SOURCES AND MECHANISMS OF FORMATION OF GASEOUS HYDROCARBONS IN SEDIMENTARY ROCKS

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Abstract

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Accepted concepts of principal stages of hydrocarbon formation fail to satisfactorily explain the accumulation of supergiant gasfields in West Siberia, U.S.S.R., such as for example Urengoy, which comprise 30% of the proven gas reserves of the world. A new mathematical model has been developed which applies the concept of activation energy distribution to the formation of gases. Characteristic differences in the molecular structure of humic and sapropelic source organic matter are expressed in different activation energy distributions. The model allows the calculation of isotope values for different types of organic matter and their dependence on maturity. Application of the model to West Siberia suggests that the supergiant gas accumulations in Urengoy are more likely formed from terrestrial organic matter through thermochemical reactions at moderate depths and are not the result of either deep, overmature, or bacteriogenic processes. The new mathematical model suggests that humic organic matter, in general, has a high methane-generating capacity at comparably low maturities of organic matter equivalent to 0.5–0.7% on the vitrinite reflectance scale.

1. Introduction

The widely suggested concept of formation of hydrocarbons says that thermogenic methane forms at the relatively late stage of geochemical transformation of organic matter (see, e.g., Tissot and Welte, 1978; Hunt, 1979; Parparova et al., 1981; Rogozina, 1983; Trofimuk et al., 1984). The scheme (Fig. 1) reproduced from Hunt (1979) illustrates this concept: independent on the type of organic matter the main stage of methane generation (disregarding microbiological methane) comes after the stage of oil formation. The corresponding depths are ⩾4–6 km. As gas deposits occur mainly at
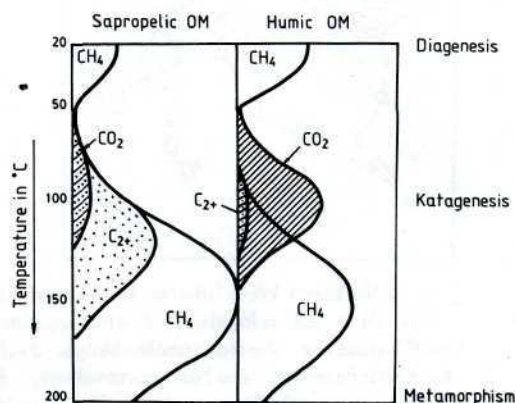

Fig. 1. Relative yield of gas during transformation of organic matter (after Hunt, 1979). The *numbers* to the left indicate subsurface temperatures in °C.

depths of 1.5–3 km extensive vertical migration of gas is implied. This concept affects the whole current strategy of gas exploration. However being applied to the actual geologic situation, it encounters many difficulties and I think that it is wrong in principle.

2. The problem of origin of gas in West Siberia

It is reasonable to make a start with the problem of the origin of gas in West Siberia. In northern West Siberia in such gasfields as Urengoy, Bovanenkovskoye, Yamburg, Medvezh'ye, Zapolyarnoye and some others (Fig. 2)
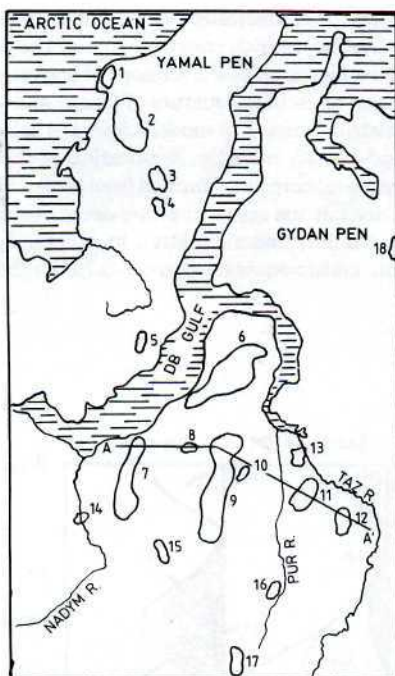

Fig. 2. Northern West Siberia: location of the major gasfields (line *AA'* = location of cross-section in Fig. 3; *1* = Kharasavey; *2* = Bovanenkovskoye; *3* = Neytinskoye; *4* = Arcticheskoye; *5* = Novoportovskoye; *6* = Yamburg; *7* = Medvezh'ye; *8* = Pestsovoye; *9* = Urengoy; *10* = Samburg; *11* = Zapolarnoye; *12* = Russkoye; *13* = Tazovskoye; *14* = Nadymskoye; *15* = Yamsoveyskoye; *16* = Vostochno-Tarkosalinskoye; *17* = Vengayakhinskoye; *18* = Messoyakhskoye).

more than 30% of the proved gas reserves of the world are concentrated*. There are many controversies about the origin of the gas. To date all the conceivable mechanisms have been proposed, from that of a microbiological origin of the major part of the gas to its generation under high temperatures at great depth. The latter view is the most widespread.

The main gas deposits of the region are situated in sediments of Cenomanian age at depths of ~ 1000–1200 m (Fig. 3). The reservoirs occupy the uppermost position in the Pokur Suite ($K_2cm + al + apt$), which is composed of sands and sandstones with interbedded shales mainly of continental origin. The thickness of the Pokur Suite is ~ 800 m. The gas consists of almost pure methane.

Another large gas accumulation occurs in the Lower Cretaceous (Neocomian complex) at depths of ~ 2500–3000 m. This is a wet gas. C_2–C_4 gaseous hydrocarbons amount to 6–10% of the gas. The Neocomian gas is accompanied with condensates. The concentration of the latter is 100–300 g per cubic meter of gas.

Oil occurs in the lower part of the Neocomian section especially in the Achimov Suite, immediately overlying the Upper Jurassic shales (Bazhenovian Suite). Underneath the thick Tyumen Suite it contains only few hydrocarbons.

Thus the occurrence of methane, gas-condensate and oil in the Mesozoic section of northern West Siberia makes up a sequence which is just opposite to that predicted by the theoretical scheme.

It has been proposed that this is due to migration of methane and condensates from great depth (Yevseyev et al., 1973). Because of its low coalification rank and the humic type of organic matter the Pokur Suite was not believed to be an adequate source for such a huge accumulation of gas in the Cenomanian deposits

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*For details on location, stratigraphy, lithology, etc., see literature on the local geology, e.g. Kontorovich et al. (1975). In English a recent compilation by Grace and Hart (1986) is relevant.
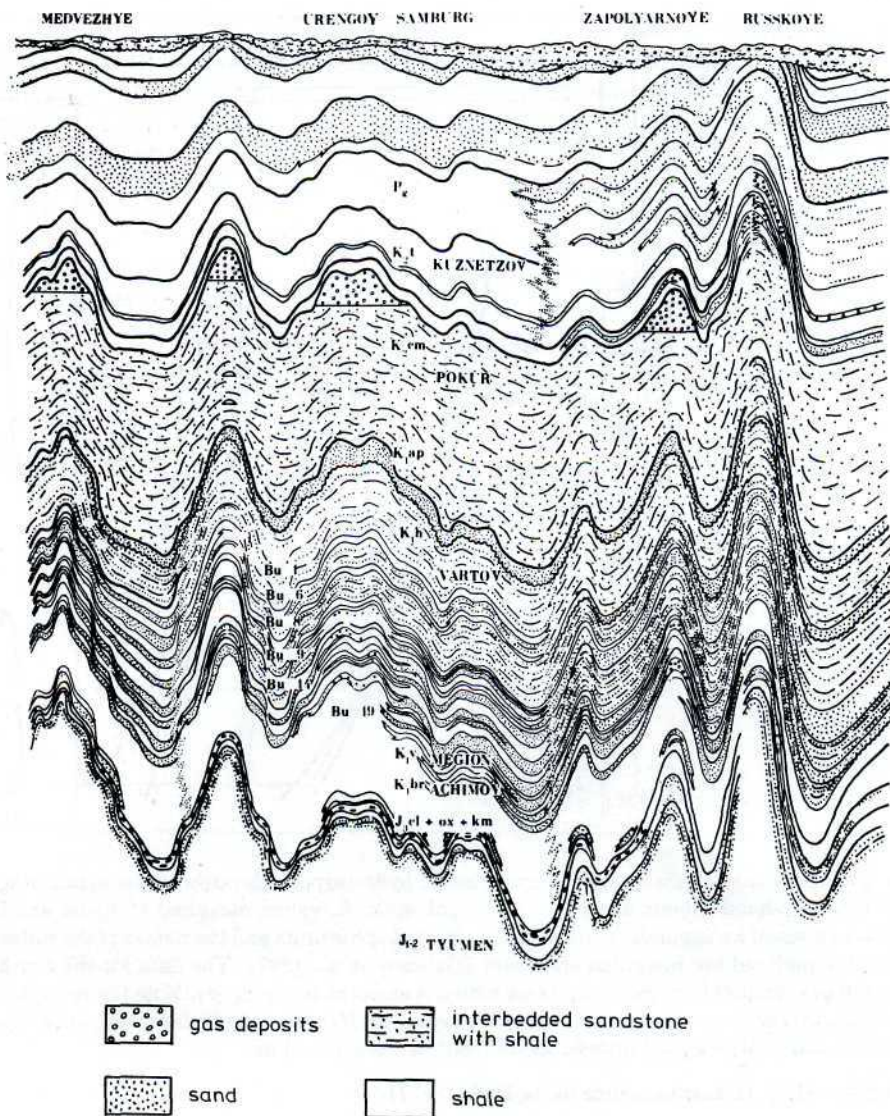
MEDVEZHYE   URENGOY   SAMBURG   ZAPOLYARNOYE   RUSSKOYE

