# THE ORIGIN OF GAS ACCUMULATIONS IN WESTERN SIBERIA

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### **ABSTRACT**

Gas fields in the north of Western Siberia are the largest in the world. The origin of these pools is an important problem for understanding gas formation in sedimentary basins. Isotopic and other organic geochemistry analyses have been used to evaluate gascondensate source rocks. A model is proposed in which humic organic matter produces methane during the condensation of aromatic rings. Sapropelic organic matter generates methane during the cracking of aliphatic structures. Our data show that gas forms by thermal transformation of kerogen mainly in gas production reservoirs: Cenomanian, Neocomian and Jurassic. Consequently, gas migration was limited in stratigraphic complexes.

## 1. INTRODUCTION

Gas accumulation in North Western Siberia is a unique natural phenomenon, as unique as petroleum accumulation in the Persian Gulf. A significant part of world gas reserves is concentrated in several supergiant gas fields such as Urengoy, Bovanenkovskoye, Yamburg, Zapolyarnoye, Medvezh'e and others. Elucidation of the nature of this gas would provide a key for comprehending the factors controlling formation and accumulation of gas in the sedimentary shell of the Earth in general.

This work intends to touch on some of the problems of gas geochemistry in the north of Western Siberia dealing with isotopes and an organic geochemistry study of the Urengoy field, the largest gas field in the world.

# 2. GEOLOGIC SETTING

The Western Siberian sedimentary basin occupies territory more than 3 million km<sup>2</sup>.

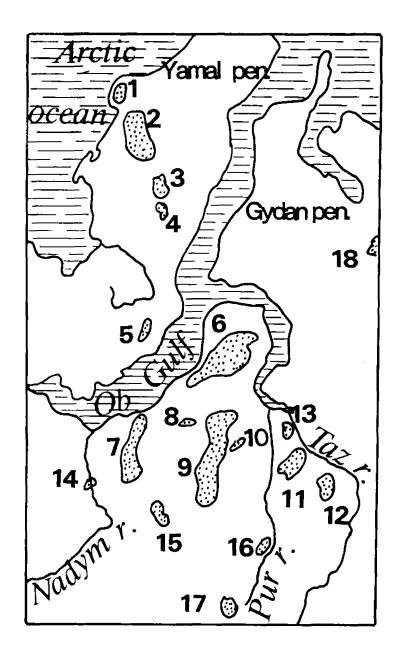


Fig. 1: Map showing location of gas fields in the north of Western Siberia. 1 = Kharasavey; 2 = Bovanenko; 3 = Neyto; 4 = Arktic; 5 = Novyy Port; 6 = Yamburg; 7 = Medvezh'ye; 8 = Pestspv; 9 = Urengoy; 10 = Samburg; 11 = Zapolyarnoye; 12 = Russkoye; 13 = Taz; 14 = Nadym; 15 = Yamsovey; 16 = East Tarkosaly; 17 = Vengayakha; 18 = Messoyakha.

bounded by the Ural Mountains on the west, the Siberian platform on the east, the Kazakhstan highlands to the south and the Arctic Ocean to the north (Fig. 1). The Precambrian crystalline foundation dips north from a depth of 4 - 6 km in the central part of the basin (so-called Middle Priob'e region) to a depth of 12 - 14 km in the Nadym and Pur-Taz regions. The maximum depth (~ 16 km) is achieved in the area between the Pur and Taz rivers (Vaipolin, 1984). The sedimentary succession consists of two major structural units. The lower, Paleozoic-Triassic, is composed of sedimentary and volcanic rocks metamorphosed in different grades and folded, while the upper, Mesozoic-Cenozoic, is a normal sedimentary succession, composed predominantly of terrigenous rocks and containing excellent reservoirs and seals. For details of the structural geology and stratigraphy, see Kontorovich et al. (1975).

In contrast to the central part of Western Siberia which is a rich petroliferous region with giant oil-fields like Samotlor, Fedorovskoye, Vartovskoye, etc., the north of Western Siberia is predominantly a gas-bearing area. The principal productive zones are in the Cretaceous section. The Turonian shales (Kuznetsov Suite) along with Paleogenic clays and limestones form a regional seal about 500 - 1500 m thick. Sediments of the Cretaceous section were deposited mainly under conditions of coastal-marine, lagoon, marsh and lake environments.

The largest gas deposits are in sediments of the Pokur Suite ( $K_{1\ ap2+al}+K_{2}c$ ) in Cenomanian sand reservoirs at a depth of 1.1 - 1.5 km. This is almost pure methane gas. Content of the heavier hydrocarbons  $C_{2}$ - $C_{4}$  does not exceed 0.15%. Aptian gas contains some condensate (0.65 - 80 g/m³). The second largest gas productive zone is in Neocomian at a depth of 2.1 - 3.6 km. In contrast to Cenomanian gas, Neocomian gas is wet. The content of  $C_{2}$ - $C_{4}$  hydrocarbons amounts to  $\sim$  6 - 10%. The content of condensate in gas deposits of the Vartov and Megion Suites reaches 100 - 350 g/m³ and in the Achimov Suite 600 g/m³. Many gas-condensate deposits have oil rims.

