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Organic Geochemistry 37 (2006) 1200–1262
Organic Geochemistry
www.elsevier.com/locate/orggeochem

Isotope organic geochemistry ☆

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Received 6 October 2005; received in revised form 2 March 2006; accepted 17 April 2006
Available online 14 September 2006

Abstract

The present-day state as well as the history of isotope organic geochemistry is reviewed. Theoretical aspects of isotope fractionation in a system of complex organic molecules, fractionation of carbon isotopes in the biosphere, isotopes as applied to study the transformation of organic matter, geochemistry of oil and gas, evolution of the carbonate–organic carbon system and aspects of astrobiology are considered.

1. Introduction

Alfred Treibs (1934) was the first to discover porphyrins in oil and identified them as derivatives of chlorophyll. This discovery was the starting point of organic geochemistry. During most of its history, the main objectives of organic geochemistry were determining the factors controlling the transformation of biogenic organic matter in the geosphere, hydrocarbon generation and alteration and other aspects advantageous for petroleum exploration. More recently, organic geochemistry has been applied to environmental studies. In the future one can expect significant developments of studies related to the evolution of the biosphere, the origin of life and extraterrestrial material.

The first in-depth isotopic study of petroleum was made by Silverman and Epstein (1958). Then Silverman (1964), Kvenvolden and Squires (1967), Eckelman et al. (1962), Frank and Sackett (1969), Park and Dunning (1961) in the USA, Müller and Wienholz (1967), May et al. (1968) in East Germany, Colombo et al. (1965) in Italy, Welte (1969) in West Germany, Botneva et al. (1969), Alexeyev et al. (1967), Lebedev (1964) in the Soviet Union developed the initial basic knowledge of petroleum isotope geochemistry. During the 1960s our group in the Gubkin's Institute carried out theoretical and experimental studies of isotope fractionation in hydrocarbon systems and studies of oil and gas in the Volga-Ural, Sakhalin and Kaspian regions. The results were published in Galimov (1967, 1968, 1969a,b, 1971), Galimov et al. (1972a,b, 1973a,b) and summarized in Galimov (1973).

☆ Alfred Treibs lecture, Goldschmidt Conference, June 2004, extended and updated by the date of submitting to *Organic Geochemistry*.

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doi:10.1016/j.orggeochem.2006.04.009

Contemporaneously, the study of biomarkers was developing. Isoprenoids and other complex biomarkers such as terpanes and steranes were found in geological samples and used in petroleum geochemistry. Important contributions to the discovery of biomarkers in oil and sediments and their application in petroleum geochemistry were made by Bray and Evans (1961), Meinschein (1961), Blumer et al. (1963), Eglinton and Calvin (1967), Maxwell et al. (1971), Blumer (1973), Petrov et al. (1974), Seifert (1977), Seifert and Moldowan (1978), Ourisson et al. (1979), Simoneit et al. (1973), and Mackenzie et al. (1982). Isotope measurements combined with the study of molecular structures, including those of biomarkers, are a common and very efficient approach in modern organic geochemistry. This paper mainly deals with isotope studies.

Early investigations were mostly based on bulk carbon isotope analysis. Regional and age-dependent variations of petroleum $\delta^{13}C$ values were reported as well as systematic differences in $\delta^{13}C$ values of oil fractions of different molecular weight and of different compound classes of oil, i.e. alkanes, aromatics, and asphaltenes. Isotope geochemistry was recognized by geologists as a useful tool in petroleum exploration but further progress was impeded by several unresolved problems: (1) inadequate background on the isotope chemistry of complex organic compounds, (2) a limited database on the isotopic composition of biological molecules which are potential precursors of petroleum constituents, and (3) poor knowledge of the behavior of isotopes in diagenetic and catagenetic processes.

Therefore, our group in the V.I. Vernadsky Institute decided to study the above problems and then developed models of oil and gas generation. This paper aims to focus on the development of this approach and the progress achieved. The collateral purpose was to bring together and coherently state the results and the ideas scattered throughout different papers and books, some in Russian, which are not easy available. The narrative on contributions from a single scientific school would have little practical value unless stated in the context of the advancements of the scientific field as a whole. Therefore, while this paper is not a comprehensive review of all aspects of organic geochemistry, I attempt to give an idea on the state-of-art in modern isotope organic geochemistry.

2. Theoretical aspects of isotope fractionation in a system of complex organic molecules

Unfortunately even today isotope chemistry is rarely used for interpretation of isotope data in papers dealing with organic geochemistry. The majority of the papers are empirical. Theoretical misinterpretation sometimes occurs. Therefore I believe that a short outline of the theoretical aspects of isotope organic geochemistry is reasonable. I will emphasize notions introduced by my colleagues and myself.

2.1. Thermodynamic isotopic factor (β factor)

By the beginning of the 1970s isotope fractionation coefficients α were known only for systems of simple compounds, containing a single exchangeable atom or equivalent atoms such as CH_4, CO_2, CO, $CaCO_3$, $C_{graphite}$, $C_{diamond}$, and HCN (Urey, 1947; Craig, 1953; Bottinga, 1969). The α value is related to the measurable δ values through a simple approximation:

$$\delta_{AX} - \delta_{BX} \approx (\alpha - 1) \times 10^3‰, \tag{1}$$

where AX and BX stand for the compounds (e.g. CH_4 and CO_2) containing element X (e.g. carbon), of which the isotope composition is under consideration. On the other hand α is theoretically determined as a ratio of values characterizing the isotope thermodynamic properties of the compared compounds. We named the thermodynamic isotopic factor β (β factor):

$$\alpha = \frac{\beta_{AX}}{\beta_{BX}}. \tag{2}$$

In turn

$$\beta_{AX} = \frac{Q_{AX^*}}{Q_{AX}} \frac{s_{AX^*}}{s_{AX}}, \tag{3}$$

where Q_{AX^*} and Q_{AX} are partition function ratios for the isotopic species (e.g. $^{13}CH_4$ and $^{12}CH_4$). The asterisk denotes the rare isotope (^{13}C in the case of carbon). s_{AX^*} and s_{AX} are symmetry numbers.

In the western literature the β notation is not widely accepted. One can instead find the expression $\ln \frac{s^*}{s} f$, which is equivalent to $\ln \beta$. Here f is the reduced partition function ratio Q_{AX^*}/Q_{AX}. Chacko et al. (2001) used the β value, but not with the same definition. They defined β as $f^{1/r}$ which is not applicable to the majority of organic compounds containing non-equivalent exchangeable atoms. Note that we used the designation *f* thereafter in a different meaning, i.e. as an extent of accomplishment of a process.

Urey (1947) and Bigeleisen and Mayer (1947) expressed the relationship of the reduced partition functions in terms of the vibrational frequencies of the isotopic forms. The most common form of this expression is:

$$\beta_{\mathrm{AX}} = \left\{ \frac{Q_{\mathrm{AX}^*}}{Q_{\mathrm{AX}}} \cdot \frac{s_{\mathrm{AX}^*}}{s_{\mathrm{AX}}} \right\} = \prod_{i}^{3N-6} \frac{v_i^* \mathrm{e}^{-\frac{hv_i^*}{2kT}} \left(1 - \mathrm{e}^{-\frac{hv_i}{kT}}\right)}{v_i \mathrm{e}^{-\frac{hv_i}{2kT}} \left(1 - \mathrm{e}^{-\frac{hv_i^*}{kT}}\right)}, \tag{4}$$

where v_i and v_i^* are vibration frequencies of the isotopic forms, h and k are Planck and Boltzmann constants, respectively, T is temperature in Kelvin. The partition function ratio contains a mass term $(m^*/m)^{3/2}$, where m and m^* are the masses of isotopes. However, this term cancels in a ratio of β factors, which defines isotope fractionation for a given element. Therefore, the partition functions are used in the reduced form (Urey, 1947; O'Neil, 1986). Hence, it follows that for a single atom $\beta \equiv 1$ by convention. The partition function ratios for the simple molecules listed above were calculated for a number of publications (Urey, 1947; Craig, 1953; Bottinga, 1969; Hartshorn and Shiner, 1972; Richet et al., 1977).

The isotope fractionation factors of hydrocarbons were unknown. Moreover, the relation between isotope fractionation coefficient (α) and isotopic characteristic (β) for polyatomic compounds containing non-equivalent carbon atoms had not been investigated. If a compound contains equivalent atoms, like carbon in C_2H_6 or oxygen in CO_2, then the β factor of the compound is calculated through β factor of its fully isotopically substituted form (n is the number of carbon atoms):

$$\beta_{\mathrm{AX}_n} = \sqrt[n]{\beta_{\mathrm{AX}_n^*}}. \tag{5}$$

In cases when a compound contains several non-equivalent atoms of an element it forms a multitude of the isotopic forms.

Propane is the simplest hydrocarbon containing non-equivalent atoms of carbon: two peripheral atoms, which are equivalent and the central one, which is different (Fig. 1). The β factors can be calculated for each isotopically monosubstituted form. The β factors of isotopic species substituted in the peripheral carbon atoms of the CH_3 groups are equal ($\beta_1 = \beta_3 = 1.1331$), whereas the β factor of the isotopic species substituted in the central atom is different ($\beta_2 = 1.1493$).

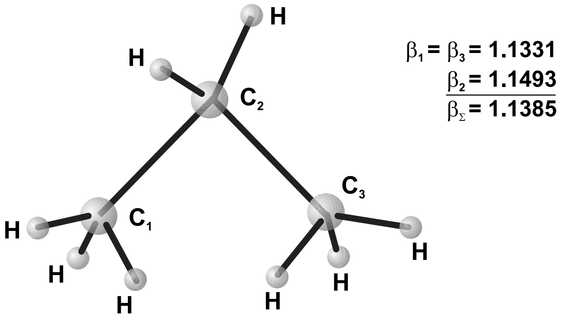


Fig. 1. Non-equivalent carbon atoms in propane.

The question arises of how to express α in this case? What is a quantity characterizing the β factor of the whole compound? I analyzed this problem and found that the β factor of a polyatomic compound cannot be determined adequately just by use of the β factor of its fully isotopically substituted form (Galimov, 1971). The accurate relation between α-value and set of β factors of polyatomic compounds is rather cumbersome. Even in the simplest case of a system containing propane and methane it appears as follows:

$$\alpha_{\mathrm{C_3H_8{-}CH_4}} = \frac{\beta_{1,2,3}}{\beta_{\mathrm{CH_4}}} \times \frac{\frac{3\beta_{1,2,3}^2}{\beta_{\mathrm{CH_4}}^2} R^2 + \frac{2\beta_1^3 + 4\beta_{1,2,3}^3}{\beta_{1,2,3}\beta_1} \frac{R}{\beta_{\mathrm{CH_4}}} + \frac{1}{\beta_{1,2,3}} (\beta_2 + 2\beta_1)}{\frac{2\beta_{1,2,3}^3 + \beta_1^3}{\beta_1} \frac{R^2}{\beta_{\mathrm{CH_4}}^2} + \frac{2\beta_2 + 4\beta_1}{\beta_{\mathrm{CH_4}}} R + 3}, \tag{6}$$

where $\beta_{1,2,3}$ denotes the β factor of the fully substituted form, R characterizes the isotopic ratio. The $^{13}C/^{12}C$ ratio is 0.011. For the other light elements, R is also $\ll 1$. In a good approximation Eq. (6) can be reduced to the simple formula:

$$\alpha = \frac{2\beta_{1(3)} + \beta_2}{3} \cdot \frac{1}{\beta_{\mathrm{CH_4}}}, \tag{7}$$

and in the generalized form the α coefficient for polyatomic compounds can be expressed as the following relationship:

$$\alpha = \frac{\frac{1}{n}\sum_i^n \beta_i(\mathrm{AX}_n)}{\frac{1}{m}\sum_i^m \beta_i(\mathrm{BX}_m)}. \tag{8}$$

Obviously the values in the numerator and denominator characterize the isotopic properties of the compared compounds as a whole. Designating them β_Σ, we obtain

$$\alpha = \frac{\beta_{\Sigma(\mathrm{AX}_n)}}{\beta_{\Sigma(\mathrm{BX}_m)}}. \qquad (9)$$

Thus, the following relationship exists between the thermodynamic isotopic factor of a compound (β_Σ) and their isotopically mono substituted forms (β_i):

$$\beta_\Sigma = \frac{1}{n}\sum_i \beta_i. \qquad (10)$$

I called this relationship a first rule of additivity (Galimov, 1982). The difference between β_Σ values calculated by using Eq. (5) on the one hand and through the accurate formula (Eq. (6)) and its approximation (Eq. (10)) on the other is not significant but it increases with an increase of R and an increasing difference between β_i values of a compound. For the particular case of propane the β_Σ values are to be 1.13847, 1.13899 and 1.13850 from Eqs. (5), (6) and (10), respectively. Note that there is a typographical error on the last page of the original paper (Galimov, 1971), which makes the numerical example presented there unrealistic. The isotope fractionation between propane and methane is $\alpha_{\mathrm{C_3H_8–CH_4}} = \frac{\beta_{\Sigma(\mathrm{C_3H_8})}}{\beta_{\Sigma(\mathrm{CH_4})}} = 1.0223$ (all for 300 K). The data calculated for some other hydrocarbons are presented in Table 1 for selected temperatures. More β factors of hydrocarbons are available from the laboratory database (Polyakov, 1996).

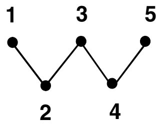
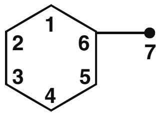
2.2. Intramolecular equilibrium isotope effect

On the basis of considerations presented above the notion on the equilibrium intramolecular isotope effect was introduced (Galimov, 1971, 1974a). The earlier understanding of the term intramolecular isotope effect was related to isotope kinetics (Roginsky, 1956). The difference in isotopic composition of an element in two non-equivalent positions is determined by the relationship of the respective β_i factors:

$$\alpha_{i(1-2)} = \frac{\beta_{i(1)}}{\beta_{i(2)}}. \qquad (11)$$

For the particular case of propane $\beta_{i(\mathrm{CH_2})}/\beta_{i(\mathrm{CH_3})} = 1.1493/1.1331 = 1.0143$ (300 K). Criss (1999) in his recent textbook speculates about intramolecular isotope fractionation as if nothing was known about it, neither theoretically nor experimentally (pp. 75–76). He overlooked the data obtained in isotope organic geochemistry. Some examples of intramolecular isotope distribution in organic molecules will be presented below. Modern instruments allow the study of intramolecular isotope distribution by the direct measurements of the differently substituted isotopic forms (Wang et al., 2004a).

Table 1
Thermodynamic isotopic factors on carbon (β^{13}C factors) of hydrocarbons for selected temperatures (extracted from Galimov, 1973)

Compound	β-factors			
	β_i, β_Σ	Temperature (K)		
		300	400	500
Methane	$\beta_i = \beta_\Sigma$	1.1136	1.0765	1.0554
Ethane	$\beta_i = \beta_\Sigma$	1.1317	1.0861	1.0610
Propane	$\beta_{\mathrm{CH_3}}$	1.1331	1.0867	1.0613
	$\beta_{\mathrm{CH_2}}$	1.1493	1.0956	1.0666
	β_Σ	1.1385	1.0895	1.0680
Butane	$\beta_{\mathrm{CH_3}}$	1.1330	1.0867	1.0613
	$\beta_{\mathrm{CH_2}}$	1.1506	1.0963	1.0670
	β_Σ	1.1419	1.0915	1.0641
Pentane 	$\beta_{\mathrm{CH_3}}$	1.1330	1.0866	1.0613
	$\beta_{\mathrm{CH_{2(2-4)}}}$	1.1506	1.0963	1.0670
	$\beta_{\mathrm{CH_{2(3)}}}$	1.1519	1.0969	1.0674
	β_Σ	1.1450	1.0925	1.0648
Benzene	$\beta_i - \beta_\Sigma$	1.1533	1.0975	1.0679
Toluene 	β_6	1.1677	1.1057	1.0725
	$\beta_{1,5}$	1.1545	1.0982	1.0680
	β_7	1.1293	1.0840	1.0593
	β_Σ	1.1527	1.0972	1.0674
Cyclohexane	$\beta_i = \beta_\Sigma$	1.1544	1.0983	1.0683

2.3. Isotopic bond numbers approximation

In order to calculate β factors from Eq. (4) one needs to know vibrational frequencies of the isotopic forms of molecules (v and v^*). They can be found by solving the equation of molecular motion (secular equation). Even in the ideal gas approach calculation of the β factor in this way has limitations. The significance of these limitations increases with increasing complexity of the organic compounds. Having dealt with the study of hydrocarbons and other multi-carbon organic molecules in the 1960s and 1970s I tried to find an approximation technique that would allow evaluation of β^{13}C factors. Eventually I came to the formulation of the method of *isotopic bond numbers* (Galimov, 1972, 1973, 1982, 1985; Polyakov, 1990, 1991).

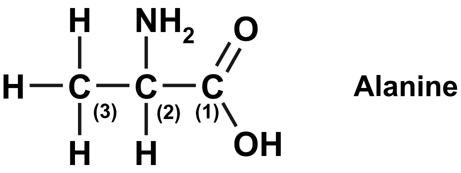
It should be noted that in the literature, particularly in the 1970s, there were many attempts to simplify the complicated procedure of calculating β factors, avoiding the necessity in each case to solve the complete system of equations for vibrational motion. Bigeleisen with co-authors (e.g. Ishida et al., 1969; Bigeleisen and Ishida, 1973; Bigeleisen et al., 1976) proposed some useful approximations. The additive method of isotopic bond numbers is not all-purpose, but it seems to be the simplest method and the most convenient one for estimating the β^{13}C-factors of carbon in complex compounds. It was acknowledged by Bigeleisen et al. (1976) that "The presented numerical examples complement the preceding theoretical confirmations [references 8 and 18 in the cited work] of Galimov's method for estimating the values of $\ln(s/s^{*})f$ in a wide range of carbon compounds by means of summing the bond numbers".

The detailed review of the isotopic bond numbers method is given in a monograph (Galimov, 1985). According to this method, the β_i factor of a mono-substituted isotopic form can be determined using the following expression:

$$\beta_i = 1 + \sum_j L_j^n + \sum_k l_k, \qquad (12)$$

where L_j is a value characterizing the jth of n bonds formed by the ith atom, to which the β_i factor is related, and l_k is a value which accounts for "distant surroundings". The l_k-value is more than an order of magnitude smaller than the respective L_j value. The l_k-value depends on the type of bond formed by the partner atoms.

Table 2 contains L_j and l_k values for different types of bonds formed by carbon for 300 K. Fig. 2 shows a comparative evaluation of β_i values for alanine by using the method of isotopic bond numbers and by solution of problems of vibrational motion of the alanine molecule. It is seen that the corresponding values are in a good concordance. Polyakov and Kharlashina (1986) and Polyakov (1990, 1991) provided a more vigorous justification of the isotopic bond numbers than I formerly did and calculated the temperature dependence of L_j-increments (Fig. 3). The advantage of the method of the isotopic bond numbers is that it can be used for evaluating the isotopic thermodynamic properties of complex biopolymers like peptides or lipids, which cannot be determined by any other way.



	Isotopic bond numbers	Solution of the secular equation
$\beta_1=1+L_{C=O}+L_{C-O}+L_{C-C}+l_{C-N}+l_{C-C}$ =	1.202	(1.197)
$\beta_2=1+2L_{C-C}+L_{C-N}+L_{C-H}+l_{C=O}+l_{C-O}$ =	1.180	(1.179)
$\beta_3=1+L_{C-C}+3L_{C-H}+l_{C-C}+l_{C-N}$ =	1.137	(1.139)
β_Σ =	1.173	(1.172)

Fig. 2. An example of the calculation of $\beta_i{}^{13}$C and $\beta_\Sigma{}^{13}$C factors of alanine using isotopic bond numbers. On the right (in parentheses) the corresponding values obtained by Polyakov and Kharlashina (1994) by solution of the equation of the vibration motion of alanine are presented for comparison.

Table 2
Isotopic bond numbers for carbon at 300 K (extracted from Galimov, 1985)

L_{C-X}		l_{C-X}	
Symbol	Value	Symbol	Value
L_{C-H}	0.0284	l_{C-H}	0
L_{C-C}	0.0464	l_{C-C}	0.0013
$L_{C=C}$	0.0785	$l_{C=C}$	0.0016
$L_{C\equiv C}$	0.088	$l_{C\equiv C}$	0.0002
L_{C-N}	0.050	l_{C-N}	0.0016
$L_{C=N}$	0.079	$l_{C=N}$	0.0016
$L_{C\equiv N}$	0.090	$l_{C\equiv N}$	0.0003
L_{C-O}	0.055	l_{C-O}	0.0019
$L_{C=O}$	0.096	$l_{C=O}$	0.0028

2.4. The rate of isotope exchange in a hydrocarbon system

Carbon isotopes easily exchange in a system such as CO_2–HCO_3^-–CO_3^{2-}. The equilibrium can be

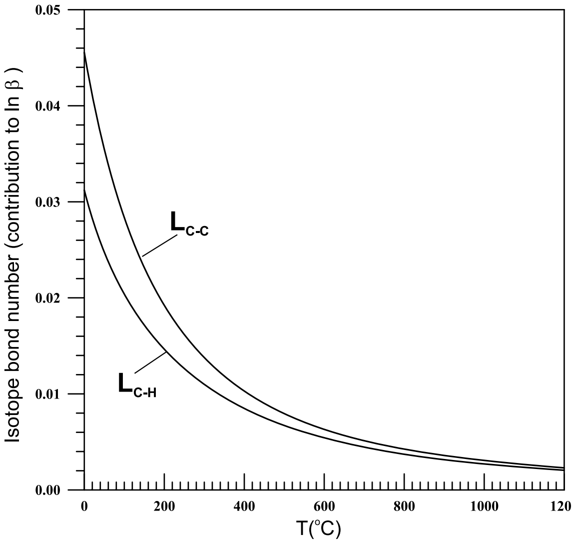


Fig. 3. Temperature dependence of the isotopic bond numbers L_{C-H} and L_{C-C}.

attained within hours and in part of the system within seconds (Skidmore et al., 2004). However, isotope exchange between hydrocarbons is very slow. Even for hydrogen atoms it takes on the order of millions of years under natural conditions. Normal alkanes preserve their δD values for 15–20 Ma (Yang and Huang, 2003) and even as long as 260–280 Ma (Dawson et al., 2004). Carbon atoms are even more resistant to isotope exchange. Experiments showed that any alteration of the carbon isotope composition in the CH_4–C_2H_6–C_3H_8–C_4H_{10} system does not occur at temperatures lower than 300 °C over 4 h (Galimov et al., 1972b). At 500 °C all the C_1–C_4 hydrocarbons become isotopically heavier by 1–2‰. This is due to a kinetic isotope effect during decomposition of the hydrocarbons, associated with the formation of pyrobitumen. The latter incorporates the isotopically light fragments of the decomposed molecules. In a natural system this type of isotope fractionation is observed during thermal alteration of oil and condensate formation (Galimov, 1973). Recently, Hill et al. (2003) experimentally studied cracking of oil hydrocarbons with increasing thermal stress and reported the same results.

CH_4–CO_2 is an important natural system. Under dry conditions there is no indication of isotope exchange between CO_2 and CH_4 at temperatures as high as 600 °C (Sackett and Conkright, 1997). In the presence of water isotope exchange occurs at a much lower temperature (Giggenbach, 1997). We used water as a possible carbon isotope exchange intermediate in our experimental study of C_1–C_4 hydrocarbons. At 500 °C water facilitates some isotope exchange (Galimov et al., 1972b). Transition metals (Ni, Pt, Pd, etc.) may catalyze the isotope exchange reactions. That carbon isotope equilibrium between CO_2 and CH_4 can be attained was experimentally demonstrated for a temperature as low as 200 °C (Horita, 2001).

2.5. The kinetic isotope effect

The kinetic isotope effect is caused by differences in the reaction rates of isotopic forms. Reactions with isotopically light species are usually faster than those that are isotopically heavy. The kinetic isotope effect α_k is determined by the ratio of the reaction rate constants of the isotopic species,

$$\alpha_k = \frac{k^*}{k}, \tag{13}$$

and may be expressed through the difference of activation energies of the reactions of the isotopic forms,

$$\alpha_k = \left(\frac{\mu}{\mu^*}\right)^{1/2} \exp -[(E^* - E)/RT], \tag{14}$$

where μ and μ^* are reduced masses of the moieties of a molecule connected by the breaking bond. To avoid confusion it should be noted that in the early literature α is used as the ratio of the rate constant of the faster reaction to that of the slower reaction. However, in modern nomenclature of isotope chemistry the rare isotope (X^*) appears in the numerator (R^*/R, β^*/β, etc.). Therefore, to maintain uniformity, the kinetic isotope effect should be presented in the form of k^*/k rather than k/k^*, and the numerical values of kinetic isotope effects will often be lower than unity.

The calculation of kinetic isotope effects is accomplished in the framework of the complex transient theory, which yields an expression including vibrational frequencies of transient complexes, which are usually unknown (Melander, 1960). By assuming that all vibrational terms except one, which corresponds to the vibration of the bond broken in the reaction, are canceled out, the general expression for the kinetic isotope effect may be reduced to the Eyring–Keugel relationship (see Melander and Saunders, 1987).

In the same approximation the following expression for calculation of the kinetic isotope effect through the isotopic bond numbers was suggested (Polyakov and Galimov, 1992):

$$\alpha_k = \left(\frac{\mu}{\mu^*}\right)^{\frac{1}{2}} \left(1 - \frac{L'_j}{\beta}\right), \tag{15}$$

where L'_j is the L_j value of the broken bond. Previously, Sundberg and Benett (1983) showed that the isotopic bond numbers may be successfully used for calculation of the kinetic isotope effect.

2.6. Isotope fractionation between product and substrate in the course of a process

If an isotope effect α occurs during the formation of a product (P) from a substrate (S), then their isotopic compositions change as a function of the extent (f) of the reaction (Fig. 4a). The value of f changes from zero at the beginning of the process to unity at its completion. Conventionally,

$$R_{[P(f)_i]} = \alpha R_{S(f)} \tag{16}$$

and when $f \to 0$, $R_{S(f)} \to R_{S(0)}$, α of the process can be measured through the isotopic composition of the product released at the initial stage of the process related to the isotopic composition of the initial substrate.

During the process isotope compositions of the product and the substrate are determined in accordance with the formulae below:

(a) Isotopic composition of the product $R_{P(f)}$ accumulated at the time f relative to that of the initial substrate $R_{S(0)}$:

$$R_{P_{(f)}} = R_{S_{(0)}} \frac{1}{f}[1-(1-f)^{\alpha}]$$
$$\delta_{P(f)} = \delta_{S(0)} + \left\{\frac{1}{f}[1-(1-f)^{\alpha}]-1\right\} \times 10^{3}\text{‰}. \tag{17}$$

It follows from Eq. (17) that in the case of full consumption of the substrate $R_{P(f=1)} = R_{S(0)}$.

(b) Isotopic composition of the residue of the substrate ($R_{S(f)}$) at the time f relative to that of the initial substrate:

$$\begin{aligned} R_{S(f)} &= R_{S(0)}(1-f)^{\alpha-1} \\ \delta_{S(f)} &= \delta_{S(0)} + [(1-f)^{\alpha-1}-1] \times 10^{3}\text{‰}. \end{aligned} \tag{18}$$

(c) Isotopic composition of the initial substrate as reconstructed from the measured isotopic composition of its residue and the product accumulated at the time f:

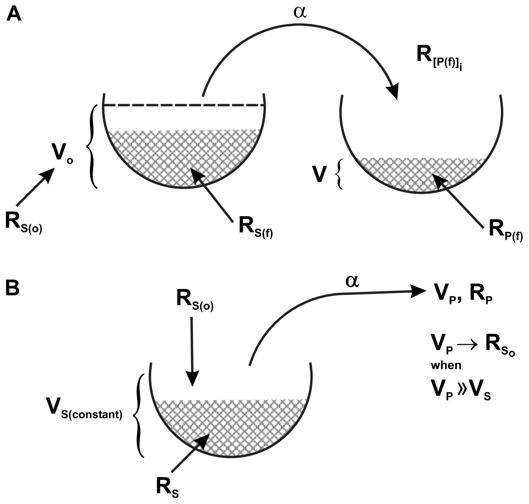


Fig. 4. Isotope fractionation between product and an initial substance in the course of a process: (A) Rayleigh distillation model. (B) Distillation with total reflux. Parameters are explained in the text.

$$\begin{aligned} R_{S(0)} &= R_{p(f)}f + R_{S(f)}(1-f) \\ \delta_{S(0)} &= \delta_{p(f)}f + \delta_{S(f)}(1-f). \end{aligned} \tag{19}$$

(d) Instantaneous isotopic composition of the increment of the product $R_{[P(f)]i}$ removed by the time f relative to the initial isotopic composition of the substrate:

$$\begin{aligned} R_{[P(f)]i} &= R_{S_0} \cdot \alpha(1-f)^{\alpha-1} \\ \delta_{[P(f)]i} &= \delta_{S(0)} + [\alpha(1-f)^{\alpha-1}] \cdot 10^{3}\text{‰}. \end{aligned} \tag{20}$$

The extent of the isotope fractionation depends on the size of the isotope effect α and the coefficient f. The coefficient f in dependence of a type of a process may stand for the accomplishment of the reaction, the coefficient of utilization, the availability of a substrate, the measure of evaporation, etc. Rayleigh was the first to study this mechanism of fractionation for the distillation process. The isotope effect α may have both kinetic and isotope exchange character. In the latter case the product should be immediately removed from the system (for a natural example see Galimov, 1991).

