EP/S/EXP/Lab.Pau n° 89/216RP

Pau, Novembre 1989

WELL 25/1-10 - NORWAY

Follow-up organic geochemical study

EP/S/EXP/Lab.Pau n° 89/216RP

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Imp. 7332 C SNEA(P) - RGM 953 006 004

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: K. LE TRAN

TITRE

: WELL 25/1-10 NORWAY

Follow-up organic geochemical study

REFERENCES

: EP/S/EXP/Lab.Pau n° 89-216RP

SUMMARY

The cutting extracts of two beds in the Draupne and Heather Formations bear the hydrocarbon imprint of the contaminant used in mud additives in that well. This is well demonstrated by GC-MS biomarker analysis (terpanes) at a molecular level, but the rock extracts are globally not much influenced as suggested by the difference in the composition.

The indicators for thermal maturation based on molecular distribution are difficult to handle because of the influence of the contaminant, nevertheless the very low concentration of biomarkers added to the high dominance of rearranged steranes suggest a high level of thermal maturation.

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1 - INTRODUCTION

The results already obtained in screening analyses and optical study of the organic matter (report EP/S/EXP/Lab.Pau 89/074 RP) have shown that the Jurassic section in well 25/1-10 has undergone extensive thermal stress, so that the entire series is beyond the oil window. Indeed the amount of extractable organic matter is very small, making the analysis of liquid hydrocarbons very difficult or even impossible.

Nevertheless, in order to get information, on one hand, on the contaminant used in drilling mud additives in that well and, on the other hand, on rock extracts attaining high thermal maturity, three samples were selected on the basis of screening analyses and analysed in detail for hydrocarbon characterisation including GC, GC-MS and carbon isotopy.

The contaminant is the sample collected at 4210m, and the other two samples are the richest in organic extract content belonging to the Upper Jurassic, one in the Draupne Formation (4260-65m) and the other one in the Heather Formation (4365m).

2 - RESULTS

Results are listed in tables 1 and 2 for the main geochemical data and table 3 for the isotopic and chromatographic ratios.

Gas chromatograms of GC analysis are presented for each sample both in synoptic overview (annexes 1, 6 and 11) and individual traces for each fraction (annexes 2, 3, 7, 8, 12 and 13). GC-MS results are given in relative abundance (fragmentograms) and in quantitative data for various ratios on the steranes and terpanes (annexes 4, 5, 9, 10, 14 and 15) .

2.1 - CONTAMINANT (SAMPLE 4210m)

The extract of the contaminant contains a small percentage of alkanes (8.4%) and aromatics (7.5%), the bulk (84.1%) being constituted by polar compounds.

The gas chromatogram of alkanes (annexes 1 and 2) shows a bimodal fingerprint with a first mode culminating at C14-C15 and a second mode, much higher, culminating at C27-C29.

The n-alkanes are, by far, the most abundant hydrocarbons as compared to iso and cyclo-alkanes, and in the C23-C33 range, there is a sharp odd preference in the n-alkanes: n-C25, n-C27, n-C29 and n-C31 are prominent (high wax range). Pristane/phytane ratio is slighly higher than 1 (1.18).

A compound, which is not a n-alkane, occurs in high abundance just before the n-C32. This compound appears in what follows to be a good marker of the pollutant; its structure has been identified by mass spectrometry as being that of the C31 aß, 22R Homohopane or in short C31 aß(R).

The aromatic hydrocarbon gas chromatogram (annexes 1 and 3) is dominated by dimethylnaphthalene (DMN) and shows high concentration of phenanthrene (P) and methylphenanthrenes (MP), the former one dominating the latter ones.

The methylphenanthrenes are dominated by the isomer 1 which predominates over the isomers 9, 2 and 3 in decreasing order. This seems to be typical of the product. The methylphenanthrene indexes MPI-1 and MPI-3 are 0.55 and 0.70 respectively.

The FPD sulfur aromatic trace (annexes 1 and 3) is dominated by the 4-methyldibenthiophene (4-MDBT) which predominates over the other isomers, 2+3 and 1-MDBT, in decreasing order. This is also typical of the product.

The terpane m/z 191 fragmentogram (annex 4) shows very high concentration of a single compound (X) which is highly prominent: this compound has been identified as being the C31 aß, 22R Homohopane. Such a pattern is particularly typical and is, as a matter of coincidence, similar to that obtained on the lignite of Yallourn, Australia (Van Dorselaar, thesis, 1975).

The sterane m/z 217 fragmentogram (annex 4) is dominated by the C29 aaR regular sterane. The rearranged steranes are present, particularly the C27 ones (C27S dia and C27R dia), but their concentration is not high.

Carbon isotope measurement on the saturated fraction was not possible because of the very small amount of saturates which constitute only 8 % of the total extract.

2.2 - DRAUPNE AND HEATHER EXTRACTS (4260/65m AND 4365m)

The gas chromatogram of alkanes of the Draupne Fm sample (annexes 6 and 7) is dominated by n-alkanes in the lower range, culminating at n-C16. But the important features are, on one hand, the marked odd preference of n-alkanes in the higher range between C23 and C33 as already mentioned for the contaminant and, on the other hand, the presence in relatively high concentration of the (X) marker also above reported for the contaminant. Pristane/phytane ratio is close to that of the contaminant (1.27).

The gas chromatogram of the alkane fraction of the Heather Fm sample (annexes 11 and 12) is similar to the preceding one with however, the difference that the n-alkane odd preference in the C23-C33 range is not as sharp and the possible presence of the (X) marker is not obvious. Pristane/phytane ratio is 1.75, i.e. slightly higher than the Draupne sample and the contaminant. The A-B plot (figure 1) shows that this sample is slighly different from the above two other samples.

The gas chromatograms of the aromatic fraction as well as total aromatics (FID) than sulfur compounds (FPD), are very similar between the two samples (annexes 8 and 13) and also with the contaminant (annex 3). Methylphenanthrene indexes MPI1 and MPI3 increase from the Draupne sample to the Heather sample (0.60 to 0.65 for MPI1 and 0.71 to 0.75 for MPI3) and are slighly higher than the contaminant (0.55 and 0.70 respectively) as shown in figure 2.

The terpane m/z 191 fragmentogram of the sample from Draupne Fm (annex 9) is identical to the contaminant above described with a single prominent peak corresponding to the C31 aß (R) Homohopane. The one of the sample from Heather Fm (annex 14) is somewhat different in that it contains C29 aß Norhopane and C30 aß Hopane in addition to the C31 aß (R) Homohopane which is also present in significant concentration, but in lower concentration than in the other samples.

