KEROGEN

INSOLUBLE ORGANIC MATTER FROM SEDIMENTARY ROCKS

Edited by
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1980

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C^{13}/C^{12} in kerogen

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I. INTRODUCTION

The carbon isotopic composition of a kerogen depends on the isotopic composition of its biological precursors as well as on the isotopic fractionation that has taken place in the course of the formation and chemical evolution of the kerogen. Regularities in carbon isotope distributions in kerogens must therefore be considered against a background of the general biogeochemical behaviour of carbon isotopes; such an approach has been attempted in this paper.

II. PRINCIPLES OF CARBON ISOTOPE DISTRIBUTIONS IN BIOLOGICAL PRECURSORS OF KEROGEN

Bioorganic carbon is known to be enriched in the C^{12}-isotope, in comparison with the carbon dioxide used for photosynthesis in plants. Different biochemical components of organisms have distinctive carbon isotope compositions. For example lipids are enriched in C^{12} while amino acids and carbohydrates are relatively depleted in the light isotope [1, 15, 42, 62, 63].

Although at one time the origin of the isotopic fractionations in biological systems remained vague, it was believed to be kinetic, i.e. the effects were dictated only by the greater mobility of the carbon-12 species compared to that of carbon-13 species and by the greater lability of C^{12}-X bonds compared to C^{13}-X bonds; briefly, by the preferential assimilation of $C^{12}O_2$ in comparison with $C^{13}O_2$ during photosynthesis.

But differences in the isotopic composition of individual biochemical compounds often proved to be regular and the observed naturally-occuring fractionations often duplicated those expected on a thermodynamic (not kinetic) basis. Investigations of this problem have led to the conclusion that in biological systems there is an ordered intra- and intermolecular carbon isotope distribution, which may in general be predicted by means of isotope thermodynamics [24]. A necessary first step in such studies was the development of convenient

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techniques for calculating the isotopic thermodynamic properties of complex organic substances.

The thermodynamic isotope exchange properties of compounds can be calculated using Urey's formula for the partition function ratio of isotopic forms of the compound, the so-called β-factor:

$$\beta = \prod_{i}^{3N-6} \frac{\nu_i^* \exp\left(-\frac{h\nu_i^*}{2\,kT}\right)\left[1 - \exp\left(-\frac{h\nu_i}{kT}\right)\right]}{\nu_i \exp\left(-\frac{h\nu_i}{2\,kT}\right)\left[1 - \exp\left(-\frac{h\nu_i^*}{kT}\right)\right]} \tag{1}$$

In this equation: ν_i and ν_i^* represent the oscillation frequencies of the isotopic species (here, the asterisk refers to a molecule containing a heavy isotope); h is Planck's constant; k is the Boltzmann constant; T is the absolute temperature, K°, and N is the number of atoms in the molecules.

The greater the value of the β-factor, the higher is tne concentration of the heavy isotope in the given compound provided that equilibrium takes place in the corresponding isotope-exchange system. For example, for the exchange reaction:

$$C^{12}O_2 + C^{13}H_4 \rightleftharpoons C^{12}H_4 + C^{13}O_2$$

we can write:

$$\delta C^{13}_{CH_4} - \delta C^{13}_{CO_2} = \left(\frac{\beta_{CH_4}}{\beta_{CO_2}} - 1\right) \times 10^3 \qquad (^\circ/_{oo}) \tag{2}$$

Carbon isotope compositions are given in δC^{13}-values and represent deviations per mil ($^\circ/_{oo}$) in the C^{13}/C^{12}-ratio of the sample from the C^{13}/C^{12}-ratio of the PDB standard.

The latter is equal to 0.0112372. Thus:

$$\delta C^{13} = \left(\frac{(C^{13}/C^{12})_{sample}}{0.0112372} - 1\right) \times 10^3 \qquad (^\circ/_{oo}) \tag{3}$$

Complete interpretation of the vibrational spectra of large molecules is extremely difficult so that precise calculations of β-factors for compounds such as complex biomolecules become impossible in practice. For such compounds the evaluation of β-factor values (with a good degree of approximation) can be done by means of a method based on the additive properties of these thermodynamic values [24, 29].

It has been shown that the β_r-value, which characterizes the molecule as a whole, is the arithmetic mean of the β_i-factors characterizing monosubstitued isotopic species of the compound; in other words characterizing carbon atoms in different position in the molecule:

$$\beta_r = \frac{1}{n}\sum_{i=1}^{n} \beta_i \qquad \text{(the first rule of additivity)} \tag{4}$$

In turn, the magnitude of the β_i-factor can, to a certain degree, be expressed through the sum of scalar values which we called isotopic numbers of bonds L_j:

$$\beta_i = 1 + \sum_j L_j \qquad \text{(the second rule of additivity)} \tag{5}$$

where L_j refers to the bonds which the carbon atom forms directly.

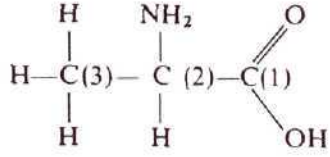
For a better approximation one can use l_k values which allow to take into account the chemical surroundings of the adjacent carbon atoms [29].

The magnitudes of L_j and l_k values, at 300° K, for different types of carbon bonds are listed in Table 9.1A. Using these values, and the additivity rules, one can estimate the β-factor of any carbon compound.

TABLE 9.1A
ISOTOPIC NUMBERS OF BONDS AT T = 300 K

Type of the bond	L_j	l_k
C – H	0.0284	0
C – C	0.0464	0.0013
C – N	0.050	0.0016
C – O	0.055	0.0019
C – F	0.056	0.0020
C = C	0.0785	0.0016
C ≡ C	0.088	0.0003
C = N	0.090	0.0003
C = O	0.0958	0.0028

If we take, for example, a molecule of the amino acid alanine:



then the values of the β_i-factors can be found as follows:

$$\beta_1 = 1 + (L_{C=O} + L_{C-O} + L_{C-C}) + (l_{C-N} + l_{C-H} + l_{C-C}) = 1.199$$
$$\beta_2 = 1 + (2L_{C-C} + L_{C-N} + L_{C-H}) + (l_{C=O} + l_{C-O} + 3l_{C-H}) = 1.180$$
$$\beta_3 = 1 + (3L_{C-H} + L_{C-C}) + (l_{C-N} + l_{C-C} + l_{C-H}) = 1.135$$

and hence the thermodynamic isotopic factor of the molecule as a whole:

$$\beta_e = \frac{1}{3}(1.199 + 1.180 + 1.135) = 1.171$$

One can see that the β_i-factors characterizing different carbon atoms in alanine are not equal. This implies intramolecular thermodynamic isotope effects.

