extracted before chromatographic separation of the extracted organic matter and of the oil. The weights and relative amounts of the various chromatographic fractions are given in Table 3. Five of the six sandstone are very rich in extractable organic matter, while the last one contains fair amounts.

The oil was seen to contain approximately 40% saturated and 25% aromatic hydrocarbons, making the SAT/ARO ratio equal to 1.7 and hydrocarbons/nonhydrocarbons equal to 2.1. Most of the sandstone cores contained hydrocarbons with the same distribution of saturated and aromatic hydrocarbons relative to the nonhydrocarbons. The two samples with lowest extractability show lower values compared to the oil, of both SAT/ARO and of hydrocarbons/nonhydrocarbons. This suggests less migrated hydrocarbons in these samples and in particular samples A-9624, supporting what was seen from the extractability data. Sample A-9620 was seen to



consist of both sandstone and claystone, and contamination of the extracted sandstone by claystone cannot be totally excluded. Thus a mixed input might be seen in this sample.

As a whole the distribution of the extractable organic matter in the sandstone cores seems to be similar to the oil.

3.5 Gas chromatography of C_{15}^{+} saturated hydrocarbons

Gas chromatograms of saturated hydrocarbons are presented in Figure 3, while data from the chromatograms are given in Table 4. The n-alkane profile of the oil is weakly bimodal, showing maxima at nC_{17} and nC_{28} . An unresolved complex mixture is seen as a hump underneath the alkanes. This low relative abundance of n-alkanes fits in guite well with what would be expected from the whole oil GC. The Pr/nC_{17} is higher in the C_{15}^{+} fraction than what was seen in the whole oil chromatogram, a fact probably caused by the separation procedure. With exception of the shallowest core all the other samples exhibit similar alkane profiles as the oil, the bimodality being more or less pronounced. The high Pr/nC_{17} is seen for all the samples. From the relative amount of the internal standard (S in Figure 3) it is obvious that sample A-9624 is less rich in alkanes than the other samples. The shallowest core, A-9620, shows a unimodal alkane distribution with maximum at approximately nC₁₆. This may indicate that the oil and the hydrocarbons in the other cores consist of mixed inputs, one source being responsible for the low molecular weight components, while the heavier components have been generated from a different source. Since the uppermost core sample consists of a mixture of sand and shale, it might be expected that the shale part of the core has been responsible for one part of the hydrocarbons. However, with the low maturity assigned to the claystones at this depth interval generation of mature hydrocarbons would not be expected. The Pr/nC_{17} and CPJ are approximately the same in this sample as in the others.

3.6 Gas chromatography of C_{15}^{+} branched/cyclic hydrocarbons

Only minor differences could be seen in the chromatograms of the branched/cyclic hydrocarbons presented in Figure 4. Some of the samples contain some n-alkanes, and A-9624 was seen to contain some unidentified peaks. These are thought to be contamination since they were seen only in the

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sample with lowest abundance of hydrocarbons. The overall distribution of the branched components and relative abundance of branched and cyclic components were seen to be similar in all the samples.

3.7 Gas chromatography of C_{15}^{+} aromatic hydrocarbons

The GC traces of aromatic hydrocarbon fractions are shown in Figure 5. Naphthalene and alkylated homologs are the major components in all the chromatograms, supporting what was seen from the saturated hydrocarbon GC's. The oil and the hydrocarbons in the cores are very similar. Even with the poor resolution of the double doublet representing methylphenanthrenes, it is apparent that the second doublet is more abundant than the first one. This indicates that the maturity of all the extracts is similar.

3.8 GC-MS analysis of saturated steranes and terpanes

Mass chromatograms representing terpanes (m/z 191) and steranes (m/z 217 and 218) are presented in Figure 6. Molecular ratios calculated from the chromatograms are given in Table 5 and 6.

Only minor differences are seen in the various ratios that are known to be affected by maturity variations (Table 5). The isomerisation reactions have reached equilibrium, implying that mature hydrocarbons are encountered in all samples. No pronounced difference could be detected between the oil and the core extracts.

Some of the ratios in Table 6 are known to be affected by both type of organic matter and maturity. Those are the Tm/Ts ratio and the relative amount of tricyclic terpanes in the m/z 191 mass chromatograms, and the relative amount of rearranged steranes in the m/z 217 chromatograms. As is seen from the table all these ratios show only minor variations, implying that not only is the maturity but also the type of organic matter similar for the oil and the core extracts.