Fig. 3. East–west cross-section (line AA' in Fig. 2) of the Cretaceous section in northern West Siberia.

(Neruchev et al., 1984). Having studied the carbon isotopic composition of methane as well as the isotope composition of Ar and He, Prasolov et al. (1981) concluded that isotopic data are in agreement with the idea of extensive vertical migration of hydrocarbons from depths of 4–5 and 6–9 km for the Cenomanian and Neocomian gases, respectively. However, the latter authors proceeded from the incorrect supposition that isotope exchange equilibrium between CH_4, CO_2 and organic carbon exists and hence temperatures of gas formation are overestimated.

In Fig. 4 our recent data on the carbon isotope composition of gaseous hydrocarbons for major productive horizons of the Urengoy field are depicted. Urengoy is the largest gas accumulation in the world. Stratification of gas deposits and the geochemical character of the gas in Urengoy are typical for northern West Siberia. Methane in the Cenomanian deposit of the Urengoy field has a carbon isotope compo-
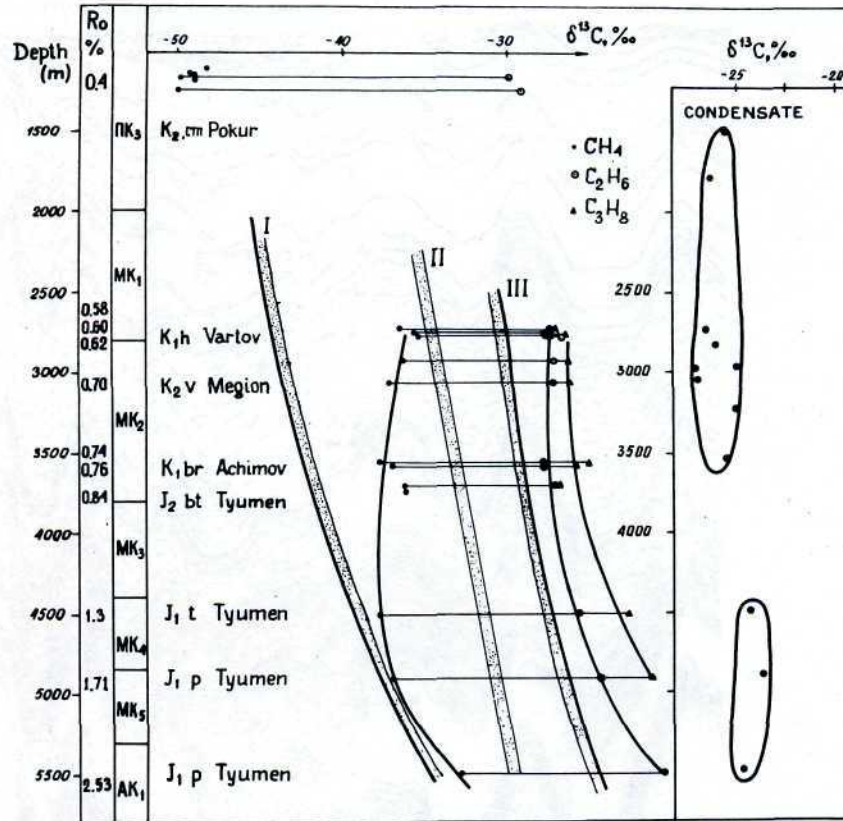
Fig. 4. Change of the carbon isotope composition of hydrocarbons throughout the sedimentary succession of the Urengoy field. At the left-hand column along with the depth scale, R_o-values measured (Lopatin and Emetz, 1984), *marks* for the successive stages of katagenesis, *symbols* for the stratigraphic units and the *names* of the suites are pointed out. The details for samples analyzed are presented elsewhere (Galimov et al., 1987). The data for the depth of 5500 m are obtained by analysis of gas samples from Samburg (area which is adjacent to Urengoy). Note the separate $\delta^{13}C$ scale (on the right) for the liquid hydrocarbons of the gas-condensate system. *I, II, III* = empirical relationships of $\delta^{13}C_{CH_4}$ and R_o (mean reflectance of vitrinite under oil) adopted from Schoell (1980) as the expressions:

$14.8 \log R_o - 41\%_o$ (*I*, marine source rocks; Stahl, 1977)

and

$8.6 \log R_o - 28\%_o$ (*III*, coal gases; Stahl, 1977)

and from Shen Ping et al. (1988) as the expression:

$8.64 \log R_o - 32.8\%_o$ (*II*, Sychuan basin, China)

sition characterized by $\delta^{13}C$-values from -50 to $-46\%_o$.

It should be noted that the values of $\sim -60\%_o$ previously reported by Yermakov et al. (1970) and Alekseyev (1974) for the Cenomanian gas of Urengoy have not been confirmed. These early, apparently incorrect data have pene-

trated into the Western literature through Meyerhoff's (1980) review and reproduced in a recent paper by Grace and Hart (1986). It has become a source of speculation on the possible microbiological origin of Cenomanian gas. In fact the actual $\delta^{13}C_{CH_4}$-values of $\sim -50\%_o$ are rather characteristic of thermogenic methane

produced at the early step of katagenesis of organic matter.

As everywhere in the north of West Siberia the Pokur Suite in Urengoy is represented by a continental sequence of sediments. Organic matter is of the humic type. Higher-plant remnants and coal seams are ubiquitous throughout the section. In the upper part of the Pokur Suite organic matter is still immature (vitrinite reflectance coefficient R_o < 0.4%). However in the adjacent depressions, the base of the Pokur Suite is lowered to a depth of ~2.5 km. Correspondingly, maturity of organic matter increases up to $R_o \simeq 0.55\%$. Hence, it is conceivable that methane was generated in the Pokur Suite from humic organic matter within a relatively wide range ($R_o = 0.4$–0.55%) although at the early stage of its geochemical transformation.

Geological conditions were very favorable for accumulation of gas in the Cenomanian reservoirs. Due to the excellent hydrodynamic intercommunications within the Pokur Suite, accumulation of gas from the whole 800-m section occurred through long-distance lateral migration. The Turonian shales (Kuznetsov Suite) formed the ideal seal (thickness of > 600 m) for the Cenomanian reservoirs.