2.7. *"Distillation with total reflux"*

In a steady-state process the amount of material in an intermediate reservoir stays constant, as the entering flux is equal to the outgoing flux (Fig. 4b). Then, regardless of the isotope fractionation effect, the isotopic composition of the reservoir remains unchanged provided that the amount of the flowing material (V_P) significantly exceeds the mass of the reservoir (V_S). In this case the isotopic composition of the entering (R_{S_0}) and outgoing (R_P) materials are equal: When $R_P \to R_{S_0}$, then $\delta^{13}C_P \to \delta^{13}C_{S_0}$. The isotopic composition of the intermediate is determined by the isotope effect of the process: $R_S \to R_P/\alpha_P$.

2.8. *Isotope fractionation in a stepwise process*

During dissolution of a crystal, isotope fractionation is small or absent, although at the very beginning of the process the observed effect might be significant. This is because the dissolution occurs "layer-by-layer". Even if α_k is significant, the resulting isotope effect tends to be zero as ultimately the entire layer goes into solution. In one of their recent works, Skidmore et al. (2004) studied the kinetic isotope effect during carbonate dissolution. In the initial stage a kinetic isotope effect as high as $-17.4‰$ was observed. However, it faded with time and disappeared after several hours (6–24 h) (Skidmore et al., 2004). This means that steady-state dissolution proceeded layer by layer. The same effect may occur during evaporation of a solid or liquid if the rate of transfer is less than the rate of evaporation. Young (2000) quantified this effect as a function of rates of evaporation and the surface diffusion.

2.9. Effect of a band of activation energies

As has been mentioned above the isotopic composition of methane produced from kerogen under natural conditions or by pyrolysis of organic matter in experiments shows much less depletion in the ^{13}C isotope than is predicted from calculation of the kinetic isotope effect for the corresponding temperature (Galimov, 1973, p. 293). At the same time, methane produced by the decomposition of an individual compound (not of a polymer like kerogen) is depleted in the heavy carbon isotope in accordance with the theoretical calculation (e.g. Frank and Sackett, 1969; Rohrback, 1979). Initially, I tried to explain this fact by the radical mechanism of gas formation (Galimov, 1973). Subsequently, I suggested that the formation of a product generated by decomposition of an irregular macromolecular substance like natural kerogen may proceed through a number of parallel reactions and, thus, should be characterized by a band of activation energies instead of single activation energy like in the case of decomposition of an individual compound (Galimov, 1974b).

Theoretical analysis of this problem showed that in a series of parallel reactions the effective isotopic fractionation is a function of the width of activation energy distribution, and, indeed, a significant decrease in isotope effect occurs when a band of activation energies is involved (Fig. 5). This explains the reduced isotope effect in the products of degradation of natural organic polymers (kerogen). In particular, it became clear why methane produced during decomposition of oil hydrocarbons is isotopically lighter than methane produced from kerogen at the same temperature (Galimov, 1973). Moreover, activation energies within the band may be distributed differently for substances of different chemical structures. This explains some important features of gas isotope geochemistry (Galimov, 1988b) considered below in the section on the geochemistry of the natural gas formation.

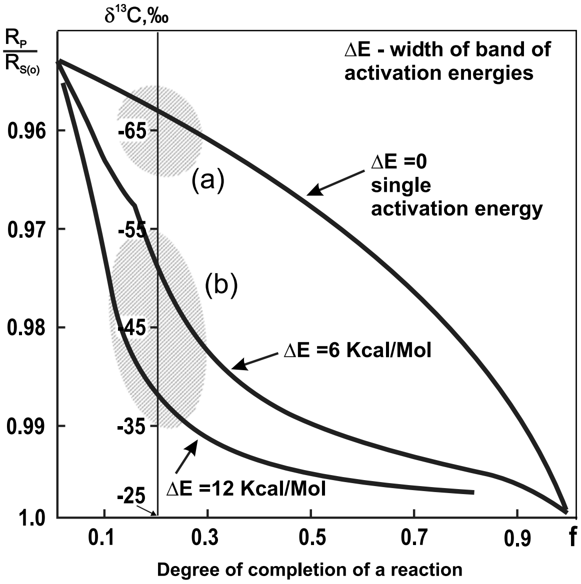


Fig. 5. Effect of a band of activation energies (Galimov, 1974). The hatched area "a" shows the grouping of $\delta^{13}C$ values obtained in experimental decomposition of individual compound (extrapolated to 300 K, e.g. Frank and Sackett, 1969; Rohrback, 1979); the hatched area "b" shows the grouping of $\delta^{13}C$ values typical for natural gases.

3. Fractionation of isotopes in the biosphere

3.1. CO_2 in atmosphere and ocean

The atmosphere contains about 0.7×10^{18} g of carbon as CO_2, and the ocean 35×10^{18} g mainly in the form of HCO_3^-. Interaction between the carbon species of the atmosphere and the ocean proceeds within the following system:

$$CO_{2(gas)} \leftrightarrow CO_{2(aq)} \tag{a}$$

$$CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3 \tag{b}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{c}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{d}$$

The turnover time between the atmosphere and the surface layer of the ocean is 5–8 years (Bolin et al., 1979; Tans et al., 1993). Isotope fractionation in this system results in the enrichment of carbonates in ^{13}C. In experiments HCO_3^- is enriched in ^{13}C by about 8‰ compared to dissolved CO_2 (Mook et al., 1974).

In the present atmosphere $\delta^{13}C$ of CO_2 is about $-7.8‰$ (Friedli et al., 1986), and $\delta^{13}C$ of HCO_3^- in the ocean is estimated to be $-2‰$ on average (Craig, 1953). The isotopic composition of the total carbon in the Earth's exospheric reservoir, including the atmosphere, hydrosphere, the living matter, and the short-term recycled carbon in the subsurface layer of the land and marine deposits, was estimated to be $\delta^{13}C = -3‰$ (Galimov et al., 1975).

The biological fractionation of isotopes leads to depletion of the biosphere carbon in ^{13}C whereas the isotope exchange of inorganic carbon in the atmosphere–hydrosphere system leads to concentration of ^{13}C in sedimentary carbonates (Fig. 6). The carbon isotopic composition of the present-day carbonates varies around $\delta^{13}C = 0‰$. The isotopic composition of the total organic carbon in the exospheric reservoirs is about $\delta^{13}C_{org} = -22‰$ (Galimov, 1999). Thus, the overall isotope fractionation factor between organic carbon and average carbon of the reservoir is about $\delta^{13}C \cong 19‰$.

During 50 years of direct monitoring of $\delta^{13}C$ of the atmospheric CO_2 a progressive depletion in ^{13}C by about $-1.3‰$ was recorded (Keeling, 1961; Friedli et al., 1986). Data on the $\delta^{13}C$ variations of CO_2 during the last hundreds years are available from the study of tree rings (Farmer and Baxter, 1974; Pearman et al., 1976; Galimov, 1976; Freyer, 1979; Sheu et al., 1996). Evolution of CO_2 content and its isotopic composition during thousands and hundred thousands of years is presently known from the study of the air trapped in ice cores obtained by drilling of the Antarctica and Greenland ice sheets (Barnola et al., 1987; Jouzel et al., 1996; Raynaud et al., 1996; Petit et al., 1999).

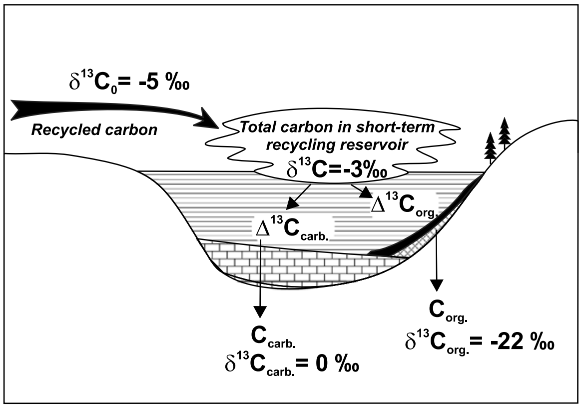


Fig. 6. Isotopic balance in a steady state of carbon fluxes in the Earth's exosphere: the "distillation with the total reflux" model is applied.

There are differences of the air CO_2 between marine, rural urban and industrial areas as well as seasonal and daily variations (Keeling, 1958; Keeling et al., 1989; Galimov, 1966; Keeling et al., 1979; Mook et al., 1983; Quary et al., 1992; Clark-Thorne and Yapp, 2003; Widory and Javoy, 2003). Plants inherit these differences. Some organisms feed on unusual substrates. For example methane-oxidizing archaea produce extremely isotopically light compounds (isoprenoid ethers, crocetane, etc.) with $\delta^{13}C$ values as low as $-50‰$ to $-70‰$ and down to $-100‰$ (Summons et al., 1994; Thiel et al., 1999).

3.2. Isotope fractionation between organisms and environment

Among the terrestrial plants two major isotopic categories can be distinguished according to their mode of CO_2 fixation (Bender, 1971; Smith and Epstein, 1971; O'Leary, 1981). The more common C_3 plants incorporate CO_2 by ribulose biphosphate carboxylation (Calvin cycle). C_4 plants are represented, for example, by maize and often by savanna and desert vegetation. They have $\delta^{13}C$ values of about $-12‰$ on the average and fix CO_2 through phosphoenol pyruvate carboxylation (Hatch–Slack cycle). There is also relatively small group of the crassulacean acid metabolism (CAM) plants. They are represented by succulents and have isotopic compositions intermediate between C_3 and C_4 plants. C_3 plants annually assimilate 119×10^{15} g of CO_2 carbon whereas 31×10^{15} g/year are fixed by C_4 plants (Lloyd and Farquhar, 1994). The contribution of CAM plants to the annual biomass production is insignificant. The average carbon isotope fractionation during photosynthetic assimilation of CO_2 is about $-18‰$ to $-20‰$ for C_3 plants and about $-4‰$ to $-5‰$ for C_4 plants.

It has been shown that autotrophic pathways of carbon fixation through the tri-carboxylic acid cycle (3-hydroxypropionate cycle) and reductive acetyl-CoA exhibit systematic differences in their degree of carbon isotope fractionation (Preuss et al., 1989; House et al., 2003). For example, lichens are less depleted in ^{13}C as compared with the other plants growing on the same piece of land (Galimov, 2000b).

Isotope fractionation during photosynthesis is a complex superposition of the isotope effects in different processes including diffusion from atmosphere, CO_2 uptake by chloroplasts, enzymatic carboxylation, photorespiration and respiration.

Isotope fractionation during primary fixation of carbon was widely considered and debated in the literature (e.g. O'Leary, 1981; Farquhar, 1989; Ehleringer et al., 1993).

The main factor, which often controls the isotope fractionation between organism and environment, is the efficiency of CO_2 uptake. For example, during a plankton bloom the depletion in ^{13}C of the biosynthesized organic matter becomes less significant due to depletion of the bicarbonate pool in the water (Schidlowski et al., 1984; Revill et al., 1994; Schouten et al., 2001; Simoneit et al., 2005). The lower $\delta^{13}C$ values of plankton in oceanic water of the temperate regions ($-20‰$ to $-23‰$) and the high latitudes ($-23‰$ to $-26‰$) compared to the equatorial waters ($-18‰$ to $-20‰$) are due to better solubility of CO_2 in colder water and consequently a higher concentration and hence availability (lower f) of CO_2 for the marine organisms (Rau et al., 1989).

Carbon isotopic compositions of living organisms vary according to the environmental conditions, and therefore the isotope analysis of sedimentary organic carbon is often used for paleoenvironmental reconstructions (Popp et al., 1997; Dawson et al., 2002). However, it should be kept in mind that $\delta^{13}C$ signatures are complex and related to a number of factors including variations of the source carbon availability, its initial $\delta^{13}C$ value, the internal isotope heterogeneity of the biomass, and different stabilities of organic compounds in degradation processes. The difference in the isotopic composition of C_3 and C_4 plants is widely used as a paleoenvironmental indicator of climate change, type of vegetation, diet of animals, etc. (e.g. Zhao et al., 2003; Jim et al., 2004). However, it has been shown that chars derived from C_4 grasses are significantly ^{13}C-depleted relative to the biological source (Krull et al., 2003). This may lead to errors in estimating the C_3–C_4 plant proportion in the geological past.

3.3. *Isotope heterogeneity of biological material*

The early works established depletion of lipids in the heavy carbon isotope (Park and Epstein, 1960) compared to the bulk isotopic composition of the organism, and, in contrast, the relative enrichment in the ^{13}C isotope of proteins and carbohydrates (Degens, 1969). Significant variations of $\delta^{13}C$ in individual amino acids were reported (Abelson and Hoering, 1961). Lignin is isotopically lighter than are polysaccharides (Galimov, 1985; Benner et al., 1987). Subsequently, many other examples of isotope heterogeneity in biological compounds were reported (Gleixner et al., 1998; Schmidt and Gleixner, 1998; Chikaraishi, 2003).

3.4. *$\delta^{13}C$–$\beta^{13}C$ correlations in biomolecules*

Initially, there was a common belief that the numerous processes in an organism should result in a complex and unpredictable isotope distribution in biological material. However, our studies showed the existence of a remarkable relationship. The development of the method of isotopic bond numbers, described above, allowed the evaluation of the $\beta^{13}C$ factors of complex organic molecules. When we applied it to biological compounds, their carbon isotopic composition revealed a correlation with the $\beta^{13}C$ value of the respective carbon both at intermolecular and intramolecular levels. The experimental data and the relevant theoretical consideration are presented in Galimov (1985). Several examples are given in Figs. 7–10.

For the first time the $\delta^{13}C$–$\beta^{13}C$ correlation was shown for lipids (Galimov and Shirinsky, 1975). For all four selected organisms there is a $\delta^{13}C$–$\beta^{13}C$ correlation (Fig. 7) with the following regression equation:

$$\delta^{13}C = \delta^{13}C_0 + æ(\beta^{13}C - \beta^{13}C_0) \times 10^{-3}, \qquad (21)$$

where $\delta^{13}C_0$ and $\beta^{13}C_0$ are the averaged values for the system under consideration. This regression equation is equivalent to Eq. (1) defining the thermodynamic isotope effect except for the coefficient æ. The coefficient æ varies within the range of 0.31–0.55 in the presented examples (instead of a unity value, which is characteristic of the equilibrium state).

The intramolecular carbon isotope distribution was studied in chlorophyll and hemine molecules (Bogacheva and Galimov, 1979; Bogacheva et al., 1980; Fig. 8a). Meinschein and coworkers from Indiana University studied intramolecular isotope effects in acetoin (Fig. 8b) and malic acid (Fig. 8c) and concluded that "the ^{13}C contents of the specific carbon atoms in malic acid from apple and sorghum increase in accordance with their β values, as predicted by Galimov" (Meinschein et al., 1984, p. 346).

During the last 10–15 years the most significant results in the field of the intramolecular isotopic study of biomolecules were obtained by the Schmidt

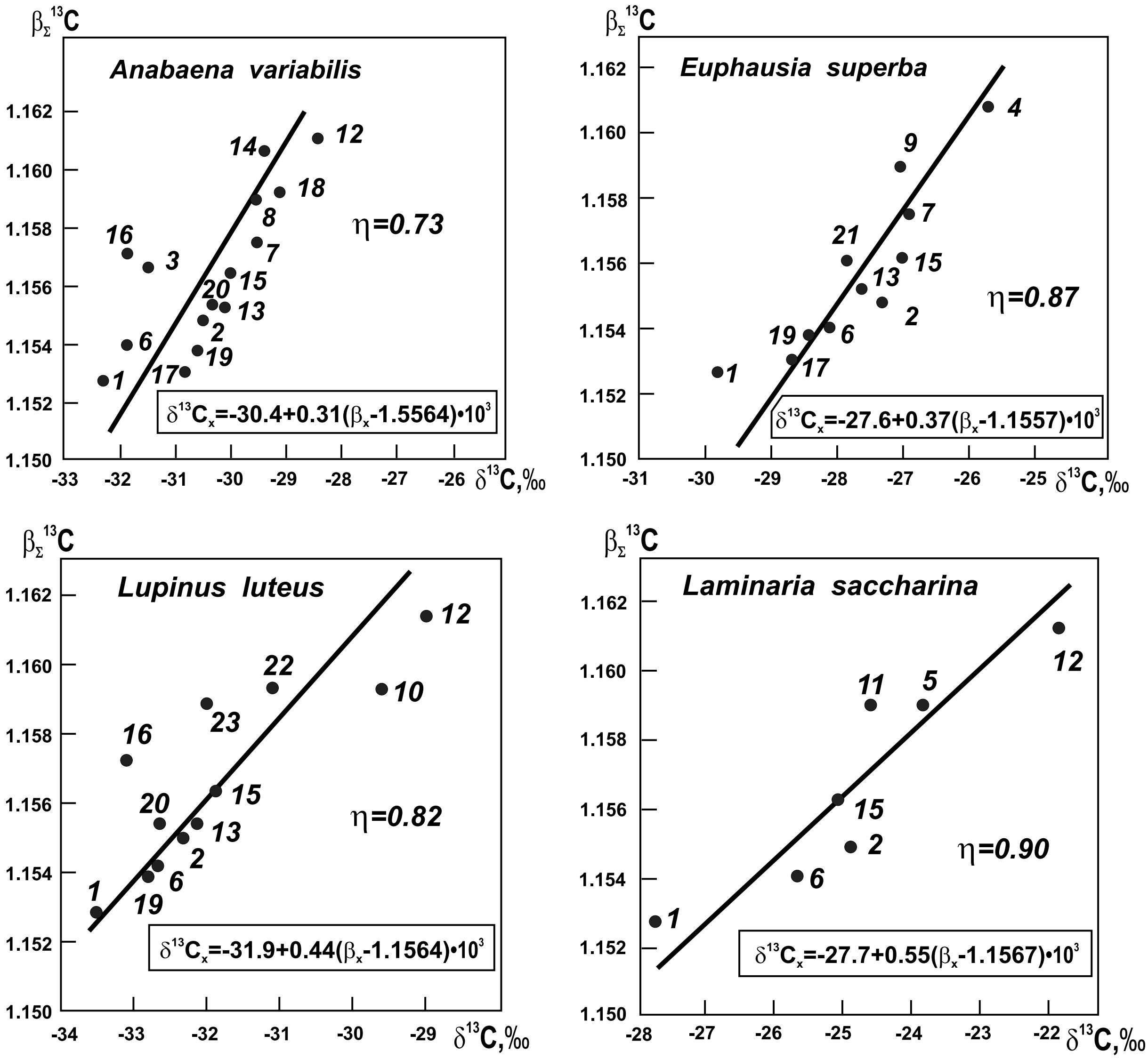


Fig. 7. $\beta_\Sigma{}^{13}$C–δ^{13}C correlation of components of the lipid fraction extracted from blue–green alga (*Anabaena variabilis*), krill (*Euphausia superba*), lupine (*Lupinus luteus*) and laminarian (*Laminaria saccharina*): 1. waxes, hydrocarbons, alcohols; 2. triglycerides; 3. β-carotene; 4. astatine; 5. carotenoid (fucoxanthine); 6. fatty acids; 7. carotenoid (echinenone); 8. sterols; 9. cholesterol; 10. β-sitosterol; 11. fucosterol; 12. chlorophyll; 13. diglycerides; 14. carotenoid (myxoxanthophyll); 15. monoglycerides; 16. phosphatidylserine; 17. sphingomyelin; 18. phosphatidylinositol; 19. lecithin; 20. cephalin; 21. cardiolipin; 22. lutein; 23. monogalactosyl glyceride (after Galimov and Shirinsky, 1975). The regression equations are shown in the boxes; η is the correlation coefficient.

group at the Technical University in Munich. The δ^{13}C–$\beta_i{}^{13}$C correlation is observed, yet rather weak, in the glucose (Fig. 9a) but stronger in the citric acid (Fig. 9b). Intramolecular isotope heterogeneity may exceed the environmental isotope variations related to geographical origin of the studied samples (Fig. 9c). The amino acids show clear δ^{13}C–$\beta_\Sigma{}^{13}$C (Fig. 10).

It was argued that the observed δ^{13}C–β^{13}C correlation is characteristic of a system of enzymatic reactions in a steady-state condition (Galimov, 1985; Galimov and Polyakov, 1990). This does not mean that all biochemical reactions must show such a relationship. Many processes in organisms are essentially irreversible and non-linear, and not in a steady state.

The origin of the δ^{13}C–β^{13}C correlation is still a matter of dispute (Monson and Hayes, 1982; O'Leary, 1988; Schmidt and Kexel, 1998; Hayes, 2001; Buchachenko, 2003; Schmidt, 2003). The

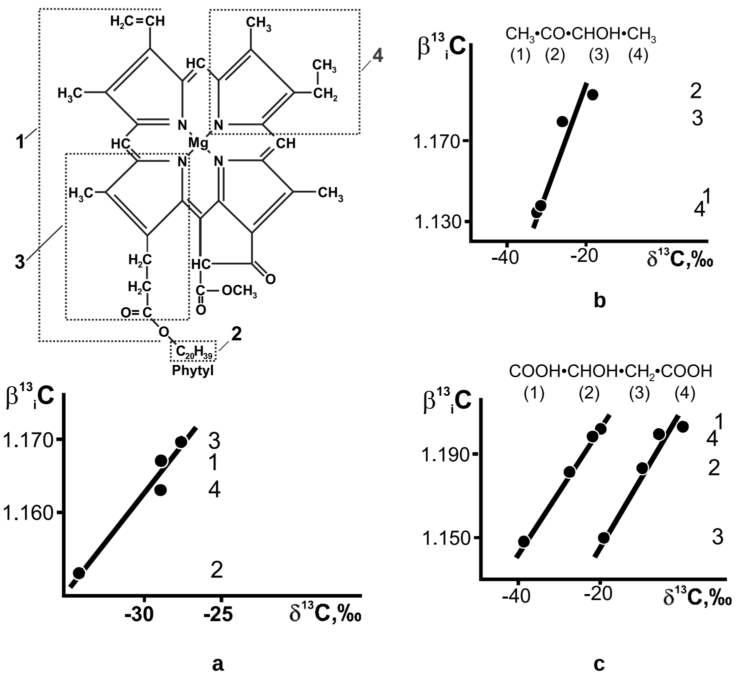


Fig. 8. Intramolecular $\beta_i{}^{13}$C–δ^{13}C correlation: (a) intramolecular carbon isotope distribution in chlorophyll (Bogacheva and Galimov, 1979); (b) intramolecular carbon isotope distribution in acetoin (experimental data by Rinaldi et al., 1974); (c) malonic acid from a C_3 plant (apple) on the left and a C_4 plant (sorghum) on the right (Meinschein et al., 1984).

major objection is that biological isotope effects are mostly kinetic rather than thermodynamic. Indeed, pure kinetic isotope effects occur in biological processes. Moreover, the theoretical expression for isotope effects in enzymatic reactions contains both the terms for thermodynamic and kinetic isotope effects (Galimov, 1985). The point is that biochemical reactions probably contain a component of reversibility in an enzyme–substrate complex even in irreversible net reactions. This leads to the "thermodynamically ordered" (equilibrium-like) isotope distribution, which is expressed in the δ^{13}C–β^{13}C correlation despite many factors which cause deviations from this relationship. It is commonly believed that there is no natural system farther from equilibrium than biological systems of living organisms. In fact, biochemical reactions per se are rather primitive and may proceed not far from equilibrium. But the system of enzymes is sophisticated. The highly organized appearance of a living entity is due to its genetic plan, which an organism carries in the form of DNA. This plan is the result of billions of years of evolution. The biosynthesis is similar to the conveyer assemblage. Each worker (analog of an enzyme) controls a simple operation. But together, they assemble a complex machine following to an algorithm prescribed by the project.

In a living organism full steady state conditions comprising the entire biological system are never achieved. Biosynthesis of some compounds is related to specific pathways and sources. For example, some hopanoids are significantly depleted in ^{13}C because methane-derived carbon is involved in their biosynthesis (Summons et al., 1994; Thiel et al., 1999; Crossman et al., 2001). Similar compounds in other organisms may show different isotopic compositions when they form by different metabolic pathways (Chikaraishi, 2003).

In a particular biosystem the β^{13}C–δ^{13}C correlation may be complicated or completely deteriorated by different kinetic isotope effects. Nevertheless, under geological conditions organic matter integrates biomass of many organisms and the relationship, which we call the biological trend, clearly manifests itself. For example, the carboxyl group may not be ^{13}C-enriched in a particular organic acid. However, CO_2 released during kerogen pyrolysis is always isotopically heavier than the total kerogen carbon, whereas the hydrocarbons are isotopically light (Tocque et al., 2005). Franks

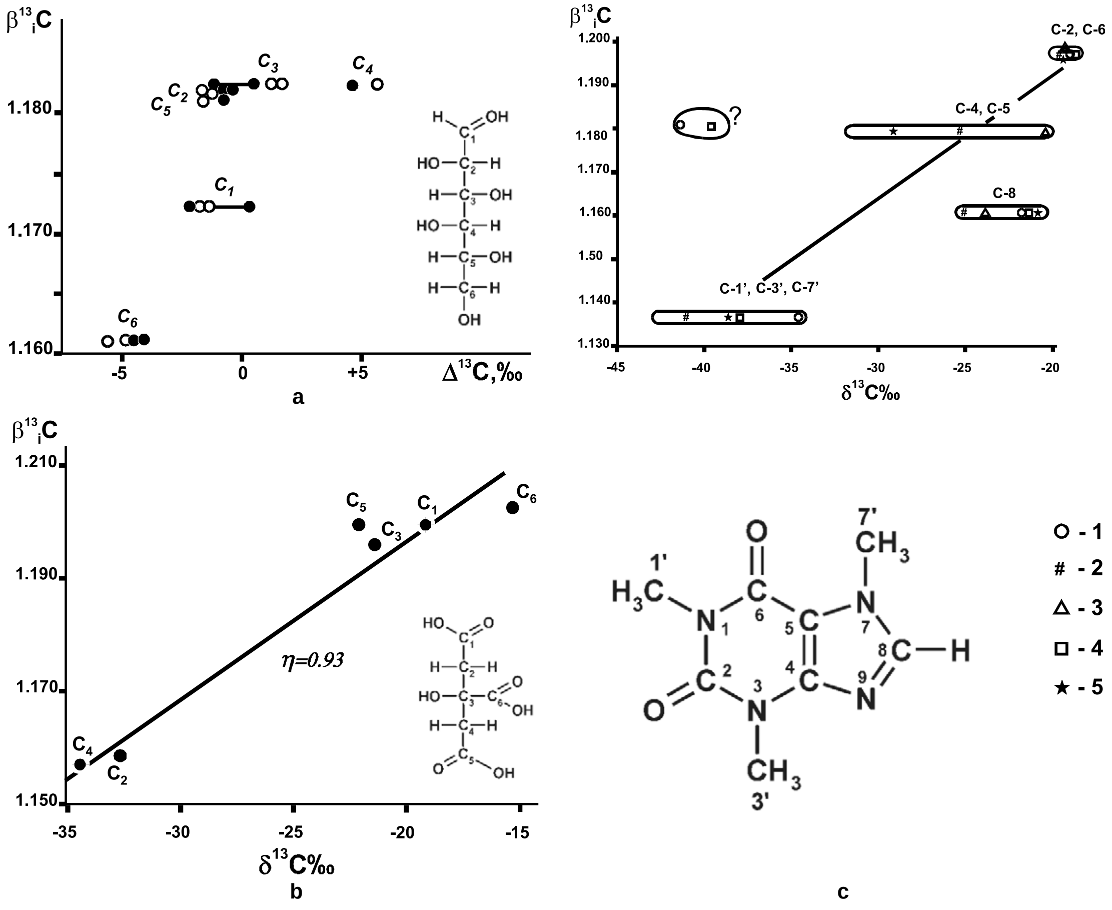


Fig. 9. Intramolecular $\beta_i{}^{13}C$–$\delta^{13}C$ correlation: (a) glucose, extracted from the C_4 plant maize (filled symbols) and the C_3 plant beet (open symbols); the measured $\delta^{13}C$ values are adopted from Rossmann et al. (1991); (b) citric acid; measured $\delta^{13}C$ values from Schmidt and Gleixner (1998); (c) purine alkoloid (caffeine) from different geographical locations: 1 – Sri Lanca; 2 – Darjeeling; 3 – Assam, 4 – China, 5 – USSR; measured $\delta^{13}C$ values from Weilacher et al. (1996).

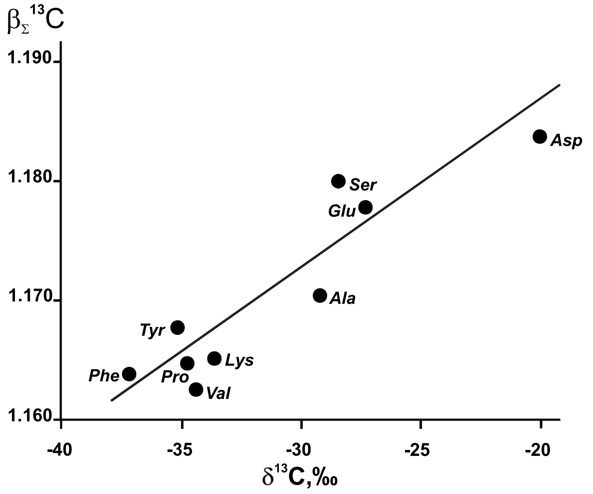


Fig. 10. $\beta_\Sigma{}^{13}C$–$\delta^{13}C$ correlation for amino acids extracted from leaves of potato. The $\delta^{13}C$ values are from Gleixner et al. (1998).

et al. (2001) and Dias et al. (2002a,b) reported that carboxyl carbon in short-chain organic acids (C_2–C_5) collected from the oilfield waters is consistently heavier ($\delta^{13}C = -12.8‰$ to $+8‰$) than aliphatic carbon ($\delta^{13}C = -22‰$ to $-30‰$). It has been concluded that the observed difference in carboxyl and aliphatic carbon in the organic acids is the result of “intramolecular isotope ordering” inherited from biological precursors (Franks et al., 2001).

