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SUMMARY

The gas components C_1-C_6 from headspace cans, well 34/10-32, are quantified and the $\delta^{13}C$ value is measured when possible on methane, ethane, propane and the butanes.

The gas components C_1-C_4 and CO_2 have been separated on two DST gas samples and the $\delta^{13}C$ value of these components have been measured. The isotopic composition of hydrogen from CH_4 has also been measured.

The stable isotope results of headspace gas from well 34/10-32 indicate a biogenic dominance at least down to the 1560 m level.

The isotope study of both the thermogenic headspace gas and the DST samples indicate a high maturity situation.

The gas may possibly be of mixed origin from two (or more) sources or derived at different maturity levels from the same source.

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1. INTRODUCTION

Headspace cans from well 34/10-32 were received and analysed June/July 1987. On cans with 200 - 300 m interval the headspace gas is quantified (C_1-C_6) and the $\delta^{13}C$ value is measured when possible on methane and the higher components ethane, propane, iso- and n-butane.

Two reservoir gas samples from the same well, DST 1; 3468 - 3482 m RKB, and DST 2; 3379 - 3385.5 and 3354 - 3365 m RKB were received and analysed September 1987. On the samples C_1-C_4 and CO_2 are quantified, and the $\delta^{13}C$ value is measured on methane, ethane, propane, the butanes and CO_2. The δD value is also measured on methane.

2. ANALYTICAL PROCEDURE

The headspace gas has been quantified by a Carlo Erba Mega HRGC 5300 gas chromatograph equipped with HWD and FID detectors and a packed column.

In order to prepare for isotopic measurements the headspace gas and the DST samples have been quantified and separated into the different gas components by a Carlo-Erba 4200 instrument. This gas chromatograph is equipped with a special injection loop in order to concentrate the samples, in the case of low concentration of the gas components. The hydrocarbon gas components were oxidized in separate CuO-ovens in order to prevent cross contamination. The combustion products CO_2 and H_2O were frozen into collection vessels and separated.

The water was reduced with zinc metal in a sealed tube to prepare hydrogen for isotopic analysis. The isotopic measurements were performed on a Finnigan Mat 251 and a Finnigan Mat delta mass spectrometer. Our $\delta^{13}C$ value on NBS 22 is -29.77 ± .06 o/oo PDB.

3. RESULTS

The composition of the headspace gas and the DST samples is given in Table 1 (headspace gas) and Table 2 (DST samples).

The results have been normalized to 100%. The stable isotope results are given in Table 3 (headspace gas) and Table 4 (DST samples).

Figure 1 shows a schematic presentation of the data.

Our uncertainty on the $\delta^{13}C$ value is estimated to be ± 0.3 o/oo and includes all the different analysis step. The uncertainty on the δD value is likewise estimated to be ± 5 o/oo.

<u>Table 1</u> Volume composition of headspace gas from well 34/10-32

SAMPLE m	IFE no.	C1 %	C2 %	C3 %	iC4 %	nC4 %	iC5 %	nC5 %	iC6 %	nC6 %	WET-NESS	iC4/nC4	sum Cn ppm
300	6613	99.7	0.19	0.13	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	3,669
327	6275*	99.4	0.02	0.03	0.19	0.32	0.00	0.00	0.00	0.00	0.01	0.60	14,079
331	6276*	99.9	0.02	0.01	0.03	0.05	0.00	0.00	0.00	0.00	0.00	0.52	24,026
334	6277*	99.6	0.02	0.03	0.14	0.22	0.00	0.00	0.00	0.00	0.00	0.63	11,044
550	6625	99.9	0.07	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	9,838
800	6632	99.8	0.11	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	4,116
1050	6639	98.7	0.90	0.41	0.00	0.00	0.00	0.00	0.00	0.00	0.01	-	145
1100	6640	99.9	0.08	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	2,323
1300	6644	99.8	0.10	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	2,289
1560	6651	99.7	0.14	0.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	2,723
1750	6656	90.8	2.84	3.58	2.18	0.63	0.00	0.00	0.00	0.00	0.09	3.48	335
1800	6657	55.3	8.24	14.12	16.47	5.88	0.00	0.00	0.00	0.00	0.45	2.80	9
1825	6658	31.0	38.41	16.11	11.28	3.22	0.00	0.00	0.00	0.00	0.69	3.50	81
1875	6660	84.9	9.21	2.67	2.90	0.37	0.00	0.00	0.00	0.00	0.15	7.80	1,347
1900	6661	47.9	21.42	8.02	5.63	2.93	4.43	5.09	2.21	2.39	0.52	1.92	1,671
1925	6662	60.6	12.14	7.98	3.62	4.03	4.25	3.76	1.54	2.08	0.39	0.90	3,697
2025	6667	54.4	13.07	13.61	3.09	5.63	3.45	3.63	1.27	1.81	0.46	0.55	5,510
2275	6672	48.8	11.22	14.15	5.12	4.88	7.08	5.12	1.54	2.07	0.51	1.05	410
2375	6673	26.6	10.26	21.39	7.68	12.35	8.42	6.70	3.38	3.26	0.73	0.62	16,270
2495	6676	37.2	13.21	18.40	5.87	7.60	6.80	5.86	2.04	2.98	0.63	0.77	18,099
2630	6677	19.7	16.06	33.58	14.60	16.06	0.00	0.00	0.00	0.00	0.80	0.91	27
2810	6678	3.8	2.08	17.99	8.05	16.57	24.15	13.73	9.94	3.69	0.96	0.49	211
2920	6679	18.4	3.57	7.65	13.27	12.76	25.51	18.88	0.00	0.00	0.82	1.04	20

