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			Private			
ADDRESS TELEPHONE			TIVALE			
TELEX	76361 energ n 76	Confidential				
REPORT TYPE	REPORT NO.		DATE			
ITE	IFE/KR/R-84/003		1984-01-04			
	REPORT TITLE	DATE OF LAST REV.				
	MUD AND RESERVOIR GAS					
	ON SAMPLES FROM WELL 3	REV. NO.				
	CLIENT Statoil, Norsk Hydro a	nd Saga	NUMBER OF PAGES			
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	CLIENT REF.		NUMBER OF ISSUES			
			20			
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SUMMARY Migrate	DISTRIBUTION					
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KEYWORDS GAS GEOCHEMISTRY, MIGRATION, BACTERIAL DEGRADATION, MATURIT						
		DATE	SIGNATURE			
Bjørg Andresen PREPARED BY Einar Brevik Arne Råheim		1984-01-04	Bjørg Andrean Znar Bruit Ame Rimin			
REVIEWED BY	,					
APPROVED BY	Karen Garder	1984-01-04	Carin Sarder.			

MUD AND RESERVOIR GAS GEOCHEMISTRY ON SAMPLES FROM WELL 31/3-1

INTRODUCTION

The samples were received on the 4th October, 1983. The main part of the work has been done in first part of December. 17 gas samples taken at 100 m intervals from the mudline at depths from 500 to 2300 m were received. Only one sample had a concentration of hydrocarbons above 1%. In spite of this, we have managed to determine the ∂^{13} Cvalue of CH₄ in most samples. Only the samples from the 1900 m, 2100 m and 2300 m depths were not analysed, because the samples were too small. The low hydrocarbon content has, however, made it impossible to do analyses on the higher hydrocarbons and CO₂. It has for the same reason also been impossible to determine the ∂D -value on CH₄.

3 samples of reservoired gas have also been analysed. We have in this case been able to determine the ∂^{13} C-values on methane, ethane, propane, butane (except 1570 m) and CO₂ (except 1574.2 m). The ∂ D-value on methane has been determined on the samples from the 1374.2 and 1570 m levels.

ANALYTICAL PROCEDURE

The natural gas has been separated into the different gas components by a Carlo-Erba 4200 instrument. The hydrocarbon gas components were oxydized in separate CuO-ovens, which enables us to collect several times when the concentration of a gas component is low. The combustion products CO_2 and H_2O were frozen into collection vessles and separated. The isotopic measurements were performed on a Finnigan Mat 251 mass spectrometer. Our $\partial^{13}C$ -value on NBS-22 is - 29.77 $\stackrel{+}{=}$.06 $^{\circ}/oo$

RESULTS

The stable isotope results are given in Table 1. The composition of the gases are given in Table II.

Interpretation

Even though the ∂^{13} C-value at 1100 m (- 48.7) suggests that a mixture of biogenic and thermogenic methane occurs at this level, the data pattern as a whole indicates that thermogenic methane migrated at least to the 700 m level.

Migrated thermogenic methane dominates to relative shallow levels (700 m). This suggests that the sealing efficiency of the cap rock is not complete.

The ∂^{13} C propane values of the reservoired gases at 1374.2, 1570 and 1574.2 m levels are all between - 14.1 to - 15.9. The butanes (when measured) are also isotopically lighter than the propane values, which is opposite to the normal trend between these two components.

The rather heavy $\partial^{13}C$ propane values together with the uncommon relation ships between the $\partial^{13}C$ values of propane and the butanes can in our view only be explained by effects from bacterial degradation.

The bulk of the methane and ethane have, however, not been effected by the bacterial degration. If this was the case, we should, according to our previous experience, have seen much heavier $\partial^{13}C$ -methane and -ethane values.

New methane and ethane must therefore have migrated into the reservoir after the bacterial degradation had stopped and could, particularly if the geological situation of the reservoir is complex, have been mixed with varying amounts of the already biodegraded methane and ethane gas components in the reservoir. For example, the difference in the ∂^{13} C-values of methane and ethane land ethane between the sample from the 1570 m level and the 1574.2/1374.2 m levels can be explained in this manner.