Thus the $\delta^{13}C$–$\beta^{13}C$ correlation, or in other words a tendency to structural and isotopic correspondence in biological material, provides a baseline for interpretation of isotope fractionation in subsequent processes of alteration of organic matter under geological conditions.

In contrast to that of the carbon isotopes the hydrogen isotope composition of biomolecules is not only controlled by the enzymatic isotope effect of hydrogenation during biosynthesis but also by the direct isotope exchange of some functional groups with the cell water (Mastalerz and Schimmelmann, 2002). As the increment of the βD factor related to the C–H bond is smaller than that related to the O–H bond, the general trend of depletion of lipids in deuterium relative to carbohydrates and the bulk organic matter is still observed (Sessions et al., 1999). Yet, the δD–βD correlation is much weaker compared to that of the carbon isotopes.

4. Fractionation of carbon isotopes on the way from living to fossil organic matter

The process of organic matter fossilization includes three main stages: (a) transformation of organic matter during its descent to the bottom of the water body in a given depositional environment; (b) diagenesis in sediments; (c) thermal alteration (catagenesis) in rocks.

4.1. Fractionation in the water column

Only 5% of organic matter from primary bioproduction in the world ocean reaches the bottom (Romankevich, 1990). Given such an essential loss of organic carbon during its descent to the seafloor it would be logical to expect a significant isotope fractionation related to this process. However, studies of the isotopic composition of organic carbon in the water column and the sediments show that the isotopic composition of organic matter in the sedimentary section is roughly close to the present-day living plankton (Galimov, 1995a).

It is known that the export of biomass from the ocean surface waters to the bottom occurs mainly in the form of organic particles (fecal pellets and macroaggregates) (Shanks and Trent, 1980; Ittekkot, 1991; Kodina et al., 1994, 1996). The predominant part of the organic matter is disintegrated in the water column by microorganisms. The finely dispersed products of disintegration remain in the water column for a long time both in suspended (POM) and dissolved (DOM) forms and are depleted in ^{13}C, whereas intact particles, which reach the bottom, preserve the isotopic composition of the primary bioproducers. Therefore, δ^{13}C of organic carbon in sediments is close to that of plankton, yet the contribution of the reworked material makes organic carbon in newly deposited sediments isotopically somewhat lighter (within 1–2‰) than its biological source (Galimov, 1995a). The exception is the basins with highly heterogeneous and movable carbon sources. For example, δ^{13}C values of organic carbon accumulated in the bottom sediments of Kara Sea are different by 3–4‰ of the δ^{13}C values of phytoplankton now present at the sea surface.

High-molecular-weight components of dissolved organic matter (HMW-DOM) both in marine and estuarine waters consist of humin (40–50%, insoluble in acids), carbohydrates (30–40%), hydrolysable amino acids (10–20%), and lipids (1–2%) (Repeta et al., 2002; Wang et al., 2004b). The total carbon of HMW-DOM has δ^{13}C values from −20‰ to −23‰ in marine waters and from −24‰ to −31‰ in coastal waters (Mannino and Harvey, 1999).

4.2. Marine versus terrestrial input

Oceanic plankton annually produces 44×10^{15} g of organic carbon (de Vooys, 1979). Most of this organic matter is recycled in the water column and in the uppermost sedimentary layer. The burial flux of organic carbon is estimated at $0.1–0.2 \times 10^{15}$ g/year. The terrestrial input of organic carbon carried by the rivers to the ocean amounts to 0.4×10^{15} g/year (Hedges et al., 1997). Hedges et al. (1997) argued that the land-derived material should compose the significant part of the buried oceanic carbon because it is more resistant to degradation. However, they also noted that the actual content of terrestrial material in marine sediments is relatively insignificant and asked: What happens to terrestrial organic matter in the ocean?

The shallow Kara Sea of the Arctic Ocean is a unique place to study the interrelation of marine and terrestrial organic matter. Two great Siberian rivers, the Yenisei and the Ob, annually discharged 1150 km^3 of the fresh water and a huge amount of land-derived material. In 1995–2003 isotope biogeochemistry of Kara Sea was extensively studied during almost annual joint Russian–German expeditions on the *R/V* “Akademik Boris Petrov” (Galimov et al., 1996, 2003). The suspended organic matter and plankton were studied at 20 stations along a 900 km profile from the open sea to the Yenisei estuary and 200 km into the river (Kodina, 2002; Fahl et al., 2003; Galimov et al., 2003). The δ^{13}C values of the particulate (suspended) organic matter (POM) varied as a function of the hydrochemical zonation, i.e. −30.9‰ to −28.4‰ in fresh river waters and −25.2‰ to −27.3‰ in marine waters (Fig. 11a) In addition to POM plankton

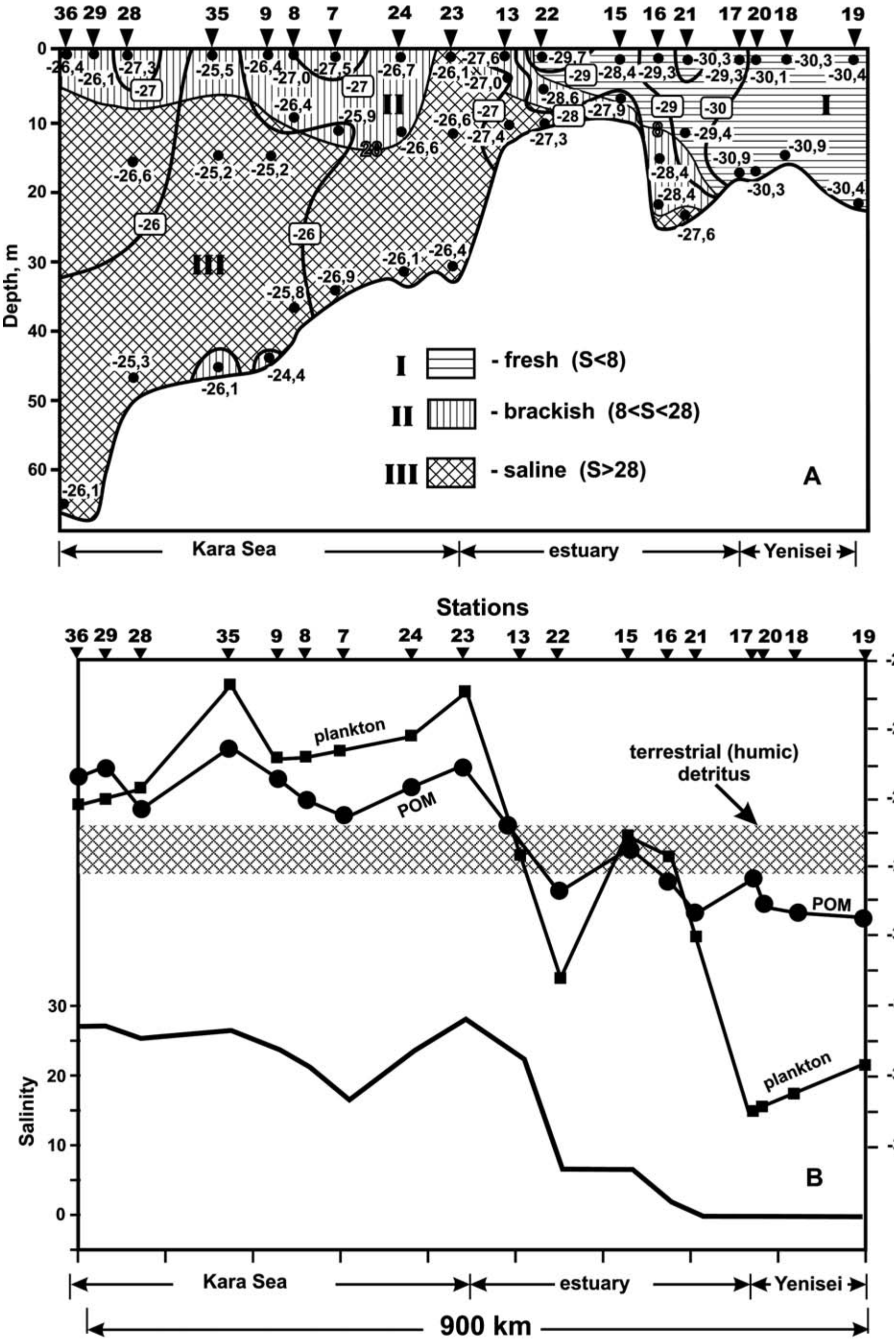


Fig. 11. Carbon isotopic composition of organic matter in a profile: Kara Sea–estuary–Yenisei River. I, II, III are the salinity zones. (A) $\delta^{13}C$ of particulate organic matter (POM) at different depths and in different salinity zones along the profile; (B) $\delta^{13}C$ of POM in subsurface water in comparison with $\delta^{13}C$ of plankton along the same profile. Samples were collected during the 34th cruise of the *R/V* "Akademik Boris Petrov" in 2000.

material was sampled and studied (Fig. 11b). The POM in the deeper water is a mixture of terrestrial and plankton components. The terrigenous detritus and humic material had $\delta^{13}C$ values of −27.5‰ to −29.1‰ and −28.5‰ on average (Kodina, 2002; Galimov et al., 2003). It is obvious that freshwater plankton is isotopically lighter and marine plankton isotopically heavier than POM. It can be calculated from these data that the suspended material carried by the river consists of 70% of terrestrial detritus and 30% of planktogenic material, whereas suspended matter in the marine part of the profile contains approximately 20% of terrigenous detritus and the contribution of the marine bioproducers is about 80%. At the distal stations the terrigenous component in the seawater becomes insignificant. Nevertheless, the $\delta^{13}C$ values of the suspended material still appear to be too low for normal marine plankton even at the high latitude. We found that this is due to the fact that the isotopically light fresh water CO_2 ($\delta^{13}C$ $-10‰$ to $-20‰$) from degradation of terrigenous organic matter in the surface water extends much further offshore than the detritus itself (Korobeinik et al., 2001; Galimov et al., 2003). The photosynthetic assimilation of the relatively light CO_2 with $\delta^{13}C$ $-3‰$ to $-8‰$ in open sea makes the marine plankton isotopically particularly light. The additional cause is the temperature effect. The isotope effects both kinetic and thermodynamic increase by 0.2–0.4‰ with 1 °C decrease of temperature. Thus, the isotopically light C_{org} is not necessarily evidence of a terrigenous input. The land-derived material is deposited mostly at close proximity to the shore at the geochemical barrier between continent and marine environment. This partly answers the question put above.

In Fig. 12 the $\delta^{13}C$ values of the total organic carbon in the bottom sediments of the Kara Sea are shown in combination with lignin content and relative abundance of *n*-alkanes in a symbolic way. Lignin is typical for land plants and does not occur in plankton. Normal alkanes with 25–31 carbon atoms are characteristic of land plant waxes, whereas the content of C_{14}–C_{19} *n*-alkanes is higher in plankton material. As expected all three parameters indicate a predominant terrestrial source of the organic matter at the Yenisei Bay. A higher content of the terrigenous component was observed in the central part of the sea. Probably, terrestrial material is delivered there by an ocean current, but also by drifting ice, rather than by distal discharge of the Yenisei and Ob rivers.

Higher contents of aromatic monomers of lignin as well as a predominance of the C_{25} *n*-alkane was observed in marine sediments at the north end of the Novaya Zemlya Island in combination with less negative $\delta^{13}C_{org}$ values of about $-22.4‰$ to $-22.5‰$. Possibly, this is a result of the presence of lichenous material in the terrigenous source.

Lichen is a principle form of vegetation on the high latitude islands, and lichens are distinguished by their isotopic composition. The $\delta^{13}C$ values of lichen samples collected on the Antarctic islands during the 33rd cruise of *R/V* "Akademic Boris Petrov" in 1999 varied mainly from $-19‰$ to $-23‰$ with an average of $-21.8‰$ for 14 samples from four islands (Galimov, 2000b).

A peculiar situation occurs in Black Sea in a profile seaward of the Danube River mouth, where hydrogen sulfide regime in the water column complicates the ordinary isotope signature due to mixing of marine and fresh water organic carbon (Galimov et al., 2002; Galimov, 2004a).

4.3. Diagenesis in marine sediments

The next step is transformation of organic matter at the sediment surface and in the uppermost subsurface layer. The main process of diagenetic transformation of organic matter is decomposition of biopolymers and reorganization of the products into a geopolymer (Eglinton, 1969; Galimov, 1980; Tissot and Welte, 1984). The exceptions are some components of biomass; which are resistant to decomposition, for instance, spores, higher plant leaf cutans, and algaenans. They preserve their chemical structure and even morphology and may form microscopically recognizable parts of the fossilized organic matter. Sometimes they represent organic carbon species of significantly different isotope composition compared to the host organic matter. For example, algaenan of *Botryococus brauni* with $\delta^{13}C$ values from $-2‰$ to $-12‰$ was reported to occur in kerogen with $\delta^{13}C$ values of $-26.4‰$ to $-25.2‰$ (Grice et al., 2003).

In marine sediments diagenetic processes successively occur in different stages, which are aerobic oxidation in the presence of molecular oxygen in the bioturbation zone, denitrification, sulphate reduction, and methanogenesis. Fig. 13 represents such a typical geochemical profile: Sulphate-reducing bacteria oxidize organic matter to CO_2, the sulphate reduction zone is succeeded by the methane generation zone where extremely isotopically light microbial methane with $\delta^{13}C$ values as low as $-100‰$ is produced. Release of phosphate and ammonia into interstitial water indicates the decomposition of organic matter. Despite all of these indications of active organic matter reworking in sediments the isotopic composition of the total organic carbon shows just a slight change within 1–2‰ to more negative values.

Organic substances in recent sediments consist of dark-brown polymers, which may be extracted with

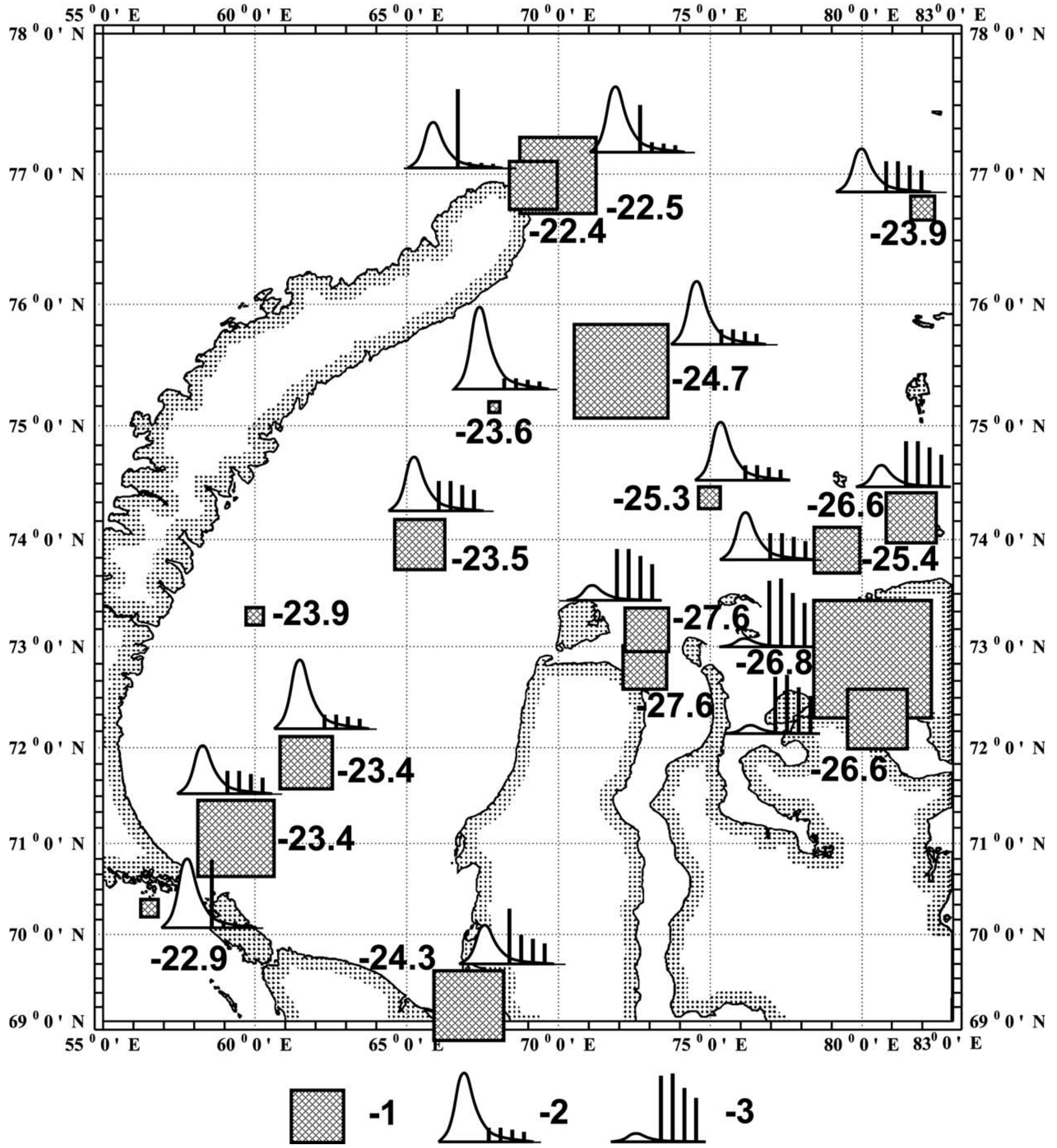


Fig. 12. Geochemical characteristics of bottom sediments in the Kara Sea. The data were obtained by studying samples collected during an expedition with *R/V* "Akademik Boris Petrov" in 2000. The δ^{13}C values for total organic carbon in the bottom sediments are shown in combination with lignin content and the relative abundance of C_{14}–C_{19} and C_{25}–C_{31} *n*-alkanes. The size of the squares is proportional to the content of vanillin in μg/g C_{org}. 1 – Relative content of lignin, 2 – *n*-alkane distribution pattern typical for planktonic organic matter; 3 – *n*-alkane distribution pattern typical for terrigenous organic matter. Numerical data and technical details are presented elsewhere (Kodina and Peresypkin, 2002).

dilute alkaline solutions. The alkaline extract is usually subdivided into two fractions: alkali-soluble but acid-insoluble humic acids (HA) and fulvic acids (FA) which are alkali- and acid-soluble; the organic matter remaining in the sediment after alkaline extraction is called humin (kerogen).

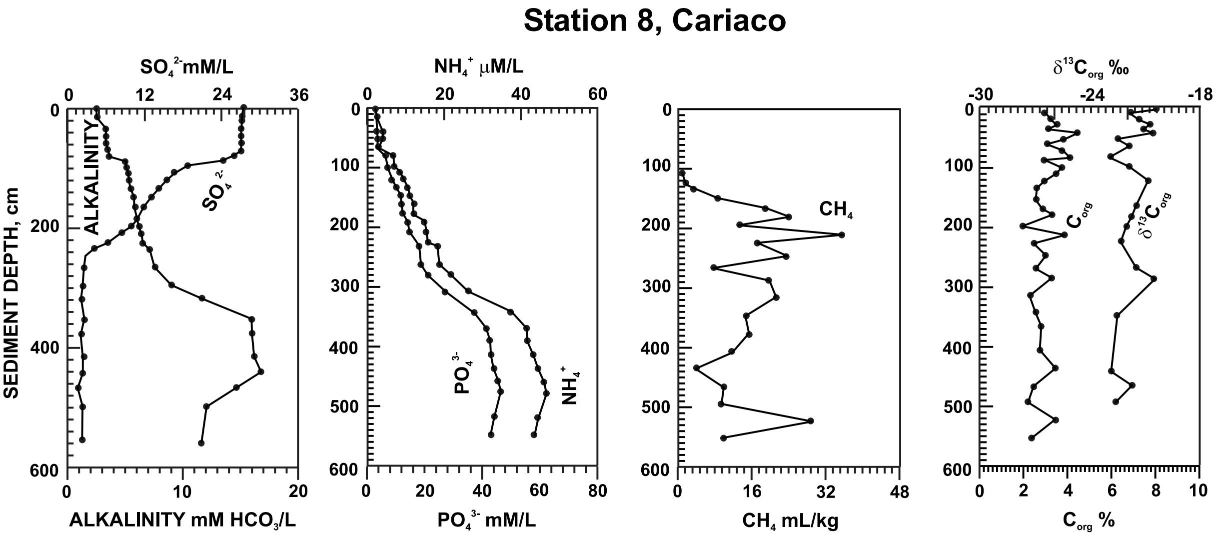


Fig. 13. Geochemical sediments profile at Station 8 (10°40′ N, 63°35′ W) in the Cariaco Basin, studied during the 14th cruise of *R/V* "Akademik Boris Petriov" in 1990 (modified from Galimov, 1995a).

Isotope studies showed that humic acids in sediments are depleted in the ^{13}C isotope as compared to fulvic acids by about 1‰ and the matured humin in turn is depleted in the ^{13}C isotope relative to the humic acids (Nissenbaum et al., 1972; Nissenbaum and Schallinger, 1974; Nissenbaum, 1974). Nissenbaum in the series of papers cited before put forward the idea that the formation of humic acids in marine sediments is related to the reaction of proteins and carbohydrates, the so-called melanoidin reaction. It involves interaction between aldehyde and amino groups and results in the formation of dark-brown substances similar to the humic acids in marine sediments.

We experimentally studied isotope fractionation during melanoidin formation (Galimov, 1980). A mixture of glucosamine and protein hydrolyzate was boiled under reflux (100 °C) for 12–30 h. The synthetic "fulvic" and "humic" acids showed depletion in the ^{13}C isotope as compared to the starting carbon of glucosamine by 0.5–1.5‰. Partly, the depletion may be due to the loss of the relatively ^{13}C-enriched carboxyl groups as Nissenbaum and Schallinger (1974) had suggested. We related this effect to the kinetic isotope effect of polymerization (Galimov, 1980, pp. 285–286) based on our previous experimental study of isotope fractionation in polymer forming reactions (Galimov, 1980 and references therein). Qian et al. (1992) repeated the isotope study of melanoidin formation and found approximately the same results. However, their statement that they allegedly proved kinetic isotope fractionation during the condensation reaction, whereas Nissenbaum and Galimov in their earlier studies just speculated about the loss of ^{13}C-enriched carboxyl groups (see p. 201 in Qian et al., 1992), is not correct. The kinetic-isotope-effect nature of the observed fractionation was already documented in Galimov (1980).

4.4. Fraction-specific isotope distribution pattern

As shown before, there is a slight change of bulk organic matter isotopic composition during diagenesis. Usually it does not exceed −1‰ to −2‰. The situation is different for particular fractions of organic matter. Isotopic composition of these fractions at the starting point corresponds to the isotopic composition of their biological precursors, but it may be significantly transformed during diagenesis.

Biological compounds can be displayed in a diagram of $\delta^{13}C$ versus $\beta^{13}C$ values. However, in the case of fossil organic matter it is difficult to use $\beta^{13}C$ values directly since the structure and the chemical composition of geochemical components are often not precisely known. Instead, the following technique can be used. There is a correlation between $\beta^{13}C$ value and polarity of an organic compound. Increase in polarity of a fraction corresponds to an increase of the $\beta^{13}C$ value (Galimov, 1985). Therefore, isotope analysis of organic matter fractions from extracts with successively increasing polarity may simulate the δ^{13}C versus β^{13}C relationship. Labels H, HB, B, and BM in Fig. 14 and following stand for the fractions eluted from a chromatographic column with solvents of increasing polarity: hexane, hexane/benzene, benzene, and benzene/methanol, respectively. Asphaltenes, designated fraction "A", are precipitated from the total extract prior to column chromatography by addition of an excess amount of pentane.

During diagenesis different compounds behave differently. Some of them are easily destroyed, others are more resistant. Proteins and carbohydrates are most easily attacked by microorganisms. However, if during diagenesis microbial activity is low or organic tissues are protected by biominerals, e.g. in diatoms, then protein/carbohydrate structures may escape biodegradation once incorporated into a macromolecular structure through mechanisms possibly similar to melanoidin formation.

The interaction of aldehyde and amino groups may form polymer structures, which contribute to asphaltenes and to some extent to the benzene–methanol fraction (BM). Polar lipids also partly fall into these fractions. Carotenoids, mono-, di- and tri-glycerides and some other less polar lipid compounds are concentrated in the hexane–benzene fraction (HB). The least polar and the most isotopically light compounds like hydrocarbons fall into the hexane fraction. Fatty acids, which are isotopically light but relatively polar, fall into the benzene fraction (B). This results in some kind of inversion in isotope distribution between fractions B and HB (Kodina and Galimov, 1984). Fig. 14 demonstrates the expected transformation of the biological organic matter during diagenesis and the occurrence of related fossil compounds in liquid chromatography fractions.

In Fig. 15 several examples of the carbon isotope distribution of fractions extracted from recent sediments are presented. The averaged shape of the curves characterizing the isotope distribution between the studied fractions is in accordance with that inferred in Fig. 14.

The isotope distribution may differ dramatically from that in Fig. 15 when organic remnants in sediments are subjected to extended microbial reworking. In Fig. 16 the data obtained during a study of sapropelic organic matter from Lake Balkhash are

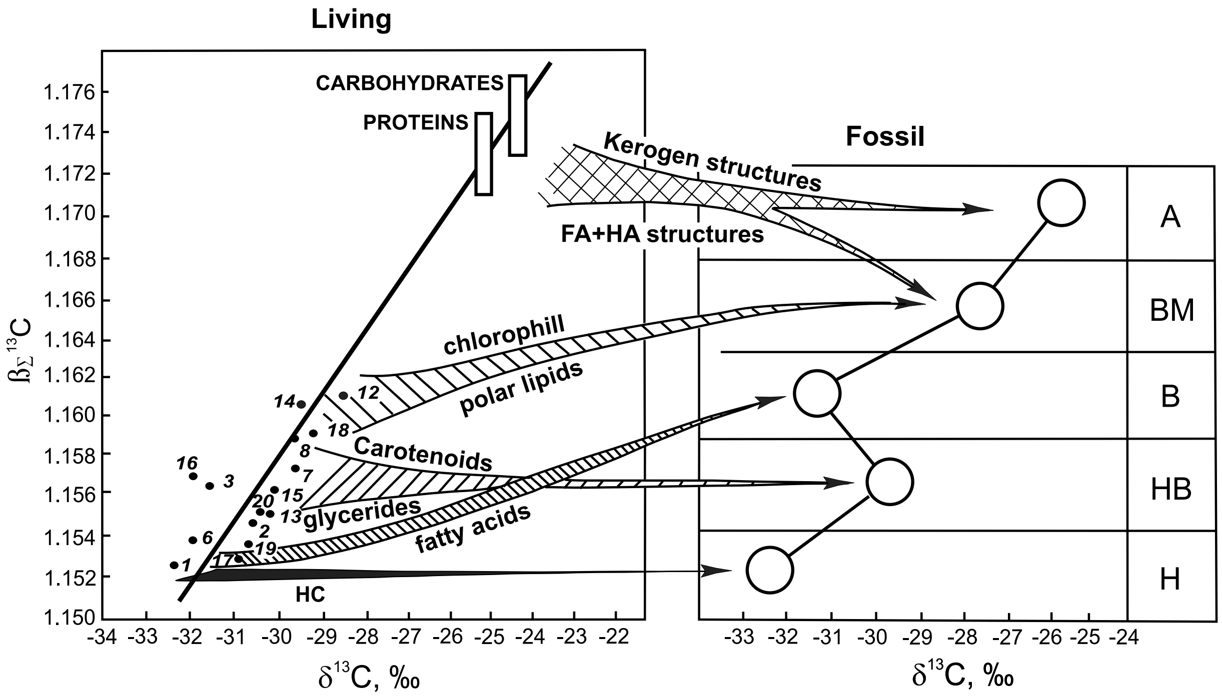


Fig. 14. Scheme showing the suggested relation between fractions of different polarity in fossil organic matter and biochemical compounds of living matter. As an example of a $\beta_\Sigma{}^{13}\mathrm{C} - \delta^{13}\mathrm{C}$ relationship in living matter the isotope distribution for biochemical components of chlorella (see Fig. 7) were selected. The numbers correspond to the fractions shown in Fig. 7 (modified from Galimov, 1995a). The isotope distribution in fossil organic matter is explained in the text.

plotted. The carbon isotope distribution pattern is almost opposite to the normal biological trend. It is suggested that in this case proteins and carbohydrates are exhaustively eliminated by microorganisms and cannot contribute to the high-molecular-weight fractions A and BM (Fig. 17). Instead, these fractions could form by means of microbial oxidation of non-polar compounds; for instance, oxidation of fatty acids. This results in the formation of isotopically light asphaltenes and components of the most polar fraction. On the other hand, since microorganisms preferentially use isotopically light alkanes, the non-polar fraction (H) is relatively enriched in the ^{13}C isotope.

Thus we distinguish two principally different ways of diagenetic transformation of biomass deposited in sediments, which results in principally different patterns of carbon isotope fractionation. The first is when components relatively depleted in the light carbon isotope like proteins and carbohydrates are partially preserved. They may be preserved under conditions unfavorable for microorganisms or be shielded by mineral particles, in particular if bound into the mineral matrix of skeleton-bearing organisms like diatoms; another factor may be a high accumulation rate or protection in some other way. It was shown by the analytical study of a diatomaceous ooze that organic matter protected by a mineral matrix (and liberated by HF) was isotopically heavier (−21.88‰) than organic matter outside the mineral matrix (−24.88‰) (Kodina and Galimov, 1984). We called the organic matter of this type "aquahumic" since the formation of humic structures through melanoidin reaction appears to be the most significant mechanism of their formation. The opposite carbon isotope distribution evolves when protein and carbohydrate structures are completely eliminated. Sapropelic organic matter forms by this way. It is essential to note that the fossil organic matter of this type is created from the initially isotopically light structures. Therefore, it must become relatively isotopically light.