The sterane m/z 217 fragmentograms of the two extracts are very similar with the marked presence of rearranged steranes (C27 and C29 diasteranes) which dominate the trace background. This feature is different as compared with the contaminant where these compounds are present, but are not dominating.

3 - CONCLUSION

The results obtained as well as gas chromatography of the saturated fraction and aromatic fractions than the GC-MS analysis of the biomarkers showed that the rock extracts of Draupne and Heather Formations are still influenced by the contaminant added repeadtedly in large quantities from the lower Cretaceous, even after thorough washing of the ditch cuttings. The sample from the Draupne Fm appears to be more affected by the contaminant than the one from the Heather. The contaminant has been established as being a lignite of natural origin and not a refined product.

The contamination effect is all the more apparent as the amount of rock extract is small, which is the case for the Jurassic in this well. This is particularly true for the molecular imprint as detected by GC-MS analysis, which is sensitive at relatively low concentration level for each individual marker. In contrast, the bulk of the extracts is globally different when one examines their composition, thus suggesting indigenous nature for the extracts in the Jurassic. As a matter of fact, the latter contain much larger proportion of hydrocarbons, both saturates and aromatics, as compared to the contaminant (62 and 73% instead of 16%).

Because of the contamination effect above stated, the characterisation of hydrocarbons of the rock extracts and the assessment of thermal maturity based on detailed molecular analysis is difficult. Nevertheless, it can be inferred from the paucity of biomarkers and the sole presence of rearranged steranes, that a high maturation level has been attained.

TABLES

TABLE: 2 25/1-10

RESULTS OF ORGANIC INVENTORY ANALYSIS

	SAMPLE	DEPTHS				R O	CK-EV	AL				LE	СО	<u> </u>		I A	TRO	SCAN			
	TYPE	Metres	Q1	on	Tmax	\$1	\$2	\$3	PI	HI	10	TOC	100	Q2	EOM	100(EOM/TOC)	SAT	ARO	POL	SAT/ARO	HC
	ND ND ND	4115.00 4145.00 4170.00 4195.00 4200.00 4205.00	N N	RI_RT RI_RT RI_RT	# #	.16 .18 .08	.27 .73 .37	.11 .43 .20	.37 .20 .18	36 47 29	14 28 16	.76 1.56 1.25	-	N N N	.068 .044 .021	8.9 2.8 1.7	53.8 34.5	17.8 22.7	28.4 42.8	3.02 1.52	.49 .25
	BO ND ND	4210.01 4220.00 4225.00 4230.00 4235.00	N	RT RI_RT RI_RT	433 # #	3.50 .17 .15	47.66 .31 .33	30.32 .11 .14	.07 .36 .32	155 29 29	98 10 13	30.83 1.05 1.13		I N	1.907 .036 .037	6.2 3.4 3.3	8.4 47.2 39.6	7.5 21.9	84.4 30.9	1.12 2.16	3.03
	ND ND	4240.00 4245.00 4250.00 4255.00	N N	RI_RT RI_RT	#	.08 .18	.23	.04 .13	.27 .40	22 24	4 12	1.03		N N	.029	2.8 2.0	41.9	21.3	39.1 36.0	1.86 1.90	.22 .19
-	ND ND ND	4260.00 4265.00 4275.00 4280.00	N N	RI_RT RI_RT RI_RT	436 # #	.44 .08	.79 .17 .20	.23 .08 .14	.36 # .35	46 18 20	13 8 14	1.71 .95		N N	.070 .015 <s< td=""><td>4.1 1.6</td><td>41.9</td><td>20.2</td><td>37.9</td><td>2.07</td><td>.44</td></s<>	4.1 1.6	41.9	20.2	37.9	2.07	.44
	ND ND	4285.00 4290.00	N N	RI_RT RI_RT	#	.07 .12	.18	.08 .10	# .31	19 24	9 9	.96 1.07		N N	.012	1.3					
	ND ND ND	4295.00 4300.00 4305.00	N N	RI_RT RI_RT RI_RT	# # 448	.07 .06	.20 .23 .29	.03 .04 0.00	.25 .22 .27	21 21 24	3 4 0	.98 1.06 1.23		N N	.012 .012 .027	1.2 1.1 2.2					
	ND ND	4310.00 4315.00	N N	RI_RT RI_RT	449 450	.14 .18	.28 .29	0.00 .10	.33 .39	24 24	0	1.20 1.19		N N	.030	2.5 2.2	51.0	17.4	31.6	2.93	.21
	ND ND ND	4320.00 4325.00 4330.00	N N N	RI_RT RI_RT RI_RT	449 449 450	.11 .17 .27	.22 .23 .37	.02 .07 .06	.34 .42 .42	21 21 27	2 7 5	1.03 1.10 1.36		N N	.018 .024 .043	1.7 2.2 3.2	51.0	15.6	33.4	3.27	.29
	ND ND ND	4335.00 4340.00 4345.00	N N	RI_RT RI_RT	450 449	.11 .06	.19 .17	.08 .07	#	18 17	8 7	1.04 1.00		N N	.029 .021	2.8 2.1	31.0	15.0	33.7	3.21	.23
	ND ND	4350.00 4355.00	N N N	RI_RT RI_RT RI_RT	453 450 446	.06 .11 .14	.19 .23 .18	.07 .11 .06	# .33 #	20 25 19	8 11 7	.97 .92 .94		N	.018 .022 .035	1.9 2.4 3.7	42.1	18.2	39.7	2.31	.21
L->	ND ND ND	4360.00 4365.00 4370.00	2 2	RI_RT RI_RT RI_RT	# 446 450	.14 .24 .09	.17 .26 .15	.07 .09 .15	# .48 #	18 25 16	8 8 16	.93 1.05 .94		N N	.023	2.5 6.1	61.1	12.0	26.9	5.09	.47
	ND ND	4375.00 4380.00	N N	RI_RT RI_RT	447 451	.15 .06	. 19 . 18	.11 .11	#	19 19	11 12	.98 .92		N N N	.020 .018 .012	2.1 1.8 1.3					
	ND ND ND	4385.00 4390.00 4395.00	N N	RI_RT RI_RT RI_RT	453 453 455	.05 .06 .05	.17 .16	.09 .06 .19	# -	19 18 16	10 7 21	.91 .86 .89		NNN	.014 .015 .012	1.5 1.7 1.3					
	ND ND	4400.00 4405.00	N N	RI_RT RI_RT	452 444	.10 .14	.19	.11	# .39	20 23	11 9	.96 .96		N N	.023 .017	2.4 1.8					
	ND ND ND	4410.00 4415.00 4420.00 4425.00	N N N	RI_RT RI_RT RI_RT	451 441 442	.11 .29 .12	.19 .30 .17	.03 .17 .09	# _49 #	20 28 20	3 16 10	.98 1.09 .86	9	N N	.025 .035 .021	2.6 3.2 2.4	46.5	18.6	34.9	2.50	.23
	ND ND ND	4430.00 4435.00 4445.00 4450.00	N N	RI_RT RI_RT RI_RT	444 443 442	.19 .14 .07	.21 .24 .16	.28 .09 .09	.47 .36 #	22 26 19	29 9	.95 .93		N N	.022 .026	2.3 2.8					
	ND ND	4455.00 4465.00	N N	RI_RT RI_RT	445 441	.11 .09	.26 .22	.11 .11	.31 .29	28 24	11 12 13	.84 .93 .89		2 2 2	.022 .030 .022	2.6 3.2 2.5	49.2	19.7	31.1	2.50	.21
	ND	4480.00	N	RI_RT	439	.15	.22	.05	.40	23	6	.98		N	.033	3.4	46.3	26.5	27.2	1.75	.24