Table 1.

	Depth m	Metha a ¹³ C ^{X)}		Ethane $\partial^{13}C^{X}$	Propane ^{3¹³C^{X)}}	i-Butane Ə ¹³ C ^{X)}	n-Butane Ə ¹³ C ^{X)}	CO ₂ ∂ ¹³ C ^X)
	500 600 700 800	-50.9 -54 -49 -45						
	900 1000 1100 1200	-35 -35.1 -48.7 -37						
MTF	1374.2 1400 1500	-41.1-3 -34.4 -41.6	137.1	-24.6	-15.9	-18.7	-22.6	+ 7.3
MFF	1570 1574.2 1600 1800 2000	-32.5 -35 -37	141.0		-15.5 -14.1		-20.4	+ 3.2
	2200	-33						

- x) Our uncertaincy on the $\partial^{13}C$ -values is estimated to be $\frac{1}{2} \cdot 3^{\circ}/\circ 0$ and includes all the different analyses steps.
- xx) The uncertainly on the ∂D_{CH_4} value is about 5 O /oo. The isotopic measurements have been performed in Mooks laboratory, Groningen, Netherland.

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Depth	Methane	Ethane	Propane	i-Butane	n-Butane	co ₂
m	00	ppm	ppm			g g
500	.71	7	5			.08
600	.20	4	1			.09
700	.31	6	2			.07
800	.30	6	2			.10
900	.15	3	1			.09
1000	.31	4	1			.11
1100	.36	5	1			.10
1200	.22	10	1			.11
1400	.44	75	10			.09
1500	1.72	123	20			.10
1600	.13	4	1			.08
1800	.13	11	3			.08
1900	.02	6	1			.08
2000	.08	5	< 1			.08
2100	.02	3	< 1			.07
2200	.07	3	< 1			.07
2300	.02	4	< 1			.06
	+		 	<u>+</u>		
1374	80	3.4%	.48	. 38	.048	0.5
1510	57	1.98	.28	.15%	<.01%	0.3
1574.2	33	3.0%	.68	.5%	.048	0.1

Table II. Composition of mud and reservoired gases.

It is in this case difficult to indicate the type of source because we do not know to what extent the $\partial^{13}C$ -values of the butanes have been changed due to bacterial degradation.

The bacterial degradation has also ruined the possibility to indicate the maturity of the source. It is, however, likely that the last gas which were derived from the source(s) was relatively dry and was probabely derived from a source where the heavier hydrocarbon gas fractions and possibly oil was already expelled.

The ∂D_{CH_4} and the $\partial^{13}C_{CH_4}$ from the 1374.2 m level (the methane which is least effected by bacterial degradation) also indicate when plotted in a ∂D_{CH_4} vs. $\partial^{13}C_{CH_4}$ plot (Fig. 1 c, in Schoell 1983) that the super imposed methane gas was formed at rather high maturity at the end of the oil window in the condensate field.

CONCLUSION

The following interpretation would fit the present data on the reservoired gases :

Biodegradation of hydrocarbons in the reservoir was followed by a period of renewed supply of predominantly dry gas.

Remark

We have made this interpretation assuming that bacterial oxydation has not occurred in any of the sample containers (vacutainers and aluminum bags). If this is the case, the ∂^{13} C-values on methane would become higher (heavier) than the real values.

We do not, however, consider this to be a serious problem in the present situation. At any rate, a relatively small bacterial degradation problem in the sample containers does not

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change our conclusion; new methane and ethane migrated into a reservoir where the existing hydrocarbons at an earlier stage had suffered bacterial degradation.

We cannot at the moment comment on the rather strange $\partial^{13}C$ -values on CO₂. These values as well as all the data from the present well must be seen in relation to the data from the other wells when the whole project is finished and a final report can be prepared.

REFERENCE

SCHOELL, M., 1983 : Genetic characterization of natural gases AAPG Dec.

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