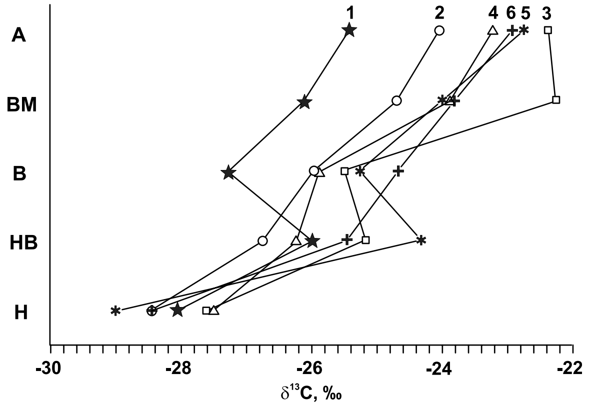


Fig. 15. Fraction-specific carbon isotopic distribution pattern for organic matter from some recent sediments: (1) Eastern Mediterranean, cored at Station 13 (34°21′9 N, 19°58′8 E, water depth 3030 m) and collected during the 14th cruise of *R/V* "Akademik Boris Petrov", subbottom depth 37–41 cm (Report, 1990); (2) South Atlantic, Angola Basin, DSDP Site 530D, core 530B–1-1, subbottom depth 140–150 cm (Kodina, 1987); (3) Red Sea, Kebrit Deep, subbottom depth 9–242 cm, sampled during the 70th expedition of *R/V* "Sonne" (unpublished data, samples were obtained from Dr. W. Michaelis); (4) Same as (3), subbottom depth 292–300 cm; (5) Gulf of California, Guaymas basin, DSDP Site 478, Core 478-6-3, subbottom depth 45.7 m (Galimov et al., 1982); (6) Same as (5), subbottom depth 72.2 m.

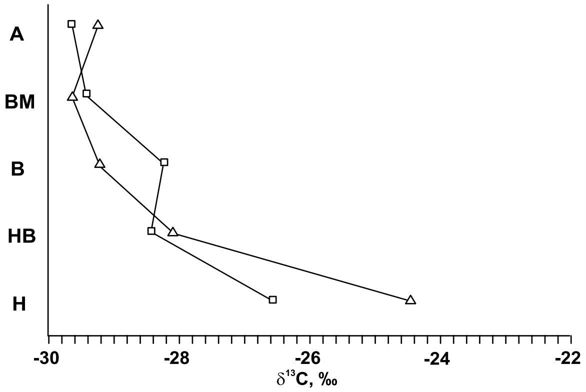


Fig. 16. Fraction-specific carbon isotope distribution pattern for a recent freshwater sapropel (Lake Balkhash, Kazakhstan); the two curves are for different pieces of the same sample (data from Kodina and Galimov, 1984).

The whole picture should be supplemented with the case of terrestrial organic matter. The coalification process does not result in significant isotope fractionation (Galimov, 1968, 1985). This conclusion was confirmed in many subsequent studies (e.g. Peterson and Fry, 1987). The carbon isotope composition of fossil wood, lignite and coal varies from −23‰ to −28‰, and mostly is around −24‰ to −26‰, which is close to the range for terrestrial plants (e.g. Bechtel et al., 2002). Schleser et al. (1999) subjected a wood sample to an artificial decay process. The δ^{13}C value of the wood carbon returned almost to the initial value after some decrease during heating. The maximum depletion in ^{13}C of about 0.7‰ was believed to be a consequence of the preferential decomposition of cellulose relative to lignin.

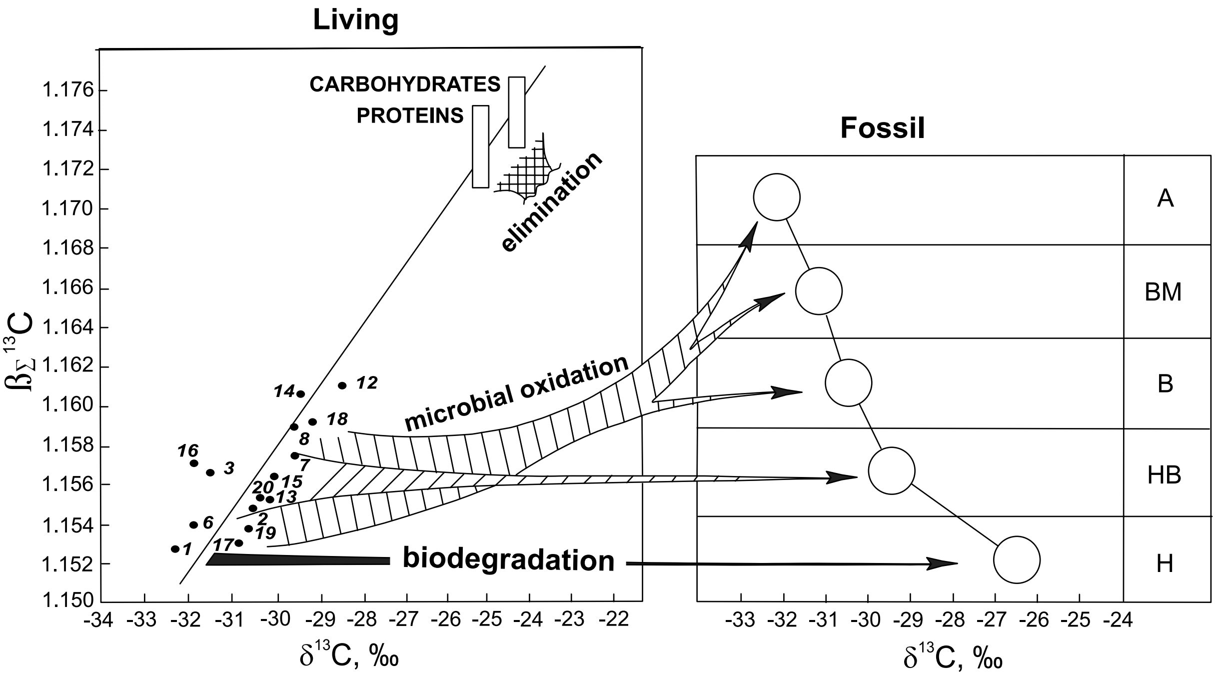


Fig. 17. Same as Fig. 14, but for organic matter subjected to active microbial reworking ("sapropelic type"). Designations are the same as in Fig. 14.

Lignin is a component of land plants, which is resistant to biodegradation and, thus, makes up a major part of humic structures of fossilized terrestrial organic matter. Lignin is isotopically lighter than proteins and carbohydrates. Therefore, the difference between polar and non-polar components in terrestrial organic matter is smaller than in the aquahumic marine organic matter (Kodina and Galimov, 1984). Eventually, three "pure race" patterns of fraction-specific isotope distribution can be distinguished (Fig. 18), though the mixed forms occur more frequently in natural conditions.

Thus, the biological signature is significantly transformed during diagenesis depending on the source of the organic material and the environmental conditions. The significance of the concept is that the specific patterns of isotope relationships in the fractions may be used to elucidate geochemically the origin of fossil organic matter, including that of crude oil.

4.5. Thermal alteration, biodegradation, oxidation

The isotope distribution pattern inherited from the diagenetic stage may be modified in subsequent processes of thermal alteration, biodegradation, and oxidation.

4.5.1. Thermal alteration

Thermal alteration was extensively studied both by laboratory simulation and under natural conditions (Rohrback, 1979; Chung and Sackett, 1979; Clayton, 1991; Rooney et al., 1995; Lorant et al., 1998; Tang et al., 2000; Hill et al., 2003; Tocque et al., 2005). We used the unique opportunity to study thermal alteration under natural conditions in sediments from the Gulf of California (Galimov and Simoneit, 1982). The recent tectonic activities

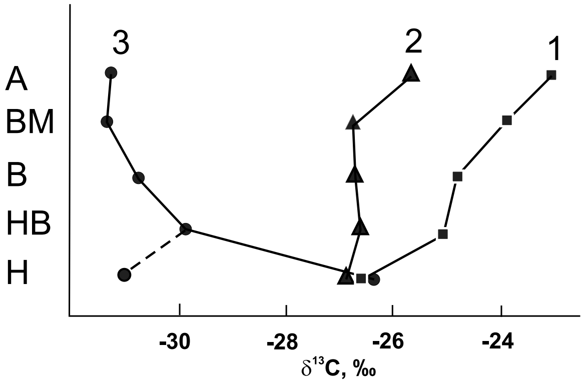


Fig. 18. Typical fraction-specific carbon isotope distribution patterns for aquahumic (1), terrestrial (2) and sapropelic (3) organic matter.

generate extremely diversified thermal conditions within this sedimentary basin, filled with lithologically uniform diatomaceous sediments. Samples were collected during Deep Sea Drilling Programme Leg 64 in the Guaymas Basin. On the basis of a number of geochemical parameters (relative content of hydrocarbons in the bitumen, presence of chlorins and porphyrins, CPI values, etc.) the samples were considered a representative series typifying thermal effects to different degrees (Galimov and Simoneit, 1982).

In Fig. 19 the samples from the Gulf of California are numbered in the order of increasing degree of maturation. The isotopic composition of the hydrocarbon fraction (H), consisting mainly of *iso*- and *n*-alkanes, was most sensitive to thermal alteration. The hydrocarbon fraction became isotopically heavier with increasing thermal stress whereas the other fractions did not show any significant isotopic shift up to a certain level of thermal stress. Only in the case of the strongly altered sample 5, which suffered hydrothermal alteration at about 300 °C in close proximity to a basaltic sill, the whole pattern of the isotope distribution is dramatically different. In the course of maturation the hydrocarbons decompose with a kinetic isotope effect and the residue becomes isotopically heavier, whereas the newly generated macromolecules incorporate the formerly isotopically light moieties and comprise the asphaltenes and polar fractions.

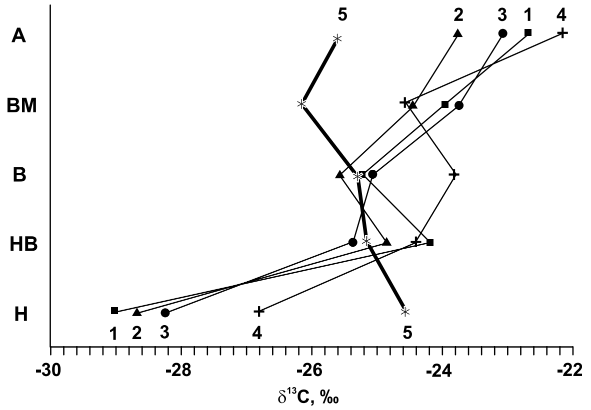


Fig. 19. Change of the carbon isotope distribution pattern as a function of the extent of maturation of organic matter, hydrothermally altered sediments from Guaymas basin, Gulf of California, DSDP Site: (1) 478-6-3, (2) 479-43-1, (3) 477-5-1, (4) 477-7-1, (5) 477-16-5. See detailed description of the cores in Galimov and Simoneit (1982). Thermal alteration increases from 1 to 5.

Recently Tocque et al. (2005) carried out a detailed laboratory study of thermal alteration of organic matter. They analyzed the products of anhydrous pyrolysis of a type II kerogen in the conversion range from 1% to 87% (Fig. 20). As a general rule, the products are enriched in ^{13}C with increasing thermal alteration. Yet at the initial stage of transformation (from 1.2% to 10%) the products become isotopically lighter, seemingly in disagreement with the theoretical expectation. The same phenomenon was reported earlier by other investigators (Lorant et al., 1998; Hill et al., 2003). The authors of the experiments believe that this phenomenon is due to specific, yet undetermined, precursors in immature kerogen. To my mind, there is a simpler explanation. Any natural sample selected for an experiment had its previous transformation history. At the beginning of the experiment the carbon, which is residual from the previous step, is released. This residual carbon is relatively enriched in ^{13}C. Then it is overweighed by isotopically lighter carbon produced by new cracking reactions, and, as the process approaches a steady state, the products become again progressively heavier.

The whole picture is complicated by superposition of primary and secondary isotope fractionation. The temperatures in an experiment (250–350 °C) are significantly higher than those occurring under natural conditions. This results not only in a different magnitude of isotope fractionation but, more importantly, also in different types of the reactions involved. Therefore, quantitative indicators inferred from pyrolysis experiments, especially on the basis of individual components, should be used with caution. We prefer to use entire compound classes (fractions) for characterization of the organic matter.

It follows from the thermal alteration experiments that the isotopic composition of fractions of different polarity, which we use, changes little under thermal stress, at least in the range of oil stability. Therefore, the pattern of the isotope distribution between the fractions represents a sustained characteristic of the organic matter, which can be used for oil–source rock correlation, as I will show later.

4.5.2. Biodegradation

Data on the isotope fractionation during biodegradation of organic matter and oil are controversial. It is known that the most biodegradable fraction is the normal alkanes. There were reports based on experiments that biodegradation changes little the

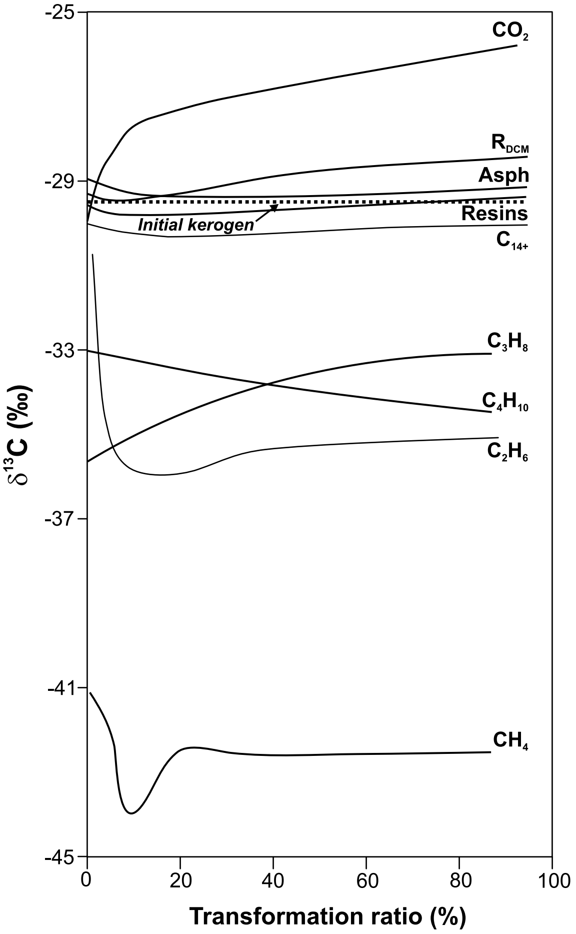


Fig. 20. Change of carbon isotopic composition of the fractions released during transformation of kerogen (after Tocque et al., 2005): C_{14+} is a fraction insoluble in *n*-pentane but soluble in dichlormethane (DCM), Asph is a part of the DCM fraction insoluble in *n*-heptane, R_{DCM} is the DCM insoluble residue.

isotope composition of alkanes (Mansuy et al., 1997; Huang et al., 1997; Mazeas et al., 2002). But other field and laboratory studies showed that biodegradation of hydrocarbons, both aerobic and anaerobic, results in 1–4‰ shift of their isotopic composition to less negative values (Kodina and Galimov, 1984; Galimov and Frik, 1985; Meckenstock et al., 1999; Stehmeir et al., 1999; Hunkeler et al., 2001; Bugna et al., 2004). Recently, Nguyen et al. (2004) showed that *n*-alkanes of biodegraded leaves change their isotopic composition by 3–4‰, whereas the $\delta^{13}C$ value of the bulk carbon of the leaves almost did not change.

Aromatic hydrocarbons are more resistant to microbial attack and do not noticeably change their carbon isotopic composition (Meckenstock et al., 1999; Ahad et al., 2000). However, Yanik et al. (2003) reported a significant change of biodegraded individual polyaromatic hydrocarbons. Recently, Sun et al. (2005) showed that during heavy biodegradation the C_{15}–C_{18} *n*-alkane fraction became enriched in ^{13}C up to 4‰, whereas the C_{19+} fraction remained unchanged.

The (H)-fraction in the young sapropel (see Fig. 17) is isotopically relatively heavy as it presents the remains of microbial processing of the biological precursors of this fraction. Sapropelic sediments enriched in organic matter are transformed to black shale in the course of catagenesis. The isotope distribution curves for several well-known black shale formations are presented in Fig. 21. One can see that the isotope distribution characterizing the ancient black shale is quite similar to that which has been ascribed to sapropelic organic matter. The only exception is the hexane fraction (H). However, the explanation is easy. In ancient black shale this fraction consists of hydrocarbons generated during catagenesis. These hydrocarbons are isotopically light and have nothing to do with the respective biodegraded fraction (in fact negligibly small) of a fresh sapropel in young sediments. The inset in Fig. 21 illustrates the transformation of the isotopic distribution pattern of the young sapropelic material into that of the matured black shale. The reverse process occurs when the black shale and oil are subjected to biodegradation.

4.5.3. Oxidation

An experimental study of oil oxidation carried out in our laboratory showed that it leads to enrichment of the BM fraction with products of oxidation of the non-polar fraction (Frid and Bannikova, 1990). The non-polar fraction, which dominates in oil, almost does not change its isotopic composition, whereas the polar BM fraction shows a significant shift of its isotopic composition toward a more negative $\delta^{13}C$ value (Fig. 22). It has been reported that oxidation may result in the formation of heterocyclic structures through cyclization of aliphatic chains (Almendros et al., 2003).

5. Identification of oil source rocks

Identification of oil source rocks is one of the most important targets in petroleum exploration. Organic geochemistry suggests two main approaches, which are based on specific chemical structures including biomarkers and on isotope composition and fractionation.

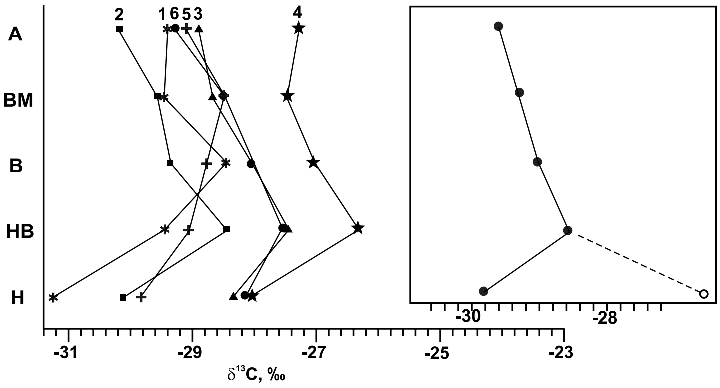


Fig. 21. Carbon isotope distribution patterns for black shale of different age. Inset: averaged curve for the studied black shales transformed from the initial curve for fresh sapropel in young sediment. 1 – Green River Pg_2, North America; 2 – Bazhenovian J_3v, West Siberia; 3 – Pripiatski D_3fr, Belorussia; 4 – Domanic D_3fr, Volga-Ural; 5 – Domanic D_3fr, Solikamsk depression; 6 – Dictionema O_2, Estonia.

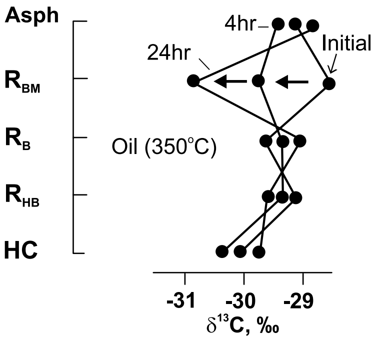


Fig. 22. Experimental oxidation of oil (after Frid and Bannikova, 1990).

5.1. Effect of primary migration

Direct comparison of the hydrocarbon composition of petroleum accumulated in a reservoir with bitumen retained in the source rock is complicated by fractionation during primary migration (expulsion of petroleum from the source rock) and the different generation stages of the oil hydrocarbons accumulated in the reservoir and those retained in the source rock. Aromatics are better retained in kerogen than saturated hydrocarbons. Within the saturated hydrocarbons, cycloalkanes are more strongly retained than normal alkanes. Theoretically, heavier *n*-alkanes are expelled more easily than light *n*-alkanes. It should be noted that methane is more soluble in kerogen than the higher-molecular-weight *n*-alkanes and consequently the former should be preferably retained (Ritter, 2003). Still, as methane is produced in greater amounts than other hydrocarbons, it quickly reaches the saturation level in kerogen and is steadily getting released. From this moment solubility of the other hydrocarbons in methane becomes significant for the expulsion mechanism, and the efficiency of different hydrocarbons expelled will depend on their partition between methane and kerogen, and later, at higher maturity, between bitumen and kerogen. Under steady-state conditions the hydrocarbon composition of expelled petroleum approaches the hydrocarbon composition of the generated petroleum, yet the hydrocarbon composition of the bitumen retained in the source rock can be quite different. This effect is similar to "distillation under total reflux".

As has been discussed in the relevant section above, the isotope fractionation in absorption/desorption and solution/dissolution processes is relatively small and not expected to discriminate between the released hydrocarbons and their retained counterparts. This is a significant advantage of the isotopic method for establishing genetic relationships between oils and their source rocks.

5.2. Oil–source rock correlation by comparison of patterns of the isotope distribution between oil fractions and putative source organic matter

The results presented in the previous sections provided a key for developing an isotopic method for the identification of oil source rocks (Galimov and Frik, 1985; Galimov, 1986; Kodina et al., 1989, 1991). In the Volga-Ural region the Lower Caboniferous Jasnopolyanian horizon (C_1jp) is one of the richest oil-bearing units. Oil also occurs at some other levels of the sedimentary profile (Fig. 23). In the same profile a few layers are sufficiently enriched in organic matter to represent a source rock. The Domanik Suite (Upper Devonian, D$_3$fr) and the Malinovian shales (Lower Carboniferous, C$_1$mn) are the most prospective ones. The latter just underlies the oil-bearing horizon, and it was widely believed to be the source rock of the oil. Yet analysis showed that the isotope distribution patterns of the oil and the organic matter of the Malinovian shales were quite different. Instead, the fraction-specific isotope characteristic of the Jasnopolyanian (C$_1$jp) oil revealed a satisfactory similarity with that of the Domanik shales. The shape of the curves corresponds to the sapropelic (black shale) type. The Domanik Suite (D$_3$fr) is an important oil source rock for the whole sedimentary succession in the Volga-Ural region.

The Okruzhnoye oilfield on Sakhalin Island represents another example (Fig. 24). Here, oil occurs in sedimentary rocks of Miocene age. The apparent source is the 600 m thick succession of siliceous rocks, which formed from diatomaceous oozes. This type of sediment is widespread around the Pacific Ocean. The counterpart of the Pileng (N$_1$pg) suite is the Monterey Formation in California.

The extract from the source rock is characterized by an isotope distribution curve with a shape typical of aquahumic organic matter (see Fig. 15). The oil accumulation in the Pileng suite has a similar isotope distribution curve. The uppermost oil accumulation in the Borovian strata (N$_1$br) in the Okruzhnoye field is characterized by a different isotope distribution curve. However, a closer look shows that this difference is due to the relative depletion of the BM fraction of the Borovian oil in ^{13}C. As it has been shown above this is a feature of oxidized oil. Thus, we conclude that the oils in both accumulations are genetically related, but the Borovian oil has been subjected to oxidation.

The study of the Novoportov oilfield, West Siberia, offers one more example of oil–oil correlation (Fig. 25) (Kodina et al., 1991). Here, in the Lower Cretaceous sequence several oil accumulations occur. The Albian (K$_1$al) and Hauterivian (K$_1$h) oils show similar isotope distribution curves with the exception of the H fraction, of which the isotopic composition in the Albian oil is clearly shifted to a more positive δ^{13}C value by about 1‰. The cause

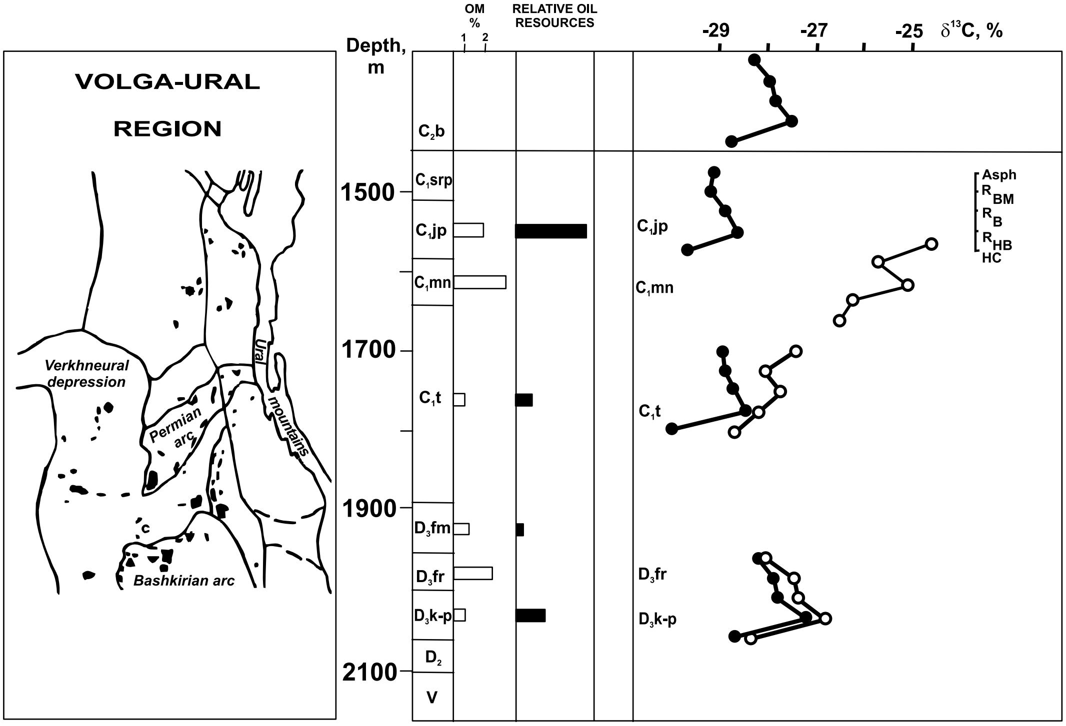


Fig. 23. Fraction-specific carbon isotope distribution patterns of oils (filled circles) and extracts (open circles) from the suggested source rocks in the profile of the Volga-Ural Region (from Galimov and Frik, 1989).

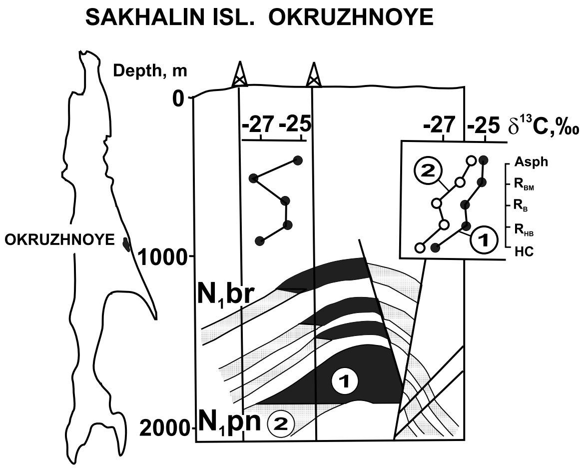


Fig. 24. Fraction-specific carbon isotope distribution patterns of oils (filled circles) and extracts (open circles) from the suggested source rocks in the profile of the Okruzhnoye field, Sakhalin.

of this enrichment in ^{13}C is biodegradation of the oil, which had migrated to the uppermost horizon of the sequence. It seems that only the δ^{13}C value of the H fraction is sensitive to biodegradation, whereas the other fractions are conservative. Hence, the fraction-specific isotope study allows to distinguish a biodegraded oil and at the same time to recognize the genetic correlation between the biodegraded oil and its intact counterpart.