Follow-up

TABLE 3

ISOTOPIC AND CHROMATOGRAPHIC RATIOS

	-	CARBON	 	CHRO	ATOGRA	PHIC I	RATIOS	 5	
+	l	RATIOS		SATURA	ATED HO	:	AROI	MATIC	HC
LAB REF.	DEPTH (m)	SAT	PR/ nC17	PH/ nC18	PR/PH	A/B	MPI1	MPI3	MP/ P
B13780 B13728 B13747	4210 4260-4265 4365	# -28.5 -27.4	.38 .39 .35	.35	1.18 1.27 1.75	1.08 1.16 1.66	.60	.71	1.89 2.20 2.37

CARBON ISOTOPIC RATIOS :

UNITS ARE IN PER MIL / PDB

SAT = SATURATED FRACTION

= ANALYSIS NOT POSSIBLE

SATURATED HYDROCARBON RATIOS:

PR = PRISTANE ; PH = PHYTANE

A = PRISTANE/nC17 ; B = PHYTANE/nC18

AROMATIC HYDROCARBON RATIOS:

MPI1 = 1.5(2MP+3MP)/(P+1MP+9MP)

MPI3 = (2-MP+3-MP)/(1-MP+9-MP)

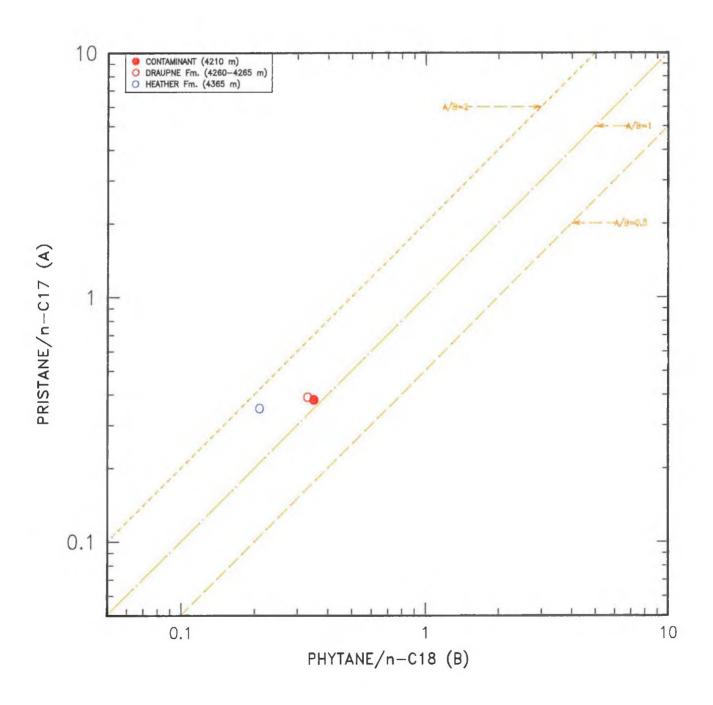
MP/P = SUM OF METHYL-PHENANTHRENES/PHENANTHRENE

FIGURES



PRISTANE/n-C17 vs. PHYTANE/n-C18

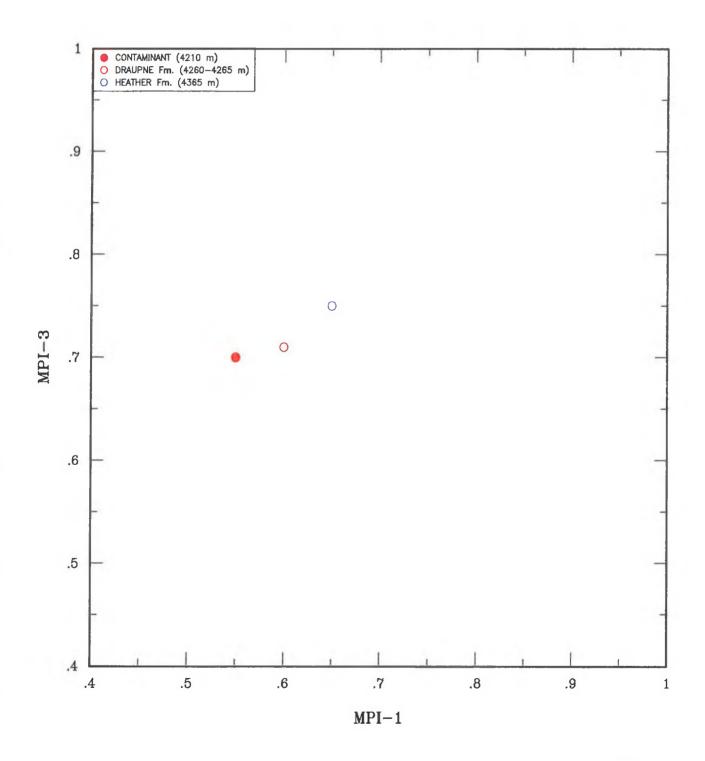
25/1-10





METHYLPHENANTHRENE INDEX

25/1-10



ANNEXES

COUNTRY

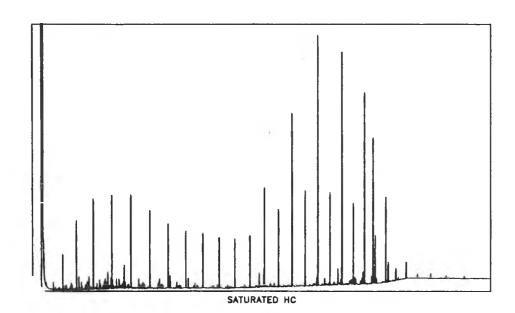
: NORVEGE

WELL

: 25/1-10

DEPTH : 4210m

IDENTIFICATION : CONTAMINANT



Composition of total product (%)