Gavrilov et al. (1972) found a correlation between $\delta^{13}C_{CH_4}$ and the content of atmospheric argon (Ar_{air}) in the Cenomanian gas of different fields of northern West Siberia. They suggested that the correlation was due to the mixed origin of the Cenomanian gas with end-member components being the indigenous gas ($\delta^{13}C_{CH_4} \simeq -60\%$ and $Ar_{air} \simeq 110$ ppm) and gas migrated from the Neocomian section ($\delta^{13}C_{CH_4} \simeq -39$ to -38% and $Ar_{air} \simeq 3$–5 ppm). Under these conditions the Cenomanian gas in the Urengoy field ($\delta^{13}C_{CH_4} \simeq -48\%$, $Ar_{air} \simeq 55$ ppm) would be composed of one-third of the gas migrated from the Lower Cretaceous. However, this is in contradiction with the hydrocarbon composition of the gas. The Cenomanian gas in Urengoy contains ethane and heavier hydrocarbons in negligible quantities

($C_{2+} \simeq 0.15\%$). If appreciable migration had taken place the content of the C_{2+} would have been much higher, allowing for a more wet character of the Neocomian gas ($C_{2+} \simeq 6$–10%). In addition, the isotopic composition of ethane in the Cenomanian deposit of Urengoy ($\delta^{13}C_2 = -29.5 \pm 0.4\%$) is different from that in the Neocomian section of the field ($\delta^{13}C_2 = -27.5 \pm 0.5\%$).

Hence the correlation between $\delta^{13}C_{CH_4}$ and Ar_{air}, mentioned above, is likely rather due to different contributions of gas from different parts of the section within the Pokur Suite rather than being due to migration of hydrocarbons from below. If the source of gas is confined to the shallow part of the Pokur Suite, methane should be rather depleted in the heavy isotope ^{13}C which is exactly observed in the Vengayakhinskoye field, where in the Cenomanian deposit methane has $\delta^{13}C_{CH_4} = -60.3\%$ (Gavrilov et al., 1972). Alternatively, when the deep part of the Pokur Suite, and consequently mature organic matter, would have been mainly involved in the formation of the deposit, relatively heavy methane should occur, such as in the Messoyakhskoye field, where methane in the Cenomanian deposit has $\delta^{13}C = -41.1\%$, and in the case that the whole section serves as a source of gas for the Cenomanian deposit the comingled methane should average at an isotopic composition of ~ -50 to -47%. Just such $\delta^{13}C$-values are characteristic of methane in all of the supergiant gasfields of the region, including the Urengoy field.

Although a partial migration from deeper sections cannot be ruled out it seems that this process is insignificant. Both geochemical and geological evidence points to the Pokur Suite as a very probable source of gas concentrated in the Cenomanian reservoirs. The Neocomian gas as it has been mentioned is quite different from the Cenomanian one.

The Neocomian section as a whole is composed of sediments being transitional from the marine to continental environment. In the upper part of the section (Vartov Suite) the com-

position of organic matter reflects essential input of terrigenous material. Downwards in the Megion and Achimov Suites organic matter tends to be more of the sapropelic type. The maturity of the organic matter ranges throughout the Neocomian section from 0.55% to 0.76% on the R_o-scale (Lopatin and Emetz, 1984).

Isotopic composition of methane in the Neocomian deposits varies from -38 to $-35‰$. This roughly corresponds to the type and the maturation level of organic matter from the corresponding stratigraphic units.

At the upper part of the Tyumen Suite (thick continental succession of Early and Middle Jurassic age) methane and C_2–C_4 gaseous hydrocarbons have a carbon isotopic composition similar to that of the hydrocarbons of the Neocomian. Hence, migration of hydrocarbons from this horizon upwards cannot be discounted.

At depths of ~ 4000–4800 m isotopically light methane appears. Downwards methane again becomes gradually isotopically heavier. C_2–C_4 hydrocarbons also continue to be enriched in ^{13}C.

In accordance with the existing concept the most favorable conditions for gas formation are attained at depths of 4500–5500 m (Neruchev et al., 1984). However, little gas occurs at this interval. An analysis of gas from this part of the section (in fact the samples were collected from the deep hole drilled in the Samburg area which is adjacent to the Urengoy field) showed that the isotopic compositions of the hydrocarbons in the deep parts of the Tyumen Suite are distinctively different from those of the Neocomian deposits. Therefore, the former is unlikely to be the source for the latter.

Condensates in the studied section are subdivided into two groups by their carbon isotopic composition (see the insertion in Fig. 4). The Neocomian condensates show throughout the whole section a uniform isotope composition with average $\delta^{13}C = -27.20 \pm 1.1‰$. Condensates which are produced in trace amounts (0.03–0.4 $cm^3 \, m^{-3}$) from Cenomanian reservoirs fall into the same range. Condensates from

the Tyumen Suite derived from depths of > 4000 m have an isotopic composition characterized by the average value $\delta^{13}C = -25.34 \pm 0.55‰$. These groups of condensates are also different in their chemical composition (Nemchenko and Rovenskaya, 1987).

Thus the observed variations in the carbon isotopic and chemical composition of hydrocarbons roughly correlate with facies and maturation of organic matter in the corresponding parts of the section. This along with the quite distinctive characteristics of hydrocarbons from the different stratigraphic units and regular change of those characteristics with depth within the stratigraphic units is apparently in contradiction with the notion that the hydrocarbons migrated from great depth to the present reservoirs. However, if it is assumed that the vertical migration was not significant other questions arise which can hardly be answered within the framework of the existing concept. If methane of the giant Cenomanian deposits, for example, would have been generated in the Pokur Suite how can it be related to the maturity of the organic matter in this section? What is the mechanism by which humic organic matter may produce significant amounts of methane at a relatively early stage of its maturity? If gases in the Neocomian reservoirs formed at the stage preceding oil formation what is then the origin of the condensates related to these gases? Why is the Tyumen Suite which contains in the studied interval mature organic matter ($R_o = 1.1$–2.0%) practically free of gas? This despite the fact that organic matter in such a stage, in accordance with the existing concept, still has a high methane generative potential.

As is known the isotope composition of gaseous hydrocarbons is related to maturity and type of initial organic matter and isotope data have been successfully used for identification of gas source rocks (Galimov et al., 1973; Stahl and Carey, 1975; Stahl, 1977; Schoell, 1980; James, 1983; Burns et al., 1984). However, the established isotopic relationships are empirical. They are not derived from the mechanisms

of formation of hydrocarbons. Therefore in many cases they do not allow adequate interpretation of isotope data. This is also true in the present case since the observed isotope relationships reveal unusual behavior. For instance, the carbon isotope composition of methane shows a reverse trend with depth within a certain interval (Fig. 4). The difference between the isotopic composition of the C_2–C_4 hydrocarbons increases with depth instead of decreasing as one would expect from theoretical considerations (James, 1983).

Below a model is presented which aims to answer these questions.

3. The model

3.1. Suggested mechanism

For sapropelic organic matter which is enriched in aliphatic structures the most probable mechanism of methane formation is cracking. In this case methane forms along with other hydrocarbons. The chemical structure of humic organic matter is characterized by an abundance of aromatic rings and heteroatoms. During geochemical transformation a condensation of aromatic rings occurs. In this connection it is of interest that aromatic rings are readily opened during hydration when an oxygen atom forms an immediate bond with a carbon atom of an aromatic ring like in phenyl, benzochinon, etc. (Gräber and Hüttinger, 1980). This process is accompanied with the liberation of CO and CH_4. As the opening of aromatic rings is a prerequisite of the aromatic condensation process and heteroatomic substituents are typical for the structure of humic organic matter it is reasonable to suggest that this kind of processes operate during geochemical transformation of kerogen.

It is likely that the carbon of CO originates from the carbon atom of the aromatic ring bound with the oxygen atom and CH_4 forms by hydration of a neighboring carbon atom:
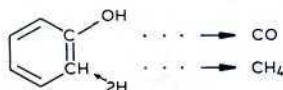

The reaction scheme of the formation of CO and CH_4 looks symmetric. Hence, activation energies of both processes as well kinetic isotope effects accompanying the formation of CO and CH_4 ought to be similar.

Actually CO is known to be one of the major components of gas released during pyrolysis of organic matter. Activation energies calculated for CO and CH_4 formation are characterized by rather close values (Rohrback, 1979).