5.3. Oil–source rock correlation based on compound-specific isotope analysis

Isotope analysis of individual compounds separated on line by gas chromatography (GC-irm-MS technique) came into practical use in the 1990s. This so-called compound-specific δ^{13}C analysis has been applied to oil–oil and oil–source rock correlations and the elucidation of petroleum generation mechanism (Hayes et al., 1990; Bjorøy et al., 1994; Rooney et al., 1998). The hydrogen-isotope-specific analysis was also used for these purposes (Sessions et al., 1999; Sache et al., 2004). The compound-specific isotope technique is an effective tool for oil–oil correlation. Its application to oil–source rock

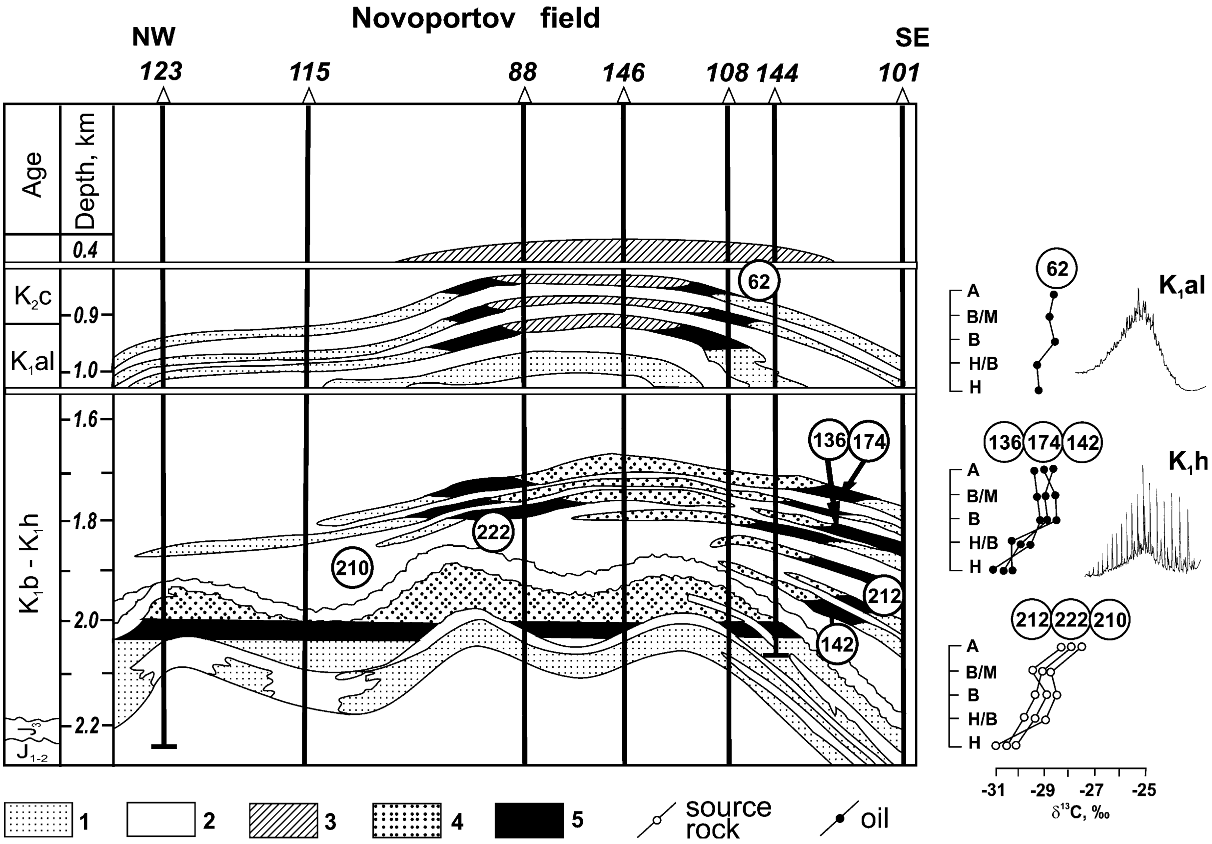


Fig. 25. Schematic profile of the Novoportov field in West Siberia, with δ^{13}C data of the fractions of the oils and the extracted organic matter (after Kodina et al., 1991). 1 – sandstone, 2 – clays, 3 – gas, 4 – condensate, 5 – oil. The figures in the circles are the sample numbers.

correlation is more problematic. The composition of the generated hydrocarbon assemblage progressively changes during chemical transformation of the initial kerogen. This additionally complicates quantitative and qualitative relations between the expelled and the retained compounds.

Recently, Odden et al. (2002) carried out a compound-specific carbon isotope analysis of thermal extracts (S_1 Rock–Eval fraction) and kerogen pyrolysates (S_2 Rock–Eval fraction) of source rocks and compared the data with those obtained for local oils and hydrocarbon fractions released by pyrolysis of asphaltenes precipitated from those oils (Fig. 26). It is obvious from their data that the *n*-alkanes of the oil studied (Tyrihans Nord) are isotopically lighter than those from the kerogen pyrolysate of the suggested source rock. And the *n*-alkanes produced by pyrolysis of the asphaltenes from that oil are more enriched in the ^{13}C isotope than the *n*-alkanes of both the oil and the pyrolysate.

The isotopic composition of every generated compound progressively changes with the increase of maturation, i.e. with the increase of the *f* value. This explains why the isotopic composition of compounds and fractions in oil usually are isotopically lighter than the same compounds and fractions extracted from the source rock. Similarly, enrichment of asphaltenes in ^{13}C relative to the host oil means that these asphaltenes represent small fragments of the initial kerogen, which have exhaustively released isotopically lighter hydrocarbons during petroleum formation. Secondary asphaltenes may be isotopically lighter than the host oil. This is valuable information extractable from this kind of isotopic study. Nevertheless, one cannot expect a close similarity of the isotope distribution pattern of *n*-alkanes even between genetically related oil and kerogen because of the stepwise process of petroleum formation and the chemical alteration of the kerogen at each step. The fingerprint patterns of the fractions eventually derived from the same source do not exhibit a closer similarity to each other than the relevant fractions of the alien oils. Moreover, within the same layer the extent of hydrocarbon generation (*f* coefficient) may vary according to facies differences, e.g. due to variations of the composition of the mineral matrix, the local density of the rock and other specific properties of the layer.

Thus at the present level of our knowledge the usefulness of compound-specific isotope analysis for oil–source rock identification is reduced to that of fraction-specific isotope analysis. However, the carbon isotopic analysis of individual hydrocar-

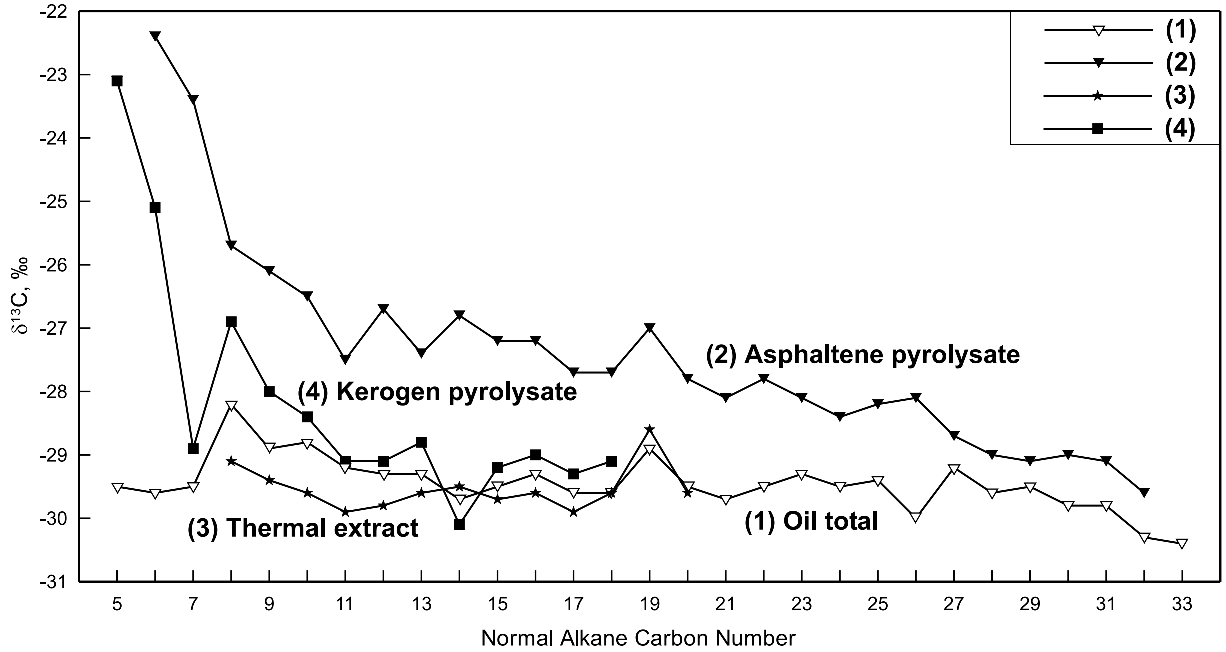


Fig. 26. δ^{13}C values of *n*-alkanes from (1) – oil (Tyrihans, North Norway), (2) – asphaltenes precipitated from this oil, (3) – thermal extract (S_1 Rock Eval fraction from kerogen of the most likely source rock, Spekk formation) and (4) – kerogen pyrolysate (S_2 Rock Eval fraction) from the same source. The data are from Odden et al. (2002).

bons promises to be a useful tool for the investigation of reaction mechanisms of hydrocarbon generation.

5.4. Biomarkers and other markers

A biomarker is a compound, which preserves an identifiable structure of its biological precursor. Biomarkers are widely used for oil–oil and oil–source rock correlations (Peters et al., 2005). By comparison of structurally similar compounds in sediments and crude oils with their probable biological precursors one may distinguish the source facies. Modification of the biomarker structure allows reconstruction of the thermal history of the oil. Some biomarkers are indicators of specific biochemical processes and environments.

Triterpenoids and sterols were studied in detail. Sterols are easily modified during diagenesis, whereas polycyclic terpenoids are more resistant. Sterols are classified as biomarkers of animals and zooplankton, algae or higher plants depending on their substitution at C-4 or C-24 (Huang and Meinschein, 1979; Mackenzie et al., 1982; Peters and Moldowan, 1993; Volkman et al., 1999). Steranes in crude oils are important biomarkers (Curiale, 2002).

Hopanoids are considered biomarkers for bacteria and cyanobacteria (Ourisson and Albrecht, 1992; Summons et al., 1999). Hopanoids are often isotopically light ($\delta^{13}C$ values of about $-50‰$ to $-60‰$; Grice et al., 2001; Neunlist et al., 2002).

Squalane is suggested to be a marker for halophilic archaea and hence a molecular indicator of hypersaline environments (ten Haven et al., 1988; Grice et al., 1998). Crocetane is depleted in ^{13}C to a value as low as $-100‰$ and has been recognized as a marker for methane oxidizing archaea (Thiel et al., 1999). Thiel et al. (2001) found that the *n*-C_{23} alkane, depleted in ^{13}C ($\delta^{13}C$ values of less than $-70‰$), is an indicator of anaerobic methane oxidation.

Isoprenoids such as penta- and tetramethylicosane were identified as components of methanogenic bacteria (Vink et al., 1998). Head-to-head linked isoprenoids are synthesized by archaea (Ward et al., 1985).

Not only biological but any organic structures, which form in sediments before expulsion of the oil from the source rock, may be used for correlation. For example, diamondoid structures emerge during catagenesis (Petrov et al., 1974). Recently it has been shown that diamondoids are resistant to biodegradation even in heavily biodegraded oil, where the hopanes are already degraded, and therefore may be used for identification of the source rock of the altered oil (Wingert, 1992; Schulz et al., 2001). Strictly speaking they are not biomarkers but markers.

The weakness of implementation of the biomarker concept in petroleum geology is that the concentration of biomarkers in crude oils and source rock extracts are low, often at the level of ppm. During migration oil may easily be contaminated by allochthonous biomarker structures picked up from the ambient rock.

It has been shown in many works that the parallel study of structures and isotope compositions of biomarkers provides valuable genetic information (Hayes et al., 1990; Macko, 1994; Popp et al., 1997; Naraoka and Ishiwatari, 2000; Huang et al., 2000; Grice et al., 2001; Schouten et al., 2001; Lu et al., 2003; Wang et al., 2004b). In our application of isotope analysis we showed that both biomarkers and bulk hydrocarbons in the studied oils of the Volga-Ural region were related to each other by their isotopic signatures indicating their common origin (Fig. 27) (Bogacheva and Galimov, 1979).

Sometimes kerogen may comprise organic matter moieties including biomarker structures which are not representative of the main part of the kerogen producing most of the oil hydrocarbons. Such an example was presented above using the data obtained by Brincat et al. (2000) for Lake Baikal sediments. Grice et al. (2003) described biomarkers related to algaenan of *Botryococcus brauni* to be unusually enriched in ^{13}C ($\delta^{13}C = -2\%$ to -12%) and to occur in kerogen with $\delta^{13}C$ values of $-26.4‰$ to $-25.2‰$, which produced isotopically light hydrocarbons ($\delta^{13}C = -26‰$ to $-35‰$). Some biomarkers in oils bear no relation to the source organic matter. They have a quite different isotope composition (Li et al., 1996; Cuishan et al., 2003) and, probably, originate from secondary alteration (biodegradation) of the oil.

6. Geochemistry of gas

6.1. Methanogenesis and methane oxidation

Methane can be formed biologically from CO_2 and hydrogen, acetate, methanol (Claypool and Kaplan, 1974; Cappenberg and Jongjan, 1978), or

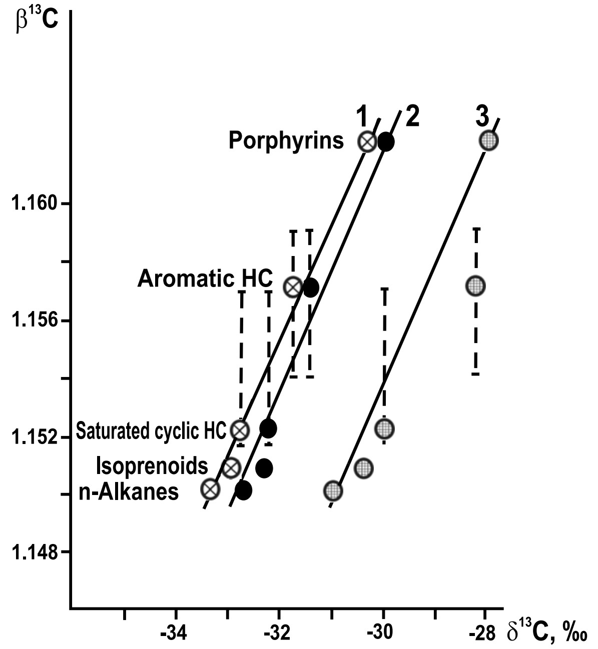


Fig. 27. Carbon isotopic composition of the main hydrocarbon fractions of oil and biomarkers (porphyrins and isoprenoids) from the same oil versus their estimated $\beta^{13}C$ factors. The samples are from the following oil fields: 1 – Severo-Ostrovnoye, 2 – Surgut, 3 – Kokuyskoye (Bogacheva and Galimov, 1979).

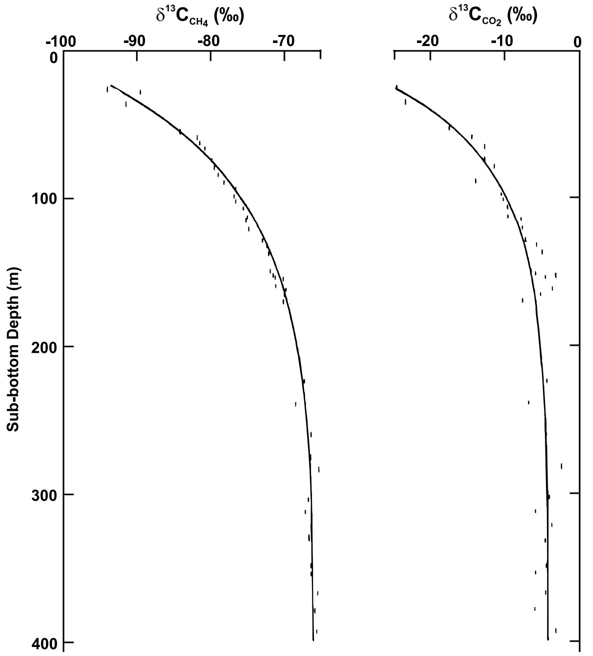


Fig. 28. Variations with depth in the carbon isotopic composition of CH_4 and CO_2 from subbottom sediments of Site 533, Deep Sea Drilling Project Leg 76, Blake Outer Ridge, Atlantic Ocean. The water depth is 3184 m (Galimov and Kvenvolden, 1983).

methylated compounds such as trimethylamine and dimethylsulfide (Oremland and Polein, 1982).

In marine sediments microbiological methane is produced almost entirely through CO_2 reduction. There exists a close parallelism in the isotopic composition of biogenic CH_4 and CO_2 in oceanic sediments (Galimov and Simoneit, 1982; Galimov and Kvenvolden, 1983). Fig. 28 illustrates such a relationship. In land environments (freshwater, marsh) the acetate fermentation predominates.

It was established long ago that methane produced in the anaerobic environment as well as under relevant experimental conditions is extremely depleted in the ^{13}C isotope (Rosenfeld and Silverman, 1959; Nakai, 1961). The $\delta^{13}C$ values of about $-60‰$ to $-100‰$ are characteristic of microbial methane. Microbial methane is depleted in deuterium as well (Schoell, 1980; Valentine et al., 2004 and references therein).

The following relationships were suggested to distinguish the nature of methane through $\delta^{13}C$ and δD measurements (Schoell, 1980; Galimov and Kvenvolden, 1983; Woltemate et al., 1984; Whiticar et al., 1986; Whiticar, 1999):

(a) CO_2 reduction:

$$\delta D_{CH_4} = \delta D_{water} - 180‰$$

$$\delta^{13}C_{CH_4} = \delta^{13}C_{CO_2} - 62‰ \quad (T = 15\ °C)$$

(b) Acetate fermentation:

$$\delta D_{CH_4} = 0.4\delta D_{water} - 323‰$$

$$\delta^{13}C_{CH_4} = \delta^{13}C_{CO_2} - 49 \pm 5‰$$

Nevertheless, significant deviations from these relationships sometimes occur in natural systems (Hornibrook et al., 1997, 2000).

The temperature dependence of isotope fractionation in the microbial CH_4–CO_2 system was experimentally determined (Fig. 29) (Balabane et al., 1987). It is generally believed that isotope fractionation during methanogenesis is due to a kinetic isotope effect. However, the actual mechanism remains unknown. The culture experiments with CO_2-reducing methanogenic archaea cultivated over the temperature range of 35–85 °C showed that the $\Delta_{CO_2-CH_4}$ values fairly well followed the isotopic exchange equilibrium line (Botz et al., 1996).

The uppermost layer in marine sediments is the zone of aerobic oxidation due to bioturbation and

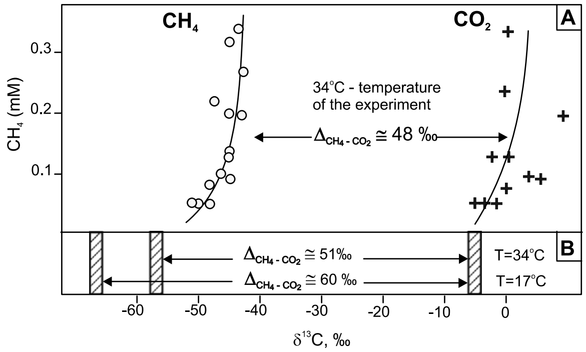


Fig. 29. Experimental study of the CO_2 reduction by *Methanobacterium formacion* (after Balabane et al., 1987). The experimental data (A) are compared to $\Delta_{CH_4-CO_2}$ (B), measured by Galimov and Kvenvolden (1983) in sediments of the Blake Outer Ridge, DSDP Leg 76.

supply of molecular oxygen. An oxidation zone is present even in an anoxic basin because of the deposition of mineral oxides (see Fig. 13). Sulphate reduction does not start before the oxygen potential has sufficiently decreased. Then, the methane generation process begins. This type of zonation is typical for marine basins with a normal redox regime.

In well-oxygenated basins organic matter is reworked and aerobically oxidized to such an extent that it becomes unusable for anaerobic microorganisms. In this case, sulphate reduction and subsequent methane generation are suppressed. Recently, we observed this situation in the Kara Sea. Fig. 30 presents the $\delta^{13}C$ versus HI/OI (Hydrogen Index to Oxygen Index ratio) plot for organic matter from the surface layer of sediments at different sites in the Kara Sea. Samples with highly oxygenated organic matter are distinguishable by their very low HI/OI ratio despite a marine planktonogenic origin of the organic matter (Galimov, 2004a). It is seen that microbial activity, both sulphate reducing and methane producing, in sediments from this area (Site 39) are only faintly expressed. In contrast, Site 75 represents a classical geochemical zonation. Decrease of the sulphate concentration with depth reflects the microbial sulphate reduction process. Simultaneously, the alkalinity increases due to the biochemical oxidation of organic matter. Input of CO_2 released during oxidation of organic matter changes the CO_2 isotopic composition from the $\delta^{13}C$ value characteristic of the local seawater to that which corresponds to organic carbon. When sulphate reduction is almost completed, methane generation starts.

A significant part of the methane generated by methanogenic archaea is oxidized by methane-oxidizing microorganisms. Methanotrophs grow on methane as their sole source of carbon and energy by oxidation of methane to formaldehyde (Hanson and Hanson, 1996; Jahnke et al., 1999). The released isotopically light CO_2 is known to be the source of carbonate minerals anomalously depleted in the ^{13}C isotope (Coleman et al., 1981) and occurring in sediments and near gas seeps. An example of this geochemical regime is shown in Fig. 31 at one of the stations studied in the Kara Sea during the 35th cruise of the *R*/*V* “Akademik Boris Petrov”. Methane invading the sulphate reduction zone is oxidized. As a result, isotopically light CO_2 appears, which, in turn, leads to the formation of carbonate minerals, in particular ikaite, significantly depleted in ^{13}C ($\delta^{13}C = -40.0‰$ to $-42.4‰$) (Kodina and Galimov, 2002; Kodina et al., 2003).

The kinetic isotope effect during methane oxidation causes residual CH_4 to become ^{13}C-enriched (Baker and Fritz, 1981; Coleman et al., 1981). This effect allows recognizing the methane oxidation process in sediments. Fig. 32 demonstrates a significant shift of the isotopic composition of methane due to its oxidation in the uppermost sediments and the anoxic water column of the Cariaco basin relative to the methane in the methanogenesis zone (Report on 14th cruise of the *R*/*V* “Akademik Boris Petrov”, Report 1990; Galimov, 2004a).

The scale of geochemical zonation is usually centimeters or meters, but sometimes it is extended over hundreds of meters as it was observed in the deep holes (Fig. 33) drilled during DSDP Leg 50 in the Moroccan Basin, Atlantic Ocean (Galimov et al., 1980a,b; Galimov and Kodina, 1982). In recent studies of the “deep biosphere” there was evidence of microbial activity in oceanic sediments as deep as about 1000 m and beyond, (e.g. Parkes et al., 1994).

Gaseous hydrocarbons heavier than methane may occur in recent sediments in aerobic conditions. They are products of biochemical destruction of a fresh plant material rather than of microbial synthesis. For example, normal and iso-alkanes (C_2–C_5), and unsaturated hydrocarbons: ethylene, propylene, and butylenes C_2–C_4 were detected at micro liter per liter level in the Kara Sea and Yenisei estuary (Galimov et al., 2003, Galimov et al., 2006). The peculiarity of geochemistry of hydrocarbon gases at the

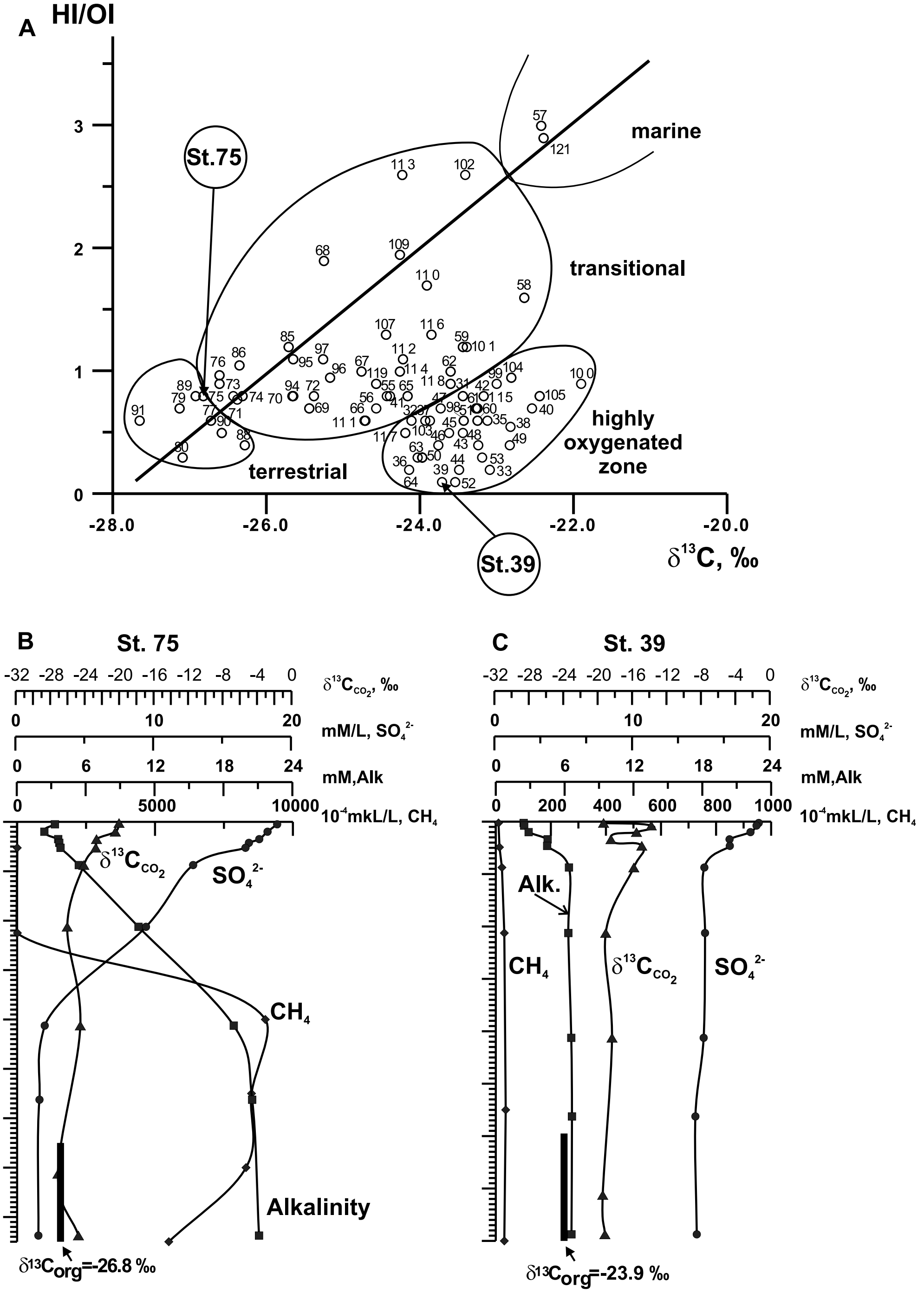


Fig. 30. Comparison of variation of the geochemical parameters in oxygenated sediments and the sediments with a normal redox regime: (A) Different redox zones in the Kara Sea: $\delta^{13}C$ vs. HI/OI for organic matter from subbottom sediments. The number next to the data point is the site number; (B) variation of geochemical parameters with depth in subbottom sediments from Site 75 with a normal redox regime; (C) the same for Site 39 with highly oxygenated sediments. The data are from Galimov (2004a).

surface conditions is a comparable content of methane (0.3–5 μl/l) and the C_2–C_5 hydrocarbons including unsaturated ones (0.1–0.5 μl/l). Apparently, this is due to the fact that this methane forms along with the heavier hydrocarbons as a product of early destruction of a biomaterial.

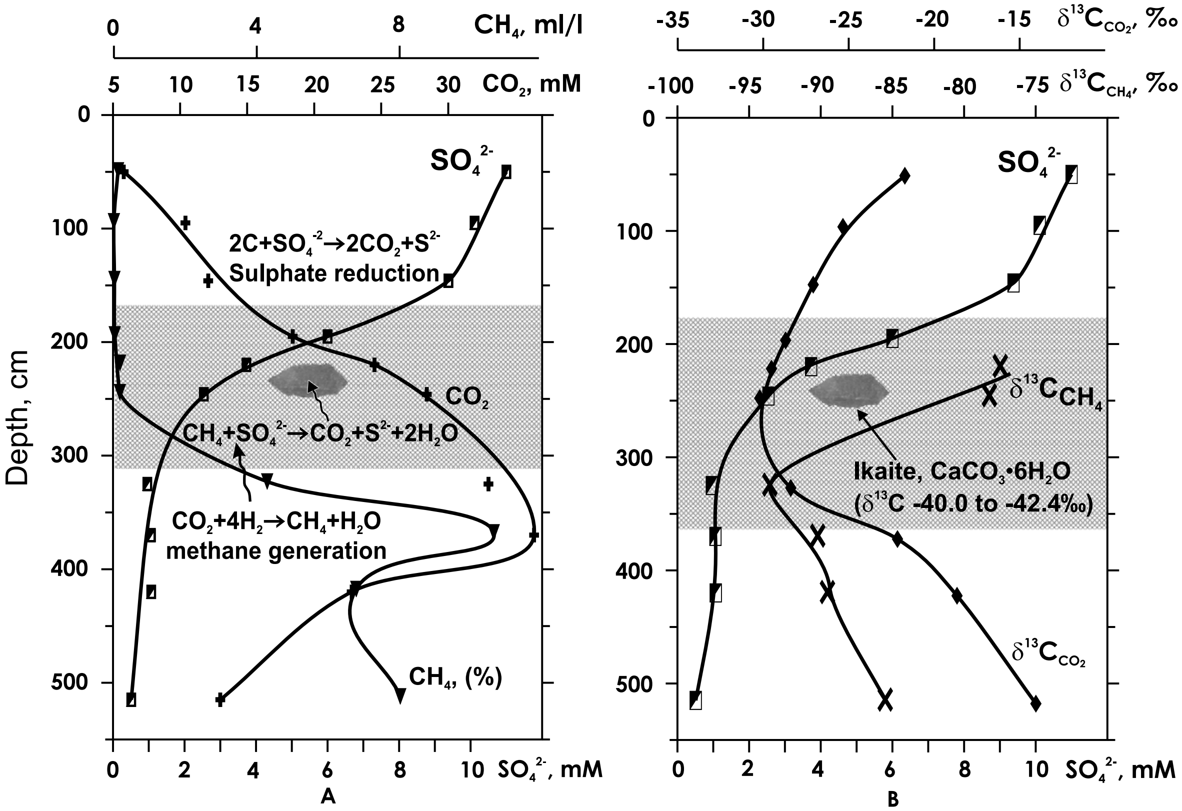


Fig. 31. Geochemical profile of sediments at station 01–26 in the Kara Sea. The samples were collected during the 35th cruise of *R*/*V* "Akademik Boris Petrov" in 2001: (A) change of concentrations of SO_4^{2-}, CH_4 and CO_2 with depth; (B) change of carbon isotopic composition $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{CO_2}$ with depth in the same profile.