Available data on the carbon isotope composition of biomolecules, and their calculated β-factors, suggests thermodynamically ordered isotope distribution in the biological systems: correspondance between experimentally measured δC^{13} and theoretically calculated β-values [24] (Fig. 9.1). In particular, such a correlation has proved to be characteristic of components in the lipid fractions of a number of the organisms [34] as shown on Fig. 9.2. It is noticeable that the same type of β_e-δC^{13} relationship is found in the lipid fraction of organisms belonging to quite distinct taxonomic groups.

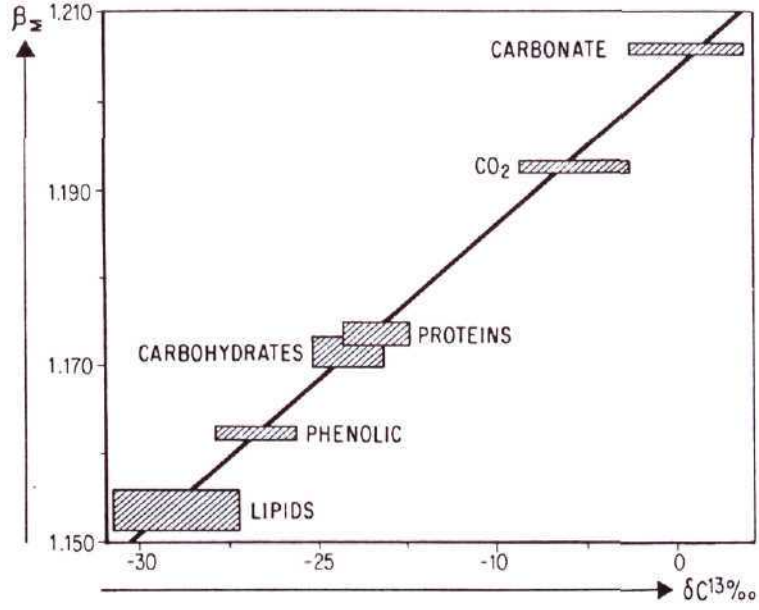


Fig. 9.1. — Correspondence between carbon isotope composition ranges of some components of biological system (including environmental CO_2 and biogenic calcite) and β-factor values of these components.

If the biological isotope effects are thermodynamically ordered the carbon isotopes will be regulated not only between biomolecules but also within them.

The β_i-factor values for carbon atoms in some functional groups, or structural positions, are listed in Table 9.1B.

TABLE 9.1B
THERMODYNAMIC ISOTOPE FACTORS (β_i-FACTORS) OF CARBON IN SOME STRUCTURAL POSITION IN ORGANIC COMPOUNDS

Structural group	Formula	β-factor
1. Methyl	$-CH_3$	1.131
2. Nitrile	$-C\equiv N$	1.137
3. Methoxy	$-OCH_3$	1.141
4. Methene	$-CH_2-$	1.149
5. Methine	$>CH-$	1.166
6. Aldehydic	$-CHO$	1.170
7. Amino	$>CH$ | N	1.172
8. Cetene	$C=C=O$	1.173
9. Phenolic	$\gtrless C-OH$	1.179
10. Carbonyl	$>C=O$	1.187
11. Carboxylic	$-COOH$	1.197

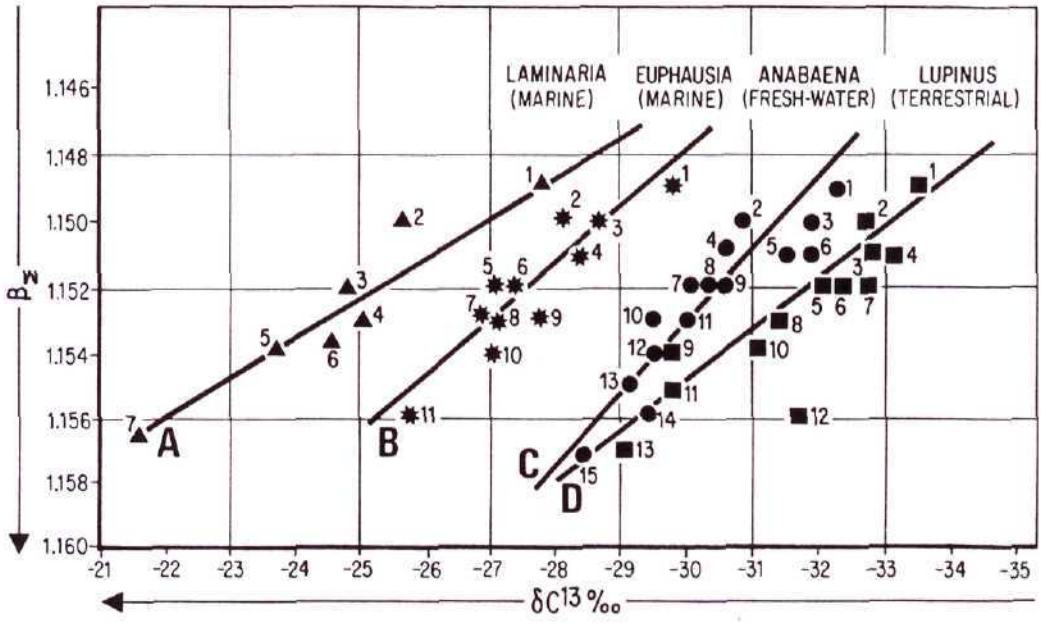


Fig. 9.2. — Carbon isotope composition of individual components of lipid fraction compared with the β-factor values of these components in some organisms [34].