In order to study the correlation between the isotopic composition of CH_4 and CO we undertook a set of experiments simulating the coalification process, with samples being selected to represent different ranks of maturity and different types of organic matter (Galimov et al., 1989a). As it is seen from Fig. 5 a clear similarity of $\delta^{13}C$-values for CO and CH_4 and a parallelism in their change during stepwise pyrolysis is observed for coals of humic (A) and sapropelic–humic (B) types. In contrast, typical sapropelic shale (Bazhenovian Suite, West Siberia) gave a small yield of CO (F). Isotopic correlation between CO and CH_4 is absent for peat (D) and anthracite (E). Apparently in the former condensation of aromatic structures has not yet started while in the latter this process is already accomplished. It is of interest to note that kukersite (C) from Estonia showed the same similarity between the isotopic composition of CO and CH_4 which is characteristic of humic organic matter. Kukersite is classified as sapropelic material. However, it has a specific chemical composition characterized by the enrichment in aromatic structures with heteroatomic substituents (Fomina et al., 1965).

Hence, there is a basis to suggest that one of the possible mechanisms of methane formation is conjugated with the process of condensation of aromatic rings.

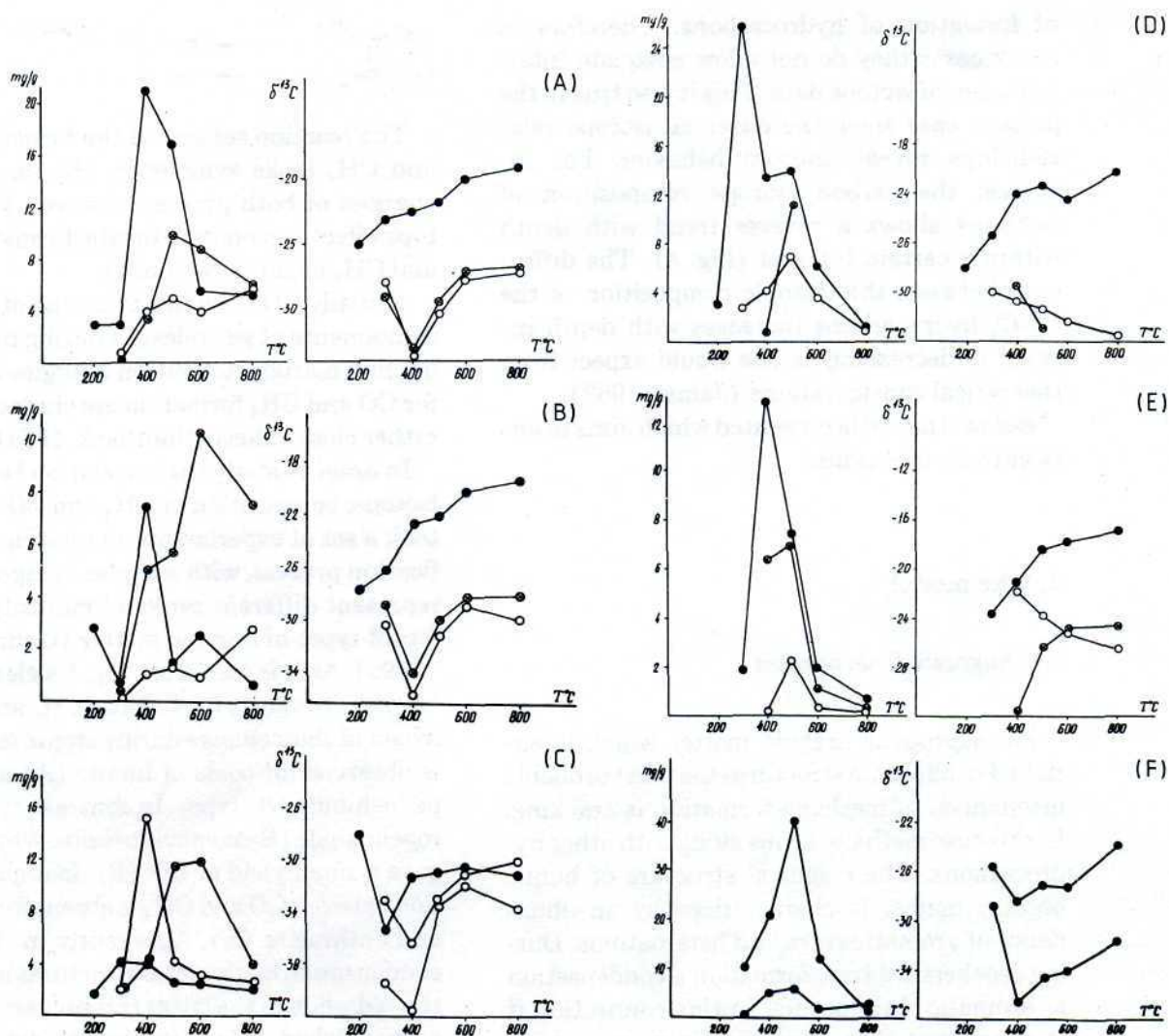The net reaction may be written as follows:

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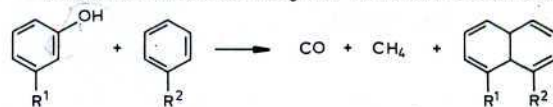
Fig. 5. Yield and carbon isotopic composition of gaseous products of stepwise (4 hr. for each temperature step) pyrolysis of organic matter of the different types (modified from Galimov et al., 1989a): A=brown coal; B=bituminous coal; C=kukersite (Estonia); D=peat, E=anthracite; F=sapropelic shale (Bazhenovian Suite). *Filled dots*: CO_2; *open circles with cross*: CH_4; *open circles*: CO.

In contrast to pyrolysis experiments CO does not occur in appreciable quantities under natural conditions as its carbon ends up as CO_2 or CH_4 depending on the redox conditions, or is incorporated into organic matter (Galimov et al., 1989a). By the same reason the relative yield of CO and CH_4 during pyrolysis is not diagnostic.

The above suggested mechanism might operate both in humic and sapropelic types of organic matter. However, the initial concentration of aromatic structures with heteroatomic substitutors is much higher in humic materials as a rule. Therefore, formation of methane by this way manifests itself earlier and more extensively in humic organic matter, whereas the

ability of sapropelic organic matter to produce hydrocarbons is realized mostly under conditions when splitting of aliphatic C–C bonds becomes effective.

3.2. Band of activation energies

The existence of different mechanisms of methane formation and the successive involvement of reacting carbon atoms from different structural positions implies that the process of methane formation is characterized by a certain set (range) of activation energies rather than by a single value.

I showed some years ago by applying this concept how one might explain the fact that methane generated from kerogen under natural conditions or under experimental pyrolysis is significantly less enriched in the light carbon isotope than methane formed under destruction of individual organic compounds (Galimov, 1974). If we assume for example a range of activation energies: $\Delta E = 12$ kcal. mol^{-1} (isotope separation coefficient $\alpha = 1.05$, degree of acccomplishment of the reaction $f = 0.5$) we obtain a calculated difference in isotopic composition of methane and initial carbon of $-5\%_0$, whereas in the case of a single-level activation energy reaction ($\Delta E = 0$ under the same conditions) the difference would be $-33\%_0$ (Fig. 6).

The same principle accounts for the fact that activation energies calculated for natural processes of transformation of organic matter (15–30 kcal. mol^{-1}) are lower than those which characterize chemical conversion of individual organic compounds (50–70 kcal. mol^{-1}; Jüntgen and Klein, 1975).