#### 3. THE PROBLEM OF THE ORIGIN OF GAS IN WESTERN SIBERIA

The origin of gas in the north of Western Siberia, in particular, of the supergiant Urengoy gas-field, is the subject of many discussions. Controversial views have been put forward. One of the most widespread ideas is that the gas migrated into the Cenomanian and Neocomian reservoirs from a great depth (Nalivkin et al., 1969; Yevseyev et al., 1973; Neruchev et al., 1984). This suggestion is based on the theoretical concept which considers the principal phase of gas formation as a stage which ends the process of generation of hydrocarbons, i.e., following the principal stage of oil formation (oil-window), corresponding to the relatively late stage of transformation of organic matter. The source of gas in the north of Western Siberia is believed to be the Lower-Middle Jurassic sediments which entered, in accordance with Neruchev et al. (1984), the principal phase of gas formation at a depth of 4.5 km. Isotopic data are sometimes

interpreted as favouring this point of view. Prasolov et al. (1981) studied isotopic composition of Ar, He and  $^{13}\text{C}/^{12}\text{C}$  of methane in the Western Siberian gases. They came to the conclusion that Cenomanian and Neocomian gases had different sources. However, these authors believe that in both cases the gas migrated from a great depth: Cenomanian from 4 - 5 km and Neocomian from 6 - 9 km. The conclusion on the deepseated source of the gas has been inferred from specific interpretation of isotopic data. Prasolov, in both the paper mentioned above and others, argues that carbon isotopic composition of methane depends on thermodynamic isotope effect and that the observed variations of the  $\delta^{13}$ C-values of methane reflect a change of temperature conditions of formation of gas. The temperatures calculated from this suggestion indicate the great depth of generation of gas, including that for methane from Cenomanian deposits.

Several authors insisted on the microbiological origin of gas in the Cenomanian deposits. This view was based on the isotopic data obtained in Alekseyev's laboratory and appeared in two papers: Yermakov et al. (1970) and Alekseyev (1974). In those papers very low  $\delta^{13}C$ -values for Cenomanian methane were reported, as example for Urengoy,  $\delta^{13}C = -59^{\circ}/_{\circ\circ}$ . Proceeding from such data Alekseyev suggested that Late Cretaceous gases are buried marsh gases.

Repeatedly, and in different contexts, considerations have been suggested about the autochthonous or mixed origin of gas in the principal productive zones (Yermakov et al., 1970; Nesterov et al., 1977). Gavrilov et al. (1972) found that there was a correlation between the carbon isotope composition of methane and the content of atmospheric argon (Ar<sub>air</sub>) for different gas deposits within the section of the Pokur Suite. They interpreted this dependence as a result of mixture in different proportion of the autochthonous gas (with low  $\delta^{13}$ C-value of about  $-60^{\circ}/_{\circ\circ}$  and high concentration of Ar<sub>air</sub>  $\simeq 110$  ppm) and gas which came from Neocomian (with  $\delta^{13}$ C-value of about  $-36 \div -38^{\circ}/_{\circ\circ}$  and Ar<sub>air</sub>  $\simeq 3 \div 5$  ppm).

It is curious that different authors have used isotopic data in support of quite different, sometimes opposite, points of view on the nature of Western Siberia gas. In this connection it seemed reasonable to undertake a combined organic geochemistry study including an isotopic study of gaseous hydrocarbons, condensates and organic matter.

### 4. SAMPLING AND METHODS

Sampling of gas probes was carried out from the mouth of bore holes. Reducing gear was used to decrease the gas pressure to 3 - 4 atm. Gas was taken in inverted 250-ml vessels initially filled with salt water.

Methane, ethane, propane and buthane were separated by gas chromatograph LXM-8MD5 which was used in preparative version with 5 m stainless steel column of 4 mm inner diameter filled by alumogel. Argon served as a carrier gas.

Hydrocarbons were directed through a copper oxide under 800°C. CO2 resulting

from oxidation was frozen at liquid nitrogen temperature, purified and used for measurement of the isotopic composition of carbon. Isotope analyses were carried out with the help of mass-spectrometer VARIAN-MAT-230. Results are reported relative to PDB standard in  $\delta^{13}$ C notation with standard deviation of about  $\pm$  0.1°/ $_{\circ\circ}$ . In several samples, the isotopic composition of hydrogen of methane was measured. Conventional technique including reducing of H<sub>2</sub>O to H<sub>2</sub> by passing over uranium (700°C) was used. Accuracy of  $\delta$ D-analysis is about  $\pm$  2°/ $_{\circ\circ}$ . Standard is SMOW.

#### 5. RESULTS

Carbon isotopic composition of methane collected in different sites from the main productive horizon (PK<sub>1-3</sub>) of the Cenomanian deposit of the Urengoy gas field is confined to a narrow range of  $\delta^{13}$ C variations from -49.94 to -48.94°/ $_{\circ \circ}$  (Table I). The ethane in two samples is characterized by  $\delta^{13}$ C -28.32 and -29.02°/ $_{\circ \circ}$ . The isotopic composition of the Neocomian gas differs significantly. Methane in studied samples has  $\delta^{13}$ C from -37.76 to -35.41°/ $_{\circ \circ}$ . The ordinary trend to depletion of methane in the light isotope with increase of depth has not been observed. Instead, methane in the Megion and Achimov Suites is isotopically lighter than methane occurring in the overlying deposits of the Vartov Suite. The ethane is isotopically very uniform (-27.4 ± 0.4°/ $_{\circ \circ}$ ) throughout the whole Neocomian section. At the top of the Tyumen Suite, within Malyshev horizon (J<sub>2</sub>bt) the isotope characteristic of gaseous hydrocarbons is similar to that for the Neocomian gas. At deeper horizons of the Tyumen Suite, gas scarcely occurs and its isotopic composition changes.

The deepest gas probes were collected from bore hole R-700 drilled in the Samburg area which is immediately adjacent to the Urengoy gas field. At a depth of more than 5 km, methane becomes isotopically heavier. The same is observed for  $C_2$ - $C_4$  hydrocarbons. It is noteworthy that at intervals  $3.7 \div 3.9$  km methane occurs which is isotopically lighter than the methane in either the overlying or the underlying deposits (Table I).