A. Laminaria saccharina (seaweed).
1. Waxes, hydrocarbons. **2.** Fatty acids. **3.** Triglycerides. **4.** Monoglycerides. **5.** Fucoxanthin. **6.** Fucosterol. **7.** Chlorophyll.

B. Euphasia superba (marine).
1. Waxes, hydrocarbons. **2.** Fatty acids. **3.** Sphyngomyelin. **4.** Lecithin. **5.** Diglycerides. **6.** Triglycerides. **7.** Echinenon. **8.** Monoglycerides. **9.** Cardiolipine. **10.** Cholesterol. **11.** Astacene.

C. Anabaena variabilis (fresh-water blue-green algae).
1. Waxes, hydrocarbons. **2.** Sphyngomyelin. **3.** Fatty acids. **4.** Lecithin. **5.** β-Carotene. **6.** Phosphatidylserine. **7.** Diglycerides. **8.** Cephalin. **9.** Triglycerides. **10.** Echinenon. **11.** Monoglycerides. **12.** β-Sitosterol. **13.** Phosphatidylinositol. **14.** Myxoxanthophyll. **15.** Chlorophyll.

D. Lupinus luteus (terrestrial).
1. Waxes, hydrocarbons. **2.** Fatty acids. **3.** Lecithin. **4.** Phosphatidylserine. **5.** Diglycerides. **6.** Triglycerides. **7.** Cephalin. **8.** Monoglycerides. **9.** β-Sitosterol. **10.** Lutein. **11.** Chlorophyll, xantophyll. **12.** Monogalactosylglyceride. **13.** Chlorophyll.

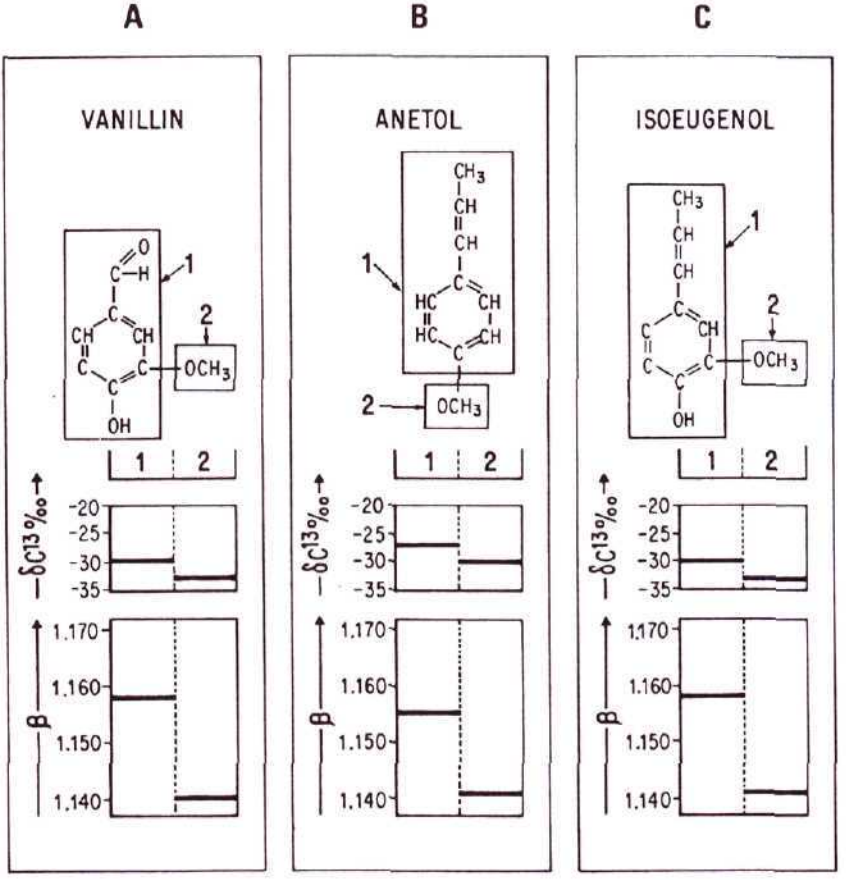


Fig. 9.3. — Thermodynamically ordered intramolecular carbon isotope distribution in some biological aromatic compounds :

A. Vanillin [30]. **B.** Anetol [84]. **C.** Isoeugenol [84]. Note that the measured isotope distribution is in correspondence with the calculated β-factor values of the same fragments.