Thus it appears that the process of methane formation from organic matter is characterized by a certain range of activation energies with the distribution function of activation energy values being unequal for humic and sapropelic organic matter respectively.
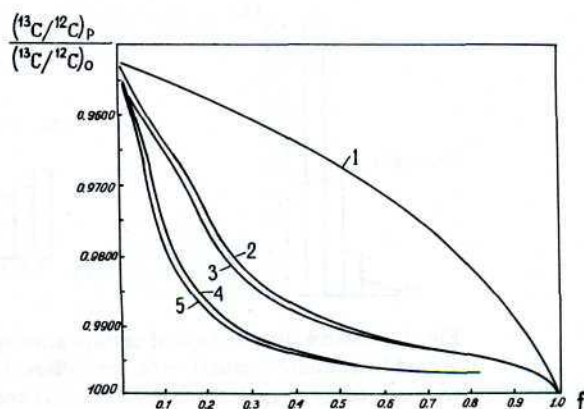

Fig. 6. Isotope fractionation ($\Delta^{13}C$) between product of reaction and starting material in dependence of the degree of completion of the reaction (f) for different widths of activation energy range (ΔE) and discreteness (n), i.e. the number of individual activation energies making up the range: (1) single activation energy ($\Delta E = 0$); (2) $\Delta E = 0.6$ kcal. mol^{-1}, $n = 100$; (3) $\Delta E = 6$ kcal. mol^{-1}, $n = 100$; (4) $\Delta E = 6$ kcal. mol^{-1}, $n = 10$; (5) $\Delta E = 12$ kcal. mol^{-1}, $n = 100$ ($E = 30$ kcal. mol^{-1}, $\alpha = 1.05$; modified from Galimov, 1974). The curves show that isotope fractionation depends significantly on the width of the range of activation energies. For a given width of the range isotope fractionation depends little on its discreteness.

3.3. Methane, $\delta^{13}C_1$–R_o

Proceeding from considerations stated above a model is suggested which implies the existence of a range of discrete activation energy levels for methane formation with a different distribution of the methane-producing sites at the corresponding levels of activation energy for sapropelic and humic organic matter. It is assumed that humic in contrast to sapropelic organic matter is relatively enriched with sites for initial methane formation at the lower E_a levels (Fig. 7). For simplicity several discrete levels of the activation energy are taken within the range of E_a-values usually observed in pyrolysis experiments.

The yield and isotopic composition of methane have been calculated for the successive stages of geochemical transformation of organic matter. The degree of the transformation is approximated by the vitrinite reflectance coefficient R_o which, in turn, may be related to
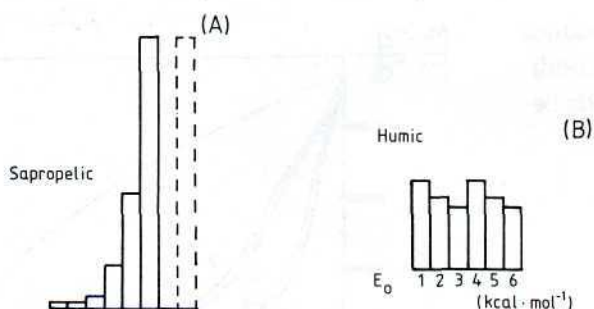
Fig. 7. Relative distribution of carbon sites which are involved in methane formation on the different levels of activation energy suggested for sapropelic (A) and humic (B) organic mater. Activation energies E_{ai}, corresponding to 1,2,3,..., are taken as: 36, 40, 44, 48, 52 and 56 kcal. mol^{-1}. Frequency factors accordingly are: $5 \cdot 10^7$, 10^9, 10^{10}, 10^{12}, 10^{13} and 10^{14} s^{-1}. Relative distributions of the initial sites C_{0i} for methane formation are respectively taken as: 1, 0.8, 0.7, 1, 0.8 and 0.7 for humic; and 0.05, 0.05, 0.15, 0.5, 1.25 and 3.0 for sapropelic organic matter.

temperature and age values (Lopatin, 1973). In the given example the time has been taken equal for all stages ($t_j = 20$ Myr.) and the characteristic temperature for the jth stage has been determined (T_j). The yield of methane c_{pi} corresponding to the ith level of the jth stage can be obtained from the following expression:

$$c_{pi}/c_{0i} = 1 - exp[-t_j$$
$$\times \{A_i \exp(-E_{ai}/RT_j)\}] \qquad (1)$$

Summation over all E_{ai} levels gives the yield for a particular stage (R = gas constant).

Calculation reveals a difference of methane evolution for the humic and sapropelic types of organic matter (Fig. 8A). As distribution functions of E_a are taken more or less arbitrary the drawing illustrates the principal idea rather than actual evolution curves.

The same model describes the dependence of the isotopic composition of methane on maturity of organic matter and, what seems to be even more important, predicts a difference between $\delta^{13}C_1 - R_o$ relationships for humic and sapropelic types of organic matter. The dependence of the carbon isotopic composition of methane on the degree of maturation of initial organic matter has long been established (Gal-

imov, 1973; Stahl, 1974). However, the cause of the difference of the relationships for humic and sapropelic organic matter remains unclear.

Isotopic composition of methane ($\delta^{13}C_{pi}$) corresponding to the ith level of activation energy is determined through the formula:

$$\delta^{13}C_{pi} = \delta^{13}C_{0i} + [(c_{0i}/c_{pi})\{1 - (1$$
$$-c_{pi}/c_{0i})^{1/\alpha}\} - 1] \times 10^3 \qquad (\%o) \qquad (2)$$

Summation of $\delta^{13}C_{pi}$'s for all the E_{ai}'s taking into account the yield (c_{pi}) gives $\delta^{13}C_1$ for the jth particular stage. The resulting $\delta^{13}C_1$ evolution curves are presented in Fig. 8B. The two curves (a and b) for each type of organic matter correspond to the extreme cases of the gas accumulation history. The left-hand curve (a) describes an instantaneous isotopic composition of methane released (under the condition that all methane generated in the previous stages is lost) whereas the right-hand curve (b) corresponds to the averaged isotopic composition of all methane accumulated at a given moment.

The known empirical curves are depicted in the same Fig. 8B. The curves I and III were found by Stahl (1977) for marine and humic organic matter, respectively. The curve II has been recently obtained by Shen Ping et al. (1988) for methane derived from predominantly continental deposits of the Sychuan and Shanganin basins of China.

The Chinese authors argued that the $\delta^{13}C_1 - R_o$ relationship for methane generated by dispersed humic organic matter differs from that of coal-type methane which Stahl (1977) dealt with. However, the difference between the curves may be interpreted also in terms of the accumulation history. Stahl's curve is fairly well approximated with the "instantaneous" curve while Shen Ping et al.'s curve is closer to the "accumulative" curve.

It should be emphasized that the calculated trends have been obtained neglecting a possible variation of the isotopic parameters involved. The isotopic composition of the initial carbon for both types of organic matter, for example,
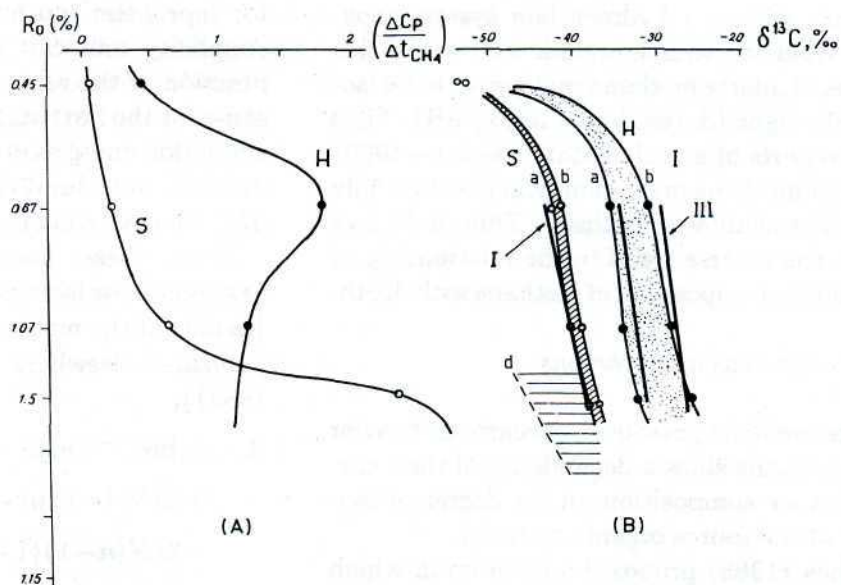
Fig. 8. Methane evolution (A) and carbon isotope composition (B) trends resulting from the model implying different distribution functions of activation energies (as is shown in Fig. 7) for sapropelic (S) and humic (H) organic matter. Calculations have been done for stages of transformation of organic matter characterizing with the following values of vitrinite reflectance coefficients: $R_o = 0.45$ ($t = 20 \cdot 10^6$ yr., $T = 70°C$), $R_o = 0.67$ ($t = 20 \cdot 10^6$ yr., $T = 100°C$), $R_o = 1.07$ ($t = 20 \cdot 10^6$ yr., $T = 120°C$), $R_o = 1.5$ ($t = 20 \cdot 10^6$ yr., $T = 145°C$). Isotopic composition of initial organic carbon: $\delta^{13}C_0 = -30‰$; kinetic isotope effect of methane formation: $\alpha = 1.03$; $a = $ "cumulative" curve, $b = $ "instantaneous" curve; I, II, $III = $ empirical relationships for sapropelic (I; Stahl, 1977) and humic (II; Shen Ping et al., 1988; III; Stahl, 1977) organic matter.