Analysis of condensates shows that, presented in trace amounts in the Cenomanian gas, they are very close in carbon isotopic composition to the condensates occurring in the Vartov Suite of Neocomian section (Table II). This group of condensates is characterized by  $\delta^{13}C \simeq 27.5 \pm 1.0^{\circ}/_{\circ \circ}$ . The next group of condensates occurred at a depth of more than 3.2 - 3.5 km, which includes condensates from the Megion and Achimov Suites of Neocomian, while from Jurassic, the average is  $\delta^{13}C - 25.7 \pm 0.7^{\circ}/_{\circ \circ}$ .

Organic matter was studied in core-samples. Carbon isotopic composition of kerogen was measured and proved to be uniform throughout the section studied ( $\delta^{13}C \simeq -25 \pm 1.5^{\circ}/_{\circ\circ}$ , Table III). Pyrolysis study was carried out by Rock Eval III chromatography.

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174

								Сопр	Composition of Gas (%)	ins (%)		lsotope	Isotope ratios ("/a,)	3	
												813c			8.
Well No	Depth (m)	γ8α	Formation	R.º (%)	Stage of	5	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> 11 <sub>8</sub>	i.C.4H <sub>10</sub>	nC4H10	<b>.</b>	C2H6	C3H8	C4H10	t
-	2	~	4	~	۰	_	200	6	2	=	;;   	=	4	~	-
							Urengoy								
264	1109 - 1137	K 2c									48.07				7
797	1137 - 1167	K2c									.49.75	29.82			
161	1200 - 1233	<b>K</b> 26									49,94	.29.02			
272	1103 - 1150	K,									-49.24				
274	1138 - 1171	$K_2^c$									.48.83				
275	1150 - 1180	$K_{2^c}$									.48.80				
<b>3</b> 5	25.73 - 82.72	ж п	91g	95'0	MK	89.6	8,2	-	0.5	0.5	-36.42	27.38	-27.09	-26.11	
311	2728 - 2733	×	BU	0.62	MK	95.3	3.2	0.3	0.1	-0	.35.59	-27.03	.26.42		7
574	2743 - 2750	¥	BC,	0.62	¥.	63 4	130	6.01	3,8	<b>4</b> S	35.41	-27.67	.27.45	26.87	
295	2916 - 2920	<b>~</b> _	BU <sub>12</sub>	0.70	MK,	7.68	6.3	2.8	0.5	0.5	.36 32	27.12	.26.32	-25.32	
\$05	3060 - 3064	×	8∪14	0.72	¥,	86.7	6.2	3.7	Ξ	<del>4</del> .	-37.07	27.08	. 26.19		7
254	3550 3566	×	۸4	62.0	MK <sub>2</sub>	9	4.0	ᅼ	0.2	0.3	37 76	.27.82	.25.04	-23.02	
510	3576 - 3584	×_	<b>A</b>	97.0	MK <sub>2</sub>	91.	5.7	2.0	4.0	0.5	16.91	27.88	-25.92		÷
	3720 - 3740			0.84	MK <sub>3</sub>	1.68	9.9	23	9.0	0.7	-36.11	27 11	.26.85	-25 50	
	3836 3852			1.05	MK <sub>3</sub>						27.42	69.12.	.22.00		
282	4504 4520	-		8.1		85.9	6.6	2.9	7.0	0.4	37.86	-25.70	-22.54	.21 73	7
282	4753 - 5034	<u>-</u> -		17.1	MK <sub>4</sub>	8.6.8	9.6	4.	9.0	9.4	-37 02	24.43	-21.34		÷
							Samburg								
R-171	2976 - 2993	ж 		6.0	MK <sub>2</sub>						-33.83	25.66	.24 IS	.23.81	
R-173	3101 - 3105	, K		6:0	MK <sub>2</sub>						-35.77	25.60	.24.03	-23.45	
R-700	3910 - 3942	۹ <sup>1</sup> *		1.06	MK <sub>3</sub>						.43.65	-31.85	.29.10	-27.51	
R-700	4012 - 4044	٦-		1.15	MK <sub>3</sub>						43.55	-31.15	.27.03	-24.45	
R-700	4244 - 4265	λ2		1.32	₩ ¥						41.13	28.00	-24.16	.2424	
R-700	4320 - 4355	32		1.37	MK 4						39.85	27.75	-24.20	.23.55	
R-700	4450 - 4460	r r		85.1	₩K 4	96.37	5.45	2.1	0.7	0.73	.35.13	.2358	-21.71	-22.14	
R-700	4592 - 4602	<u>-</u> -		17.1	MK <sub>4</sub>	95.93	3.1	9.0	0.17	0.14	.33.65	.22.87	-22.08		
R-700	5480 - 5490	۲.		2.53	ΑK	96.33	2.98	0.47	60.0	0.07	-33.12	-20.54			

Vitrinite reflectance coefficients  $R_{m}^{O}$  were measured by study of coal inclusions in argillaceous sediments by use of a POLARM-311 microscope in accordance with the technique described by Lopatin and Emetz (1984). In the studied interval of depths (2.7 - 5.5 km)  $R_{max}^{O}$  changes from 0.59 to 2.56% and approximated the regression equation  $R_{max}^{O} = 2.09 \cdot 10^{-8} h^{2.14}$  (where h-depth) according to Puisson law (the correlation coefficient 0.97).