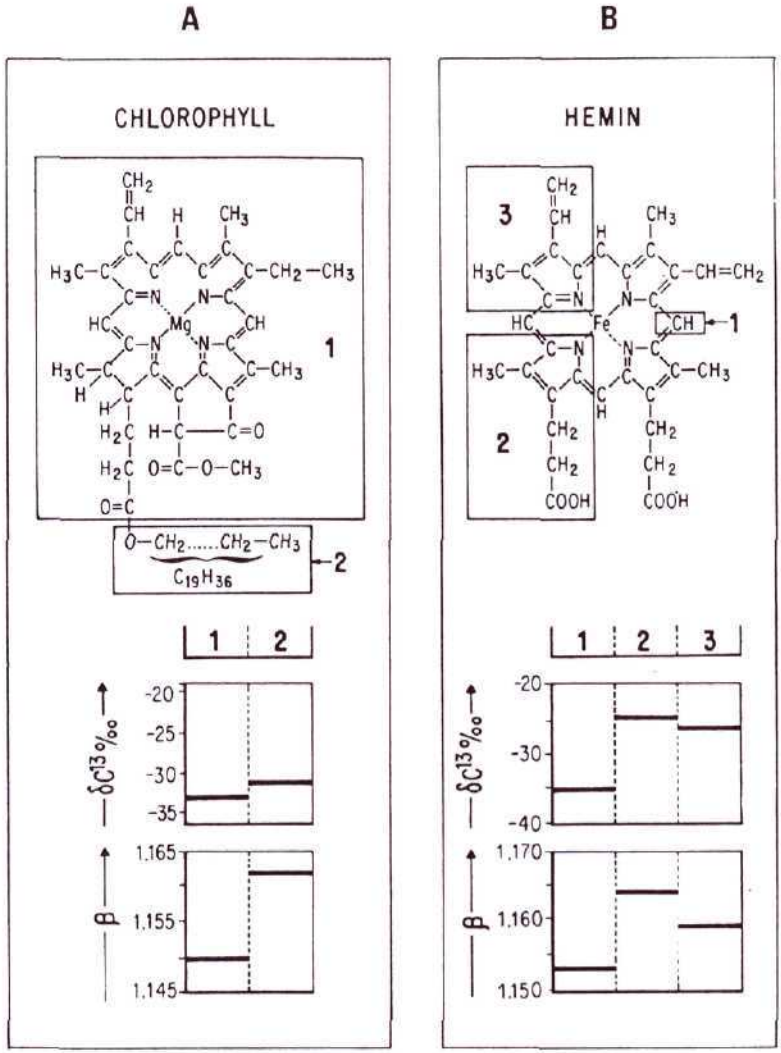


Fig. 9.4. — Thermodynamically ordered intramolecular carbon isotope distribution in:

A. Chlorophyll [31] of biological origin. **B.** Hemin.

Abelson and Hoering [1] showed that carboxyl groups of amino acids were enriched in the C^{13}-isotope compared to the molecule as a whole. Now this fact may be interpreted in terms of the difference of the corresponding β-values.

In our laboratory experiments were undertaken to study the intramolecular carbon isotope effects in biomolecules and to check the hypothesis of thermodynamically ordered intramolecular carbon isotope distributions. Thus, the relative concentration of the C^{13}-isotope in the methoxy groups of a number of aromatic lignin monomers was investigated [30]. In contrast to the carboxyl group, the carbon in a methoxy group has a low β_i-factor (Table 9.1B). Accordingly, the above experiment showed that the carbon in the methoxy groups of the aromatic compounds investigated was relatively depleted in the C^{13}-isotope. The data for the vanillin from a reed is shown in Fig. 9.3A. Similarly, it has been established that a distinction exists between the measured carbon isotopic compositions of certain fragments of hemin and chlorophyll molecules as expected from estimated β-factor values of these fragments (Fig. 9.4)[31]. Experimental results for acetic acid, and acetoin, obtained by Meinschein *et al.* [49] and Rinaldi *et al.* [66] are also consistent with the concept of a thermodynamically ordered carbon isotope distribution within these molecules (Fig. 9.5).

It has been supposed that the appropriate isotope fractionation takes place within enzyme-substrate complexes at each step of the enzyme-controlled formation of a biomolecule

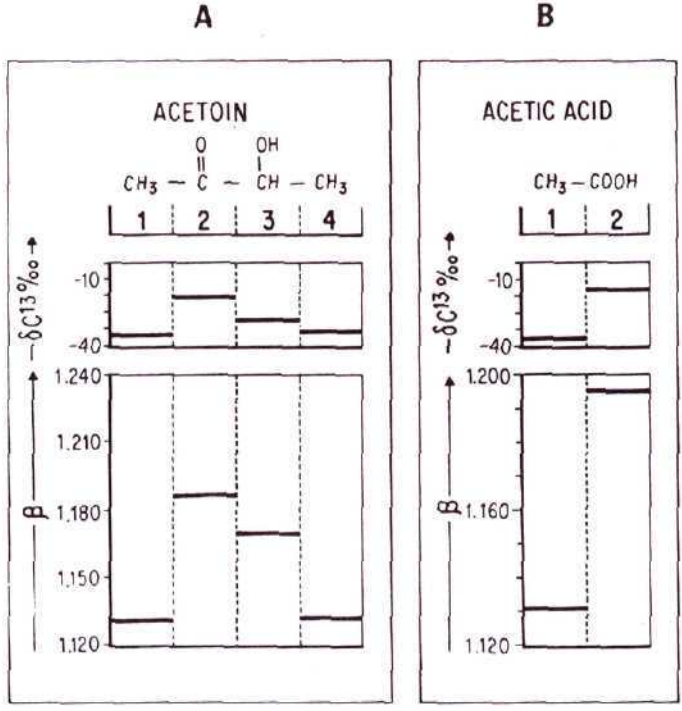


Fig. 9.5. — Thermodynamically ordered intramolecular carbon isotope distribution in :

A. Acetoin [66] of biological origin. B. Acetic acid [49].

[27, 29]. Analysis of this model indicates that the magnitude of the thermodynamic component of the biological isotope effect which occurs during enzymatic reaction is dependent on two quantities:

(a) β-factor ratios of the product and the substrate.

(b) The χ-value which depends on the kinetic constants (not confuse with kinetic isotope effects) of the reaction.

This gives the following relationship for biological isotope effects of enzymatic reaction in its simple version:

$$\delta C_A^{13} - \delta C_B^{13} = \overline{\chi}\left(\frac{\beta_A}{\beta_B} - 1\right) \times 10^3 \qquad (‰) \qquad (6)$$

χ-value may change from zero to unit. Under the normal conditions χ-value varies around 0.5. The changeability of this factor predetermines dependence of the biological isotope effects on the pathways of the biosynthesis and environment conditions. β_A- and β_B-values in expression (6) may represent both β_e-and β_i-factors and expression (6) may correspondingly describe intermolecular or intramolecular carbon isotope effects.