is assumed to be equal ($\delta^{13}C = -30‰$). The isotopic separation coefficient $\alpha = 1.03$ has been used as being independent of temperature, type of organic matter and activation energy level. Intramolecular isotope heterogeneity has been neglected as well. In fact all these factors may affect isotope fractionation. However, it is of interest that the model seems to adequately explain observations without any additional conditions.

The distribution function for hydrogen involved in the formation of methane is not necessarily the same as that for the carbon sites. Therefore, the difference of the methane evolution curves for humic and sapropelic material observed for carbon isotopes should not be observed for hydrogen isotopes. This answers the question:

"why the hydrogen isotopic fractionation is the same for both humic (i.e. predominantly aromatic) and liptinitic (i.e. predominantly aliphatic) precursor materials"

which Schoell (1980, p. 658) raised having criticized justly an explanation by Sackett (1978).

At high temperatures methane begins to form not only from polymers but also as a result of the destruction of individual compounds (mainly hydrocarbons) that formed at previous stages. One can expect that methane of such an origin has to be relatively enriched in the light carbon isotope. This idea has been suggested some years ago (Galimov, 1973, p. 306, fig. 78). In the framework of the present model formation of methane under the conditions of destruction of hydrocarbons may be taken into account by an additional high-level activation energy difference (designated by the dotted line in Fig. 7). In principle, two situations are possible: (1) when methane forms in source rocks, isotopically light methane is added to isotopically heavy methane which forms from mature organic matter; and (2) when methane is derived from oil destruction in a reservoir, i.e.

it forms within a hydrocarbon system separated from the source organic matter. In this case particularly methane may prove to be isotopically light (dotted line d in Fig. 8B). Thus at deep parts of a sedimentary basin ($\sim$4000–4500 m) methane may occur which isotopically resembles shallower methane. This could give rise to the reverse trend in the relationship of the isotopic composition of methane with depth.

3.4. C_{2+} gaseous hydrocarbons

Like methane gaseous hydrocarbons heavier than methane show a dependence of their carbon isotope composition on the degree of maturity of the source organic material.

James (1983) proposed a diagram in which the empirical data were approximated by curves inferred from the concept that the isotope distribution in a hydrocarbon system is controlled by thermodynamic isotope effects and their temperature dependence. Although James' diagram can be useful for practical purposes as it is based on empirical data his theoretical approach is hard to accept. It is unlikely that thermodynamic isotope effects can be realized in natural hydrocarbon systems.

I believe that C_2–C_4 hydrocarbons form first, by splitting of corresponding fragments from the polymer matrix of kerogen. Then, under high temperature cracking of previously liberated individual compounds including hydrocarbons of greater molecular weight becomes more and more important as a source of low-molecular-weight hydrocarbons.

The first stage may be regarded in the same manner as in the case of methane formation. Following the logic of the model one again could assume a set of reactions leading to formation of C_2–C_4 molecules from kerogen which is characterized by a range of activation energies $\Delta E'_a$. It is likely that lipid-like material serves as a principal source of aliphatic structures independent of the type of organic matter. Therefore the distribution function of activation energies should not be systematically different for sapropelic and humic organic matter. For simplicity one can assume the distribution function of the range $\Delta E'_a$ to be even, and the same for the next stage. However, the range of activation energies on the decomposition of individual compounds is assumed to be narrow: $\Delta E''$ (see insertion in Fig. 10 on p. 90).

From these assumptions the following expression for isotopic shift Δ_n may be inferred [details of the mathematical treatment will be published elsewhere (Galimov and Poliykov, 1989)]:

$$\Delta_n = [(\ln\epsilon_1)^{-1}\{\exp(-w) - \exp(-\epsilon_1 w)\}$$
$$+ 2\lambda N\{1 - \exp(-\epsilon_2 w)\}\epsilon_2 w \exp(-\epsilon_2 w)$$
$$- 2\lambda N(n-1)\{1 - \exp(-\epsilon_2 w)\}^2 w\epsilon_2]$$
$$\times (\alpha - 1)\left(n[1 - (\ln\epsilon_1)^{-1}\{E_1(w)\right.$$
$$\left. - E_1(\epsilon_1 w)\} + \lambda N\{1 - \exp(-\epsilon_2 w)\}^2]\right)^{-1}$$

$$(3)$$

where $\epsilon_1 = k_2/k_1$ and $\epsilon_2 = k_3/k_1$ (k_1, k_2 and $k_3 =$ rate constants corresponding to E_{a1}, E_{a2} and E_{a3}, respectively); $\lambda =$ proportion between concentrations of initial carbon leading to C_2–C_4 hydrocarbons formation through splitting of kerogen and destruction of hydrocarbon precursors, respectively; $w = kt$ serves as a measure of transformation of organic matter; $\alpha =$ isotope separation coefficient; and $E_1(w)$ and $E_1(\epsilon, w) =$ integral exponent functions of type:

$$E_1(x) = \int_x^\infty \exp(-x)x^{-1}dx$$

The following steps lead to this expression. The yield of c_n from the polymer matrix of kerogen is described as a first-order reaction:

$$c'_{p(n)}/c'_{0(n)} = 1 - \exp(-kt) \qquad (4)$$

Analogously, for the isotopic species:

$$c^*_{p(n)}/c^*_{0(n)} = 1 - \exp(-k^*t)$$
$$= 1 - \exp[-(k + \delta_k)t] \qquad (5)$$

and assuming

$\delta_k t \ll 1$

then

$$c''^*_{p(n)}/c^*_{0(n)} = 1 - \exp(-kt)$$

$$+ (kt/n)\exp(-kt)(\alpha - 1) \quad (6)$$

The yield should be averaged on the activation energy range:

$$[c'_{p(n)}/c'_{0(n)}]_{av} = \int [1 - \exp(-w)]\varphi(w)dw \quad (7)$$

where $\varphi(w)$ is the distribution function of w. The distribution function of activation energies is assumed as:

$$\varphi(E) = (E_{a2} - E_{a1})^{-1}$$

Hence,

$$\varphi(w) = 1/(w \ln \epsilon_1) \quad (8)$$

$$\left[\frac{c'_{p(n)}}{c'_{0(n)}}\right]_{av} = \int\limits_{\epsilon_1 w}^{w} \frac{1 - \exp(-w)}{w \ln \epsilon_1} dw$$

$$= 1 - \frac{E_1(w) - E_1(\epsilon_1 w)}{\ln \epsilon_1} \quad (9)$$

and

$$[c'^*_{p(n)}/c'^*_{0(n)}]_{av} = [c'_{p(n)}/c'_{0(n)}]_{av} + 1/(n \ln \epsilon_1)$$

$$\times [\exp(-w) - \exp(-\epsilon_1 w)](\alpha - 1) \quad (10)$$

Formation of the C_n molecule from C_N (in fact low-molecular-weight n-alkane from higher-molecular-weight n-alkane) may be described by the following formula:

$$c''_{p(n)}/c''_{0(n)} = 2[1 - \exp(-kt)]\exp[-(n-1)kt]$$

$$+ (N - n - 1)[1 - \exp(-kt)]^2$$

$$\times \exp[-(n-1)kt] \quad (11)$$

The term $[1 - \exp(-kt)]$ describes formation of C_N from a higher-molecular-weight precursor while the term $\exp[-(n-1)kt]$ describes the stability of the C_n molecule against further fragmentation. The latter decreases with increase of n. The yield of C_n depends on the number of ways $(N - n - 1)$ by which this molecule can be formed. The first addendum at the right-hand part of eq. 11 accounts for the contribution of terminal sites of the C_N compound to the formation of the C_n product while the second addendum is the analogue for the internal sites of C_N. An example of the calculation for $N = 8$ is presented in Fig. 9B. It shows satisfactory agreement with the experimental data (Fig. 9A).