N	Well No.	Depth (m)	Formation name	Geologic age	δ13 <sub>C</sub> (°/ <sub>°°</sub> )
1		1150 - 1200	PK <sub>1-3</sub>	K <sub>2</sub> c	-26.64
2	80	1784 - 1800	PK <sub>21</sub>	$K_1$ al	-27.37
3	665	2746 - 2751	BU <sub>g</sub>	$\mathbf{K}_{1}^{1}\mathbf{h}$	-27.80
4	615	2923 - 2928	BU <sub>12</sub>	Κįν	-28.61
5	504	2970 - 2974	$BU_{12}^{12}$	Κ <sub>1</sub> ν	-25.92
6	504	3046 - 3050	BU14	Κįν	-28.29
7	504	3224 - 3228	вU <sub>16</sub>	Κ <sub>1</sub> ν	-25.96
8	655	3558 - 3583	BU <sub>19-21</sub>	K, b	-25.56
9	282	4504 - 4520	17-21	J <sub>1</sub>	-25.11
10	282	4753 - 5034		J,	-24.95
11*	700	5480 - 5490		J <sub>1</sub> P	-25.98

TABLE II.
CARBON ISOTOPE VALUES FOR CONDENSATES
FROM URENGOY GAS FIELD

### 6. DISCUSSION

First, it should be noted that the extremely negative values ( $\delta^{13}C \simeq \sqrt{-60^{\circ}/_{\circ o}}$ ) reported by Yermakov et al. (1970) and Alekseyev (1974) for Cenomanian methane of the Urengoy field have not been confirmed. Therefore the idea of microbiological origin of Cenomanian gas based on this data (Meyerhoff, 1980; Grace and Hart, 1986) should be abandoned although some contribution to methane being related to the microbiological process should not be ruled out.

The equations are known which link isotopic composition of methane ( $\delta^{13}C_1$ ) with vitrinite reflectance coefficient ( $R^0$ , %), characterizing degree of maturation of initial organic matter. These equations are different for organic matter of different types:  $\delta^{13}C_1 = 14.8 \log R^0 - 41^\circ/_{oo}$  for sapropelic organic matter;  $\delta^{13}C_1 = 8.6 \log R^0 - 28^\circ/_{oo}$  (Stahl, 1977) and  $\delta^{13}C_1 = 8.64 \log R^0 - 32.8^\circ/_{oo}$  (Sheng Ping et al., 1988) for humic organic matter. Hydrogen isotopic composition is approximated by equation  $\delta D_1 = 35.5 \log R^0 - 152^\circ/_{oo}$ , which does not depend on the type of organic matter (Schoell, 1980). In Figure 2, a change of isotope composition for methane with depth for the Urengoy field is shown.

The curves corresponding to the regression equations mentioned are also presented. They have been fitted to the section studied, taking into account R<sup>O</sup> data obtained for the Urengoy field (Fig. 3). The curve suggested by Stahl (1977) for methane, which

<sup>\*</sup> from the Samburg area.

Table III. Results of mass spectrometric analysis ( $\delta^{13}\text{C},\,^{\circ}\!/_{\!\circ\!\circ}$ ) of the Kerogen from shale samples of urengoy gas field

Sample	Well No.	Depth (m)	Age	R <sub>m</sub> , %	δ <sup>13</sup> c,°/ <sub>00</sub>
1	566	3040.7	к <sub>1</sub>	0.67	-24.07
2	200	3239.0	$\mathbf{K}_{1}$	0.69	-25.10
3	254	3509.4	к <sub>1</sub>	0.79	-25.94
4	266	3578.0	K <sub>1</sub>	0.80	-26.84
5	266	3649.0	$J_3^3$	0.82	-27.65
6	266	3650.2	$J_3^3$	0.82	-26.22
7	266	3713.0	$J_3^3 J_3^2$	0.90	-23.62
8	254	3713.6	$J_3^2$	0.90	-23.81
9	254	3789.0	$\mathbf{J}_2$	0.90	-24.46
10	266	3913.5	$J_2$	1.05	-25.65
11	254	3997.4	<b>J</b> <sub>2</sub>	1.06	-24.77
12	254	3998.2	J <sub>2</sub>	1.06	-25.10
13	266	4022.5	$\mathbf{J}_2$	0.98	-26.64
14	266	4314.0	J <sub>2</sub>	1.03	-25.76
15	266	4193.0	J <sub>2</sub>	1.27	-24.23
16	266	4335.6	J <sub>1</sub>	1.30	-24.57
17	266	4495.8	J	1.67	-24.82
18	266	4496.5	J	1.67	-25.54
19	266	4606.4	J <sub>1</sub>	1.70	-25.37
20	266	4707.1	J <sub>1</sub>	1.71	-25.08
21	266	4927.4	J <sub>1</sub>	1.81	-27.46
22	266	5010.5	J <sub>1</sub>	1.86	-26.82
23	266	5013.0	J <sub>1</sub>	1.86	-27.47

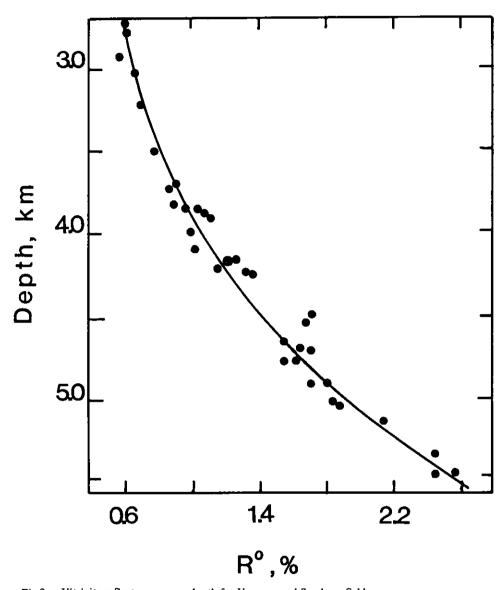


Fig 2: Vitrinite reflectance versus depth for Urengoy and Samburg fields.

originated from marine organic matter, approaches experimental data in Cenomanian (the Pokur Suite) and the Middle-Late Jurassic (the Tyumen Suite) intervals. However, these are just the intervals in which the sediments are presented predominantly by continental facies. Late Jurassic and the beginning of Cretaceous were the only times of marine environments in the north of Western Siberia.