ASPHALTENES

AROMATIC HC : 7.5

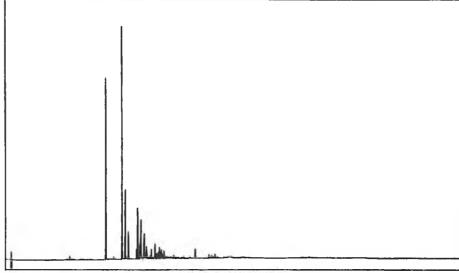
RESINS

: 84.1

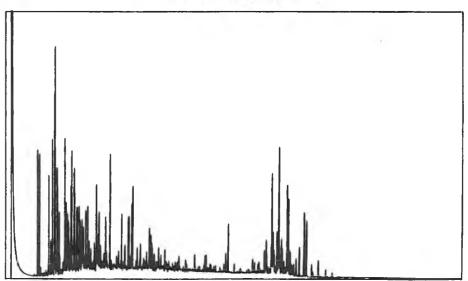
SATURATED HC : 8.4

S/A

: 1,12



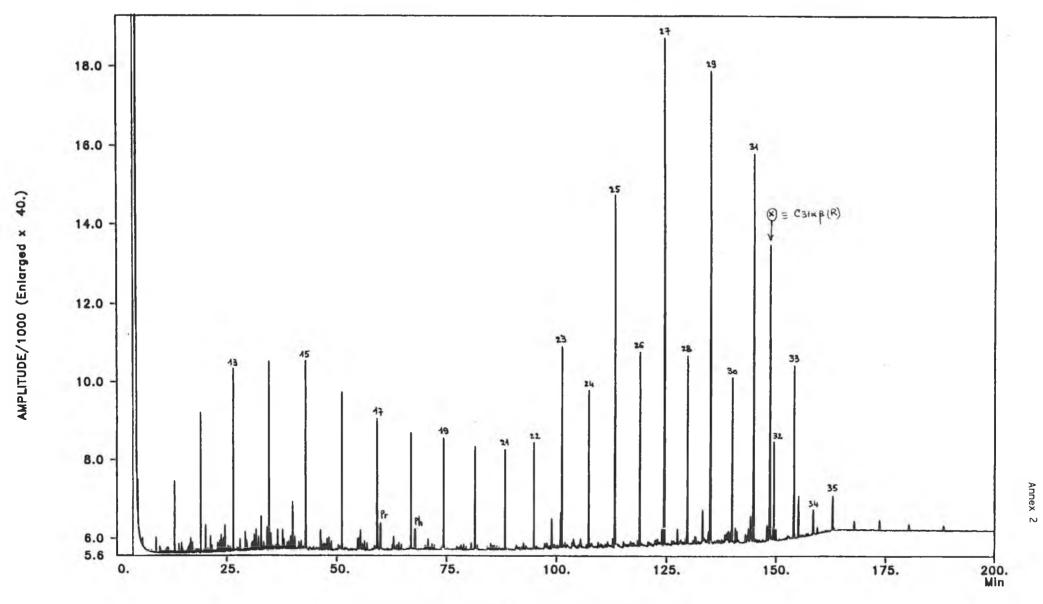
SULFUR COMPOUNDS



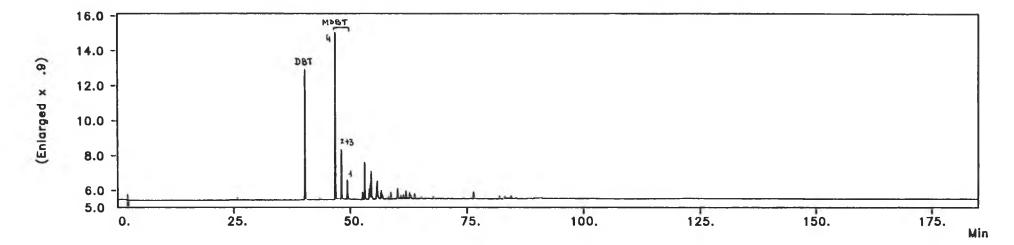
AROMATIC HC

Annex 1

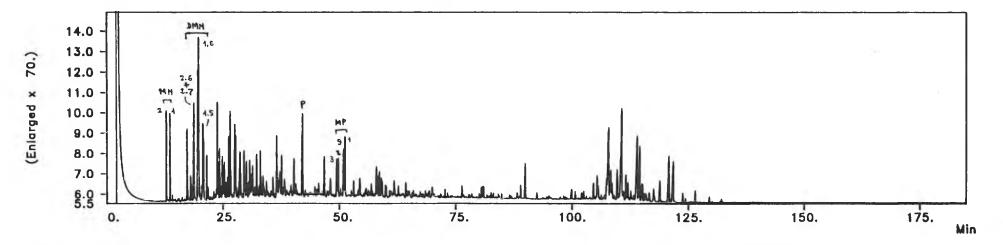
CHROMATOGRAM OF THE SATURATED HC



NORVEGE 25/1-10 4210.0 m

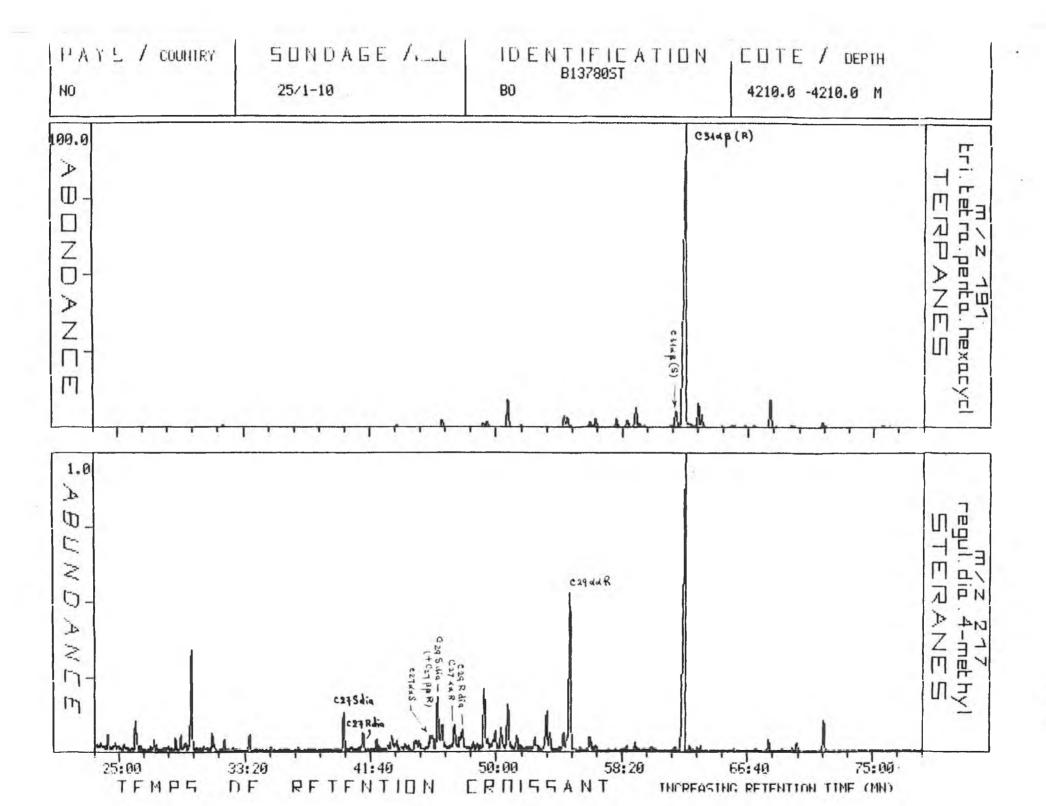


FPB13780NO



FIB13780NO

25/1-10 4210.0 m



S N E A (P) Computerized GC/MS Analyt	ical Repo	Organic Geochemistry rt on Steranes and Terpanes	nr. 1806
Sample	1/1-10 10. 0	B13780. BO NO (Meters)	.!
STERANES	Arese	TERRANES	Areas
C21 Sterane	nd nd 1117. 3240. 2011. 1788. 980. 3222. 1681. 11910. 74072.	C23 tricyclic C24 tetracyclic Ts	ns ns nd 24742. 59410. nd nd nd nd 5187590.
C30 tricyclic,22 S C30 tricyclic,22 R 29 Desmethyl Hopane. C28 Bisnorhopane C29/5 (RT.> 29 ab). 18 a(H) Oleanane Gammacerane C33 ab S Homohopane. C33 ab R Homohopane. C35 Hexacyclic	ns ns ns 90151. ns ns nd	C35 ab S Homohopane. C35 ab R Homohopane.	nd nd
	RESUL		
27 bb S / 27 aa R 27 aa S / 27 aa R 27 S dia / 27 aa R . 22 4-Me st / 27 aa R % 20 S C27 % bb C27	1.12 0.64 N / A N / A 38.35 64.37	C29 DHop / C29 Hop . v C28 BNHop / C29 Hop - v C29/5 / C29 Hop 18 aH Olean/C30 Hop . v Gammacerane/C30 Hop . v 30/3(R&S) / C29 Hop - v 30/3(R&S) / 23/3 2.35Hex/C35Hop(R&S) .	. low. . low. 1.06 . low. . low. . low.
29 bb S / 29 aa R 29 aa S / 29 aa R 27 S dia / 29 aa R 22 4-Me st / 29 aa R % 20 S C29 % bb C29	N / A		7 / A N / A N / A
C29 H / C30 H Tm / Ts	1.42 N/A N/A N/A N/A		
23/3 / 21 st TT / ST	N / A 70.03		

Country NO 25/1-10

Lithology

Age/Formation

DRAUPNE Fm

elf aquitaine

Identification 4260 4265 M (Lab. Ref. B13728) TOC (%) 1.71 S2 (mg/g) .79 HI (mg/g) 46 1.71 .36

Tmax (C) 436

EOM .0967

SAT HC ARO HC

NSO

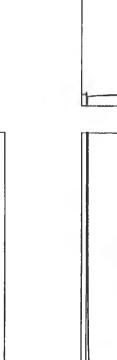
35.80 (% EOM) 15.80 (% EOM) 48.40 (% EOM)