* Analysed april 1987

Table 2 Volume composition of DST samples from well 34/10-32

Sample	IFE no.	C_1 %	C_2 %	C_3 %	$i-C_4$ %	$n-C_4$ %	CO_2 %	ΣC_1-C_4	$\frac{\Sigma C_2-C_4}{\Sigma C_1-C_4}$	$\frac{i-C_4}{n-C_4}$
DST 1 3468-3482 m	6774	82.6	3.5	1.2	0.03	0.07	12.6	87.4	0.05	0.46
DST 2 3379-3385.5 3354-3365 m	6775	84.7	8.2	3.0	0.34	0.64	3.1	96.9	0.13	0.54

Table 3 Isotopic composition of headspace gas samples from well 34/10-32

Sample m	IFE no.	$\delta^{13}C$ PDB				
		C_1	C_2	C_3	$i-C_4$	$n-C_4$
300	6613	-69.5				
327	6275*	-73.1				
331	6276*	-73.5				
334	6277*	-71.5				
550	6625	-67.7				
800	6632	-69.8				
1100	6640	-68.5				
1300	6644	-57.3				
1560	6651	-56.1				
1850-1900	6660	-31.3				
1900-1950	6662	-39.6	-31.4	-29.7		-26.9
2000-2050	6667	-40.0	-27.3	-26.9		-28.0
2300-2350	6673	-41.3	-26.1	-25.5	-25.4	-29.6
2450-2540	6676	-40.2	-26.1	-26.1	-28.8	-26.3

* Analysed April 1987

Table 4 Isotopic composition of DST samples from well 34/10-32

Sample	IFE no.	C_1 $\delta^{13}C$ PDB	C_1 δD SMOW	C_2 $\delta^{13}C$ PDB	C_3 $\delta^{13}C$ PDB	$i-C_4$ $\delta^{13}C$ PDB	$n-C_4$ $\delta^{13}C$ PDB	CO_2 $\delta^{13}C$ PDB	CO_2 $\delta^{18}O$ PDB
DST 1 3468-3482 m	6774	-39.6	-183	-26.6	-25.5	-25.8	-26.4	-13.6	- 6.1
DST 2 3379-3385.5 3354-3365 m	6775	-39.9	-194	-28.4	-26.5	-25.5	-26.7	-12.6	-12.8

4. INTERPRETATION

The stable isotope results of headspace gas from well 34/10-32 indicate a biogenic dominance at least down to the 1560 m level.

From the 1900 m level and downwards the gas samples may be divided into two different groups based on the $\delta^{13}C$ values of ethane and n-butane. The headspace gas from the 1900 m level and the DST 2 samples are characterized by relatively light $\delta^{13}C$ ethane values compared to the other samples.

The two headspace samples from the 2000 - 2050 m and 2300 - 2350 m levels have lighter $\delta^{13}C$ n-butane values than the other headspace and the DST samples.

The rather heavy $\delta^{13}C$ values of ethane, propane and n-butane may indicate a biodegraded environment.

The $\delta^{13}C$ values of the headspace gas from the 1900 - 1950 m follow the same smooth trend from methane to n-butane, exluding i-butane, which is generally found in unaltered gases (James 1983*).

A source LOM between 10 and 11 is found when plotted on James' maturity diagram, Figure 2 (James 1983), e.g. that the gas was formed at a relatively high maturity level in the oil window.

The three other headspace samples and the two DST samples show an opposite trend with $\delta^{13}C$ n-butane values lighter than or at the same level as the $\delta^{13}C$ propane values. This present isotopic pattern together with the groups of heavy and lighter $\delta^{13}C$ ethane and n-butane values indicate a mixed gas situation.