# S<sub>o</sub> (mg HC/g rock)

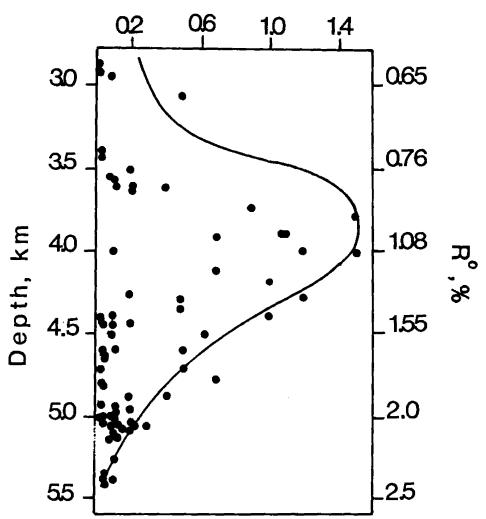


Fig. 3: Plot of the S<sub>o</sub> pyrolysis peak in milligrams per gram of rock versus depth for Jurassic Cretaceous gas source rocks in the Urengoy and Samburg gas fields.

Recently a model has been suggested (Galimov, 1988) which considers methane formation as a process characterized by a band of activation energies, with the distribution function of activation energies being different for different types of organic matter. In humic organic matter, those structures predominate which can be initial for methane carbon under relatively low activation energies, while sapropelic organic matter contains more structures whose involvement in methane formation requires relatively

high activation energies. This model formalizes the concept that methane formation from humic organic matter is linked to the process of condensation of aromatic rings, whereas in sapropelic organic matter, methane is produced mainly during the process of cracking of aliphatic structures. Several important consequences follow from this model.

The first is that humic organic matter is able to produce methane at a relatively early stage of its geochemical transformation. Significant part of methane generative potential might be realized at the stage corresponding to  $R^{O} = 0.4 \cdot 0.7\%$ , i.e., at the stage before and during oil window. This is in serious contradiction to the widely accepted dogma that principal gas formation commences after oil window (Neruchev et al., 1973; Hunt, 1979; and many others).

Secondly, the model explains the empirically established dependence of carbon isotopic composition of methane on a degree of catagenesis of the initial organic matter. Moreover, different dependence for different types of organic matter follows from the model. To date, the difference between  $\delta^{13}C_1-R^0$  curves for humic and sapropelic type of organic matter have not been satisfactorily explained. It follows too from the model that for the same type of organic matter the  $\delta^{13}C_1-R^0$  relationship may be different, depending on gas accumulation history. It has been shown that the equation  $\delta^{13}C_1=8.6\log R^0-28^\circ/_{\circ\circ}$  found by Stahl (1977) best describes an instantaneous isotopic composition of the released methane (i.e., the case where methane generated at previous stages has been lost), whereas the equation  $\delta^{13}C_1=8.6\log R^0-32.8^\circ/_{\circ\circ}$ , suggested by Sheng Ping et al. (1988), corresponds to the case where the whole previously generated methane is accumulated.

Calculations showed that the curves  $\delta^{13}C_1 - R^0$  for different types of organic matter converge at the initial point corresponding to the  $\delta^{13}C_1$ -value about  $-60^{\circ}/_{\circ\circ}$ . In other words, methane produced at the early stage of maturity of both humic and sapropelic organic matter should have similar isotopic composition.

Thirdly, it follows from the model that a gas-condensate system can form at a relatively early stage. Methane (as well as  $CO_2$ ), liberated in significant amounts at the early stage of transformation of humic organic matter, may carry off liquid hydrocarbons from source rocks in soluble gas form. Thus, gas-condensates may be separated before migration of hydrocarbons in a liquid phase becomes possible. This model is significant for understanding the origin of gas in the north of Western Siberia.

Sedimentary deposits of the Pokur Suite are enriched in humic organic matter. Coal seams are ubiquitous throughout the section. In our opinion this humic organic matter is a source of gas in Cenomanian deposits. The isotopic composition of methane ( $\delta^{13}C = -49 \div -48^{\circ}/_{\circ \circ}$ ) corresponds to the relatively early stage of transformation of organic matter. As mentioned above methane generated by humic or sapropelic organic matter at the early stage is isotopically undistinguished. Therefore  $\delta^{13}C$ -values for methane from the Cenomanian deposit, seem to fall on the line extrapolating the  $\delta^{13}C_1$ -R° relationship for sapropelic organic matter.

Apparently, the whole section of the Pokur Suite was involved in gas formation. In

depressions adjacent to the Urengoy megaswell the base of the Pokur Suite is lowered to a depth of 2400 - 2500 m where R<sup>O</sup>-values, characterizing maturity of organic matter increase to 0.53 - 0.57%. Owing to excellent hydrodynamic communication within the Pokur Suite, accumulation of gas from the whole section, together with long distance lateral migration, could occur. Thus, in fact, methane in Cenomanian deposits at a depth of 1000 - 1200 m appears to be a product of accumulation of gases generated by humic organic matter in a relatively wide range of its geochemical transformation (R<sup>O</sup> from 0.4 to 0.57%). A factor which, along with favourable reservoir and gas generative conditions, was responsible for accumulation of Cenomanian gas was the thick 630 m seal formed by Turonian shales.