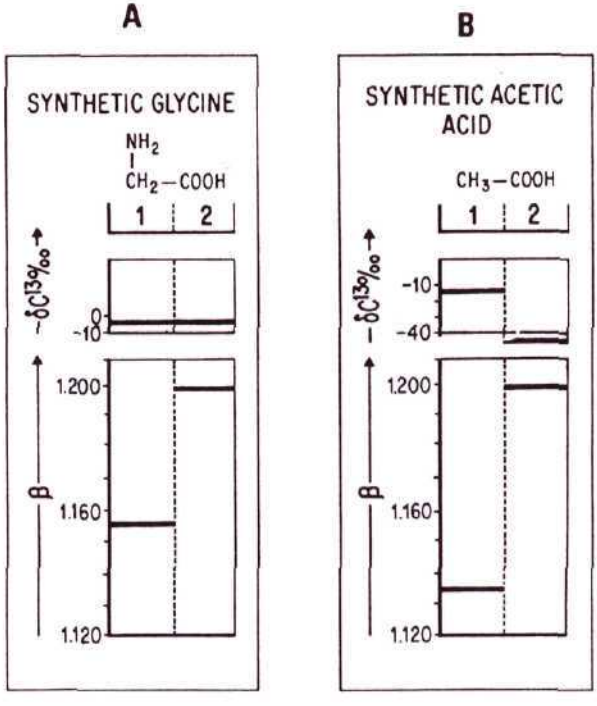


Fig. 9.6. — Lack of thermodynamically ordered carbon isotope distribution in compounds abiogeneously synthesized:

A. Glycine [84]. **B.** Acetic acid [49].

Thus, it is possible to evaluate carbon isotope distributions in different constituents of organisms, on some general basis, without resort to measurements in every case. Moreover, one can predict alterations in the carbon isotopic composition of organic matter (OM) during diagenesis. It is clear, for example, that elimination of functional groups with carbon enriched in C^{13} (high β_i-value) such as carboxyl, or formyl, results in the enrichment of the OM in the light carbon isotope. Alternatively, removal of isotopically light methyl or methoxy groups should produce OM richer in the heavy isotope.

Since the β-factor is temperature dependent, the carbon isotope composition of organisms will depend on the temperature of biosynthesis.

It should be emphasized also that the thermodynamically ordered isotope distribution appears to be a purely biological phenomenon. In other words the carbon isotope composition of **chemically synthesized** compounds should not be expected to correspond to β-factors of these compounds. For example, in contrast to biogenically produced carboxyl carbon, which is relatively enriched in the C^{13}-isotope, the carbon atoms of carboxyl groups formed by abiogenic oxidation will most likely be enriched in the C^{12}-isotope, due to kinetic isotope effects. Data presented in Fig. 9.6 confirm this proposition. Differences in intramolecular carbon isotope distributions in biogenic and abiogenic compounds may therefore be used to determine the biological or nonbiological origin of terrestrial and extraterrestrial compounds [24, 27, 34].

III. RELATIONSHIPS INHERITED BY FOSSIL ORGANIC MATTER FROM ITS BIOLOGICAL SOURCE

Terrestrial plants are enriched in the C^{12}-isotope by 5-8‰ when compared with marine ones (Fig. 9.7). This may be caused by more high degree of utilization of the ambient CO_2 by water plants. The another reason is difference between the isotopic composition of the carbon sources: the atmospheric CO_2 ($\delta C^{13} = -7‰$) and the seawater bicarbonate ($\delta C^{13} = -2‰$). Data in Fig. 9.2 also exemplify the influence of environmental carbon. Displacement of the lines along the horizontal axis, for various organisms, is also due to differences in the isotopic composition of the source carbon.

Difference in δC^{13}-values between OM of terrestrial and marine origin is preserved in fossil OM, but at a somewhat reduced level. Thus, if the difference between terrestrial and marine plants is about 8‰, for humic substances, and appropriate kerogens, it may amount to 3 to 5‰ only.

In transitional environments δC^{13}-values change gradually from about -20 to $-23‰$, characterizing open sea deposits to about -26 to $-28‰$, characterizing intracontinetal reservoirs [74]. The contribution of terrestrial OM to the total organic carbon of marine sediments, evaluated on this basis, becomes negligible at a distance of 60-100 km offshore [8]. However, due to undercurrents, continental material may be deposited as much as 1 000 km from its point of origin. The increased C^{12} content of deep sea sedimentary OM does not always appear to be related to the contribution of organic terrestrial matter. This might be due to more profound transformations of the OM within the massive water column. Temperature variations both throughout the water column, and during geological time also play a part.

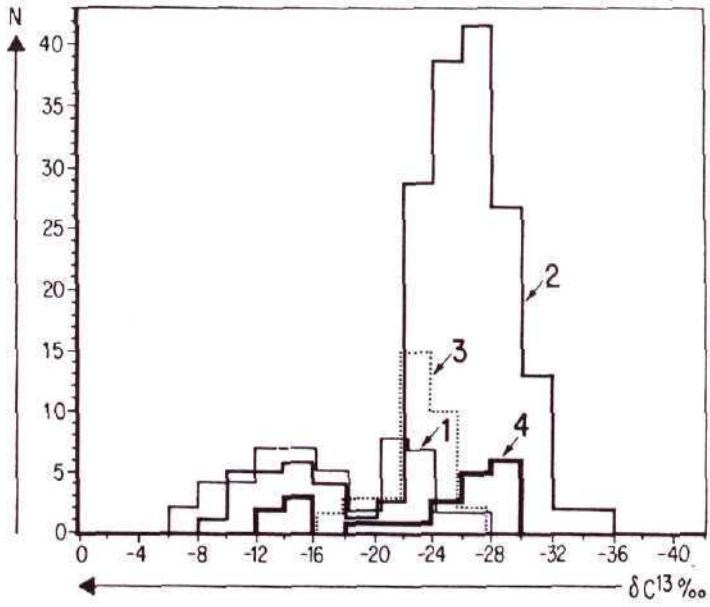


Fig. 9.7. — Carbon isotope composition of plants and humic acids from burial OM in marine and continental environments:

1. Marine plants. 2. Land plants. 3. Humic acids from marine sediments. 4. Humic acids from soils and lake sediments.
δC^{13} – Values for humic acid samples are taken from: [65, 55, 7, 2, 57, 53]; marine and land plants data are taken from: [70, 79].