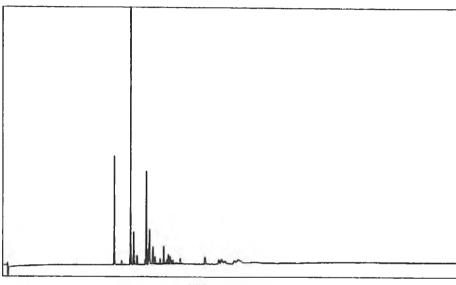
SHALE GREY-BROWNISH GREY, SLIGHTLY SILTY-SILTY, MICROMICACEOUS

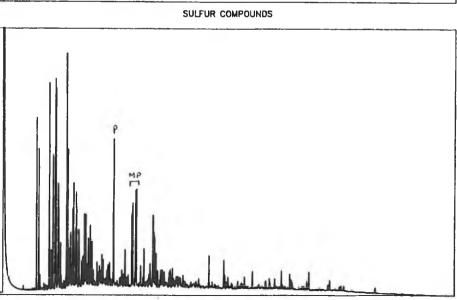
SATURATED HC

d13C SAT

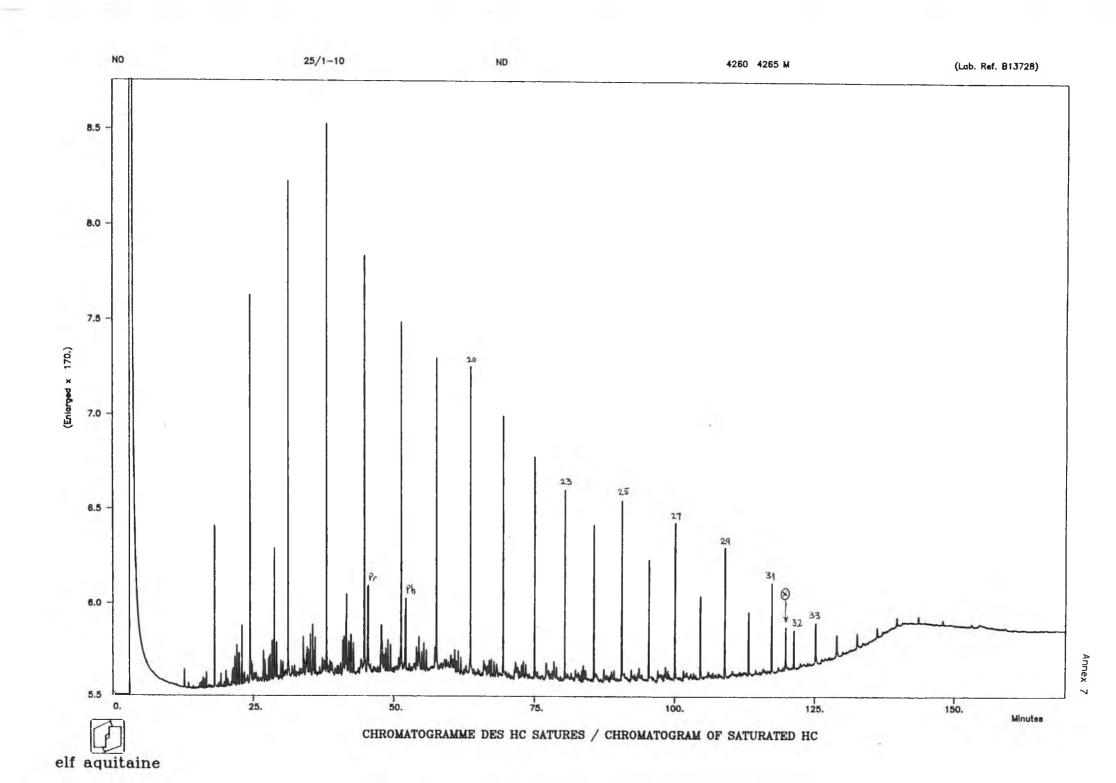
-28.5

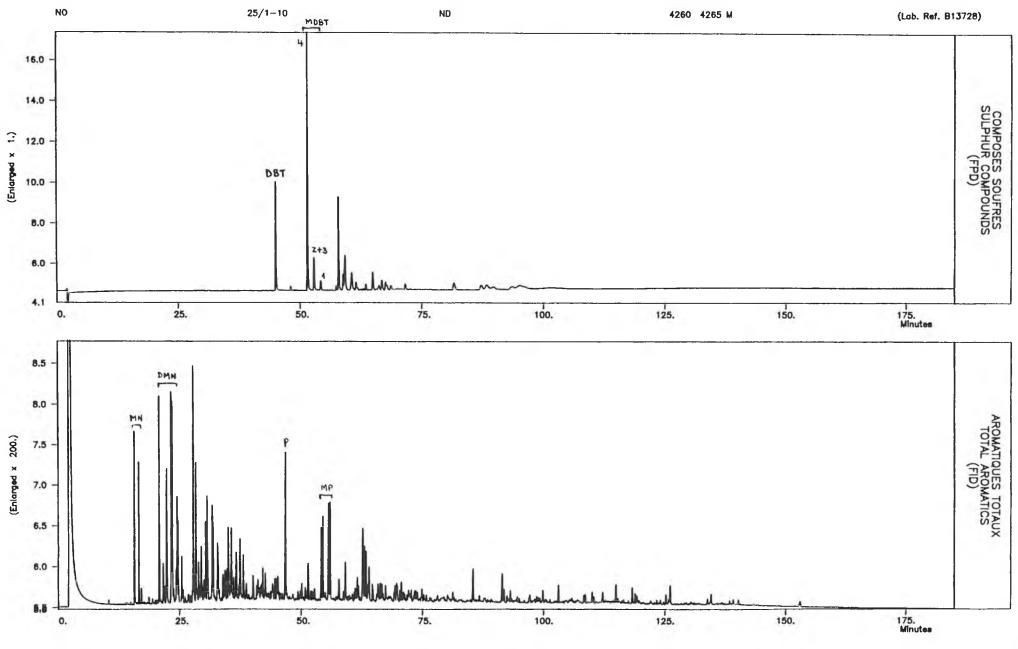






AROMATIC HC

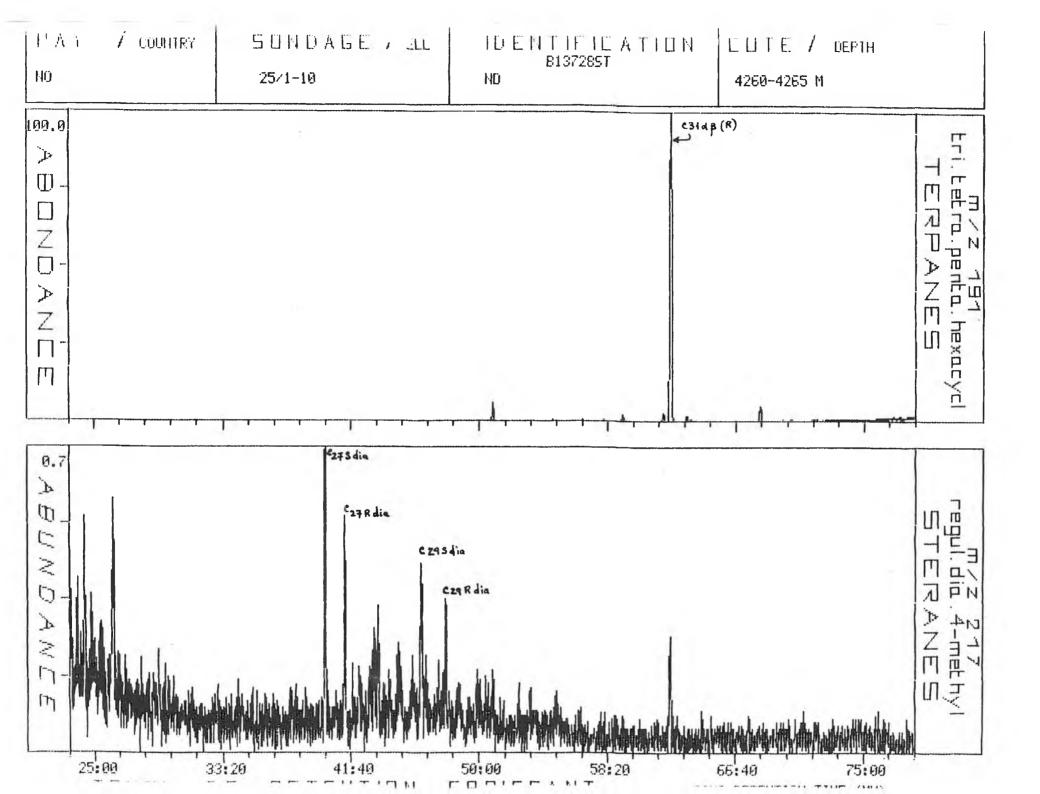






CHROMATOGRAMME DES HC AROMATIQUES/ CHROMATOGRAM OF AROMATIC HC

William C



S N E A (P) Computerized GC/MS Analyt	ical Repo	Organic Geochemistry rt on Steranes and Terpanes nr.	1804
Sample	5/1-10 260.	B13728. ST NO to 4265. (Meters)	!
Acquisition File Name : B1 Submitted by	3728STM	Mag tape / september 21. , 1989.	
STERANES	Areas	TERPANES	Areas
C21 Sterane C22 4-Methyl Sterane C22 Sterane C27 S Diasterane C27 aa S Sterane C27 bb R Sterane C27 bb S Sterane C27 aa R Sterane C29 aa S Sterane C29 aa R Sterane C29 bb R Sterane C29 bb R Sterane C29 bb S Sterane	nd nd 666. nd nd nd nd nd nd nd	C23 tricyclic C24 tetracyclic Ts	ns ns ns ns ns ns ns ns ns