The gas is at least derived from two different sources with one source dominating from the C_1-C_3 range and the other dominating from C_4 and higher. Gases derived from the same source but at different maturity levels is an alternative possibility.

The relationship between the $\delta^{13}C$ values of propane and the n-butane may also indicate a high maturity situation.
A high maturity situation is in accordance with the combined use of $\delta^{13}C$ and δD methane values of the DST samples. A high maturity in the condensate field of the oil window is indicated when the results are plotted in Figure 3 (Schoell 1983**).

If it is assumed that C_1-C_3 are dominately derived from one source the $\delta^{13}C$ values of methane, ethane and propane can be used to indicate the maturity level of the DST gas by using James' maturity diagram (James 1983), Figure 2.

A source LOM between 11 and 12 may thus be indicated, e.g. that the gas was formed at a relatively high maturity level in the oil window. The DST 1 sample seems slightly more mature than the DST 2 sample.

5. CONCLUSION

The stable isotope results of headspace gas from well 34/10-32 indicate a biogenic dominance at least down to the 1560 m level.

The isotope study of both the thermogenic headspace gas and the DST samples indicate a high maturity situation. The gas may possibly be of mixed origin from two (or more) sources or derived at different maturity levels from the same source.

* James, Alan T. (1983): Correlation of Natural Gas by Use of Carbon Isotopic Distribution between Hydrocarbon Components, AAPG, Vol. 67, No. 7, July 1983.

** Schoell, M. (1983): Genetic Characterization of Natural Gases, AAPG, Vol. 67, No. 12, December 1983.

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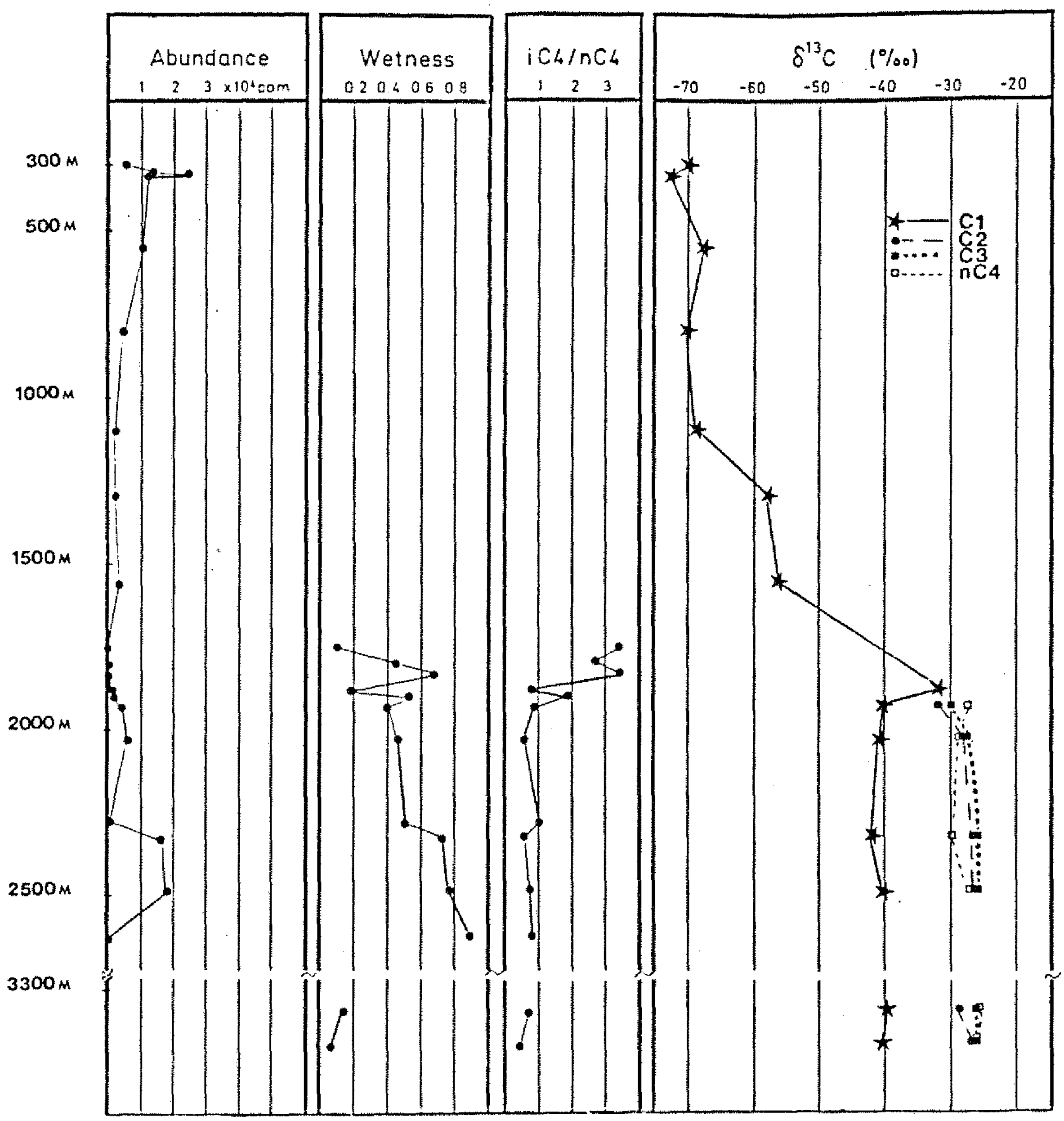