For the isotopic species one can obtain correspondingly:

$$c''^*_{p(n)}/c''^*_{0(n)} = c''_{p(n)}/c''_{0(n)} + n^{-1}[2Nw$$

$$\times \{1 - \exp(-w)\}\exp(-nw)$$

$$- 2N(n-1)w\{1 - \exp(-w)\}^2$$

$$\times \exp\{-(n-1)w\}](\alpha - 1) \quad (12)$$

Taking $c''_0 = \lambda c'_0$ and representing the isotopic shift $\Delta^{13}C$ as a relation:

$$(c^*_p/c^*_0 - c_p/c_0) \equiv c_p/c_0$$

we finally arrive at the expression written before (eq. 3). Results of calculations for C_1, C_2 and C_3 by use of eq. 12 are shown in Fig. 10. The following quantities have been used: $\alpha = 1.030$, $k_3/k_1 = 10^{-6}$, $k_2/k_1 = 3 \cdot 10^{-6}$, $\lambda N = 0.5$.
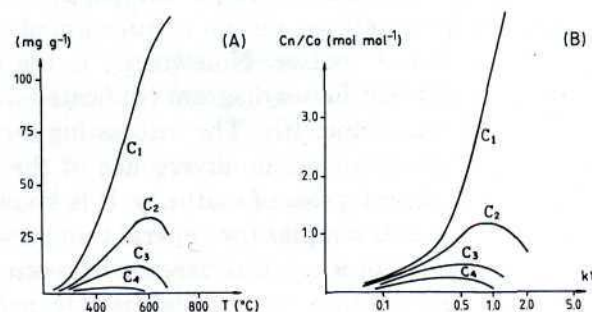

Fig. 9. Yield of methane (C_1) and its heavier (C_n) homologous alkanes: (A) experimentally observed during pyrolysis of organic matter under different temperatures (adapted data from Rohrback, 1979); and (B) calculated from destructive model by using the formula:

$$c_n/c_0 = 2[1 - \exp(-kt)]\exp[-(n-1)kt]$$

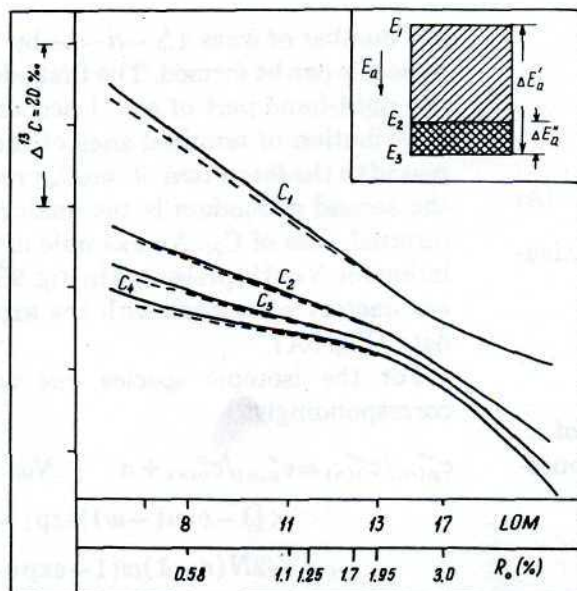$$+ (N - n - 1)[1 - \exp(-kt)]^2$$

$$\times \exp[-(n-1)kt]$$

Fig. 10. Calculated isotopic shifts for different hydrocarbons (C_1–C_4) plotted against R_o. The *dotted lines* represent corresponding curves from the diagram of James (1983) (LOM scale is presented to make both diagrams comparable). In the insertion the distribution functions of activation energies used for the calculation are graphically shown.

The calculated curves satisfactorily approximate the experimentally observed dependence of the carbon isotopic composition of gaseous hydrocarbons on the maturation of the source organic matter. Noteworthy is the similarity with the James diagram (indicated with dotted lines in Fig. 10). The interesting result of our calculation is the divergence of the curves at higher degrees of maturity. It is known that in natural samples the general trend toward a decrease of isotopic difference between C_1–C_4 alkanes with increase of degree of transformation of organic matter frequently changes to the opposite trend beyond some level of the maturity. Because of this effect James (1983) confined the validity of his diagram to a LOM-value (level of organic matter maturation) of ~ 13 ($R_o \simeq 1.95\%$) although this was not in agreement with the logic of his approach since under high temperatures thermodynamic isotope effects were more likely to be realized.

The proposed model explains the observed dependence. At higher degrees of maturity (at higher temperature) low-molecular-weight hydrocarbons are themselves involved in the destruction process. This results in the depletion of the light carbon isotope of the alkanes involved. The divergence of $\delta^{13}C_{(n)}$-values corresponds to this stage. Methane, partly ethane, may temporarily become isotopically lighter than the previously generated portions of the same gases. This effect should be taken into account when interpreting the dependence of $\delta^{13}C_1$ on R_o.

Exhausting of the source of liquid hydrocarbons after the accomplishment of petroleum generation (by the end of the oil-window) results in subsequent depletion in the light carbon isotope of middle- and low-molecular-weight hydrocarbons because the generation of isotopically light gas at their expense is not compensated further by producing new portions of hydrocarbons from kerogen. Therefore, condensates and then gaseous hydrocarbons become more and more isotopically heavier.

4. Consequences and application

If the suggested model provides reasonable interpretations of empirical relationships one can conclude that its basic assumptions are valid. One of the consequences following from the model is that humic organic matter can produce significant quantities of methane at the early and middle stages of its transformation. The supergiant gas deposits in northern West Siberia can now be rationalized by this reaction scheme. Previously some authors (e.g., Stroganov, 1973; Monnier et al., 1983) suggested that thermogenic methane can form at low temperature and shallow depth and presented relevant examples. However, such occurrences were perceived to be insignificant. The present model gives them a more appropriate basis. Moreover, huge accumulations of gas in northern West Siberia, particularly the methane deposits in the Cenomanian, indicate the actual scale of the process of early formation of gas.

Another interesting consequence of the model

is related to the origin of condensates. Formation of a gas-condensate system requires large amounts of gas in order to retain liquid hydrocarbons in solution. In general this is achieved at elevated temperatures. Therefore, condensates are considered to be a product of the late stage of geochemical evolution of organic matter. However, in the case of humic material the necessary proportion of gas to liquid hydrocarbons is already achieved at the early stage. Normally liquid hydrocarbons can leave source rocks when the amount of newly generated hydrocarbons exceeds some critical volume. Then a system of fractures allows hydrocarbons to force their way from a source rock to a reservoir. This process characterizes the mature (oil-window) stage ($R_o \simeq 0.6$–1.1%) and is typical for organic matter with high hydrocarbon potential (sapropelic type). Humic organic matter is a poor source for liquid hydrocarbons. It is unlikely that the latter in this case would leave the source rock by itself. However, humic organic matter generates gas. Methane (and CO_2) can serve as a carrier for liquid hydrocarbons. Therefore, even being in small concentrations (because of the early stage of transformation or poor quality of organic matter) liquid hydrocarbons may escape from a source rock in a gas-condensate state and form deposits before onset of the main stage of oil formation. This mechanism could explain not only late (normal) condensates but also early condensates related to the humic or transitional type of organic matter (Fig. 11).

Such condensates actually have been suggested (Kozlov, 1975; Powell and McKirdy, 1975; Connan and Cassou, 1980; Snowdon and Powell, 1982). These condensates often exhibit a peculiar composition which indicates their terrigenous or relatively immature parent material: high pristane/phytane ratio, sometimes higher odd-over-even predominance of n-alkanes.