OPTIONAL ANALYSIS	Areas	OPTIONAL ANALYSIS	Areas
		C35 ab S Homohopane. C35 ab R Homohopane.	nd nd
	RESUL	rs :	
29 bb S / 29 aa R 29 aa S / 29 aa R 27 S dia / 29 aa R 22 4-Me st / 29 aa R % 20 S C29	7//4 7//4 7//4	C29 DHop / C29 Hop . N / C28 BNHop / C29 Hop . N / C29/5 / C29 Hop N / 18 aH Olean/C3O Hop . N / Gammacerane/C3O Hop . N / 30/3(R&S) / C29 Hop . N / 30/3(R&S) / 23/3 N / 2.35Hex/C35Hop(R&S) . N / C35H(R&S)/C33H(R&S) . N / 29+3OHop/C35 H(R&S) . N /	A A
% bb C29 21 st / 22 st 22 4-Me st / 22 st	N / A N / A		
C29 H / C30 H Tm / Ts	N / A N / A N / A		
23/3 / 21 st TT / 5T	N / A 25. 94		

Country NO 25/1-10

Identification ND 4365 M

(Lab. Ref. B13747)

TOC (%) 1.05 S2 (mg/g) .26 HI (mg/g) 25 PI .48

Tmax (C) 446

EOM

.0738

SAT HC 57 ARO HC 11

NSO

57.70 (% EOM) 11.70 (% EOM) 30.60 (% EOM)

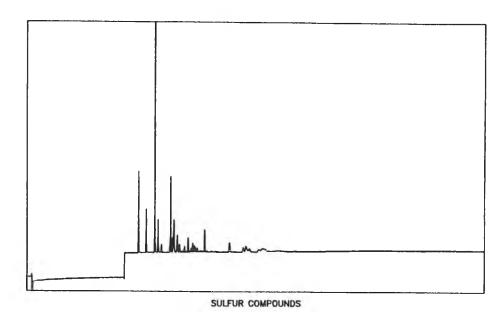
Age/Formation HEATHER Fm

Lithology

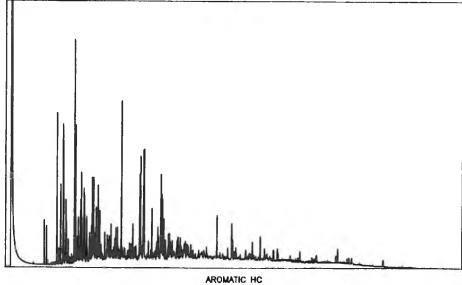
SHALE GREY-BROWNISH GREY, SLIGHTLY SILTY-SILTY, MICROMICACEOUS

SATURATED HC

d13C SAT -27.4

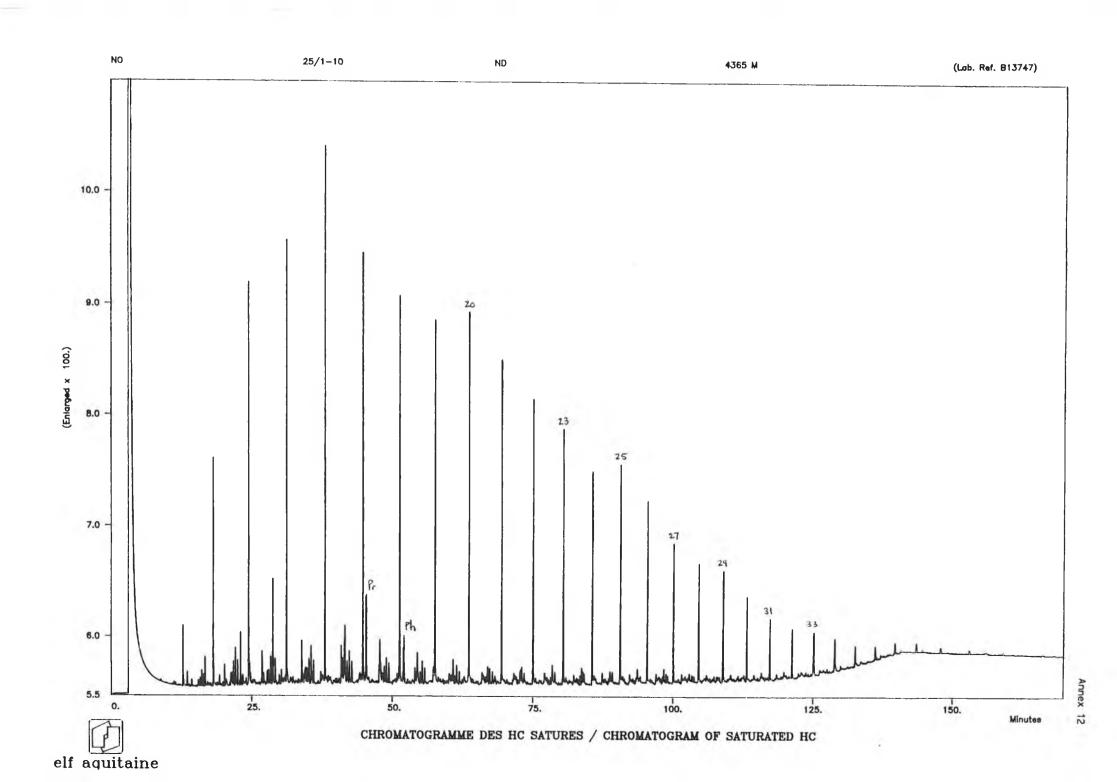


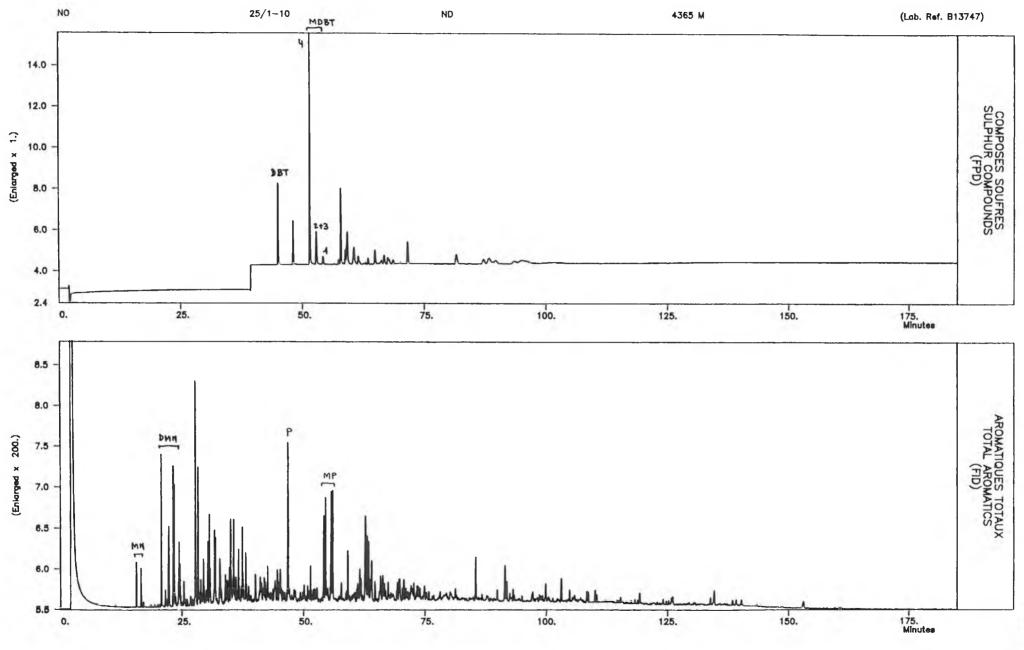




elf aquitaine

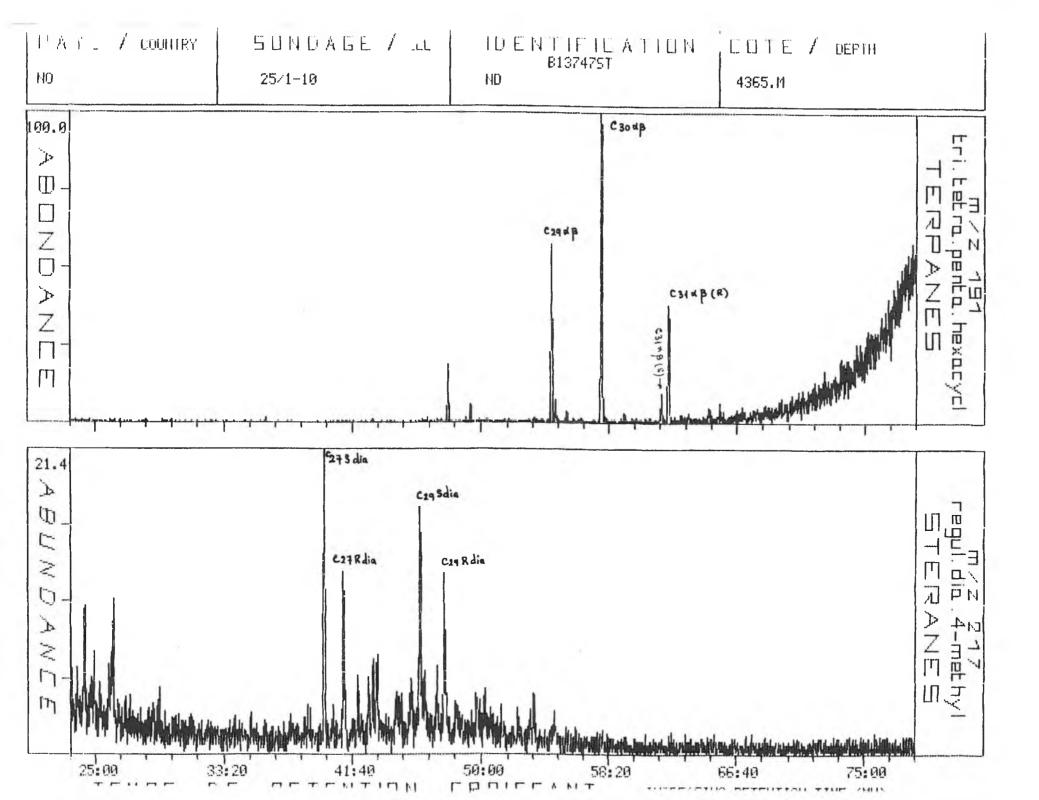
Annex







CHROMATOGRAMME DES HC AROMATIQUES/ CHROMATOGRAM OF AROMATIC HC



S N E A (P) Computerized GC/MS Analy	tical Repo	Organic Geochemistry rt on Steranes and Terpanes nr.	1805
Well Depth	365. 137475TM)	Mag tape / september 21. , 1989.	
STERANES	Areas	TERPANES	Areas
C21 Sterane	nd nd 1146. nd nd nd nd nd nd 12990.	TERPANES C23 tricyclic C24 tetracyclic Ts	ns 834, 258, 2646, 4600, ns 431, 1676, ns 13998,