Figure 1 Composition of headspace and DST gas from well 34/10-32

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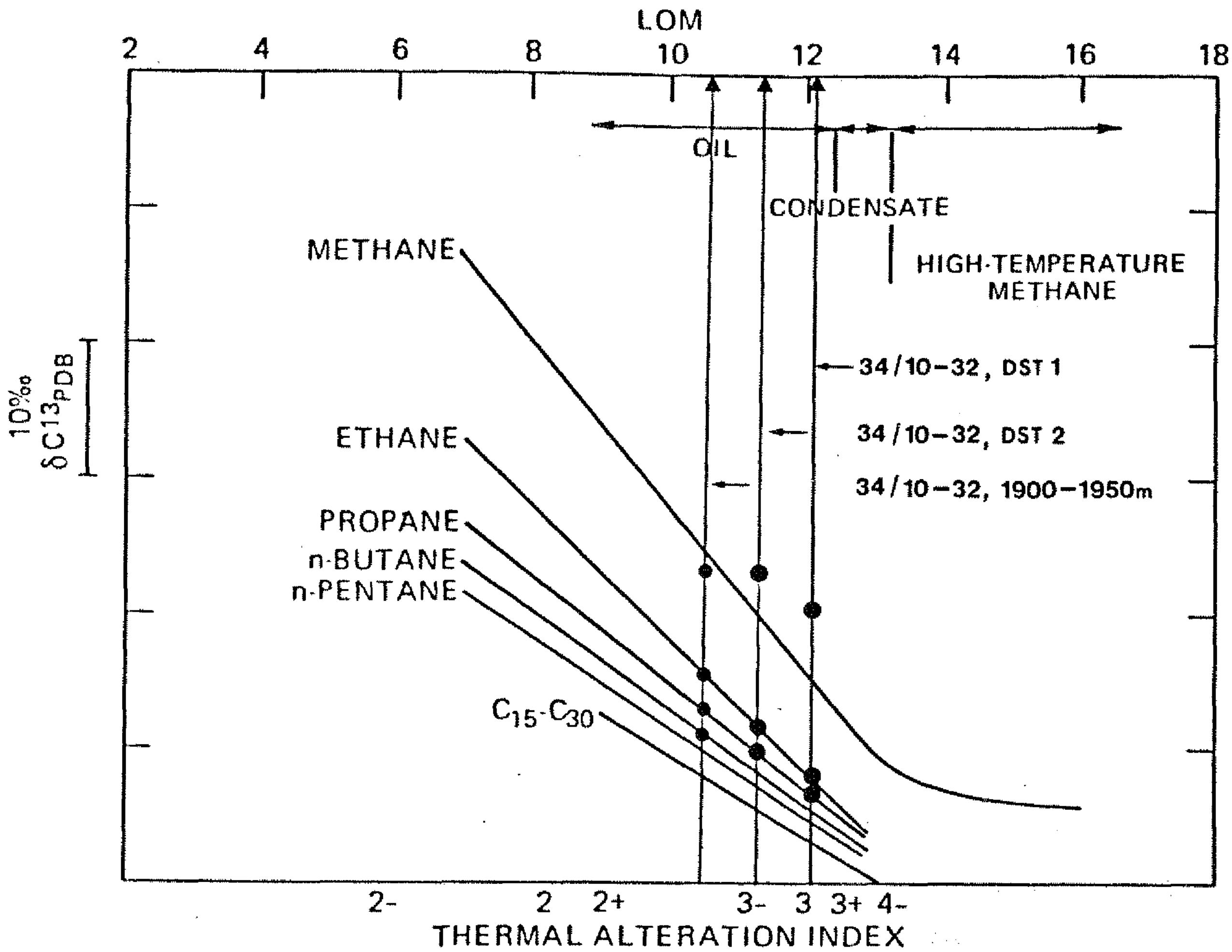

Figure 2 Carbon isotopic separations of gas samples from well 34/10-32 are plotted on the maturity diagram (after James, 1983). A source LOM between 10 and 12 is indicated for the gas.