The carbon isotopic composition of the early condensates also should differ from that of the late condensates. The latter as a rule are en-
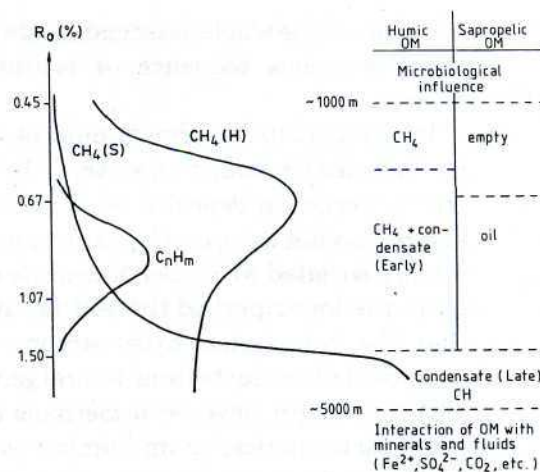

Fig. 11. Proposed hydrocarbon zonality related to katagenetic transformation of organic matter.

riched in the heavy carbon isotope. This is due to active fragmentation of gasoline-range hydrocarbons during the late condensate formation stage. As this process does not occur during the early condensate formation one cannot expect that they would be enriched in the heavy carbon isotope.

Coming back to the discussion on the origin of the West Siberian gas it is noteworthy that the situation described here is intrinsic to the hydrocarbon systems in the sedimentary strata of northern West Siberia.

Supergiant deposits of methane in the Cenomanian with $\delta^{13}C$-values of -50 to $-46\%o$ give an impressive example of an accumulation of gas derived from predominantly humic organic matter in its relatively early stage of transformation ($R_o \simeq 0.4$–0.55%). Some contribution of methane from microbiological processes is conceivable. Methane anomalously enriched in the light carbon isotope ($< -60\%o$) sometimes occurs, usually in small pools. Highly naphthenic condensates with acyclic components amounting from 60% to 95% are intrinsic (although scarce) to the Pokur Suite. These condensates are lacking n-alkanes which probably results from biodegradation (Goncharov, 1987). However, microbiological methane as well as naphthenic condensates are minor con-

tributors to the whole gas-condensate system of the Cretaceous sequence of northern West Siberia.

In contrast to the almost pure methane deposits in the Cenomanian section, the Neocomian hydrocarbon deposits, as it was discussed before, contain wet gas (C_{2+} on average 6–10%) often associated with gas-condensate and some oil in the lower part of the section. It is likely that the Neocomian hydrocarbon system is composed of products from several generations. The first might have been methane and early condensates derived from humic organic matter. The proper source is the moderately mature organic matter in the Vartov Suite ($R_o \simeq 0.55$–0.72%). Also migration of hydrocarbons from the continental Tyumen Suite at the time when its organic matter was at the same maturation stage cannot be discounted. Indeed gas in the Malyshev horizon (J_2bt) is very similar to the gas in the Vartov gas deposits (see Fig. 4). The next conceivable source is a source rock of marine facies of the Bazhenovian Suite and partly the Achimov and Megion Suites. It is reasonable to assume that the sapropelic organic matter in these sediments, at sufficient maturation level, might generate higher gaseous and liquid hydrocarbons which can migrate into the Neocomian system. Migrating gas from the Tyumen Suite through oil-prone sediments of the Upper Jurassic might play a role in the formation of deposits composed of wet gases with high concentration of condensate (up to 600 g m^{-3}) and sometimes with oil in the lower part of the Neocomian. The relative proportion between gas from different sources changes throughout the Neocomian section. This is accordingly reflected in the change of the isotopic composition of the methane (see Fig. 4).

The Tyumen Suite in the uppermost section retains gas derived from humic organic matter similar to the Neocomian gas. Appearance of methane at the deeper horizons ($\sim$4000–4500 m) that is isotopically lighter than methane in the overlying section, despite the increase of maturity of organic matter, is probably due to

beginning destruction of hydrocarbons at those depths. Indeed this is correspondingly accompanied by a divergence of isotopic trends for higher hydrocarbons. Condensates occurring in these layers show an appreciable enrichment in the heavy carbon isotope. That does mean that these are late-stage condensates.

With increasing depth (4500–5500 m) methane again becomes isotopically heavier. The ethane and propane as well as the butane also tend to be heavier. Their carbon becomes noticeably heavier ($\delta^{13}C \simeq -22$ to $-20‰$) than the kerogen carbon ($\delta^{13}C = -26‰$). These trends continue at greater depth ($\sim$5500 m). In addition, concentration of C_2–C_4 begins to decrease. At a level of 4500 m the gas still contains more than 10% of C_{2+} hydrocarbons (e.g., C_2H_6, 9.9%; C_3H_8, 2.9%; C_4H_{10}, 0.7% — Urengoy field, well N282, 4504–4520 m) whereas at a depth of 5500 m the C_{2+} content falls to 3.5% (C_2H_6, 2.9%; C_3H_8, 0.5%; C_4H_{10}, 0.1% — Samburg area, well P-700, 5480–5490 m). This suggests deep degradation of the whole hydrocarbon system.

Thus based on the concept developed here the observed change of isotopic and compositional characteristics of hydrocarbons throughout the section of the Urengoy field may be regarded in terms of change of type and maturation of organic matter at the corresponding depth. This would mean that the hydrocarbons have been accumulated approximately in the same intervals of the section (within 500–1000 m) in which they were generated.

The concept that the gas deposits of northern West Siberia formed through vertical migration of gas from depths of $\sim$4.5–5.5 km (Nalivkin et al., 1969; Yevseyev et al., 1973; Neruchev et al., 1984) and even greater $\sim$7–9 km (Prasolov et al., 1981) is inconsistent with experimental data. It has been inferred from the belief that gas forms mostly at the late stage of organic matter transformation and consequently at great depth.

In the studied section organic matter at depths of $\sim$4500–5500 m has a rank corre-

sponding to R_o-values of 1.75–2.5%. This stage is believed to correspond to the main stage of gas formation. However, this part of the section does not contain appreciable quantities of gas. In addition experimental simulation of carbonization of organic matter and mass-balance calculations (Rogozina et al., 1974) show that organic matter has still a high methane generation potential up to the latest carbonization stage. Obvious disagreement between coalification experiments, in fact carried out under conditions of closed system, and conditions observed in nature is probably due to the fact that under high temperatures organic matter begins to react with oxides like SO_4^{2-}, FeO and even CO_2. Therefore, oxidation of organic matter rather than production of such reduced compounds as methane and other hydrocarbons appears to be characteristic of this stage. This must be especially true for organic matter dispersed in rock. On the contrary, concentrated forms like coal layers and petroleum pools might actually act as sources of gas even at great depth. However, such concentrated forms comprise a negligible volume in the mass balance of organic matter in the sedimentary record.

5. Conclusions

Thus the following conclusions can be drawn:

(1) Humic organic matter can yield at low level of maturity ($R_o = 0.45$–0.7%) amounts of methane sufficient to form supergiant gas fields.

(2) The mechanism of early formation of methane from humic organic matter is probably related to the process of condensation of aromatic structures with heteroatomic substitutions.

(3) A model is suggested based on the concept that methane formation is characterized not by a single activation energy, but by a range of activation energies, with the distribution functions being quite different for different types of organic matter. The model allows the explanation of major empirical trends observed in the isotope geochemistry of gaseous hydrocarbons.

(4) Apart from condensates forming in the final stage of oil formation, early condensates, preceding the oil-window, can form. Their presence is closely associated with early gas formation.

(5) Accumulation of huge gas deposits in the Cretaceous section of the northern part of West Siberia is due to favorable geologic conditions for accumulation and preservation of gas produced from humic organic matter in its relatively early stage of geochemical transformation. These are mainly hydrocarbons generated in situ. There is no indication of migration of gas from great depth as some investigators have suggested.

(6) The existing concept of sequential formation of hydrocarbons should be modified.

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