6.2. Methane in atmosphere

During the last 200 years the concentration of methane in the atmosphere changed from about 750 to 1400 ppbv. The isotopic composition of methane in the present atmosphere varies from $\delta^{13}C = -47.0‰$ to $-47.5‰$ and the hydrogen isotope composition from $\delta D = -90‰$ to $-75‰$ (Breas et al., 2001). Seasonal and latitudinal isotopic variations of the atmospheric methane carbon were observed (Bergamaschi et al., 2000; Lassey et al., 2000). The $\delta^{13}C$ value of the atmospheric methane depends on the relative contribution of methane from different sources including wetlands, marine sediments, natural gas seeps, methane produced by animals and termites, and human activity. The isotope composition of the emitted CH_4 is significantly modified by subsequent isotope fractionation processes, in particular oxidization of methane in the atmosphere and in sediments, and in biomass smoldering. The major contributors of atmospheric methane produce isotopically light methane, mostly from $-55‰$ to $-75‰$, with about $-65‰$ on average. Therefore, the fact that atmospheric methane is about 20‰ heavier is mainly related to isotope fractionation during its oxidization.

The pre-historic concentration of CH_4 in the atmosphere was reconstructed by the study of air inclusions in ice cores from Antarctica (Vostok) and Greenland (Jouzel et al., 1993, 1996; Raynaud et al., 1993, 1996). The content of CH_4 in air varied from 300 to 700 ppbv in the past.

6.3. Methane in land environments

Methane is produced in swamps, marshes, bogs, rice paddies, flood plains and freshwater sediments. Global emission of CH_4 from wetland is estimated to be 50–360 Tg/yr and from rice fields 60–140 Tg/yr (Breas et al., 2001). The $\delta^{13}C$ values from wetland sources vary from about $-50‰$ to $-85‰$. The carbon isotopic composition of methane emitted from rice fields is estimated to be $-70‰$ to $-55‰$. The global annual emission from cattle and animals

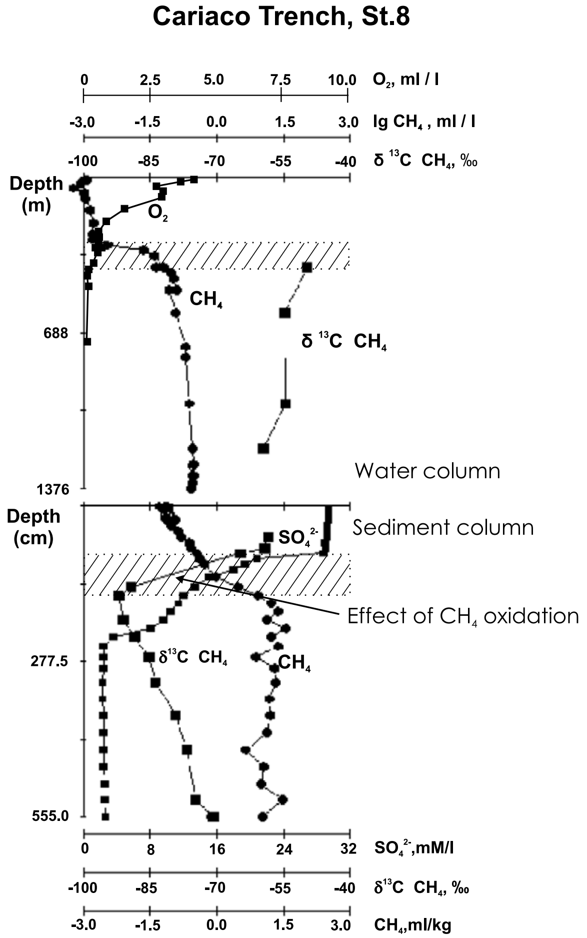


Fig. 32. Variation of geochemical parameters in the water column and the sedimentary profile at Station 8 in the Cariaco basin, as measured during the 14th cruise of *R*/*V* "Akademic Boris Petrov". The data are from the Report on the 14th Cruise of the *R*/*V* "Akademic Boris Petrov" (1990) and Galimov (1995a).

amounts from 70 to 100 Tg of CH_4, which is similar to the emission from rice paddies, and its $\delta^{13}C$ value varies approximately in the same range.

In some earlier works termites were reported to be significant contributors to the global emission of methane, but recent studies estimate CH_4 emission by termites at 1.5–7.9 Tg/yr, i.e. only from 0.3% to 1.5% of the total global CH_4 emission (Sugimoto et al., 1998).

6.4. The gas hydrate phenomenon

Gas hydrate is a snow-like substance in which methane and other low-molecular-weight hydrocarbons as well as non-hydrocarbon gases are held within cages of water molecules (Sloan, 1998). The peculiar feature of gas-hydrates is that under high pressure they remain stable at temperatures above 0 °C ($P = 70$ atm, $T = 10$ °C; $P = 250$ atm, $T = 20$ °C; $P = 462$ atm, $T = 25$ °C). As temperatures of the deep oceanic water are 2–4 °C and thermal gradient beneath the sea floor is about 30 °C/km, it is easy to calculate that under a water column of 2 km gas hydrates may exist over a zone as thick as 500 m.

Presence of gas hydrates is reflected by geophysical and geochemical properties of the host sediments: (1) the velocity of acoustic waves increases when the gas-water mixture becomes solid; (2) The thermal gradient decreases because of the higher thermal conductivity of gas hydrates; (3) A bottom-simulating reflector (BSR) appears (which transects stratigraphic layers) due to diagenetic alteration of sediments at the bottom of the gas hydrate zone. These anomalies are used for gas hydrate exploration.

Kvenvolden (1995) and Milkov (2005) provided comprehensive reviews of the occurrence and isotopic composition of gas hydrates. Hydrate-bound methane in the oceanic sediments is characterized by a wide range of carbon and hydrogen isotopic compositions: $\delta^{13}C$ from $-74.7‰$ to $-41.9‰$ and δD from $-242‰$ to $-115‰$ (Milkov, 2005).

It is noteworthy that hydrates rarely show the $\delta^{13}C$ values from $-70‰$ to $-100‰$ typical for microbial methane in oceanic sediments. As formation of gas hydrates is apparently not accompanied by isotope fractionation (Sassen et al., 2001; Milkov, 2005) this means that thermogenic gas may significantly contribute to the formation of gas hydrate accumulations.

Gas hydrate formation may prevent dissipation of methane generated by microorganisms and lead to its accumulation. Yet, the concentration of methane often is not sufficient to form a gas hydrate zone. Migration of thermogenic gas may supply the necessary concentration. Such sites, as we noted (Galimov and Shabaeva, 1985a,b) may be traced with a specific type of the relationship between $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{CO_2}$ (Fig. 34). It is seen that in Hole 567A (Middle American Trench, DSDP Leg 84), where gas hydrate was not recorded, the change in CH_4 carbon isotope composition with depth is parallel to that in CO_2. The gradient of $\delta^{13}C$ values with depth for CH_4 and CO_2 appears to be lower than that shown in Fig. 28. This is obviously due to a lower microbial activity at greater water depth (5500 m). The pictures are quite different at Sites

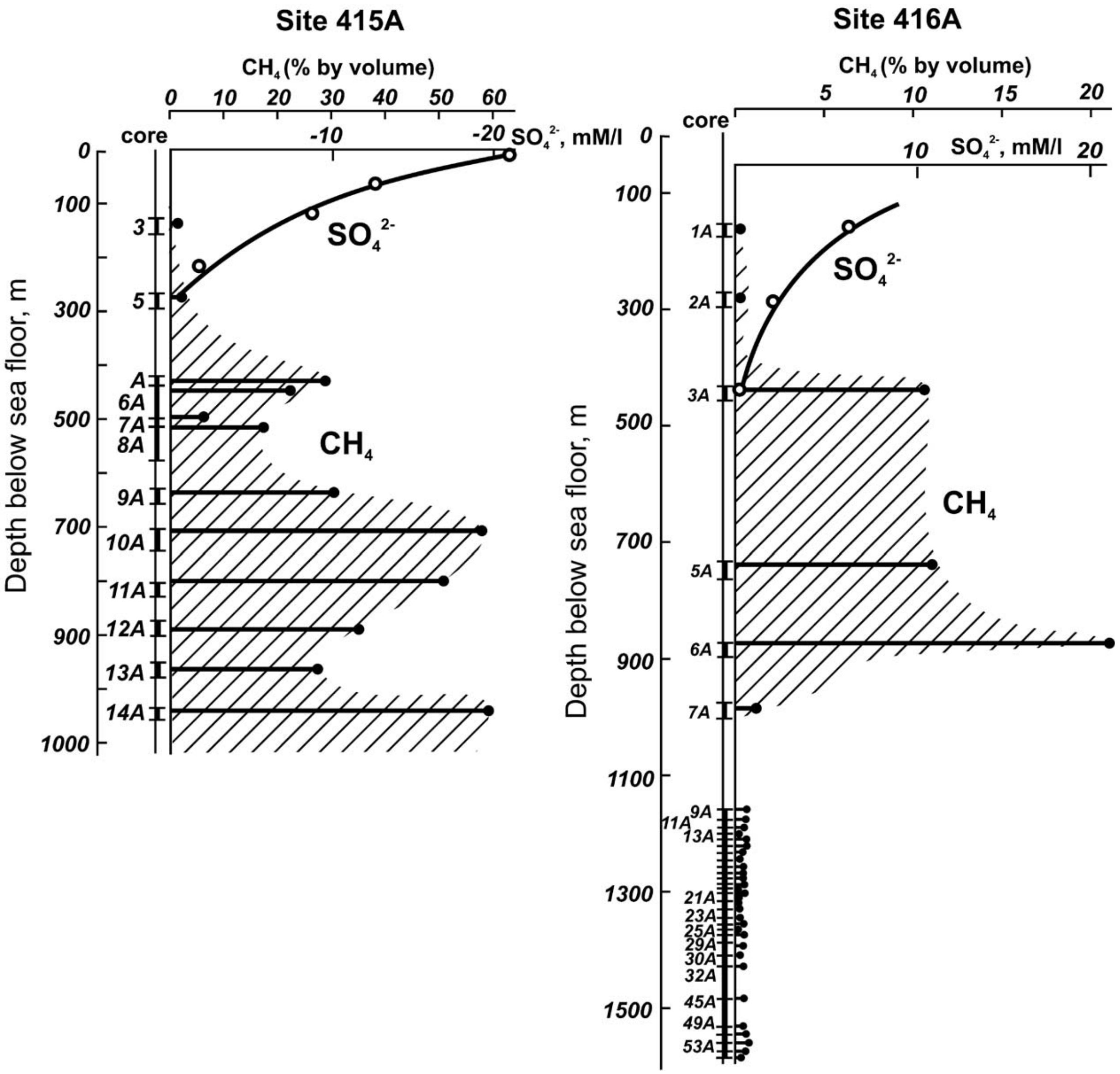


Fig. 33. Geochemical zonality (sulphate reduction and methane generation zones) in deep Holes 415A and 416A drilled in the Moroccan Basin, Atlantic Ocean, during Deep Sea Drilling Project Leg 50 (Galimov and Kodina, 1982).

568 and 570, where gas hydrate zones were detected. The $\delta^{13}C$ values measured for methane at Site 570 varied from −42‰ to −32‰ below 270 m. These $\delta^{13}C$ values are typical for thermogenic methane, and the relationship between $\delta^{13}C$ of CH_4 and CO_2 is inverted at 270 m depth. We suggest that the most probable cause of this phenomenon is the migration of thermogenic gas from deeper sediments. Indeed, direct measurement of carbon isotopic composition of a gas hydrate sample from Site 570 at the Middle American Trench gave a $\delta^{13}C$ value of −41.9‰ (Kvenvolden and McDonald, 1985).

The $\delta^{13}C$ values typical for thermogenic gases obtained by direct measurement of the isotopic composition of gas hydrate samples also were reported for hydrates from the Gulf of Mexico ($\delta^{13}C = -42.2$‰ to −48.4‰) (Sassen et al., 1999; Milkov, 2005), offshore Vancouver Island (−42.7‰ to −43.4‰) (Pohlman et al., 2005), the Caspian Sea (−44.8‰) (Ginsburg and Soloviyev, 1998).

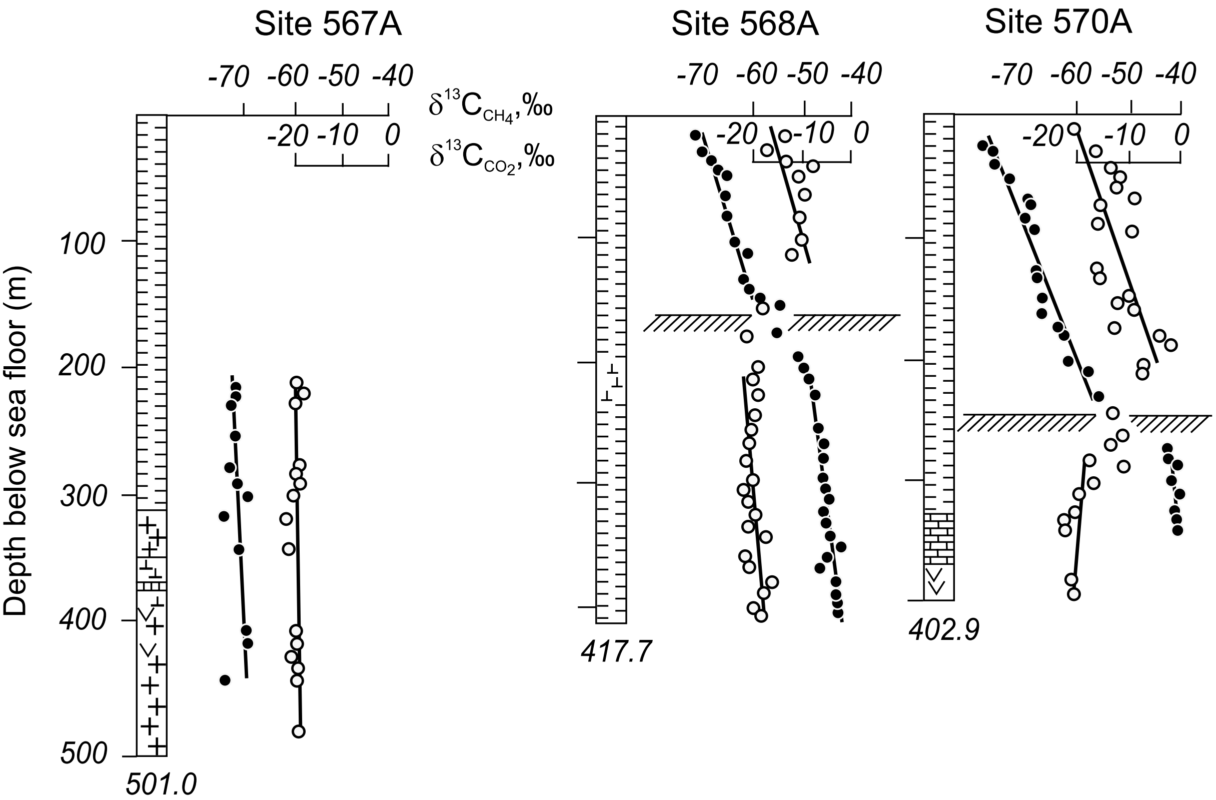


Fig. 34. Carbon isotopic composition of CH_4 and CO_2 interstitial gases in sediments of the Middle American Trench. Samples were collected from Holes 567A, 568 and 570 drilled during Deep Sea Drilling Project Leg 84, water depth 5500 m (Galimov and Shabaeva, 1985b). The lower boundary of the gas hydrate zone is marked. Water depth: Hole 567A – 5050 m, Hole 568 – 2010 m, Hole 570 – 1698 m.

Favorable pressure–temperature conditions within the thermodynamic stability zone of hydrates exist over a significant part of the ocean bottom (Galimov and Kodina, 1982). Based on the observed methane concentrations in oceanic sediments, huge accumulations of gas hydrates beneath the ocean floor may be expected (Kvenvolden, 1995). However, the actually accessible resources and accumulations potentially valuable for industrial utilization will be much more limited, if they are mostly related to sites of gas migration from deep-seated gas sources. Thus, the exploration for gas hydrate accumulations should include the evaluation of the presence of hydrocarbon source rocks and their gas generation potential in the relevant sedimentary basins.

Enigmatic incidents described as allegedly happening in the so-called Bermuda Triangle might be related to the sporadic gas release from gas hydrate accumulations. The great amount of oscillating gas bubbles ascending from the bottom may produce psychologically intolerable infrasound and cause electric and magnetic perturbations affecting navigation systems. The gas bubbles saturating the surface water dramatically decrease the buoyancy of water vehicles. We tried to test this hypothesis during Leg 14 of the *R*/*V* "Academic Boris Petrov" in 1990 on our way to the Cariaco basin through the Bermuda Triangle (Report on the 14th cruise, 1990). The idea was the following: The Cretaceous Hatteras Formation, containing black shale layers with organic matter contents up to 17%, occurs in sedimentary successions of this region (Dillon et al., 1976). It may serve as an effective source of thermogenic gas. In the case of a gas break-through the isotopic composition of methane in subbottom sediments should change from values typical for indigenous microbiological gas to those characteristic of migrated thermogenic gas. Three sites were studied. One of them was located on the Blake-Bahama Outer Ridge (Site 4, 31°15′ N 74°51′3 W, water depth 3160 m), and two others were in the abyssal plane of the Bermuda Triangle area (Site 5, 28°19′8 N 73°28′2 W, 4590 m, and N6, 25°50′

N 70°44′ W, 5450 m). The analysis of core samples retrieved from those sites did not record the expected change of the gas isotopic composition (Report on the 14th cruise, 1990). Thus the suggested mechanism was not proved, yet not ruled out.

Recently massive release of CH_4 from gas hydrate accumulations was proposed as a factor of global climate change in the geological past (e.g. Dickens, 2003; see additional references and discussion in Section 7).

6.5. Dependence of $\delta^{13}C$ of thermogenic methane on maturity of the initial organic matter

The increase of the content of ^{13}C isotope in methane with increasing burial depth of sedimentary rocks was one of the most important facts established early in gas isotope geochemistry (Galimov, 1968; Sackett, 1968). The factors which control the isotopic composition of thermogenic hydrocarbon gases are the following: (1) kinetic isotope effect depending on the extent of depletion (coefficient f) of molecular structures suitable for gas isotope generation; (2) the ranges of activation energies and distribution functions of activation energy of the gas-producing reactions, which, in turn, depend on the chemical structure and the type of organic matter; (3) temperature dependence of the kinetic isotope effect; (4) intramolecular isotope heterogeneity; and (5) isotopic composition of the initial organic matter. The factors are itemized in the order of their decreasing relative significance.

The effect of isotopic composition of the initial source is obvious but relatively small, as the range of natural $\delta^{13}C$ variation of the initial organic matter is within about 8–12‰, whereas the $\delta^{13}C$ values of thermogenic methane vary within ~50‰.

The significance of factors (1) and (2) was not recognized initially. Considering the variation of $\delta^{13}C$ of methane in geological sequences the authors of the early works (Alexeyev et al., 1967; Sackett, 1968) suggested that geological age was the determining factor. The alternative opinion was that burial depth rather than age was important and was proved by analyzing gas from different depths but of the same age (Galimov, 1968, 1969a,b). The gradient in the isotopic composition of methane with depth was believed to be due to the temperature gradient, since the kinetic isotope effect of gas formation depends on temperature.

Subsequently, I stressed the role of intramolecular isotope distribution and forwarded the hypothesis that during catagenesis methane production shifted from isotopically light carbon rich in C–H linkages to the isotopically heavier carbon poor in C–H bonds (Galimov, 1973). It followed from this consideration that the isotopic composition of gas should depend on the extent of chemical transformation (maturity) of the organic matter generating the gas. On this basis the method of identification of the gas source rocks was developed. The qualitative relationship of $\delta^{13}C_{CH_4}$ with the rank of coalification was applied for the first time to interpret the origin of gas accumulations including the giant Gazli field in the Amu-Daria depression, Middle Asia (Galimov et al., 1973a,b). The approach is evident from the Fig. 35, adopted from the cited work. Later, Stahl and Carey (1975), Stahl (1977), Schoell (1977, 1980), and James (1983) gave examples of successful application of the isotope technique of gas source-rock identification.

The idea of the dependence of gas isotope composition on the maturity of organic matter was proved to be robust. However, I had overestimated the role of intramolecular isotope heterogeneity among the causes of isotope fractionation during gas formation. Actually, the intramolecular isotope heterogeneity plays its role. However, the different generation mechanisms are more significant as discussed below.

6.6. The concept of different mechanisms of gas formation from humic and sapropelic organic matter

Stahl (1974) established an empirical but quantitative relationship between $\delta^{13}C$ values of methane and vitrinite reflectance (R_0). The latter is a measure of maturation of organic matter in sedimentary rocks. Interestingly, this relationship showed different $\delta^{13}C_{CH_4}$–R_0 trend lines with depth for methane generated from humic and sapropelic organic matter (Fig. 36). There was no obvious theoretical reason for this (Schoell, 1983). The Chinese scientists Dai et al. (1987) and Shen Ping et al. (1988) argued that Stahl's curve for humic organic matter was not reproducible and suggested a different curve for methane derived from coaly or humic material. Yet, the reason for the difference between the trends was not understood at all.

I brought forward an explanation based on my previous consideration (Galimov, 1974b) that when

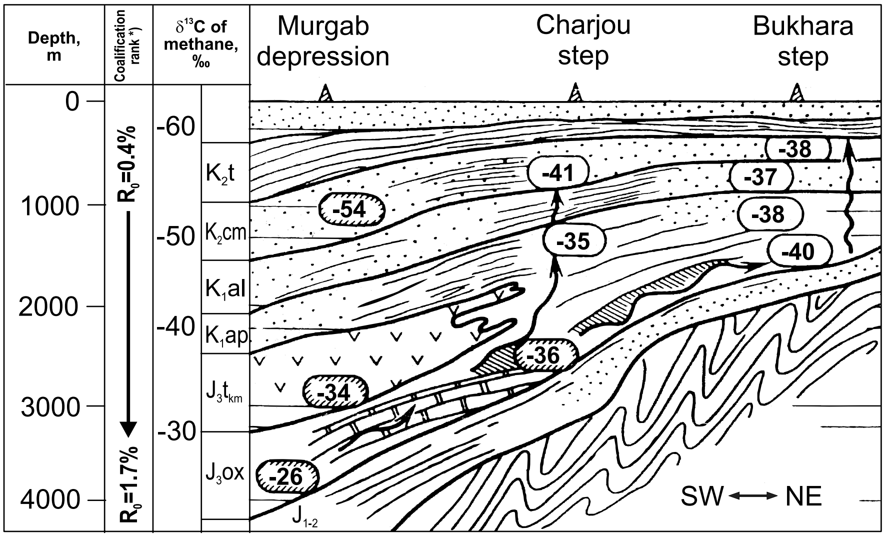


Fig. 35. An example of the identification of a gas source rock and of migration pathways (reproduced from Galimov et al., 1973b). The figures in the hatched ovals are the δ^{13}C values of methane, which was generated within the stratigraphic level where it occurs. The numbers in the open ovals characterize methane migrated from greater depth. In the columns on the left the range of the vitrinite reflectance coefficient and the δ^{13}C values of methane at the appropriate depth levels are indicated. Note that in the original paper the coalification ranks accepted in Russian literature (in Cyrillic letters) are indicated.

methane forms from a complex organic matter structure such as kerogen, the process is characterized by a set (band) of activation energies. Different structures may be involved in methane formation, and the distribution of activation energies may not be equal for humic and sapropelic organic matter (Galimov, 1988b, 1989).

Actually the most probable mechanism of methane formation from sapropelic organic matter, which is enriched in aliphatic structures, is the cleavage of C–C bonds. This process requires relatively high activation energy. Humic organic matter is characterized by an abundance of aromatic rings and heteroatoms. There is a good reason to suggest that one of the possible mechanisms of the methane formation in humic organic matter is related to the process of condensation of aromatic rings (Galimov, 1988b), and this process is characterized by lower activation energy. Thus, the range of activation energies for humic and sapropelic organic matter should shift, to the lower and higher ends, respectively, of the band of activation energies of methane formation. The calculation of the isotopic evolution curves based on this model describes the dependence of the isotopic composition of methane on the maturity of organic matter and the difference between the $\delta^{13}C_{CH_4}$–R_0 relationships for humic and sapropelic types of organic matter.

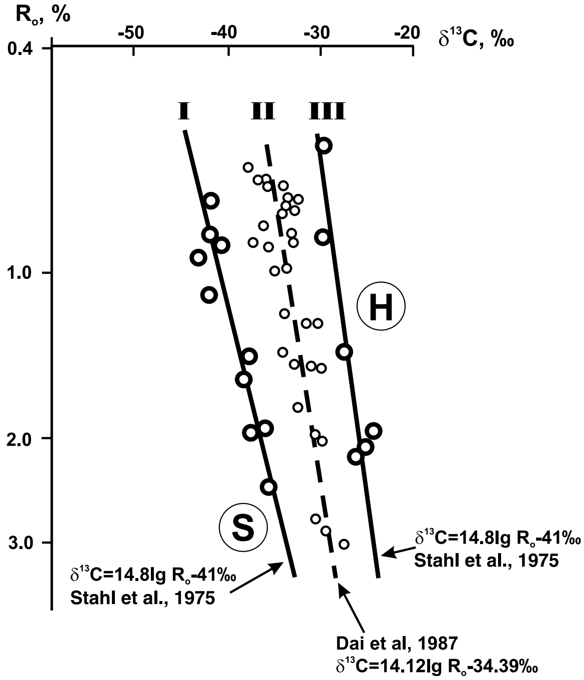


Fig. 36. $\delta^{13}C_{CH_4}$–R_0 for humic (H) and sapropelic (S) organic matter. References are given in the text.

The distribution functions for humic and sapropelic organic matter were selected to fit best the known empirical curves. The two isotope curves (“a” and “b”) for each type of the organic matter correspond to the extreme cases of the gas generation history (Fig. 37B). The left-hand curve (a) describes the instantaneous isotopic composition of methane released (under the condition that all methane generated in the previous stages was lost), whereas the right-hand curve (b) corresponds to the averaged isotopic composition of the total mass of methane generated at the given time. Thus, the difference between the curves given by Stahl (1977) on the one hand and Dai et al. (1987) and Shen Ping et al. (1988) on the other can be interpreted in terms of the generation history. Stahl’s curve is fairly well approximated by the “instantaneous” curve (a), whereas the curve established by the Chinese scientists is closer to the “cumulative” line.

The capability of the model to explain the major isotopic relationships provides a basis for its implementation in gas geology. It follows from the model that significant gas generation should take place at a relatively early stage of humic organic matter transformation. This was in contrast with the existing paradigm that main gas generation occurred in the final stages of maturation of organic matter (e.g. Hunt, 1979). Thus, the concept of main gas generation at a late stage should be corrected.

It was believed in accordance with the existing paradigm that methane in the huge gas deposits accumulated in the relatively shallow Cenomanian section of the northern part of West Siberia migrated upward from greater depth. In contrast to this, the model suggested above allowed the explanation that the gas in the Cenomanian reservoirs was generated and accumulated almost in situ (in the Pokur Suite) from humic organic matter at a relatively early stage of its geochemical transformation (for details see Galimov, 1988b; Galimov et al., 1990). Cramer et al. (1998) made a calculation using our model with a set of parallel reactions and additionally took into consideration the temperature dependence of the kinetic isotope effect. They came to the same conclusion that low-mature coaly organic matter of the Pokur Suite is the most likely source of the West Siberian gas in the Cenomanian rocks.

Another 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 a late stage of geochemical evolution of

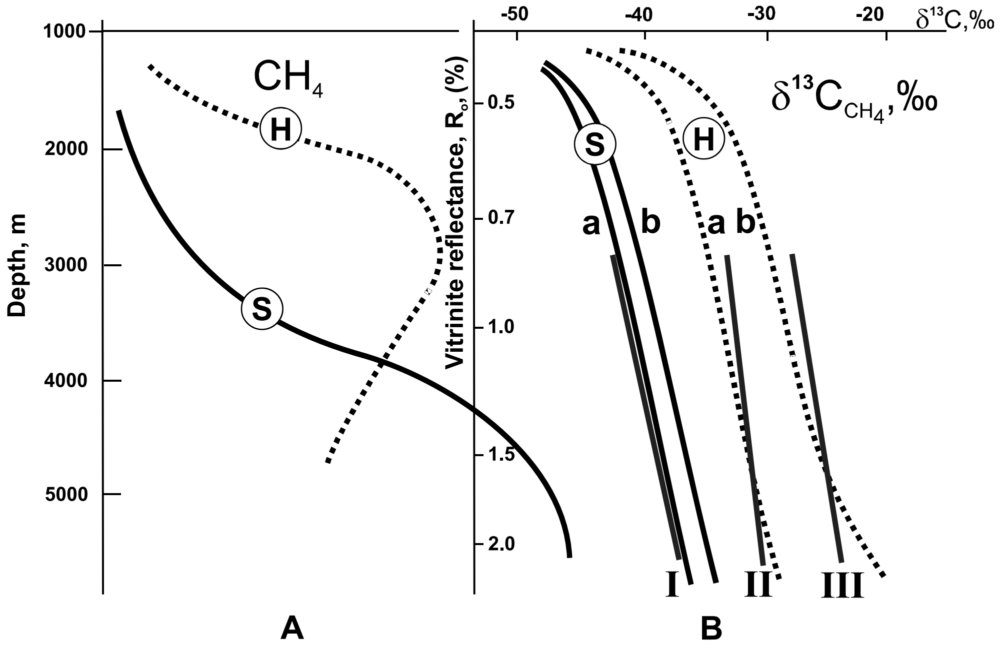


Fig. 37. Methane evolution (A) and carbon isotope composition (B) trends resulting from the model implying different distributions of activation energies for sapropelic (S) and humic (H) organic matter: *a* = “cumulative” curve, *b* = “instantaneous” curve (Galimov et al., 1988). Isotopic composition of the initial organic carbon: $\delta^{13}C_0 = -25‰$; the kinetic isotope effect of methane formation is $-30‰$.

organic matter and thermal cracking of oil. However, in the case of humic material the necessary proportion of gas to liquid hydrocarbons is already achieved at an early stage. Methane (and CO_2) can serve as a carrier for liquid hydrocarbons. Therefore, liquid hydrocarbons even in small concentrations (because of the early stage of transformation and the poor quality of the organic matter) may escape from a source rock in a gas-condensate state and form deposits before the onset of the main stage of oil formation. Such condensates actually have been suggested to occur (Kozlov, 1975; Powell and McKirdy, 1975; Connan and Cassou, 1980; Snowdon and Powell, 1982).