Geochemical characteristics of Neocomian gas differ significantly from those of Cenomanian. Formerly the idea of a common source for the whole Cretaceous gas complex was generally supported (Yevseyev et al., 1973; Neruchev et al., 1984). Prasolov et al. (1981), having taken into account isotopic data, concluded that Cenomanian and Neocomian gases had different sources. However, this author suggested that both sources were at a great depth: Cenomanian gases migrated from a depth of 4 - 4.5 km, while Neocomian from a depth of 7 - 8 km. This conclusion was based on the erroneous concept, developed by Prasolov and Lobkov (1977), which related isotopic fractionation in hydrocarbon systems to thermodynamic isotopic effects, regardless of type or maturity of organic matter. This concept contradicts the fairly well established relationships.

In Figure 2, the points corresponding to isotopic composition of Neocomian methane, fall between the lines describing  $\delta^{13}C_1 - R^0$  relationships for marine and humic organic matter.  $\delta^{13}C$ -values decrease with increase of depth which is in agreement with expanding marine environments from the Vartov to the Megion and Achimov Suites.

The isotopic characteristic of methane in Neocomian deposits is approximated by the curve suggested by Sheng Ping et al. (1988) rather than by Stahl's curve. Chinese scientists established their version of  $\delta^{13}C_1$ –R° relationship by studying the Sychuan and Shanganin sedimentary basins in which, during Mesozoic and Cenozoic time, sediments of coastal-marine, lagoon, limnic, fluvial and swampy facies were accumulated. Similar environments were expanded in the north of Western Siberia during accumulation of sediments of the Pokur and Tyumen Suites.

The observed correlation between isotopic characteristics of gas and geochemical state (type and maturity) of organic matter in the corresponding stratigraphic units implies mainly singenetic origin of gas in the Neocomian section.

Also, the data obtained disagree with the idea of a significant contribution of gas from Neocomian to Cenomanian deposits. As mentioned above, the correlation between isotopic composition of methane and the content of atmospheric argon discovered by Gavrilov et al. (1972), served as a principal argument in favour of this suggestion. Cenomanian gas was considered a mixture of indigenous gas (with  $\delta^{13}C_{CH_4} = -60^{\circ}/_{\circ\circ}$  and  $Ar_{air} = 110$  ppm) and gas migrated from the Neocomian section (with  $\delta^{13}C_{CH_4} = -60^{\circ}/_{\circ\circ}$ 

 $-38^{\circ}/_{\circ \circ}$  and  $Ar_{air} = 3$  - 5 ppm). If this were so, Cenomanian gas in the Urengoy field  $(\delta^{13}C_{CH4} = -48^{\circ}/_{\circ \circ})$  and  $Ar_{air} = 55$  ppm) would be composed of one third of the gas migrated from Neocomian. However, this is not in agreement with hydrocarbon and isotopic composition of the gas. Indeed, if appreciable migration had taken place, the content of the  $C_{2+}$  would be higher than 0.15% allowing for the wet character of Neocomian gas  $(C_{2+} = 6 - 10\%)$ . In addition, the carbon isotope composition of ethane in the Cenomanian deposit of the Urengoy field  $(\delta^{13}C_{2} = -29.5 \pm 0.4^{\circ}/_{\circ \circ})$  is different from that in the Neocomian section  $(\delta^{13}C_{2} = -27.5 \pm 0.5^{\circ}/_{\circ \circ})$ .

Apparently the observed correlation  $\delta^{13}C_1$ —Ar<sub>air</sub> is due to the different (in each case) proportion of gas from different depths within the Pokur section. In fact, when the source of gas was restricted by the shallow part of the Pokur Suite, methane must have been isotopically light (close to  $-60^{\circ}/_{\circ o}$ ). On the contrary when the deep part of the Pokur Suite containing more mature organic matter is a single source for given gas deposit, relatively heavy methane should occur (about  $-40^{\circ}/_{\circ o}$ ). In general, the isotopic composition of the gas reflects the contribution of the gas from several sources. When the whole Pokur section works for accumulation of a gas deposit, the isotopic composition of methane appears to be close to the value of about  $-47 \div -49^{\circ}/_{\circ o}$ , which is characteristic of Cenomanian methane in all supergiant gas fields in the north of Western Siberia, including Urengoy.

In the lower part of Neocomian (the Megion Suite), income of wet gas and oil from the Achimov Suite and the Bazhenovian Suite (Upper Jurassic) is noticeable. These sediments enriched with organic matter of sapropelic type entered into the oil window.

The isotopic and chemical composition of gas in the Middle-Lower Jurassic section of the Urengoy field is different to that which is characteristic of gas in the Neocomian section. This testifies against vertical migration of gas from high depth as several investigators cited above believed. Nevertheless, some migration of gas from Jurassic into Cretaceous sediments should not be excluded. In this connection, attention has to be paid to the fact that the isotopic characteristic of gas from the Vartov Suite of the Neocomian  $(\delta^{13}C_1 = -35.8^{\circ}/_{\circ\circ}, \delta^{13}C_2 = -27.3^{\circ}/_{\circ\circ}, \delta^{13}C_3 = -26.9^{\circ}/_{\circ\circ}, \delta^{13}C_4 = -26.5^{\circ}/_{\circ\circ})$  is similar to that of gas from the Malyshev horizon at the top of the Tyumen Suite  $(\delta^{13}C_1 = -36.1^{\circ}/_{\circ\circ}, \delta^{13}C_2 = -27.1^{\circ}/_{\circ\circ}, \delta^{13}C_3 = -26.8^{\circ}/_{\circ\circ}, \delta^{13}C_4 = -25.5^{\circ}/_{\circ\circ})$ . It is possible that gas from the Tyumen Suite contributed to the formation of gas deposits in Neocomian reservoirs. The rise of the Urengoy structure began in Late Cretaceous. By this time the top of the Tyumen Suite was at a depth of about 2.2 km. Consequently, gas of very early generation, similar to gas accumulated in the Cenomanian gas deposits, was lost by the Tyumenian sediments. However, gas generated in these sediments when they were at a depth of 2.2 - 4.2 km, i.e., at the stage MK<sub>1</sub>-MK<sub>3</sub> of catagenesis, could be preserved. The Middle-Lower Jurassic section contains much less gas and the Neocomian section more gas than one could expect proceeding from gas generative capacity of the corresponding rocks (Neruchev et al., 1984). Therefore, it