The calculated carbon isotopic separations between gas components are plotted on the vertical axis using a sliding scale that is simply the algebraic difference, in parts per mil, between the isotopic compositions of the natural gas components. The scale does not possess a fixed origin, but is oriented with the more depleted $\delta^{13}C$ values at the upper end. Use of this sliding scale allows the maturity of a gas to be assessed without prior knowledge of the isotopic composition of the gas source.

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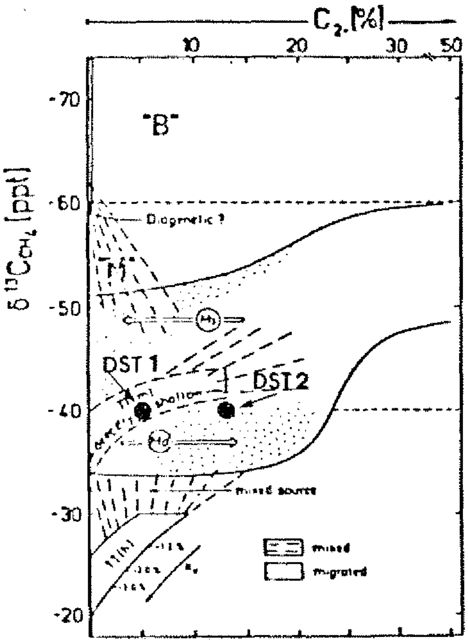

Figure 3a

Variations of molecular composition in natural gases related to the isotope variations of methane.

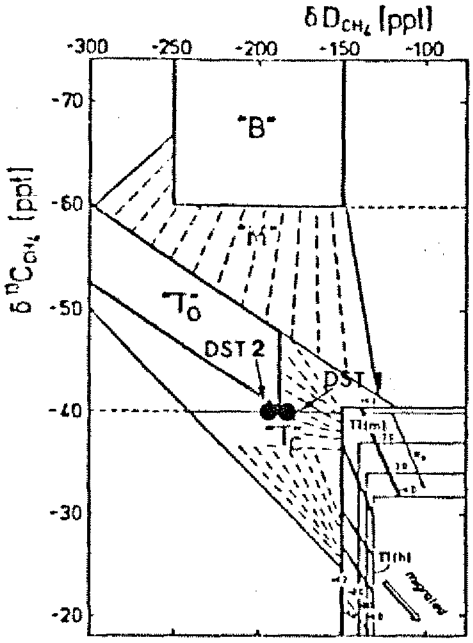

Figure 3b

Carbon and hydrogen isotope variations in methanes.

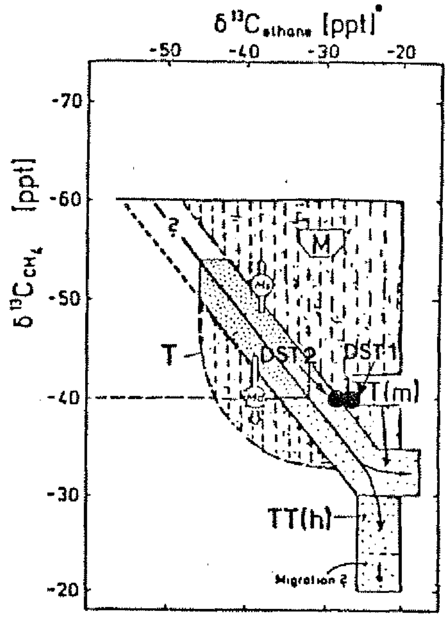

Figure 3c

Carbon isotope variations in ethane related to carbon isotope variations in methane.

The principle for the genetic characterization of natural gases is that the primary gases (B-biogenic gas, T-associated gas, TT-non-associated gas) are defined by fields of compositional variations. These primary gases may become mixed and form various mixtures "M" of intermediate composition. "TT(m)" and "TT(h)" are non-associated gases from marine source rocks and coal gases from N.W. Germany, respectively, compositional shifts due to migration are indicated by arrows Md (deep migration) and Ms (shallow migration), respectively. "T_0" are gases associated with petroleum in an initial phase of formation. "T_C" are gases associated with condensates. (Schoell 1983).