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SERVIZIO STUDI GEOLGICI
E LABORATORI

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WELL 33/6-1

OFFSHORE NORWAY

HEAD SPACE ANALYSES AND CARBON
STABLE ISOTOPES IN METHANE

BA 79-119-1

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ONLINE

For the well 33/6-1 45 out of 66 samples were found valid for the isotopic analysis of the methane. The results of both gas chromatograph and isotopic analyses are reported in Table 1. The first column indicates the depth (meters), the second column shows the content of methane in the gas mixture, columns 3 to 6 show the results of GC analyses, column 7 shows the isotopic composition of the methane according to the international isotopic standard PDB.*

The plotting of the above results shows for head space analysis the variation in composition of the desorbed gas with respect to the depth. In the upper section the gas mixture is mainly composed by pure methane. At 1770-1820 m higher hydrocarbons are detected. With increasing depth the presence of higher hydrocarbons becomes stronger and stronger, at 2050 m in the desorbed gas are heavily present higher hydrocarbons. The gas composition remains more or less the same down to the bottom of the well.

The $^{13}\text{C}/^{12}\text{C}$ isotopic ratio in methane ranges from values of -72.67 to -43.77 per mil vs. PDB. The isotopic variation has a regular tendency and deeper samples have less negative values (are less depleted in ^{13}C).

It is possible to differentiate three main blocks: in the first one, starting from 470 m, the isotopic ratio changes very fast up to 1070 m; in the second part the previous trend is less evident (1120-1770 m); finally, in the third part $^{13}\text{C}/^{12}\text{C}$ ratio changes a little and, starting from 1970-2000 m this ratio remains constant on an average value of -45 per mil vs. PDB.

In this last part there is lack of samples valid for isotopic analysis (2800-3550 m) however vitrinite reflectance values show that the rock has reached the same degree of maturity so it is supposed the $^{13}\text{C}/^{12}\text{C}$ isotopic ratio in methane remains constant and in the range of -45 per mil.

The enclosed drawing shows the evidence of a close relationship between isotopic ratios in methane and degree of maturity. Immature rocks produce

* Isotopic ratio is reported as:
$$\left[\frac{^{13}\text{C}/^{12}\text{C} \text{ sample}}{^{13}\text{C}/^{12}\text{C} \text{ standard}} - 1 \right] \times 10^3 \text{ parts per 1000 (‰)}$$

and the standard is PDB.

PDB, a Lower Cretaceous belemnite from Pee Dee formation of South Carolina, USA, serves as an arbitrary standard in reporting most literature values.

mainly pure methane whose isotopic value is very negative (-70 to -60 per mil). On the other hand mature rocks produce gas in which higher hydrocarbons are present while the isotopic value of the methane is less depleted in ^{13}C (-50 to -40 per mil).

Sampling

At the drilling site the cuttings are roughly washed and placed in a 1 liter glass jar up to 2/3 of the volume. Some ^{or distilled water?} salted water is added to prevent any bacterial activity which is the greatest source of erroneous results. The concentration of the salt water is 100 gr/l, it is highly recommended to use water absolutely free from dissolved hydrocarbons. The glass jar is carefully closed and turned upside down to provide a good gas tightness: in case of small leakages the finest particles of the cutting will easily seal the jar. One important feature of the glass jar is its sampling valve which is made by teflon and brass. The inside part is made by teflon so no corrosion problem by salt water occurs.

GC Analysis

At the laboratory the first analysis carried out is a gas chromatographic analysis. From the glass jar, by syringe, 5 ml of the gas mixture are sampled after the injection of an equal volume of salted water: this operation is required to keep the inside pressure constant, any forced desorption caused by pressure lowering produce wrong results.

The gas chromatograph is equipped with a flame ionization detector (FID) with Porapak-Q column 2.5 m long, temperature programmed. The output signal is sent to an integrator which is part of the Data System HP 3354 which performs the calculations. The composition of the gas mixture contained in the jar is measured and the content of methane is calculated. Very small quantities of methane are now required for an analysis, a concentration as small as 0.5% is useful to run the analysis, so the content of methane is important to decide either to measure the isotopic ratio or not.

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Isotopic Analysis

The isotopic analysis of the methane is carried out in two steps: preparation and mass spectrometer analysis. The preparation is needed because methane cannot be introduced into the mass spectrometer, it is therefore necessary to convert it into carbon dioxide. For this first step a special high-vacuum preparation line is used. Of course not all the samples are suitable for an isotopic analysis. For very small samples it is necessary to use a special technique, being 0.05 ml the smallest quantity of gas on which is possible to perform an isotopic analysis. The final accuracy of this method is reasonably good and results within ± 1 per mil are produced.