seems possible that Neocomian gas partly migrated from Jurassic. However, this does not mean that this gas came from a great depth. By the time the suggested migration of Jurassic gas into Neocomian deposits occurred, the Tyumenian sediments were not much deeper than the present position of Neocomian sediments. Whereas at the top of the Tyumen Suite ( $J_2$ bt, the Malyshev horizon), gas has isotopic characteristic which is normal for that generated by humic organic matter at the stage  $MK_2$ , gas from the Toarcian (at a depth > 4.5 km) shows features which are characteristic of the destructive gas. At the late stages of catagenesis of organic matter and under elevated temperatures, previously generated hydrocarbons become a source for methane. Methane of such an origin has to be comparatively isotopically light, as we already pointed out in our previous work (Galimov, 1973, see p. 306 and Fig. 78).

Two situations are conceivable. The first, when methane forms in source rock. Then isotopically light methane derived from destruction of hydrocarbons is added to isotopically heavy methane derived from mature kerogen. The next situation is realized when methane forms at the expense of hydrocarbons accumulated in a reservoir, i.e., in a system isolated from initial organic matter. In this case, particularly isotopically light methane can occur. Indeed, methane in the Toarcian sediments of the Urengoy field is enriched in the light isotope in contrast to the normal trend. The inverted enrichment of methane in the light carbon isotope is clearly manifested at a depth of 3.7 · 4.2 km in the Samburg area (see Table I and Fig. 2). In addition, divergence of  $\delta^{13}\text{C-values}$  for  $C_2\text{-}C_4$  hydrocarbons is observed at this interval which is also an indication of the destructive process (Galimov, 1988). The normal trend is convergence of  $\delta^{13}\text{C-values}$  of  $C_2\text{-}C_4$  hydrocarbons with an increase in the degree of transformation of organic matter (James, 1983).

With the increase in depth, the isotopic characteristic of gas reflects a pattern of more pronounced destruction of hydrocarbon systems. Ethane and propane become isotopically heavier ( $\delta^{13}C = -22 \div -20^{\circ}/_{\circ \circ}$ ). Their carbons become heavier than kerogen carbon. Methane again becomes depleted in the light isotope as it forms at the expense of precursors continuously getting heavier. While at the beginning of the hydrocarbon destruction process, gas contained relatively high concentration of C2+ (e.g.,  $C_2H_6 = 9.6\%$ ,  $C_3H_8 = 2.4\%$ ,  $C_4H_{10} = 0.6\%$ ), at a depth  $\ge 5.5$  km, the concentration of  $C_2$ - $C_4$  hydrocarbons clearly decreases ( $C_2H_6$  = 2.9%,  $C_3H_8$  = 0.5%,  $C_4H_{10}$  = 0.1%). At the same time, there is no indication of rapid growth of methane production which one would expect following the concept of "main phase of gas formation". The pyrolysis study shows that the concentration of gas absorbed in organic matter (peak So in the pyrograms) reaches a maximum at the stage corresponding to  $R^{O} = 0.9 \cdot 1.4\%$ (Fig. 4) and drops with increase of degree of catagenesis ( $R^0 \ge 1.8$ ). In the studied section of the Urengoy gas field the highest So-values have been fixed in organic matter from the Pokur Suite (3.04 mg HC/g kerogen), the lowest being from Neocomian (0.74 -1.25 mg HC/g kerogen) and the least concentration of gas shows organic matter from argillites of Middle-Lower Jurassic (0.34 - 0.83 mg HC/g kerogen).

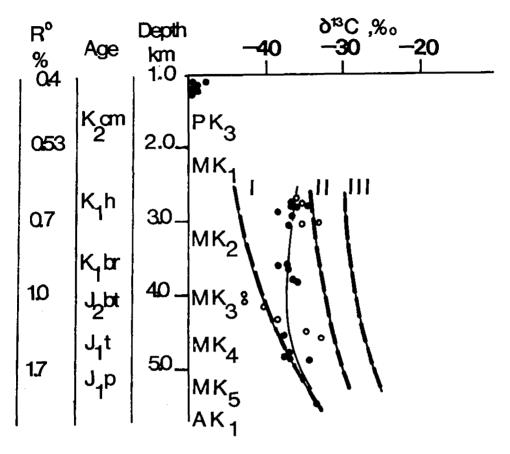


Fig. 4: Carbon isotopic composition of methane in the Urengoy (filled circles) and Samburg (open circles) gas fields. I, II, III = empirical dependencies of  $\delta^{13}C(CH_4)$  on  $R^0$  (mean reflectance of vitrinite under oil) adopted from Schoell (1980) as equations:  $\delta^{13}C = 14.08 \log R^0 - 41^0/_{00}$  (I, marine source rocks, Stahl, 1977) and  $\delta^{13}C = 8.6 \log R^0 - 28^0/_{00}$  (III, coal gases, Stahl, 1977) and from Sheng Ping et al. (1987) as equation:  $\delta^{13}C = 8.64 \log R^0 - 32.8^0/_{00}$  (II, Sychuan basin, China).

Thus, the whole pattern of isotope and chemical zonality of gas throughout the section of the Urengoy gas-field is not compatible with the idea of formation of gas deposits by way of migration of gas from great depth. Apparently, gas formed mainly within corresponding stratigraphic units, although partial migration of gas from Jurassic to Neocomian deposits is quite admittable.