Of the last three ratios in Table 6 the relative amount of bisnorhopane (Z/E) is known to be characteristic of part of the Kimmeridge Formation in the North Sea. The values for this ratio are very consistent throughout the whole core interval. Only minor variation were also seen for the relative amount of the two unidentified components (Y/E and X/E).



From the triangular diagram showing the molecular weight distribution of regular steranes (Figure 7) a similar trend as above was seen. All the samples cluster together within a fairly narrow range of values. All the molecular ratios and the general distribution of steranes and terpanes suggest that the hydrocarbons extracted from the sandstone cores and the oil from the same depth interval originate from the same type of source rock.

3.9 GC-MS analysis of aromatic hydrocarbons

The total ion chromatograms of the aromatic hydrocarbons showed similar distribution to the gas chromatograms and are not presented. Distributions of alkylated benzenes, naphtalenes and phenanthrenes are presented as composite mass chromatograms in Figure 8.

The same trend as seen from the previously discussed data could be revealed from these mass chromatograms. Only minor differences were detected, implying the samples to be very similar. The methyl phenan-threnes (m/z 192) exhibit the same distribution between the first and second doublet, assigning similar maturity to all the samples.

3.10 δ^{13} C isotope analysis

Carbon isotope ratios of saturated and aromatic hydrocarbon fractions are presented in Table 7. The values are seen to be very consistent for the saturated hydrocarbons, a slightly higher value is seen for the sample that showed lowest extractability. For the other samples the ratio varies between -28.7 and -28.9, indicating the oil to be similar to the core extracts. The variation for the aromatic hydrocarbons is more pronounced, sample A-9620 and A-9624 giving higher values than the rest of the samples. Values of -27.4 and -27.5 were found for the oil and four of the cores, supporting the theory about these samples being similar. This variation between the samples may indicate that mixed input of hydrocarbons from two different sources has taken place.



4. CONCLUSION

All analyses show that the hydrocarbons in the sandstone cores are very similar to the oil sample.

One core which contained lower abundance of migrated hydrocarbons, showed characteristics somewhat different to the other samples. This could imply a certain extent of mixed inputs, but the main part of the hydrocarbons in the sandstone cores has most probably been generated from the same source rock as the oil. The shallowest core (A-9620) was seen to contain more low molecular weight alkanes than the other cores.



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<u>Table 1</u> : APJ	gravity			
JKU no.	Code	Depth (m)	APJ gravity	
A-9617	FMT 1	1574.2	24.3 ⁰	



	A-9617
	% of total oil
nC	0.03
nC ₂	0.08
MC_	0.3
nC.	0.07
MC ₄	0.2
nC _c	0.09
2.2DMC	0.07
CyC _F +2MC ₅	0.6
3MC ₅	0.3
nC ₆	0.1
MCyC ₅ +2.4DMC ₅	1.0
۲٫۷۵ و ۲٫۷۵ و	1.4
2MC ₆ +3MC ₆	0.4
lcis3DMCyC ₅	0.3
ltr3DMCyC5	0.2
2.2.4TMC5	0.5
nC ₇	0.02
benzene+2.2DMC6+MCyC6	2.9
MC ₇	0.1
toluene	0.9

<u>Table 2</u>: Light hydrocarbons $C_2 - C_8$



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Abbreviations:

nC ₂	ethane
nC ₃	propane
MC ₃	methylpropane
nC4	butane
MC ₄	methylbutane
nC ₅	pentane
2.2DMC ₄	2.2 dimethylbutane
CyC ₅ +2MC ₅	cyclopentane + 2 methylpentane
3MC ₅	3methylpentane
nC ₆	hexane
MCyC ₅ +2.4DMC ₅	<pre>methylcyclopentane + 2.4 dimethylpentane</pre>
СуС _б	cyclohexane
2MC ₆ +3MC ₆	2 methylhexane + 3 methylhexane
lcis3DMCyC ₅	lcis 3 dimethylcyclopentane
ltr3DMCyC ₅	ltr 3 dimethylcyclopentane
2.2.4TMC5	2.2.4 trimethylpentane
nC ₇	heptane
2.2DMC ₆	2.2 dimethylhexane
MCyC ₆	methylcyclohexane
MC ₇	methylheptane
nC ₈	octane

Тавъе в За

CONCENTRATION OF SOM AND CHROMATOGRAPHIC FRACTIONS

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™ A 6 6 6 6 **3.b**

WEIGHT OF BOM AND CHROMATOGRAPHIC FRACTIONS

(Weight opm OF rock)

	IKU-I	No		DEFTH	= = =	EOM		sat.		аалаала Аго.				Non HC	
1 == T T	A 96	17	2	1574.20	222	955 955	1	409		241	1	450		306	I I I T
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L T	A 96	21	:	1567.86	:	22127		8422		6017	2	14439	:	7688	T
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I. I	A 96)	25	;	1378.59		19232	1	8478		5548	:	14026	:	5206	I I

DATE : 10 - 11 - 33.