C30 tricyclic, 22 S C30 tricyclic, 22 R 29 Desmethyl Hopane. C28 Bisnorhopane C29/5 (RT.> 29 ab) 18 a(H) Oleanane C33 ab S Homohopane. C33 ab R Homohopane. C35 Hexacyclic	ns ns nd nd	C35 ab S Homohopane. C35 ab R Homohopane.	
27 hh S / 27 aa R			
29 bb S / 29 aa R 29 aa S / 29 aa R 27 S dia / 29 aa R 22 4-Me st / 29 aa R % 20 S C29	7 / A A A A A A A A A A A A A A A A A A	C29 DHop / C29 Hop . V.low C28 BNHop / C29 Hop V.low C29/5 / C29 Hop . V.low C29/5 / C29 Hop . V.low Gammacerane/C30 Hop. V.low Gammacerane/C30 Hop. V.low G30/3(R&S) / C29 Hop V.low G30/3(R&S) / C3/3 N / C35H(R&S)/C35H(R&S). N / C35H(R&S)/C35H(R&S). N / C39+30Hop/C35 H(R&S). N /	Ä A
% bb C29	N / A		
C29 H / C30 H Tm / Ts	O.30 N/A - 20.27 N/A		
23/3 / 21 st TT / ST	N / A 1.07		