#### REFERENCES

- Alekseyev, F.A., 1974. Zonality in oil and gas formation in the earth's crust based on isotope studies. Geologiya Nefti i Gaza, N 4, p. 62-67 (in Russian).
- Galimov, E.M., 1973. Isotopy ugleroda v neftegazovoy geologii. Nedra, Moscow, 384 p. In English: Galimov, E.M., 1975. Carbon isotopes in oil and gas geology, NASA, TT-682, Washington D.C., 387 p.
- Galimov, E.M., 1988. Sources and mechanisms of formation of gaseous hydrocarbons in sedimentary rocks. Chem. Geol., 71, p. 77-95.
- Gavrilov, Ye.Ya., Zhurov, J.A. and Teplinskiy, G.I., 1972. Correlation between isotope composition of argon and carbon in natural gases. Dokl. Akad. Nauk SSSR, 206, N 2, p. 448-451.
- Grace, J.D. and Hart, G.F., 1986. Giant gas fields of Northern West Siberia. American Assoc. Petr. Geol. Bull., Vol. 70, N 7, p. 830-852.
- Hunt, J.M., 1979. Petroleum geochemistry and geology. W.H. Freeman and Company, San Francisco, 617 p.
- James, A.T., 1983. Correlation of natural gas by use of carbon isotopic distribution between hydrocarbon components. American Assoc. Petr. Geol. Bull., 67, N 7, p. 1176-1191.
- Kontorovich, A.E., Nesterov, I.I., Salmanov, F.K., Surkov, V.S., Trofimuk, A.A. and Erv'e, Yu.G., 1975. Geology of oil and gas of Western Siberia. Nedra, Moscow, 678 p.
- Lopatin, N.V. and Emetz, T.P., 1984. New data on catagenesis of deep buried Jurassic sediments of the Urengoy region. Dokl. Akad. Nauk SSSR, Vol. 279, N 4, p. 954-958 (in Russian).
- Meyerhoff, A.A., 1980. Petroleum basins of the Soviet Arctic. Geol. Mag., Vol. 17, p. 101-186.
- Nalivkin, V.D., Yevseyev, G.P., Kruglikov, N.M., Sverianov, G.P., Tchernikov, K.A. and Shablinskaya, N.G., 1969. Principal stages of the development of the West Siberian basin and its gas bearing. In: Proc. VNIGRI, Vol. 272, p. 18-46 (in Russian).
- Neruchev, S.G., Rogozina, E.A. and Kapchenko, L.N., 1973. The main phase of gas formation—a stage of catagenetic evolution of sapropelic DOM (dispersed organic matter). Geologia i Geophizika, N 10, p. 14-17 (in Russian).
- Neruchev, S.G., Zelichenko, I.A., Rogozina, E.A., Parparova, G.M. and Trushkov, P.A., 1984. Geochemical peculiarities of transformation of dispersed organic matter and quantitative estimation of oil and gas formation in the Mesozoic deposits of West Siberia. In: Principal problems of oil and gas-bearing of Western Siberia, Proc. VNIGNI, Leningrad, 132 p. (in Russian).
- Nesterov, I.I., Ryl'kov, A.V., Kulakhmetov, N.H., Poteriayeva, V.V., Poteriayev, A.G., Stavitskiy, B.P., Shchepetkin, J.F. and Ushatinskiy, I.N., 1977. Vertical migration

- of hydrocarbon and its influence on habitat of oil and gas deposits. Proc. SapSib-NIGNI, Tyumen, Vol. 17, p. 35-40 (in Russian).
- Prasolov, E.M. and Lobkov, V.A., 1977. On the conditions of formation and migration of methane (the carbon isotope composition). Geokhimiya, N 1, p. 122-134 (in Russian).
- Prasolov, E.m., Kamenskiy, I.L., Meshik, A.P., Subbotin, E.S., Suravtseva, L.N. and Yakovlev, O.N., 1981. Formation of gas fields in Northern West Siberia with reference to isotope data. In: Origin and making up the composition of natural gases based on isotope geochemistry data. Leningrad, p. 64-82 (in Russian).
- Schoell, M., 1980. The hydrogen and carbon isotopic composition of methane from natural gases of various origins. Geochim. Cosmochim. Acta, 44, p. 649-661.
- Sheng Ping, Shen Qixiang, Wang Xiaubin and Xu Yangchang, 1988. Characteristics of the isotope composition of gas—from hydrocarbon and the identification of coaltype gas. Scientia Sinica, Ser. B, Vol. 31, N 6.
- Stahl, W.J., 1977. Carbon and nitrogen isotopes in hydrocarbon research and exploration. Chem. Geol., 20, p. 121-149.
- Stahl, W.J. and Carey, B.D., 1975. Source rock identification by isotope analysis of natural gases from fields in the Val Verde and Delaware Basins, West Texas. Chem. Geol., 16, p. 257-267.
- Vaipolin, J.V., 1984. Structure of crystalline foundation and thickness of the transitional complex in West Siberia. In: Principal problems of oil and gas in West Siberia. Nedra, Moscow, 679 p. (in Russian).
- Yermakov, V.I., Lebedev, V.S., Nemchenko, N.N., Rovenskaya, A.C. and Grachev, A.N., 1970. Carbon isotope composition of natural gases of the north of West Siberian plane as related to the question of their genesis. Dokl. Akad. Nauk SSSR, 190, N 3, p. 683-686.
- Yevseyev, G.P., Kruglikov, N.M., Nalivkin, V.D., Sverianov, G.P. and Tchernikov, K.A., 1973. Relation between oil andgas in the Mesozoic deposits of Northern West Siberia. In Proc. Zap. SibNIGNI, Vol. 70, p. 71-81 (in Russian).