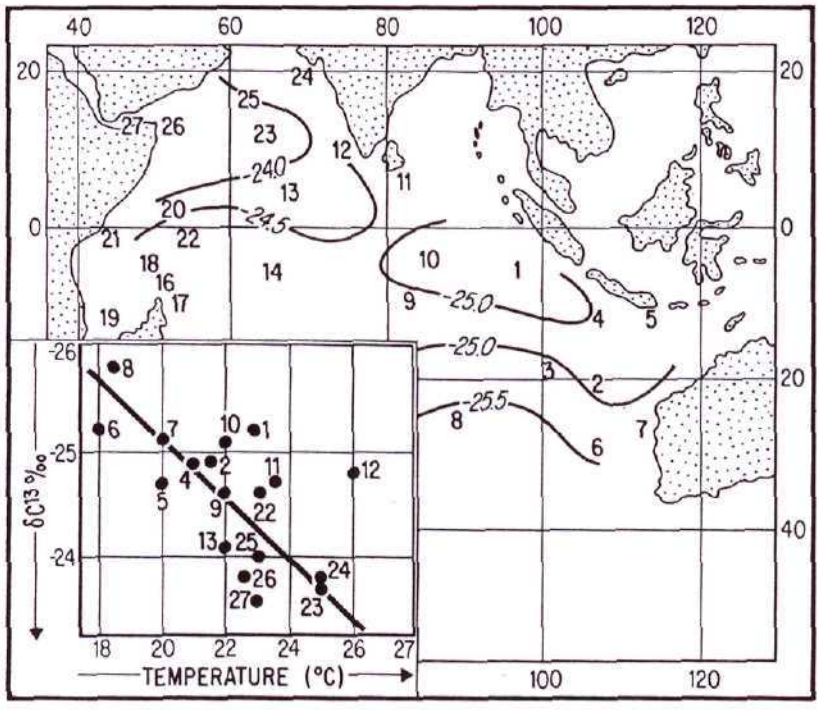


Fig. 9.8. — Temperature dependence of carbon isotope composition of the lipid fraction of plankton collected in Indian Ocean [35]. The figures mark the sites of sampling.

The theoretical temperature dependance of the thermodynamic carbon isotope effects for fossil OM is about 0.2-0.4‰ per 1° C; the same values are observed for naturally-occurring carbon compounds [29].

Attention has been paid before to correlations between the isotopic composition of organisms and their environmental temperature [15, 72] but correlations were ascribed to the influence of indirect factors. We have found [8] a definite correlation between the carbon isotope composition of the lipid fraction of plankton, collected at different latitudes in the Indian Ocean, and the corresponding average annual water temperature (Fig. 9.8).

The dependance of the isotopic composition of sedimentary OM on paleo-temperature, and its relationship with the history of glaciation was noted by Rogers and Koons [68] who showed that the organic carbon of periods of glaciation is 1-2‰ lighter. The ideas of Rogers *et al.* [68, 67] were criticized as being speculative [2] or as being valid in specific circumstances only [73]. These criticisms are invalid since the dependence of the isotopic composition of kerogen on paleotemperature may be a consequence of the thermodynamic nature of the biological isotope effects for which the temperature dependence is a fundamental property. Another thing is that the temperature dependence may be strongly masked by other factors. In some cases the dependence of the organic carbon isotope composition on temperature may be indirect [14, 15]; in several experiments this temperature dependence was not revealed [10]

It is known that the so-called C_4-plants, fixing CO_2 through phosphoenolpyruvate (Hatch-Slake's cycle) are enriched to a lesser extent in the C^{12}-isotope when compared with the usual C_3-plants fixing CO_2 through ribulose 1.5 diphosphate (Calvin cycle). If δC^{13}-values of the usual terrestrial plants are taken to be in the -22 to -28‰ range then the δC^{13}-values of the C_4-plants (and succulents) range from -13 to -19‰ [5, 79, 86]. The lower (left) maximum in the histogram for land plants (Fig. 9.7) corresponds to the C_4-plants. The low water and gas transfer and, in consequence, high degree of retention and utilization of CO_2 is a characteristic of these plants. Hence the χ-values is small during the biosynthesis of the primary products of CO_2-assimilation. Indeed, the isotope composition of the aspartic and malic acid carbon and other primary products of C_4-plant photosynthesis, was found to be close to the isotope composition of the initial carbon dioxide [86]. Carbon in the soil at sites where mainly C_4-plants grow (e.g. maize fields) is pronouncedly depleted in the light isotope as compared with the usual soil carbon (the left maximum in the histogram for soil humic substances, Fig. 9.7).

IV. DIAGENETIC ALTERATION OF ORGANIC CARBON ISOTOPE COMPOSITIONS DURING KEROGEN FORMATION

When an organism dies the mechanism providing the thermodynamically ordered isotope distribution ceases. Therefore, the isotopic distributions inherited from the various biological systems are preserved in the original molecules of the buried organic compounds. When subsequent bond formation, or bond breaking, occurs isotope fractionation may take place owing to the greater lability of C^{12}-C^{12} compared to C^{12}-C^{13}-linkages. This type of isotope fractionation is known as the kinetic effect. The more complete the

chemical reconstruction of the original biomolecules the poorer is the relationship between the isotopic composition and the β-factor value of the compound.

Humic substances in recent sediments are considered to be early form of kerogen and are usually defined as dark-brown polymers that may be extracted from soils and sediments by dilute alkaline solutions. The alkaline extracts 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 OM remaining in sediments after extraction by alkalis is called humin. Fulvic acids have lower molecular weights compared to humic acids. The percentage of native functional groups, as well as heteroatoms, in FA (C: 30-40%, H: 6-8%, O: 45-55%, N: 4.5-5.5%) is higher than in HA (C: 50-55%, H: 5.5.-6.5%, O: 30-35%, N: 1-4%) which themselves are less altered than humins (H). With increasing diagenetic transformation the fulvic acid content decreases at the cost of a rising humic acid content; that in turn drops as the humin content rises [7, 53, 54]. Indeed, the percentages of humic acids and humin in sediments are usually complementary.

The transformation of biomolecules begins in the water column and continues during sedimentation. As the first new polymers are formed there is an initial enrichment in the C^{12}-isotope relative to the plankton carbon [88].