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TABLE 1

Depth m	Methane %	C1 %	C2 %	C3 %	C4+ %	Delta 13C vs. PDB
470	.70	100.00	.00	.00	.00	-72.67
520	1.30	100.00	.00	.00	.00	-72.09
570	1.30	100.00	.00	.00	.00	-71.80
620	1.20	100.00	.00	.00	.00	-72.11
670	1.30	100.00	.00	.00	.00	-71.14
720	.20	100.00	.00	.00	.00	----
770	.40	100.00	.00	.00	.00	-68.82
820	.80	100.00	.00	.00	.00	-70.15
870	.70	100.00	.00	.00	.00	----
920	.40	100.00	.00	.00	.00	-68.22
970	.30	100.00	.00	.00	.00	-69.25
1020	.80	100.00	.00	.00	.00	-68.52
1070	.40	100.00	.00	.00	.00	----
1120	.40	100.00	.00	.00	.00	-64.84
1170	1.10	100.00	.00	.00	.00	-60.78
1220	3.10	100.00	.00	.00	.00	-57.69
1270	1.00	100.00	.00	.00	.00	-61.06
1320	.80	100.00	.00	.00	.00	-56.33
1370	1.80	100.00	.00	.00	.00	-66.68
1420	1.90	100.00	.00	.00	.00	-61.36
1470	1.70	100.00	.00	.00	.00	----
1520	.70	100.00	.00	.00	.00	-55.29
1570	.70	98.00	1.70	.00	.00	-53.78
1620	2.20	98.10	1.60	.20	.00	-54.52


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TABLE 1 (cont.)

Depth m	Methane %	C1 %	C2 %	C3 %	C4+ %	Delta 13C vs. PDB
1670	1.00	98.10	1.90	.00	.00	-54.22
1720	.60	100.00	.00	.00	.00	-54.30
1770	1.10	74.00	9.60	1.70	.80	----
1820	.30	83.80	8.60	7.60	.00	-52.75
1870	.60	67.20	7.90	13.20	11.50	-50.68
1920	.20	41.40	6.80	14.50	19.90	-48.27
1970	.40	61.80	6.40	9.60	12.30	-49.58
2050	3.20	14.80	7.60	24.40	32.30	-46.47
2100	1.80	14.10	6.40	21.20	29.00	-46.70
2150	.90	16.40	8.20	24.00	27.70	-45.99
2200	.60	20.50	6.30	16.00	24.70	-45.62
2250	1.50	25.10	9.90	21.50	22.90	-45.42
2300	1.80	27.60	12.80	19.90	22.00	-44.30
2350	1.10	24.30	9.20	21.50	25.30	-45.10
2400	1.40	10.40	5.70	19.40	30.00	-43.77
2450	.60	12.30	7.00	20.50	27.80	-44.17
2500	.40	9.40	6.00	19.50	28.30	-43.78
2550	.50	20.80	10.50	21.10	22.20	-44.10
2600	.50	20.10	14.70	28.30	22.30	-44.55
2650	.06	20.10	8.30	21.30	24.40	----
2700	.13	25.60	10.90	26.40	23.40	-44.88
2750	.24	47.10	6.90	14.60	12.90	-45.78
2800	.05	43.30	7.60	11.40	23.20	----
2850	.05	39.50	6.30	12.80	26.70	----

TABLE 1 (cont.)

Depth m	Methane %	C1 %	C2 %	C3 %	C4+ %	Delta 13C vs. PDB
2900	.04	22.60	5.90	12.70	12.50	----
2950	.22	39.60	5.40	10.90	11.30	----
3000	.18	30.00	6.70	17.00	28.70	----
3050	.08	54.10	9.90	16.10	12.10	----
3100	.07	51.60	9.70	16.90	14.70	----
3150	.03	21.00	6.90	25.70	15.80	----
3200	.05	23.70	13.50	24.60	21.90	----
3250	.03	49.40	13.90	20.70	15.90	----
3300	.12	32.00	14.70	20.90	18.90	----
3350	.15	49.40	25.60	13.50	7.20	----
3400	.25	53.10	23.20	12.20	5.80	----
3450	.15	31.50	31.90	25.40	8.10	----
3500	.24	23.70	26.70	32.30	13.60	----
3550	.37	7.60	10.20	27.90	26.60	-45.12
3600	3.47	27.90	23.50	27.70	12.60	-46.20
3649	1.72	29.10	22.70	28.10	12.70	-45.60
3700	1.20	20.00	18.80	29.20	18.20	----
3750	.64	5.10	8.00	30.00	29.00	-44.98

		Geochemical Log:	
		<h1>WELL 33/6-1</h1> <p>(OFFSHORE NORWAY)</p>	
Drawing N°: 1890	Up-to-date:	Enclosure to: HEAD SPACE ANALYSES AND CARBON STABLE ISOTOPES RATIO IN METHANE	End. N°: 1
Scale: 1:10000	Date: OCTOBER 79	Compiled by: T. RICCHIUTO	Drawn by:

