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Isotopic ratios of carbon and hydrogen isotopes in gases from block 15/9

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Title

Isotopic ratios of carbon and hydrogen isotopes in gases from block 15/9

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The chemical composition of subsea gas samples collected in the vicinity of the well head (well 15/9-13) have previously been determined. The sampling procedure was described and analytical results were discussed (Lab 83.31).

The ratios of $^{13}C/^{12}C$- and D/H-isotopes in methane are used for genetic characterization and determination of maturity of natural gases. Such data was found to be of interest to gain additional information about the origin of the sampled gas from well area of 15/9-13. As control, samples from 15/9-13 DST 1 and DST 2 and 15/9-11 DST 1 were analysed.

Samples

The sample from the 15/9-13 wellhead position has been stored in an Al-bag for five months. The DST-samples from 15/9-11 and 15/9-13 were transferred to Al-bags from pressurised bottles just before shipping of the samples. The analysis was done by Isot, Geoch. Inst., M.Schmitt, D-3160 Lehrte.

GC-analysis

The composition of the samples was determined by standard gaschromatographic methods. As in the previous report the wellhead sample is shown to be methane with traces of C^{2+} hydrocarbons. The C^{2+} concentration of the reservoir gases is approximately 20 Vol %.

Isotopic ratios of carbon - and hydrogen isotopes in methane

Methane was separated by gaschromatography from the heavier components and transferred to an oxidation line together with the carrier gas, He. The methane was oxidised to CO_2 and water, which were trapped at liquid nitrogen temperature. CO_2 was separated from water at dry ice/methanol temperature and the resulting water reduced to hydrogen. The hydrogen was trapped in activated charcoal at liquid nitrogen temperature. The carbon (CO_2-sample) and hydrogen (H_2-sample) isotopic composition were determined by mass spectrometry. The isotopic ratios $R=^{13}C/^{12}C$ (or D/H) are normalised to standards by:

$$\delta\ (^{13}C \text{ or } D) = ((R \text{ sample} - R \text{ standard})/R \text{ standard})\ 1000^{o}/00$$

The standards are PDB for $\delta\,^{13}C$ and SMOW for δ D.
Results are given in Table 2.

Discussion

The $\delta^{13}C$-values for reservoir gases group well at values of -40, in agreement with data from other wells in block 15/9. The $\delta\ ^{13}C$-value for the wellhead sample is -53.0. The uncertainty in the experimental values is less than one unit.

The main observation is that the wellhead sample is depleted in ^{13}C as compared to the reservoir gas. Generally, the limiting value for biogenic gases is assumed to be -55 to -60, but no exact limit can be defined.
For the δ D-values there is a large overlap region for gases of biogenic and thermogenic origin. The analysis gives as result higher δ D-values for the reservoir gases than for the wellhead sample. The δ D-value for the wellhead sample is close to the average of -200 found for biogenic gases.

Correlation plots of $\delta^{13}C$- δD and $\delta^{13}C$-(C_{2+}) show that the samples fall into two groups. The reservoir samples can be classified as "associated gases"- thermogenic gases with high C_{2+}-content. The wellhead sample fall into the "mixing" region - a mixture of biogenic and a biogenic gases.

Migration of reservoir gases with the measured properties through formations containing shallow biogenic gases would, however, lead to mixtures with higher C_{2+} content and higher $\delta^{13}C$-values than measured for the wellhead sample.

The classification of the wellhead sample as "mixed" can most likely be explained by processes in young sediments producing a mixture of biogenic and nonbiogenic gases. This explains the relative high $\delta^{13}C$-value to what generally is observed for biogenic gases and also the trace amounts of C_{2+}.

The non-reservoir origin of the wellhead gas is from the present data most likely.

Literature:

1) Statoil Report LAB 83.31.
2) M.Schoell Geoch. and Cosmoch. Acta (1981).
3) M.Schoell J.geol.Soc. (1983).
4) W.J.Stahl Geoch. and Cosmoch. Acta (1978).
5) References in above reports.

Table 1

Composition of gas samples from block 15/9

Component	Concentration (Vol%)			
	15/9-11 DST 1 107	15/9-13 DST 1 3	15/9-13 DST 2 2	15/9-13 Wellhead 1
Methane	78.30	83.07	81.57	99.77
Ethane	10.89	9.89	10.56	0.12
Propane	7.38	5.38	6.13	0.10
i-Butane	0.93	0.62	0.76	0.01
n-Butane	1.10	0.77	0.79	0.01
i-Pentane	0.20	0.16	0.12	0.00
n-Pentane	0.14	0.11	0.08	0.00
Hexane	0.07	0.00	0.00	0.00

Table 2

Isotopic composition of carbonisotopes in PDB-units and hydrogenisotpoes in SMOW-units for gas samples from 15/9.

Sample	13C	D
15/9-11 DST 1	-43.0	-227
15/9-13 DST 1	-39.7	-248
15/9-13 DST 2	-42.6	-230
15/9-13 Wellhead	-53.0	-219