Investigations of the carbon isotope composition of humic acids (Table 9.2) reveal, as a general rule, that humic acids are enriched in the C^{12}-isotope as compared with fulvic acids. Maturated humin carbon, in turn, is enriched in the C^{12}-isotope as compared with humic acids. These effects are more distinct for the organic carbon in sediments ($\Delta C^{13}_{HA-FA} = -1.9‰$) than for that in soils ($\Delta C^{13}_{HA-FA} = -0.7‰$). The formation of humic acids in soil is due to the transformation of lignin [45]. The formation of humic acids in marine sediments is supposed to be related to the reaction of proteins and carbohydrates. This is the so-called melanoidin reaction and involves the reaction of aldehyde and amino groups resulting in the formation of dark-brown substances similar to the humic acids of marine sediments [41, 44].

A relevant experiment on isotope fractionation during melanoidin formation was carried out in collaboration with Drozdova. A mixture of glucosamine and protein hydrolyzate was boiled under reflux (100° C) for 12, 18 and 30 hours. The melanoidin-forming character of this reaction has been demonstrated previously [17]. Data on experimental conditions, and results, are tabulated (Table 9.3) and show the following:

(a) Synthetic "fulvic" and "humic" acids are enriched in the C^{12}-isotope as compared to the starting carbon of glucosamine.

(b) Humic acids are richer in the C^{12}-isotope than the corresponding fulvic acids.

(c) Enrichement of humic acids in the C^{12}-isotope increases as the heating period increases, while enrichment of fulvic acid drops.

(d) Insoluble melanoidins ("humin") appeared to be the lightest fraction isotopically.

Thus the carbon isotope distribution in our experimental polymers coincides with the isotope distribution in the corresponding native polymers. This fact suggests that melanoidin formation is a sufficiently good model for the humidification of OM. The fact that fulvic acids are depleted in the C^{12}-isotope, as humic acids are enriched in it, indicates that fulvic acids are intermediate between a starting protein-carbohydrate complex and humic acids.

TABLE 9.2
CARBON ISOTOPE COMPOSITIONS OF HUMIC SUBSTANCES

Location, sample	δC^{13} (‰)			
	Fulvic Acid (FA)	Humic Acid (HA)	Humin (H)	ref.
MARINE SEDIMENTS				
Atlantic ocean, Mid-Atlantic Ridge, Hole 26 JOIDES, 5168 m water depth				
Depth 100 m		−24.7	−25.1	2
Depth 230 m		−25.8	−26.6	2
Depth 478 m		−24.4	−25.6	2
Average		−25.0	−25.8	
		$\Delta C^{13}_{H-HA} = -0.8$		
Pacific ocean				
Tanner Basin	−20.3	−22.0		1
Santa Barbara basin	−19.1	−22.7		1
Santa Cruz basin	−20.7	−21.8		1
San Pedro channel	−21.7	−22.7		1
Long Basin	−20.3	−22.3		1
Average	−20.4	−22.3		
	$\Delta C^{13}_{HA-FA} = -1.9$			
LITTORAL				
Hawaii, Kaneobe Bay,				
N° 1	−23.3	−24.2		1
N° 2	−24.4	−24.9		1
Florida, Humate cemented sand,				
N° 1	−24.1	−25.7		1
N° 2	−24.1	−25.7		1
California, Newport Marsh	−17.4*	−19.1*		1
Average	−24.0	−25.1		
	$\Delta C^{13}_{HA-FA} = -1.1$			
SOIL				
Nova Scotia, forest	−26.3	−26.2		1
Hawaii, Canefield	−18.2*	−14.8*		1
Israel				
Alluvial	−26.8	−28.1		4
Basaltic	−27.8	−28.4		4
Terra Rosa	−28.6	−29.4		4
Brown alluvial	−26.1	−27.0		3
Mountain rendzina	−25.6	−26.6		3
Valley rendzina	−28.1	−28.9		3
Arid	−24.8	−25.7		3
Peat	−17.4	−18.0		3
Hula peat	−20.8	−19.2		1
Canada, forest, Saanich Inlet	−27.0	−29.1		1
Average	−26.8	−27.5		
	$\Delta C^{13}_{HA-FA} = -0.7$			

(*) no taken into account while calculation of mean value
(1) Nissenbaum and Kaplan [55]
(2) Aizenshtat *et al.* [2]
(3) Nissenbaum and Schallinger [57]
(4) Nissenbaum [53]

Enrichment of the polymers in the C^{12}-isotope may be due both to the removal of the C^{13}-isotope-enriched functional groups (carboxyl,-formyl,-keto etc.) and to the kinetic isotope effect that accompanies the polymerization.

TABLE 9.3
δC^{13}-VALUES OF THE PRODUCTS OF MELANOIDINE REACTION

(Glucosamine 1 g, protein hydrolysate 0.012 g in the experiments 2 and 3, and 0.018 g in the experiment 1, H_2O – 15 ml, pH = 8.0)

Isotopic composition of the starting components:

glucosamine: – 26.14‰
protein hydrolysate: – 19.24‰

Experiment	Brown solution		Black precipitate			
	There is no precipitate with HCl. High-molecular substances are removed by dialysis		Dissolved in 1N NaON, precipitated in 3N HCl		Insoluble melanoidines	
	Fulvic Acids (FA)		Humic Acids (HA)		Humin (H)	
	δC^{13} (‰)	yield (%)	δC^{13} (‰)	yield (%)	δC^{13} (‰)	yield (%)
1. Heating for 12 h.	– 27.00	11.4	– 27.47	0.6	–	trace
2. Heating for 18 h.	– 26.68	10.7	– 29.19	2.0	–	0.33
3. Heating for 30 h.	– 26.32	3.6	–	trace	– 36.42	6.1