The late condensates are slightly enriched in the heavy carbon isotope compared to oil. This is due to fragmentation of gasoline-range hydrocarbons during condensate formation at a late stage of maturation. The late condensate represents a residual part of hydrocarbons formed by cracking. In contrast, the early condensates do not show ^{13}C isotope enrichment of this kind.

In order to prove the concept, I used a model with assumed activation energy distributions for humic and sapropelic organic matter. The distribution functions were adjusted to obtain calculated $\delta^{13}C_{CH_4}$ evolution curves, which would match the empirical relationships (Stahl's curves) for both types of organic matter. The assumptions are proved to be sufficiently valid to the extent that they provide a reasonable interpretation of the generalized empirical relationships and allow inferring the general consequences for gas generation (Galimov, 1988b). Implementation of the suggested model for exploration purposes requires the reconstruction of the actual distribution of activation energies intrinsic to the studied organic matter. This is a difficult task.

The specific model for a given case requires many factors to be taken into account, which are mainly unknown. The common approach to reconstruct the distribution of activation energies is the pyrolysis experiment. It is based on the assumption that the reaction rates characterizing a process under natural conditions can be determined by extrapolation of the data obtained experimentally at higher temperatures. The validity of this assumption is limited. Pyrolysis experiments are widely used for simulation of the lower-temperature natural processes on a geological time scale. However, it should be kept in mind that an increase of temperature not only accelerates a reaction but can also principally change the reaction pathway. This is especially true when one deals with the formation of a compound from a macromolecule of irregular chemical structure. The distribution of activation energies may strongly depend on temperature, and the character of this dependence is different for different substances. The various forms of catalysis may have an influence on the distribution of activation energies in natural systems (Galimov, 1973; Mango, 1996). Pressure also is important (Weng et al., 2003). Therefore, laboratory pyrolysis experiments are principally inadequate approximations of the natural processes of the generation of methane and other hydrocarbons. This explains the widely varying and irreproducible results of such experiments (Cramer et al., 1998; Berner et al., 1995; Andersen et al., 1995).

The concept outlined above was adopted by Berner and Faber (e.g. 1996). In a series of articles they described an approach that they presented as a new model. The "new" was an attempt to obtain the distribution of activation energies for particular gas source rocks by a pyrolysis experiment. They ignored the above-mentioned difficulties. Pyrolysis provides the activation energies of the reactions proceeding during pyrolysis but not of those proceeding under natural conditions. As a result, incorrect conclusions will be drawn from the interpretation of the pyrolysis data (Berner and Faber, 1996; Patience, 2003).

Patience (2003) raised the question: "What is coal gas?" His answer was that coal gas is relatively dry (>90% methane) and isotopically heavier ($\delta^{13}C_1 = -22‰$ to $-38‰$) than gas from marine source rocks. This does not take into account the dependence of the gas isotopic and chemical composition on maturity of the source organic matter. The late-generated gas from marine organic sources may be heavier and dryer than the early generated gas from humic organic matter.

For the same reason considering the $\delta^{13}C_1$ vs. $\delta^{13}C_2$ relationship has a little significance because similar values of the relationship may result from various combinations of different types of initial organic matter with different maturation levels and with different thermal and migration histories.

Several authors tried to test the applicability of my model (e.g. Littke et al., 1999) to explain the origin of the giant gas accumulations in northern West Siberia. The possibility of the formation of significant amounts of gas at an early stage of transformation of humic organic material was questioned. It followed from the pyrolysis experiments of the authors that only about 2% of the methane generation capability of the organic matter was realized by the time corresponding (by extrapolation) to gas formation in the Cenomanian. The pyrolysis experiments were carried out with samples from the Pokur Suite, i.e. with samples that had already produced gas in the Cenomanian time. The experimental activation energy distribution obtained by pyrolysis (Fig. 38B) is different from the calculated model function, which is in a good agreement with the actual isotopic data for the Cenomanian gas (Fig. 38A). It should be noted that for the 800 m-thick Pokur suite, which we identified as a gas source rock for the Cenomanian gas in West Siberia, even a 2% yield is sufficient to explain the known resources.

Schoell et al. (1997) proposed that the Cenomanian methane was generated by bacteria from coal-derived CO_2. They argued that the CH_4 yield during the early coalification is too small (0.01 ml/g coal) to explain the actual reserve of the gas ($\sim 30 \times 10^{12}$ m^3). Indeed, huge amounts of CO_2 are released during coalification. But a comparably large amount of hydrogen, four times greater in volume, is needed to convert CO_2–CH_4. The authors did not consider the hydrogen source. In young sediments methanogenic bacteria coexist with hydrogen-producing bacteria. Coal and plant debris are not an appropriate substrate for them. Also, Schoell et al. (1997) probably underestimated the methane yield, with their value of only 0.01 ml CH_4/g coal, at the level of maturity of the Pokur organic matter. If one adopts the 2% yield following Littke et al. (1999), which is still very small, it would give 200×10^{12} m^3 of CH_4, exceeding by an order of magnitude the proven reserves of the gas accumulation. The simultaneously released CO_2 despite its large amount would form carbonate cement in the rock at a concentration of less than 1%.

The study of the hydrogen isotopes provides an additional argument (Galimov, 1995b). Land plants growing at high latitudes, where meteoric waters are substantially depleted in deuterium, can have δD values of up to 80‰ lower than marine plants. Correspondingly, the fossil derivatives from these land plants should be depleted in deuterium. Indeed, the δD values of CH_4 in the West Siberian gases are about 50‰ below the empirical δD_{CH_4}–R_0 relationship given by Schoell (1980). Thus, the δD data

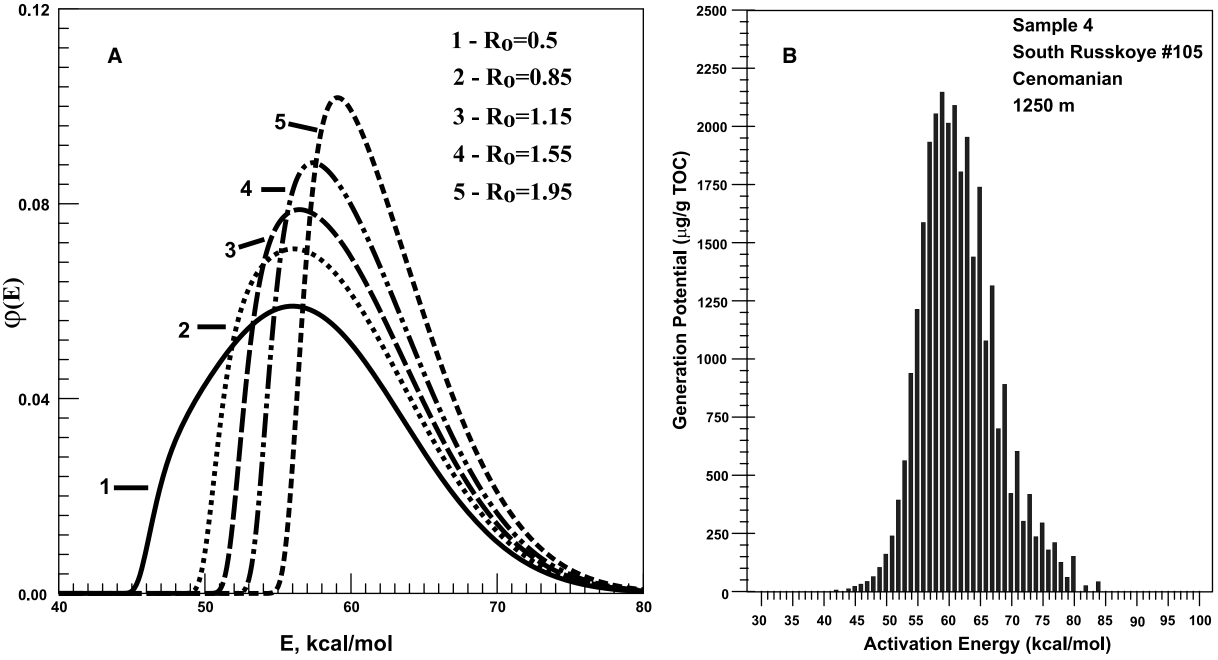


Fig. 38. Theoretically calculated distributions of activation energies of methane generation (Polyakov and Galimov, 1992) compared to those experimentally obtained by a pyrolysis experiment (Littke et al., 1999): (a) Curve (1) fits best to the empirical data; the shape of the curve evolves with increasing maturity; the starting point of the curve indicates the degree of maturation of the initial organic matter. (b) Activation energy distribution for a sample from the Pocur Suite (well 411, depth 1250 m).

independently indicate that continental humus material was the main source of methane for the West Siberian gas accumulation.

In spite of all the difficulties and uncertainties mentioned above the technique based on the attempt of reconstructing the initial and evolved chemical structure of the organic matter and its hydrocarbon producing potential is a prospective approach for the identification of gas source rocks. In any case, it promises something more than just differencing gases of biogenic, thermogenic and mixed origin, which is still in practice (e.g. Huang et al., 2003; Liang et al., 2003).

6.7. Carbon isotope distribution in the C_2–C_4 system

Along with methane higher-molecular-weight hydrocarbons form during catagenesis. Experiments (Rohrback, 1979) and the observation of the behavior of the C_2–C_4 hydrocarbon system under natural conditions showed that these hydrocarbons consecutively appear and disappear with the increase of temperature (maturation of the initial organic matter). Fig. 39 shows the results of experimental thermolysis of a liquid hydrocarbon system (after Hill et al., 2003). Methane and bitumen are the end members. The yield of the C_2–C_5 fraction first increases with the increase of the thermal stress and then declines.

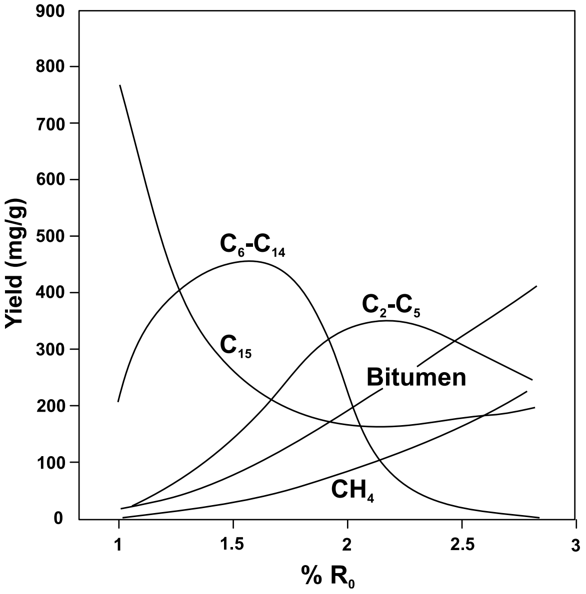


Fig. 39. Changes in yield of studied fractions as a function of increasing thermal stress (after Hill et al., 2003).

We developed a model (Galimov, 1988b; Polyakov and Galimov, 1992), which simulates the observed pattern of the temperature evolution of the C_1–C_4 system. The model was based on the idea that the low-molecular-weight C_1–C_4 alkanes are formed by cleavage of the C–C bonds of a C_N higher-molecular-weight precursor. The calculation results in yields of the C_1–C_4 hydrocarbons that are in agreement with the experimental data.

Application of the same model to the calculation of isotope fractionation with some simple assumptions concerning the distribution of activation energies and the magnitude of the kinetic isotope effect (constant at 1.030) gives results approximating well the experimental data, in particular those compiled by James (1983); yet we have a different opinion of the isotope exchange in hydrocarbon systems (see Galimov, 1988b).

The interesting result of our model is the divergence of the isotopic curves for C_1–C_4 hydrocarbons at higher maturity levels (higher temperatures). Under these conditions, according to the model, the low-molecular-weight hydrocarbons are involved themselves in the decomposition process. Methane and ethane partly consume the isotopically light moieties and may temporarily become isotopically lighter than the previously generated portions of the same gas (Galimov, 1988b). The divergence of the $\delta^{13}C$ values in the C_1–C_4 system corresponds to this stage.

Recently, Patience (2003) described two pyrolysis experiments, one carried out under closed conditions and the other one under open conditions. The first shows a divergence in the isotopic signature between the C_1–C_4 hydrocarbons with increasing temperature whereas the second one shows a convergence with increasing temperature. This, to my mind, improperly was interpreted as approximations to the conditions found in nature in coals (closed) and marine source rocks (open) with inefficient and efficient expulsion, respectively (Patience, 2003). In fact, the divergence observed in the closed-vessel experiment is due to consecutive decomposition of the C_4, C_3 and C_2 compounds, when the pyrolysis temperature exceeds 450–500 °C. The remaining higher hydrocarbons become enriched in the heavy isotope whereas the isotopically light moieties feed ethane and finally methane making them isotopically lighter, or at least slowing down their enrichment in the ^{13}C isotope independent of coal or marine organic matter as the source. Obviously, in the open system the newly formed hydrocarbons escape, at least partly, the immediate decomposition, and all compounds become more and more heavy in accordance with the reservoir exhaustion mechanism.

6.8. Reverse isotope distribution in C_1–C_4 system: organic compounds in igneous rocks

If we turn to the mantle and the lower crust environment, i.e. the domain of non-biological processes, we observe a different pattern of isotope distribution, yet controlled by the same type of kinetic isotope effect. It was shown that $\delta^{13}C$ of the average earth crust carbon is about $-5‰$ (Galimov, 1968). Deep-sitting diamonds of the ultramafic mineral paragenesis are characterized by a median value of $\delta^{13}C = -4.6‰$ (Galimov, 1991). The gaseous emanations of the mantle (CO_2, CH_4, CO) have $\delta^{13}C$ signatures, which are close to this value. The first discovery of the anomalously isotopically heavy mantle methane with $\delta^{13}C = -3.2‰$ to $-7.9‰$ was reported from a study of fluid inclusions in minerals of ultramafic rocks from the Khibiny, Lovozero, and Ilimaussaq intrusions (Galimov and Petersilie, 1967; Galimov, 1973).

The kinetic isotope effect of C–C bond breaking/formation controls the production of natural gaseous hydrocarbons both in sedimentary and magmatic rocks but with opposite patterns of isotope fractionation (Galimov, 1973). The C_1–C_4 gases in sedimentary rocks are produced via degradation of kerogen, i.e. by breaking of C–C bond. The same compounds in magmatic rocks are products of consecutive polymerization through the creation of C–C bonds. Therefore, their depletion in the heavy carbon isotope, in contrast to their sedimentary counterparts, rises with increasing carbon number. Fig. 40 taken from my earlier work (Galimov, 1973), illustrates this phenomenon for natural magmatic hydrocarbons. The original diagram is modified here by the data obtained later by Des Marais et al. (1981) during spark discharge experiments. The C_1–C_3 hydrocarbons synthesized in that experiment (asterisks) showed the same isotope distribution pattern as the C_1–C_3 hydrocarbons in igneous rocks. It should be noted that the $\delta^{13}C$ values of C_1–C_4 hydrocarbons of magmatic origin are well approximated with the theoretical curve "A", calculated by using Eq. (15) for 400 °C whereas the degradation kinetic isotope effect (curve "B") in the range of 50–150 °C, which is typical for gas generation in sedimentary rocks, predicts a greater fractionation than is actually observed. The cause of this was already discussed. Thus, biogenic and non-biogenic low-molecular-weight hydrocarbons are distinguishable because of different mechanisms of their formation, and hence their different isotope distribution pattern.

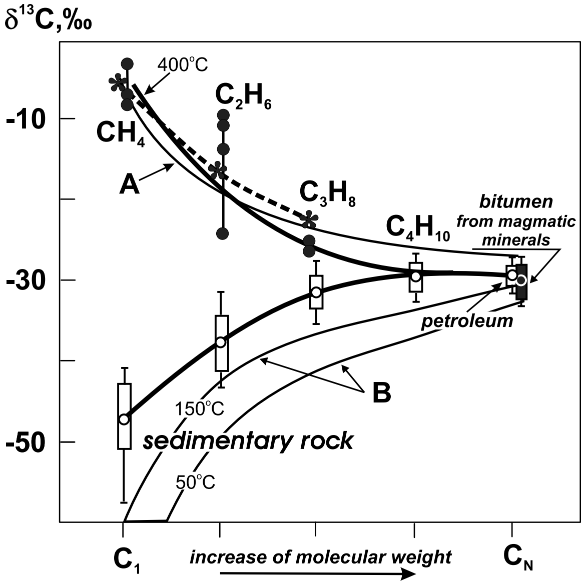


Fig. 40. Inverse relationship of C_1–C_4 hydrocarbon gases produced by cracking (in sedimentary rocks) and synthesized from simple precursors (Galimov and Petersilie, 1967, 1968; Galimov, 1973). The filled symbols are $\delta^{13}C$ values for the C_1–C_3 hydrocarbons and the averaged value for bitumen extracted from the gas–liquid inclusions in minerals of magmatic rocks; curve "A" corresponds to the calculated kinetic isotope effect during formation of C_1–C_4 hydrocarbons from a simple precursors. The open symbols stand for the averaged $\delta^{13}C$ values of the hydrocarbons from sedimentary rocks; curve "B" is the same as "A" but for gas produced by cracking of a macromolecular precursor. The asterisks gives trends found for C_1–C_3 hydrocarbons synthesized in a spark-discharge experiment (Des Marais et al., 1981).

Recently, Du et al. (2003) observed the reverse isotope distribution in the C_1–C_4 system during experimental pyrolysis of lignite at higher temperatures (500–700 °C) and pressure (1–3 GPa). They related the observed carbon isotope distribution to the effect of pressure. Other than Du et al. (2003), I suggest that pressure does not significantly affect the carbon isotope effect. A genuine, yet small carbon isotope effect of pressure is known for the diamond-graphite equilibrium system (Polyakov and Kharlashina, 1994) at pressures exceeding 40 GPa. However, the increase of pressure in a C_1–C_4 system can shift the chemical equilibrium toward the higher hydrocarbons, and this may induce partial transformation of C_1 to the higher homologues accompanied by the enrichment of C_1 and depletion of C_{2+} with the ^{13}C isotope. Accordingly, there is no new phenomenon in the Du et al. (2003) observation, and there is no need for an appeal for precautions in the identification of biogenic/abiogenic gas.

Occurrence of methane with relatively high $\delta^{13}C$ values was reported for methane–hydrogen gas seeps from ultramafic rocks in the Zambales Ophiolite, Philippines ($\delta^{13}C$ values about $-7‰$) (Abrajano et al., 1988) from the East Pacific Rise ($\delta^{13}C = -18‰$ to $-15‰$) (Welhan and Craig, 1983). One of the possible sources of abiogenic methane is serpentinisation and hydration of ultramafic rocks (Welhan, 1988; Sherwood Lollar et al., 1993; Berndt et al., 1996). However, some experiments indicate that the potential for methane synthesis during serpentinization may have been overestimated (McCollom and Seewald, 2001).

Bitumen occurring in igneous rocks is believed to be synthesized from simple precursors (CO, CH_4, etc.) under high-temperature and high-pressure conditions, i.e. they are a product of abiogenic synthesis. Indigenous bitumen found as inclusions in minerals of magmatic rocks is depleted in the ^{13}C isotope almost to the same extent as biogenic bitumen and kerogen in sedimentary rocks (Galimov and Petersilie, 1967, 1968; Galimov, 1991). In particular, bitumen inclusions in the alkaline ultramafic rocks of the Kola Peninsula showed $\delta^{13}C$ values from $-32.3‰$ to $-26.7‰$. Whether the indigenous bitumen is a form of hydrothermally altered and recycled sedimentary organic matter or a genuine product of synthesis from simple precursors, with the $\delta^{13}C$ value accidentally coinciding with the $\delta^{13}C$ values of sedimentary organic carbon, remains an open question. Some olivine and garnet crystals from kimberlite rocks had gas-liquid inclusions, which contained organic compounds. The measurements showed that the organic carbon was isotopically light with $\delta^{13}C = -23‰$ to $-32‰$ (Galimov, 1988a, 1991; Galimov et al., 1989).

6.9. Diffusion and interphase isotope fractionation

Petroleum and its components in nature are subjected to processes of evaporation–condensation, solution, diffusion, absorption–desorption, etc., during their formation and migration. Experimental studies showed that isotope fractionation related to these processes is relatively small and sometimes reveals an unexpected character.

It is known that the gas diffusion isotope effect is determined by the ratio of the diffusion coefficients (D) and correspondingly the reverse ratio of the square roots of the masses of the isotopic species:

$$\alpha_{kd} = D^*/D = \sqrt{m/m^*}. \tag{22}$$

As the diffusion coefficient of the species with the lighter isotopic is greater, a compound should become depleted in ^{13}C during diffusion. The concept of isotope fractionation by diffusion in natural gases was employed in the early literature to explain the observed change of isotopic composition of gaseous hydrocarbons in a vertical profile of sedimentary basins (e.g. Colombo et al., 1968).

The ratio in Eq. (22) is sufficiently rigorous only for the case of self-diffusion and the diffusion of gas through a medium not interacting with gas. However, when gas migrates through an active medium, the effect may be the opposite. Indeed, the diffusion effect in a liquid is determined by the relationship

$$\alpha_k \approx \sqrt{\frac{m}{m^*}} e^{-\frac{\Delta E}{RT}}, \tag{23}$$

where ΔE is the difference of the activation energies of the displacement of the isotopic species of a compound moving through the liquid. The ΔE value may have different signs. If the interaction between gas and liquid is stronger for the isotopically light molecules, then gas molecules containing the heavy isotope can migrate faster than the isotopically light molecules resulting in isotope effect opposite to the ordinary diffusion effect.

For the first time the “inverse” isotope effect was established in an investigation of methane samples from the dispersion aureole of a subsurface artificial gas reservoir at Kaluga near Moscow (Galimov, 1967). The gas samples were collected from the pumping site of the gas reservoir and from control wells at different distances from the gas body (Galimov, 1967; Fig. 90 in Galimov, 1973). It was found that with increasing distance from the pumping site methane is enriched in ^{13}C. It was suggested that isotope separation upon filtration through wet rock is caused by preferential fixation of the isotopically light methane.

In addition to the field study we undertook an experiment to determine quantitatively the magnitude of the isotope effect in the system $CH_{4(gas)}$–$CH_{4(water\ solution)}$ (for details see Galimov, 1973, pp. 314–315). The experiment showed that the light isotope of methane carbon was indeed preferentially retained in the water phase, although the effect was small ($\alpha_k = 1.0003$). The report on this study caused a discussion at the Symposium on Stable Isotopes in Leipzig in 1967 with Italian researchers, who considered the diffusion isotope fractionation to be a major factor that causes the observed depletion of methane in ^{13}C from greater depth to the surface in the Tertiary basin in Northern Italy. Later, they set up an experiment of filtration of gas through a wet medium and confirmed our results (Colombo et al., 1968, p. 156).

As the pore space of sedimentary rocks is filled with water, the mechanism of isotope fractionation induced by migration of gas is not due to the porous character of the medium, but to gas transport in a liquid. This effect can manifest itself in non-stationary processes. Under steady-state conditions this type of isotope effect is negligible. However, a minor isotope effect cannot be ruled out when the gas migrates within the body of a free gas pool or escapes the pool because of a leakage in the cap rock.

Prinzhofer and Huc (1995) referred to me as an advocate of a significant role of diffusion in isotope fractionation of natural gases (among other "Russian authors" in contrast to the "western community" recognizing the principal role of "genetic events", p. 282). The reference to Galimov (1973), however, is a misunderstanding, because in fact I am a longstanding opponent of the diffusion concept and repeatedly emphasized the relatively minor role of the diffusive processes in the general pattern of carbon isotope fractionation in natural processes.

In gas–oil pools the relative concentrations of individual constituents (C_1–C_4) in the gas cap above an oil and dissolved in the oil are quite different. The dissolved gas is richer in the higher homologues. Yet, the isotopic composition of the same component in oil and gas phase is similar. Only methane shows a hardly noticeable difference as Prinzhofer and Huc (1995) correctly noted. And this difference is due to a somewhat higher presence of the heavy isotope ($\sim$0.5‰) in the gas phase. This is about the same order of magnitude of isotope fractionation, which is observed in the water–methane system ($\alpha = 1.0003$, i.e. 0.3‰) (Galimov, 1973).

We observed a similar effect in an experimental study of carbon isotope fractionation during degassing of petroleum. Petroleum with dissolved gas was collected by a special sampler under natural pressure (15 MPa). Then the petroleum was subjected to differential degassing. The experiment was described in Galimov (1973, pp. 315–316). No noticeable systematic variation in the isotopic composition of hydrocarbons (C_1–C_4) liberated at different stages of degassing occurred, although for methane we noted a small enrichment in ^{13}C (0.5‰) in the gas liberated in the last portion.

Vaporization of liquid hydrocarbons was reported to have no or only a small isotope effect (Bjorøy et al., 1994; Ahmed and George, 2004; Poulson and Drever, 1999; Huang et al., 1999; Wang and Huang, 2001). During vaporization of dichloromethane and trichloroethane the vapor was enriched in the ^{13}C isotope (less than 1‰). The δD was also higher in the vapor phase. The isotope effect for hydrogen is by an order of magnitude greater than that for carbon.

Having emphasized the minor significance of the diffusion isotope effect in petroleum migration (Galimov, 1973; Fuex, 1980) one should not neglect it in particular cases. However, the new attempts to employ diffusion as a major factor of isotope geochemistry of natural gas (Pernaton et al., 1996; Prinzhofer and Pernaton, 1997) do not appear convincing. Some authors described an alteration of the isotope composition of oil caused by migration (Silverman, 1965; Curiale and Bromley, 1996). But this change is not due to the isotope effect. The cited authors measured $\delta^{13}C$ values of the total oil. As petroleum is a multicomponent system and different components have different isotope compositions, the obvious change of chemical composition during migration is reflected in the change of the petroleum isotopic composition as a whole. This cannot be considered an isotope fractionation.

7. $\delta^{13}C$ variation of organic and carbonate carbon during the geological history

Carbon occurs in the biosphere and in the sedimentary system in two major forms: carbonate and organic. Broecker (1970) reviewed the available isotopic data and suggested that the present-day ratio of carbonate to organic carbon (C_{carb}/C_{org}) approximately equals 4:1 and has remained nearly constant over geologic history.

The carbon isotope analysis of the ancient Precambrian carbonates was used to demonstrate that carbon in the atmosphere from the beginning of the geological record was presented in the form of CO_2 rather than CH_4 (Galimov et al., 1968). Yet the initial Earth's atmosphere could have contained CH_4 and CO (Galimov, 2000a, 2005b).

The $\delta^{13}C$ variations of carbonate (Fig. 41A) and organic carbon (Fig. 41B) through geologic time were first documented by a systematic study of samples from the Russian platform (Galimov et al., 1973a, 1975). A specific aspect of that work was that the isotopic composition of averaged samples was measured. Each sample analyzed was composed of thousands of samples collected throughout the Russian platform and mixed in proportion to the local abundance and thickness of the stratigraphic unit. This collection prepared by the Academician Ronov during his scientific career provided extraordinarily representative results for the studied stratigraphic units. These data-points are represented in Fig. 41 by the enlarged circles. The data for some geological periods not adequately represented by the mixed samples were supplemented by the analysis of individual samples. The most notable discovery was of the Early Proterozoic carbonates anomalously enriched in the ^{13}C isotope ($\delta^{13}C$ varied from +8‰ to +12‰). The periods of enrichment of carbonates in ^{13}C correspond to periods of tectonic activity. However, organic carbon does not show similar deviations of $\delta^{13}C$ values. In general, the organic carbon in the Precambrian exhibits a significantly wider $\delta^{13}C$ range with a frequent occurrence of isotopically light samples. The peak of the relative enrichment of carbonates in ^{13}C occurred in the Late Carboniferous and Permian. The $\delta^{13}C_{carb}$ value for the Russian Platform is +4.5‰ (average of 520 samples) in the Late Carboniferous and +3.4‰ (average of 715 samples) in the Early Permian (Galimov et al., 1975). These $\delta^{13}C$ values are lower than those for the above-mentioned Precambrian epochs; however, they were the highest average values obtained for Phanerozoic carbonates. Moreover, the Carboniferous organic carbon is less depleted in ^{13}C. The $\delta^{13}C_{org}$ values increase up to −24.3‰ (average of 272 samples) in the Carboniferous and up to −26.0‰ (average of 386 samples) in the Permian whereas the average $\delta^{13}C_{org}$ values in the earlier Phanerozoic periods vary from −27.2‰ to −29.7‰.

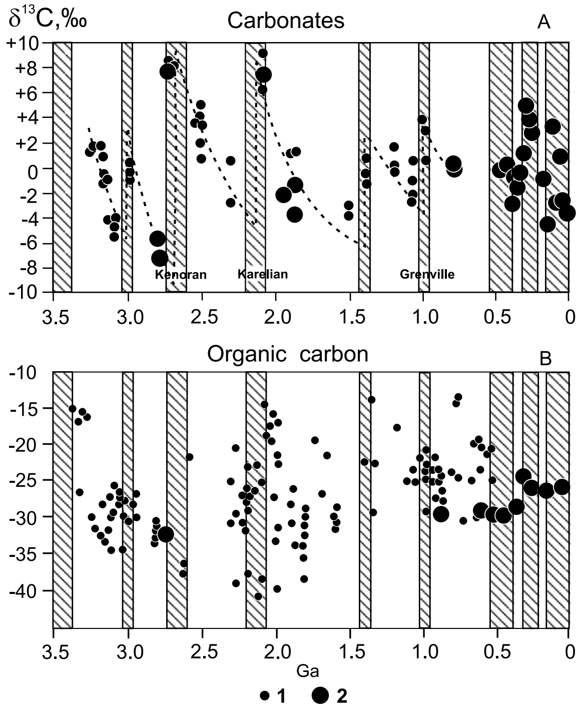


Fig. 41. Variations of $\delta^{13}C$ of carbonate (A) and organic carbons (B) over geologic time (after Galimov et al., 1973a,b, 1975; with refinement of the sample age). (1) individual sample, (2) mixed probe composed of more than hundred samples of rocks of the respective geologic age.

The other early studies were carried out by Welte et al. (1975), Eichmann and Schidlowski (1975), and Schidlowski et al. (1976). Welte et al. (1975) made a compilation of the available data from the literature for Phanerozoic samples and obtained a trend similar to Galimov et al. (1973a,b). Eichmann and Schidlowski (1975) did not find anomalous $\delta^{13}C$ values for carbonates in the studied samples from Early and Middle Precambrian ($\delta^{13}C$ varied from −2.2‰ to +4.1‰). But later Schidlowski et al. (1976) reported such carbonates in the Lomagundi sequence in Southern Africa and, thus, supported to the notion that the observed ^{13}C enrichment of carbonates was a global rather than a local phenomenon. The age of the events is around 2.1 and 2.5 Ga.

Carbonates enriched in ^{13}C were recorded in various regions of the world in Precambrian formations dated within an interval of 2.0–2.7 Ga (Baker and Fallick, 1989; Melezhik and Fallick, 1994). Later, large positive $\delta^{13}C_{carb}$ excursions (up to +12‰) were recorded in the Neoproterozoic (Kaufman and Knoll, 1995), the Late Cambrian (Glumac and Walker, 1998; Saltzman et al., 1998), the Late Silurian (Munnecke et al., 2005), the Late Ordovician (Cramer et al., 2005), and the Early Carboniferous (Saltzman et al., 2000). Decoupling of C_{org} and C_{carb} production and burial are believed to be responsible for the major $\delta^{13}C_{carb}$ excursions. While this is a likely mechanism, it cannot explain all the observations (Galimov, 1999). The “snowball” hypothesis was involved (Bekker et al., 2003, 2005). But there is evidence that the excursions appeared in interglacial rather than glacial periods (Glumac and Walker, 1998; Munnecke et al., 2005).

A different trend was found in the Cenozoic (Galimov, 1995a). The analysis of the data on the carbon isotopic composition of organic material in oceanic sediments showed that the $\delta^{13}C_{org}$ values shift since the Late Eocene–Early Oligocene from $-25‰$ to $-29‰$, typical of Mesozoic sediments, to $-21‰$ to $-25‰$, typical of present-day material (Fig. 42).

The behavior of the carbonate branch of the carbon cycle also changed. Our data on the organic carbon are compared with the variation of $\delta^{13}C$ values in carbonates with time. The latter dependency was obtained by Degens (1989). Like for organic carbon, the carbon isotopic composition of carbonates shifts by 2–3‰ in $\delta^{13}C$ from the Eocene to the present time. However, this shift is opposite to that of the organic carbon isotopic composition.

A model of the global isotope balance relevant for interpretation of these observations was suggested (Galimov, 1999). Under steady-state conditions the carbon flux into the surface reservoir (atmosphere, hydrosphere, and biosphere) is balanced by carbon leaving it by fluxes of organic and carbonate carbon (see Fig. 6). According to the isotope fractionation under “distillation with total reflux” (see the relevant earlier paragraph) the balance equations may be presented in the following form:

$$\delta^{13}C_{org} = \delta^{13}C_0 + \xi\Delta^{13}C$$
$$\delta^{13}C_{carb} = \delta^{13}C_0 - (1-\xi)\Delta^{13}C,$$

where $\xi = C_{carb}/(C_{carb} + C_{org})$ and $\Delta^{13}C = \delta^{13}C_{org} - \delta^{13}C_{carb}$. A three-dimensional diagram was calculated by Galimov (1999). If one accepts that $\delta^{13}C_0$ is a constant through geological time and equal to $-5‰$ then the diagram is reduced to a two-dimensional form shown in Fig. 43.

The hatched area shows the most typical ranges of $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ during the geologic history. The diagram shows that variations in the proportions of organic and carbonate carbon (i.e. the $C_{carb}/[C_{carb} + C_{org}]$ value), which are usually considered a possible cause for global changes in the carbon isotope composition with geological time, cannot alone produce the whole range of $\delta^{13}C$ of carbonate and organic carbon observed in nature.

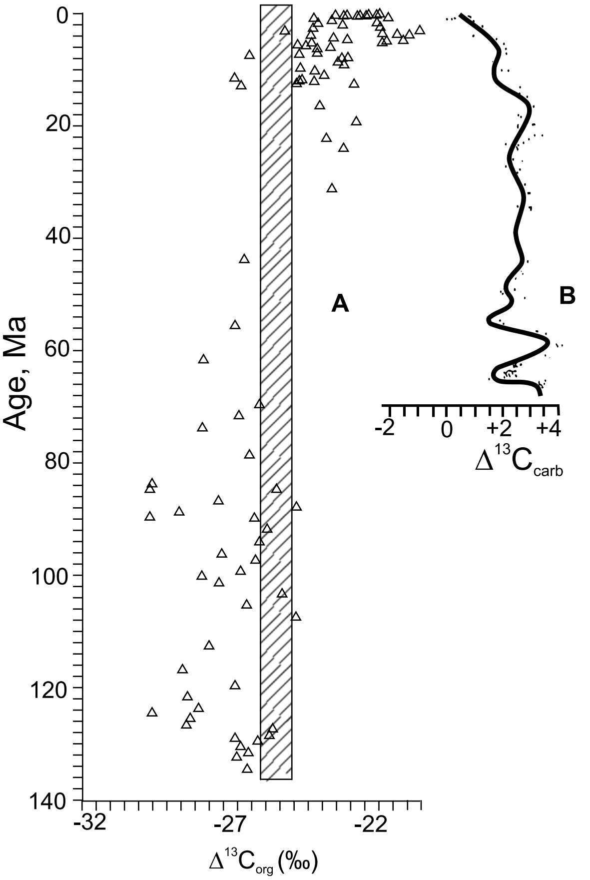


Fig. 42. Variations of the isotopic composition of organic (A) and carbonate (B) carbon with geologic age. Data on $\delta^{13}C$ for organic carbon are results of our study of core samples obtained during Legs 50, 64 and 138 of the Ocean Drilling Program. The initial data are published elsewhere (Galimov et al., 1980b; Galimov and Simoneit, 1982; Galimov, 1995a). The relationship for carbonates is after Degens (1989). The latter is consistent with the data obtained on deep-sea sediments. The hatched vertical bar is the $\delta^{13}C$ variation range for terrestrial carbon; it remains relatively constant during geological time.

As an example, field *D* corresponding to the Precambrian ^{13}C-enriched carbonates requires a stronger isotope fractionation between organic and inorganic carbon ($\Delta^{13}C$) than the fractionation is at present. Practically this means a higher isotope fractionation during biological carbon fixation. It is noteworthy that isotope fractionation during chemosynthesis is larger by 4–6‰ than that during photosynthesis (Ruby et al., 1987). Therefore, organic matter in anoxic environments may be additionally depleted in ^{13}C due to the contribution of bacterial biomass. In particular, strongly ^{13}C-depleted material may be contributed by biota

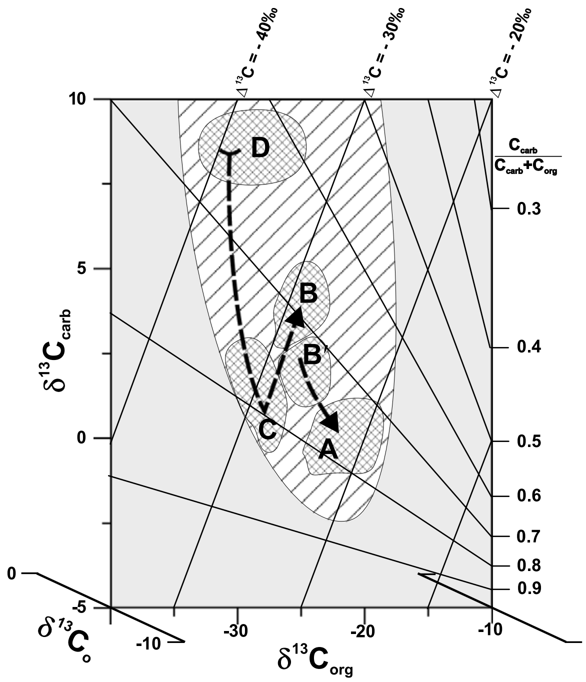


Fig. 43. Dependence of the isotopic composition of carbonate ($\delta^{13}C_{carb}$) and organic carbon ($\delta^{13}C_{org}$) on the mass ratio of carbonate and organic carbon $C_{carb}/(C_{carb}+C_{org})$ and the isotope fractionation ($\delta^{13}C$) between organic and inorganic materials in the surface carbon reservoir of the Earth, based on a constant isotopic composition of the initial carbon of $\delta^{13}C_0 = -5‰$. The scales will change correspondingly if $\delta^{13}C_0$ varies. See text for explanation.

involved in the anaerobic cycling of methane carbon. Thiel et al. (2003) found extremely isotopically light ($\delta^{13}C$ as low as $-78.9‰$) triterpenoids of the hopane series from bacterial lipids in mats associated with methane seeps in the Black Sea. Biosynthesis of hopanoids is compatible with an anoxic environment and is believed to have an early evolutionary origin (Rohmer et al., 1984).

In the diagram for $\delta^{13}C_0 = -5‰$ (Fig. 43), data points for the present-day biosphere plot within field A with the center at $\delta^{13}C_{carb} = 0‰$ and $\delta^{13}C_{org} = -22‰$. Thus, the present-day ratio of carbonate to organic carbon is 0.77:0.23, and taking into account the isotope composition of the present reservoir of total carbon ($\delta^{13}C = -3‰$) (Galimov et al., 1975) the value of the biospheric carbon isotope fractionation is $\Delta^{13}C = -19‰$.

The $\delta^{13}C$ excursions may be caused by the change of the $\delta^{13}C_0$ value, e.g. due to invasion of isotopically light CO_2 induced by massive oxidation of biogenic material, or vice versa, due to the flux of ^{13}C-enriched CO_2 generated by the intensification of carbonate metamorphism. Some authors argue that sharp $\delta^{13}C$ changes in sedimentary carbon recorded at the Triassic–Jurassic boundary (Dickens et al., 1997; Dickens, 2003), in Late Paleocene (Katz et al., 1999; Palfy et al., 2001), in Early Cretaceous (Jahren et al., 2001), in Neoproterozoic times (Kennedy et al., 2001; Jlang et al., 2003), and in Toarcian carbonates in the Jurassic (Hesselbo et al., 2000) are related to the massive release of methane from gas hydrates. The prominent feature of the $\delta^{13}C$ excursions caused by a change of $\delta^{13}C_0$ must be a coherent unidirectional shift of $\delta^{13}C$ values of both organic and carbonate carbon.

In general the global trends can be related to changes in the tectonic activity of the Earth and to climatic changes. The change in the intensity of bioproductivity was the most important event in both cases. A global anoxic regime may be induced by an increase of volcanic activity, which resulted in a higher inflow of nutrients to the ocean, and, in turn, increased the bioproductivity. In the absence of an adequate oxygen supply this leads to the preservation of the deposited organic matter and the establishment of an anoxic regime. Eventually, carbonates appear anomalously enriched in the ^{13}C isotope, and the organic carbon is relatively depleted in ^{13}C (Galimov, 1999). Global cooling also leads to an increase of bioproductivity due to an intensification of water circulation and nutrient supply. However, in this case the oxygen circulation results in recycling of most of the deposited organic matter. Eventually, it leads to the depletion of carbonates in ^{13}C and to a relative enrichment of the organic carbon in the ^{13}C isotope, as it was observed in the Cenozoic trend (Galimov, 1999).

One more feature should be noted. As is known, the carbon isotopic composition is widely employed for the identification of terrigenous, as isotopically light, and marine, as isotopically heavier, organic carbon. This proxy is valid for the present-day situation. However, as follows from Fig. 42, marine organic carbon older than the Oligocene is isotopically lighter than the land-derived carbon. Therefore, the mentioned simple method of identification of terrestrial and marine organic matter is not universally applicable.

8. Organic geochemistry and astrobiology

The experience of organic geochemistry can be used to determine fundamental geochemical consequences of the presence of life and provides a tool for identification of the vestiges of life. To achieve these goals one needs a better understanding of the essence of prebiotic and early biotic evolution.

To date a great variety of organic compounds has been identified in interstellar space, in meteorites and comets (e.g. Yang and Epstein, 1983; Wright et al., 1989; Ohishi et al., 1992; Cronin and Chang, 1993; Jewitt et al., 1997; Zinner, 1997; Irwine, 1998). Microstructures resembling microorganisms were reported to be present in the Martian meteorite ALH 840011 (McKay et al., 1996), although the arguments were not quite convincing (Galimov, 1997).

The development of the reliable identification of biogenic products has a crucial importance for the evaluation of the origin of life. Traditionally, carbon isotope analysis is used to search for traces of life in ancient sedimentary rocks and extraterrestrial material. Contrary to the current belief (e.g. Wright et al., 1989; Schidlowski, 1993; Mojzsis et al., 1996) the relative depletion in the ^{13}C isotope of total carbon in organic materials is not conclusive evidence of its life-related origin. It occurs both in biogenic and non-biogenic natural substances. To be able to distinguish a life-related origin of organic matter one needs to find properties which are unique for the chemistry of life.

Among the available extraterrestrial material carbonaceous chondrites are known as carriers of significant amounts of organic compounds. The ranges of isotopic variations in the carbon substances from carbonaceous chondrites are shown schematically in Fig. 44. The data are mostly from Cronin and Chang (1993) for the Murchison meteorite with additional data from some other sources as cited below.

The carbonaceous matter mainly consists of insoluble, structurally heterogeneous macromolecular material. Its carbon is isotopically relatively light. The isotope effects of polymerization and partial degradation could affect the isotope composition of the hydrocarbons and the polymer material (Yuen et al., 1984; Sephton et al., 2000).

More than 70 species of amino acids were identified in carbonaceous meteorites. They show a significant enrichment in the ^{13}C isotope relative to both the macromolecular carbon and its terrestrial counterparts. Organic matter from carbonaceous chondrites (amino acids, in particular) also shows significant enrichment in ^{15}N and *D*. The hydrogen isotopic composition of amino acids is characterized by δD values from about +700‰ to +2500‰ (Epstein et al., 1987; Pizzarello et al., 1991). Another important group of individual components,

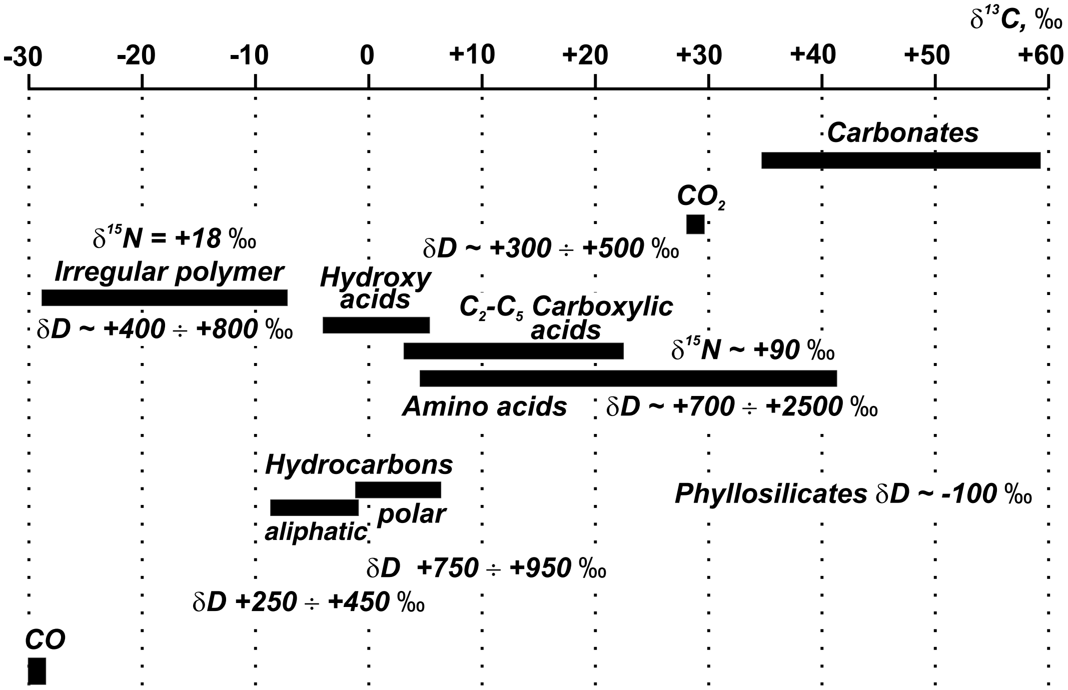


Fig. 44. Isotopic composition of organic substances in carbonaceous chondrites. See text for references.

identified in the carbonaceous chondrites, is hydroxy carboxylic acids. They are structurally similar to amino acids, but contain an OH group instead of the NH_2 group of amino acids. The isotopic composition of hydroxy carboxylic acids is slightly different from that of amino acids. The hydroxy acids in the Murchison were reported to have $\delta^{13}C = +4‰$ and $\delta D = +573‰$. The substances in Fig. 44 are schematized along the vertical axis in approximate accordance with their β factors: carbonates and CO_2 have the highest $\beta^{13}C$ values, whereas CO has the lowest one, and organic carbon is intermediate. Among the organic compounds hydrocarbons have $\beta^{13}C$ values lower than amino acids and hydroxy carboxylic acids. Looking at the diagram the impression arises that there is some trend reflecting a correspondence between the established range of the $\delta^{13}C$ values for a given type of carbon and its position on the diagram defined by its $\beta^{13}C$ characteristic. However, the polymer carbon will not comply with this trend, and if CO and CO_2 (carbonate), for which the direct isotope exchange cannot be ruled out, are to be excluded from consideration, the trend disappears.

Isotope data are available for some individual amino acids (Fig. 45) (Engel et al., 1990). There is no $\beta^{13}C$–$\delta^{13}C$ correlation for meteoritic amino acids (compared to Fig. 10 for biological amino acids). Thus, we can conclude that the criterion stated above being applied to organic material in carbonaceous chondrites does not reveal their biological origin.

The anomalous enrichment of the carbonaceous chondrites in the heavy isotopes ^{13}C, ^{15}N, and D is believed to be a strong indication that these meteorites retained interstellar components (Robert and Epstein, 1982; Tielens, 1983; Yang and Epstein, 1983; Langer et al., 1984; Turner, 1990; Anders and Zinner, 1993; Lecluse and Robert, 1994; Hoppe et al., 1995; Cassen and Chick, 1997; Charnley et al., 1997; Wielen and Wilson, 1997).

Since the pioneering experiments by Miller and Urey of 1950s, the efforts of much research dealing with the origin of life has been focused on the synthesis of organic compounds that could be of prebiological significance. It is now well established that synthesis of organic compounds may occur in the interstellar dust, comets, protoplanetary grains and bodies, including meteorite parent bodies, and in different environments on the surface of planets. Therefore, a variety of organic compounds, including complex structures certainly existed on the early Earth. They created an initial background for prebiotic evolution. But prebiotic evolution proper, to my mind, begins from adenosine triphosphate (ATP) formation (Fig. 46). The full details of the proposed concept can be found elsewhere (Galimov, 2001). ATP is suggested to play a key role since its hydrolysis (ATP–ADP conversion) materializes the mechanism of ordering and evolution of complexity (Galimov, 2004b). The main content of prebiological evolution was reduced to a process of ordering of organic structures, including synthesis of peptides from amino acids, with increasing role of selective

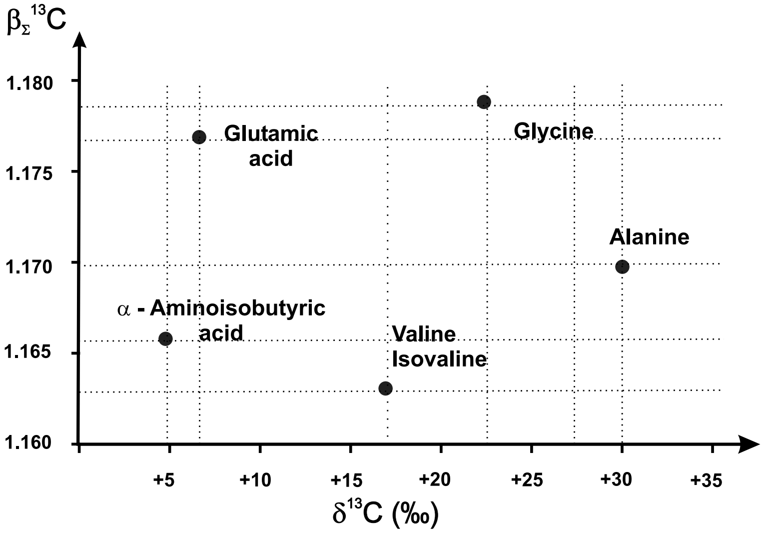


Fig. 45. Comparison of $\beta_\Sigma{}^{13}C$ and $\delta^{13}C$ values for amino acids from the Murchison meteorite. See text for references.

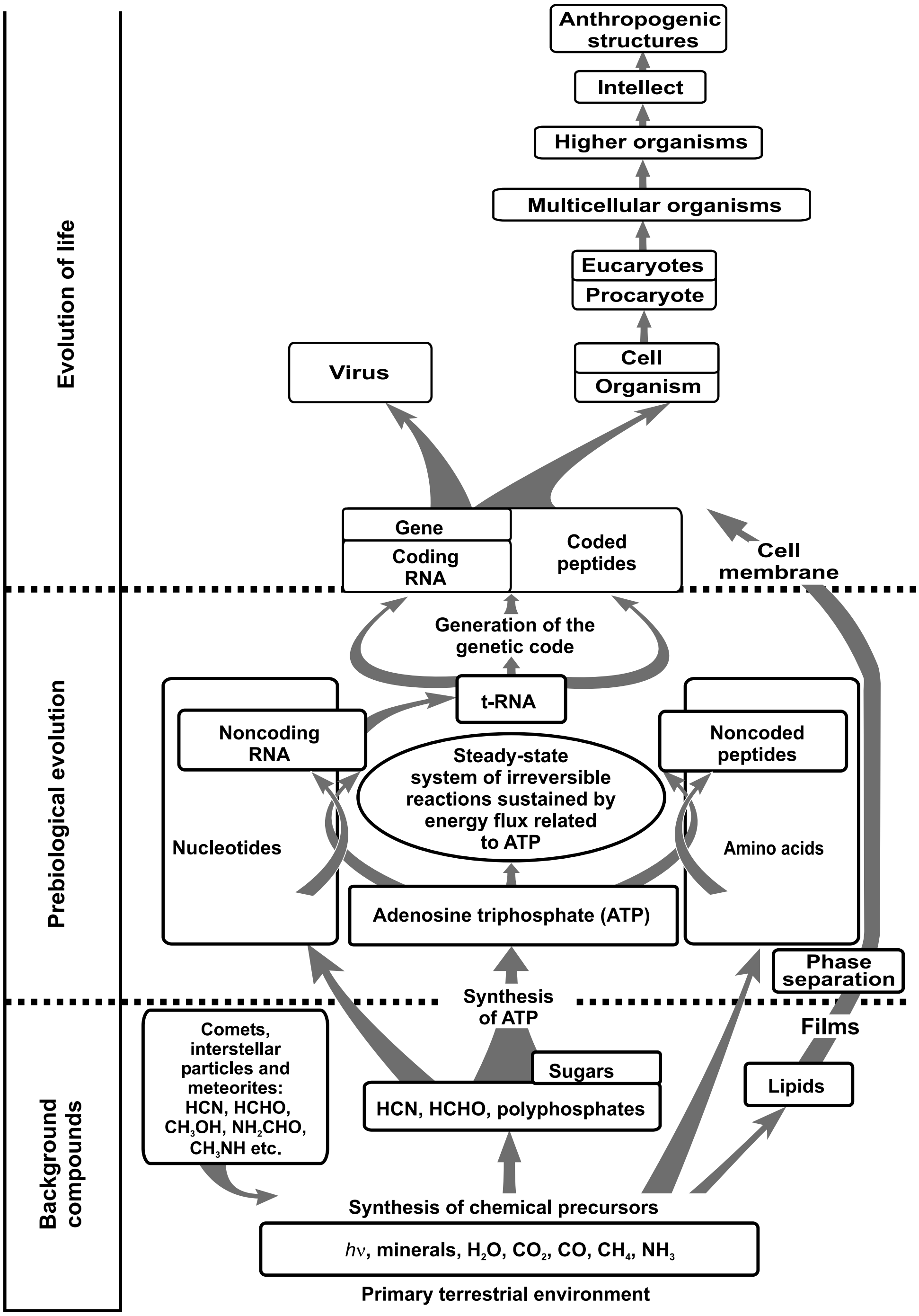


Fig. 46. Suggested pathways of early Life and subsequent its evolution (from Galimov, 2001).

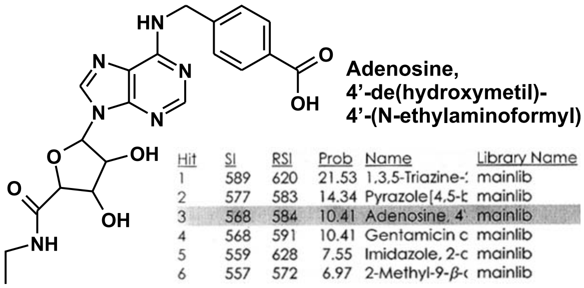
catalysis, and synthesis of nucleotide chains, with appearance of a mediator (such as tRNA) between structures of amino acids and nucleotides, and, eventually, formation of the genetic code. The appearance of the genetic code accomplished prebiotic evolution and initiates the evolution the life as we know it.

Although ATP is a rather complex molecule, both organic moieties of this compound, adenine and ribose, have HCN and formaldehyde (HCOH) as simple precursors (Orò, 1961; Ponnamperuma et al., 1963; DeGraaf et al., 1998; Krishnamurthy et al., 1999). However, HCN and formaldehyde tend to interact with the formation of cyanohydrine, and this prevents subsequent synthesis of adenosine and other RNA precursor molecules (Shapiro, 1995). Therefore, to produce ATP, specific conditions should exist (Galimov, 2005a).

The presence of a reduced atmosphere (containing carbon as CH_4) is of a crucial importance for the implementation of the ATP way of prebiotic evolution. The composition of the Earth's initial atmosphere is a subject of discussion in the recent geologic literature. The concept of a CO_2-containing (neutral) initial atmosphere gained common acceptance. However, the idea of the reduced initial atmosphere has reemerged recently with a new argumentation (Kasting et al., 1993; Sagan and Chyba, 1997; Galimov, 2000a, 2005b).

Recently we have set some experiments to synthesize compounds, which could be structurally close to ATP or its immediate precursors (Lupatov and Galimov, 2006). Proceeding from the above mentioned concept, the CH_4 and N_2 system with small addition of oxygen (0.1%) was selected. The reactions were initiated with short impulses of the electric discharge. We have identified more than 100 organic compounds in the products of the experiments, including alkene and alkinecyanides, amines, aromatic and heterocyclic compounds, and ethers of nucleonic bases. Among others, adenosine was identified with noticeable probability (Fig. 47).

Unfortunately we were not able to measure the isotopic composition of the synthesized adenosine. However, the fraction, which contained adenosine with the other similar structures, showed $\delta^{13}C$ value 12‰ lower than the initial CH_4 carbon. Study of the isotope fractionation related to synthesis of complex prebiotic molecules is promising. I believe that the isotopic evidence will play a decisive role in deciphering of the life concept.



Hit	SI	RSI	Prob	Name	Library Name
1	589	620	21.53	1,3,5-Triazine-	mainlib
2	577	583	14.34	Pyrazole[4,5-	mainlib
3	568	584	10.41	Adenosine, 4'	mainlib
4	568	591	10.41	Gentamicin c	mainlib
5	559	628	7.55	Imidazole, 2-c	mainlib
6	557	572	6.97	2-Methyl-9-β-	mainlib

Fig. 47. Identification of adenosine by GC-MS in products of synthesis from CH_4–N_2 system (with small oxygen admixture) during the electric discharge experiment (Lupatov and Galimov, 2006).

Acknowledgements

I thank Prof. Dr. Jürgen Rullkötter for very helpful suggestions and corrections made in the manuscript, and anonymous reviewer for useful comments.

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