TABLE *** 3.c**

COMPOSITION IN % OF MATERIAL EXTRACTED FROM THE ROCK

I I I	1.1	KU-No		DEFTH		Sat EOM	63 84 64 84	Ano EOM	12 12 12 12	HC EOM	55 \$* \$. \$\$	SAT Gro	11 40 FC 41	Non HC Efim	88 84 85 85	HC Non HC
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T			:		2		3		:				1		2	
I	A	9620	2	1406.22	2	30.3	3	22.6	:	52.9	2	134.0	2	47.1	:	112.1
1			;		:		2		:		:				\$	
I	A	9621	2	1567.86	2	38.1	2	27.2	:	65.3	:	140+0	ï	34.7	;	197.8
T.			:		:		:				2		\$		\$	
I	Ĥ	9622	:	1571.89	:	40.8	2	28.6	2	69.4	5	142.4	**	30.6	2	227.0
τ			3		:		3		2		2		4		3	
Ι	A	9623	:	1573.03	2	43.7	:	28.7	ĩ	72.4	2	152.1	3	27.6	3	261.9
Ι			2		:		3		3		:		4		;	
I	A	9624	2	1576.32	:	22.4	:	24.4	5	46.8	2	91.8	ž	53.2	1	87.9
I			3		;		*		:		2		:		:	
I	A	9625	ĩ	1578.59	:	44.1	:	28.8	:	72.9	:	152.8	2	27.1	3	269.4
r			:		:		:		3		3		2		3	

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].			:	DEPTH	2	PRISTANE	1	PRISTANE	2		1
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I			*	(m)		n-C17	2	PHYTANE	2		1
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Ι			:		2		:				1
1	A	9617	2	1574.20	2	1.1		2.0		1.0	I
I			2		2		2		2		I
I	A	9620		1406.22	2	1.2	2	2.3	\$	0.9	1
].			:		2		2		2		1
1	A	9621	*	1567.86	:	1.1	2	1.9	2	1.0	I
I			2		2		:		2		Ι
r	Α	9622	2	1571.89	2	1.1	2	1.9	2	1.0	Ι
I					2		2		*		I
I	A	9623	2	1573.03	:	1.1	2	2.1	:	1.0	ĩ
1			:				2		2		I
I	Α	9624	2	1576.32	2	1.1	2	2.3		1.0	ľ
].			2		2		2		2		I
J.	A	9625		1578.59	2	1.1	2	2.0	*	0.9	I
I			2		2		*		*		I
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TABULATION OF DATA FROM THE GASCHKOMATOGRAMS

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Table 5:

			m/z	191	z /w	217
JKU Code	Depth (m)	Sample type	αβ/αβ+βu])	%22S ²)	%20S ³)	%88 ⁴)
A-9617	1574.2	0i1	0.90	63.1	52.4	75.3
A-9620	1406.22	<pre>Sst.core (clst?)</pre>	0.90	63.0	49.5	72.8
A-9621	1567.86	Sst. core	0.89	58.1	54.4	75.9
A-9622	1571.89	Sst. core	0.89	58.3	52.9	75.2
A-9623	1573.03	Sst. core	06.0	56.1	57.7	72.3
A-9624	1576.32	Sst. core	0.91	59.6	49.6	71.1
A-9625	1578.59	Sst. core	0.90	58.8	55.6	73.2

1) E/E+F in Figure 7 2) J_1/J_1+J_2 in Figure 7 3) q/q+t in Figure 7 4) 2(r+s)/2(r+s)+q+t in Figure 7.

Table 6: Molecular ratios calculated from sterane and terpane mass chromatograms.

				z/u	191		m/z 217
JKU Code	Depth (m)	Sample type	Tm/Ts ¹)	τrj/e ²⁾	Z/E	X/E	rearr./reg. ³⁾
A-9617	1574.2	0i1	0.61	0.14	0.24	0.30	0.9
A-9620	1406.22	Sst. core (clst?)	0.64	0.20	0.22	0.27	1.0
A-9621	1567.86	Sst. core	0.62	0.18	0.23	0.30	0.9
A-9622	1571.89	Sst. core	0.61	0.14	0.26	0.29	1.0
A-9623	1573.03	Sst. core	0.57	0.10	0.22	0.16	1.1
A-9624	1576.32	Sst. core	0.76	0.23	0.22	0.15	1.0
A-9625	1578.89	Sst. core	0.48	0.13	0.24	0.19	1.1
1) B/A in Fi	gure 7						

2) Q/E in Figure 7
3) a+b/h+k in Figure 7

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JKU Code	Depth (m)	Sample type	SAT	ARO	
A-9617	1574.2	0i1	-28.8	-27.5	
A-9620	1406.22	Sst. core (clst?)	-28.9	-27.0	
A-9621	1567.86	Sst. core	-28.7	-27.4	
A-9622	1571.89	Sst. core	-28.9	-27.5	
A-9623	1573.03	Sst. core	-28.7	-27.4	
A-9624	1576.32	Sst. core	-28.4	-26.4	

1578.59 Sst. core -28.7 -27.5

<u>Table 7</u>: δ^{13} C isotope values for saturated and aromatic hydrocarbons.

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Reference value for NBS-22: - 29.8.

A-9625

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Figure 1

Gas chromatogram of whole oil

MCy-C5	-	methylcyclopentane
Cy-C ₆	-	cyclohexane
MCy-C ₆	-	<pre>methyl-cyclohexane</pre>
Pr	-	pristane
Ph	-	phytane

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Figure 2

GC-chromatograms of light hydrocarbons (C_2-C_8)

A	-	propane (nC ₃)
В	-	methylpropane (MC ₃)
С	-	butane (nC ₄)
D	-	methylbutane (MC ₄)
E	-	pentane (nC ₅)
F,	-	$cyclopentane (CyC_{5})+2$ methylpentane (2MC ₅)
F_2	-	3-methyl-pentane (3MC ₅)
G	-	hexane (nC ₆)
G,	-	methylcyclopentane $(MCyC_5)+2.4dimethylpentane (2.4DMC_5)$
H	-	cyclohexane (CyC ₆)
H,	-	2methylhexane (2MC ₆)+3methylhexane (3MC ₆)
J	-	heptane (nC ₇)
J	-	benzene + 2.2dimethylpentane (2.2DMC ₅) + methylcyclo-
		hexane (MCyC ₆)
J	-	methylheptane (mC ₇)
J_2^-	-	octane (nC ₈)
ĸ	-	toluene



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Figure 3

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Gas chromatograms of C_{15}^{+} saturated hydrocarbons

- Pr pristane
- Ph phytane
- S squalane (internal standard)
- * isoprenoid alkanes











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Figure 5

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Gas chromatograms of $\mathrm{C}_{15}^{}\mathrm{+}$ aromatic hydrocarbons

N = naphtalene MN = C₁-naphtalenes DMN = C₂-naphtalenes TMN = C₃-naphtalenes P = phenanthrene MP = C₁-phenanthrenes DMP = C₂-phenanthrenes





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Figure 6a

Mass chromatograms representing terpanes (m/z 191)

А	T _s , 18α(H)-trisnorneohopane	^C 27 ^H 46	(111)
В	T_{m} , 17 $\alpha(H)$ -trisnorhopane	C ₂₇ H ₄₆	(I,R=H)
С	17α(H)-norhopane	C ₂₉ H ₅₀	(I,R=C ₂ H ₅)
D	17ß(H)-normoretane	C ₂₉ H ₅₀	(II,R=C ₂ H ₅)
E	17α(H)-hopane	C ₃₀ H ₅₂	$(I, R=C_3H_7)$
F	17β(H)-moretane	C ₃₀ H ₅₂	(II,R=C ₃ H ₇)
G	17α(H)-homohopane (22S)	C ₃₁ H ₅₄	(I,R=C4H9)
Н	17a(H)-homohopane (22R)	C ₃₁ H ₅₄	$(I, R = C_4 H_9)$
	+ unknown triterpane (gammacerane?)	••••	
I	17β(H)-homomoretane	C ₃₁ H ₅₄	(II,R=C ₄ H ₉)
J	17 _a (H)-bishomohopane (22S,22R)	C ₃₂ H ₅₆	$(1, R=C_5H_{11})$
К	17a(H)-trishomohopane (22S,22R)	C ₃₃ H ₅₈	$(I, R=C_6H_{13})$
L	$17\alpha(H)$ -tetrakishomohopane (22S,22R)	C ₃₄ H ₆₀	$(I,R,=C_7H_{15})$
М	$17\alpha(H)$ -pentakishomohopane (22S,22R)	C ₃₅ H ₆₂	$(I, R=C_8H_{17})$
Z	bisnorhopane	C28H48	
Х	unknown triterpane	C ₃₀ H ₅₂	
Ρ	tricyclic terpane	C ₂₃ H ₄₂	(IV,R=C ₄ H ₉)
Q	tricyclic terpane	C ₂₄ H ₄₄	$(IV, R=C_5H_{11})$
R	tricyclic terpane (17R,17S)	C ₂₅ H ₄₆	$(IV, R=C_6H_{13})$
S	tetracyclic terpane	C ₂₄ H ₄₂	(V)
Т	tricyclic terpane (17R,17S)	C ₂₆ H ₄₈	$(IV, R=C_7H_{15})$





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Mass chromatograms representing steranes (m/z 217 and 218)

ð	$13B(H), 17\alpha(H)$ -diasterane (20S)	С ₂₇ Н ₄₈	(III,R=H)
b	13β(H),17α(H)-diasterane (20R)	C ₂₇ H ₄₈	(III,R=H)
с	13α(H),17β(H)-diasterane (20S)	C ₂₇ H ₄₈	(IV,R=H)
d	13a(H),17g(H)-diasterane (20R)	C. ₂₇ H ₆₈	(IV,R=H)
е	138(H),17u(H)-diasterane (20S)	C ₂₃ H ₅₀	(III,R=CH ₃)
f	13β(H),17α(H)-diasterane (20R)	С ₂₈ Н ₅₀	(III,R=CH ₃)
g	13a(H), 17B(H)-diasterane (20S)	C , H , N	(IV,R=CH ₂)
	+ 14a(H),17a(H)-sterane (20S)	28 50 ((1,R=H)
h	$13\beta(H), 17\alpha(H)$ -diasterane (20S)	C.,,,H _E .,	(III,R=C ₂ H _c)
	+ $14\alpha(H)$, $17\alpha(H)$ -sterane (20R)	C , H 40	(11,R=H)
i	14B(H), 17B(H)-sterane (20S)	27 48 C ₄₇ H ₄₀	(II,R=H)
	+ $13a(H), 17B(H)$ -diasterane (20R)	27 48 C.,,H _{CO}	(IV,R=CH ₂)
j	$14\alpha(H), 17\alpha(H)$ -sterane (20R)	28 50 C.,,H.,,	(I,R=H)
k	$13\beta(H), 17\alpha(H)$ -diasterane (20R)	27 48 CH _{E 2}	(III,R=C ₂ H _r)
ו	$13_{\alpha}(H), 17_{\beta}(H)$ -diasterane (20S)	CapHep	$(III, R=C_0H_c)$
៣	$14\alpha(H), 17\alpha(H)$ -sterane (20S)	29 52 C.,,,H.,,	(I.R=CH ₂)
n	$13\alpha(H), 17\beta(H)$ -diasterane (20R)	28 50 C.,,H,	(III,R=C,H_)
	+ 146 (H).176 (H)-sterane (20R)	29 52 CoHe c	(II.R=CH ₂)
0	148(H),176(H)-sterane (20S)	28 50 CapHeo	(II.R=CH ₂)
• D	$14_{\rm u}({\rm H})$, $17_{\rm u}({\rm H})$ -sterane (20R)	28 50 CH.	(I.R=CH_)
G	$14_{\alpha}(H), 17_{\alpha}(H)$ -sterane (20S)	-28-50 CooHeo	(I,R=C_H_)
r	14B(H).17B(H)-sterane (20R)	- 29 - 52 CHeo	(II.R=C ₀ H _c)
	+ unknown sterane	-29-52	2.5
5	14B(H), 17B(H)-sterane (20S)	C	(11.R=C_H_)
t	$14_{G}(H), 17_{B}(H)$ -sterane (20B)	°29''52 CH_o	(1,R=C,H_)
u u	$5\alpha(H)$ -sterane	-29''52 Co. H. c	$(V_R = C_H_)$
v	$5\alpha(H)$ -sterane	~21''36 C	$(IV_{R}=C_{R}H_{-})$
•		~22''38	(, ~3.7)









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Figure 7

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Triangular plots showing molecular weight distributions of $C_{27}^{}$, $C_{28}^{}$ and $C_{29}^{}$ regular 148(H), 178(H)-steranes





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Figure 8

Mass chroamtograms representing aromatic hydrocarbons

m/z	92 + 106	monoaromatic hydrocarbons
m/z	142	C _l -naphtalenes
m/z	156	C ₂ -naphtalenes
m/z	170	C ₃ -naphtalenes
m/z	178	phenanthrene
m/z	192	C ₁ -phenanthrenes
m/z	206	C ₂ -phenanthrenes

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