TABLE 9.4
ISOTOPE EFFECT OF POLYMERISATION REACTIONS

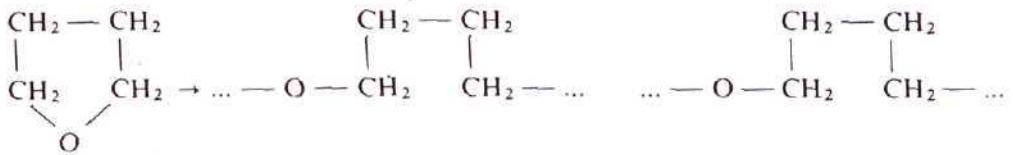
Reaction	δC^{13} (‰)		ΔC^{13}_{p-m}
	Monomer	Polymer	
Polymerisation of tetrahydrofurane...	– 34.15	– 37.30	– 3.15
Polymerisation of 1.3-dioxolane	– 28.97	– 33.20	– 3.23

When passing from fulvic acids to humic acids and then to higher molecular weight humic acids the percentage of functional groups decreases [48, 65, 75, 81]. Nissenbaum and Schalinger [57] indicated that the loss of carboxyl-groups was responsible for the increase in the C^{12}-isotope content of humic acids as compared to fulvic acids. Indeed, carbon atoms

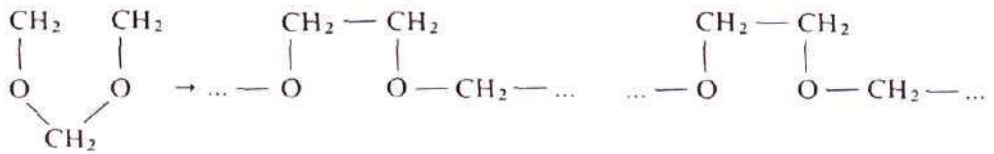
of carboxyl,-keto-groups and carbon atoms concerned with aldehyde- and hydroxy-groups are to be enriched in C^{13}-isotope. On the other hand, it is known that elimination of functional groups, specifically decarboxylation, results in the enrichment of the lost CO_2 in the C^{12}-isotope [6]. Thus, there is a competition of two trends and the net effect generally results although not always, in the elimination of CO_2, that is somewhat enriched in the C^{13}-isotope and consequently enrichment of the residual OM in C^{12}-isotope.

Polymerization seems to be one more possible source of isotopic fractionation during the diagenesis of OM. It follows, from general considerations, that the polymerization reactions should be accompanied by small isotope effects [50].

In cooperation with Berman and Klimov we have investigated two suitable polymerization reactions. The first of them involves the polymerisation of tetrahydrofuran:



the other, the formation of polydioxolane by polymerizing 1,3-dioxolane:



Both reactions proceed with a catalyst at normal pressure and temperature (20° C). The yield of polymer (100-200 monomer units) is 20-25% and the reactions are not accompanied by the formation of artefacts. Therefore, a distinction between the isotope composition of the starting monomer and the resultant polymer may be ascribed only to the polymerization effect.

As seen in Table 9.4, the polymer is richer by nearly 3‰ in the light isotope. The extent of fractionation is comparable with that observed in the process of natural polymer formation in the series: fulvic acids-humic acids-humin.

The evolution of the isotopic composition of OM during diagenesis is illustrated schematically in Fig. 9.9. Obviously decomposition of biopolymers to monomers and repolymerization of the latter to resistant geopolymers is the leitmotiv of the early diagenetic transformation of sedimentary OM. The loss of the isotopically heavy CO_2, associated with carboxyl and other functional groups, as well as the polymerization isotope effect, specify the observed changes in the isotopic composition of the geopolymers, i.e. their enrichment in the C^{12}-isotope.

Humic acids are inclined to produce complexes with lipophilic compounds such as alkanes, fatty acids, pigments and other lipids [44, 59, 52, 64]. Therefore, the reaction of lipids and pigments with humic acids should result in a further enrichment of geopolymers in the C^{12}-isotope.

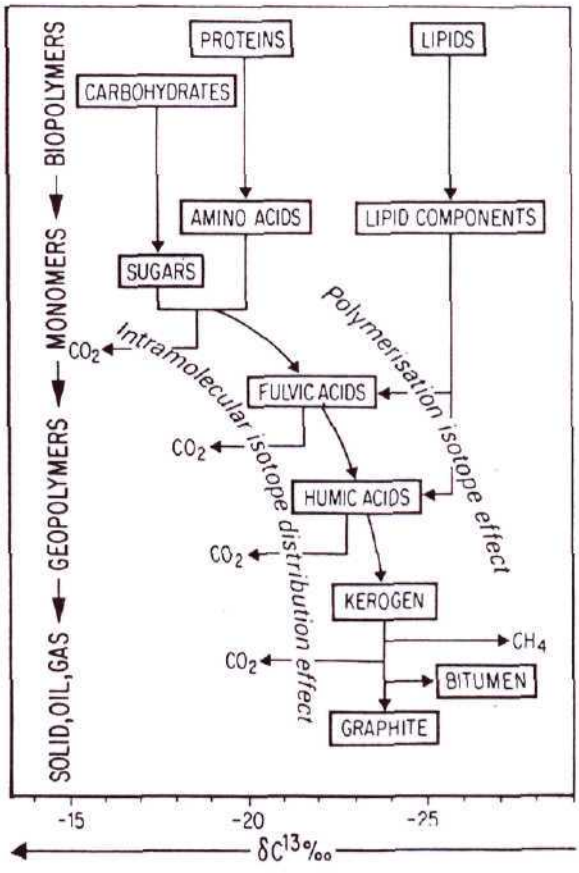


Fig. 9.9. — Sketch of diagenetical change of carbon isotope composition of OM on the pathway from biopolymers to kerogen.

V. RELATIONSHIP BETWEEN THE CARBON ISOTOPE COMPOSITION OF KEROGEN, CO_2 AND CH_4

Together with the degradation of polymeric biochemical compounds to monomers, followed by their repolymerization and stabilization in the form of kerogen, elimination of organic carbon occurs as a result of CO_2 and CH_4-formation. Diagenetic methane generation is usually related to reactions of the following two types [78, 11]:

$$\text{(a)}\ CH_3COOH \rightarrow CH_4 + CO_2$$

$$\text{(b)}\ CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Methane-producing bacteria are obligate anaerobes and therefore methane forms after the oxygen reserve is completely exhausted, usually beneath the sulphate-reducing zone.

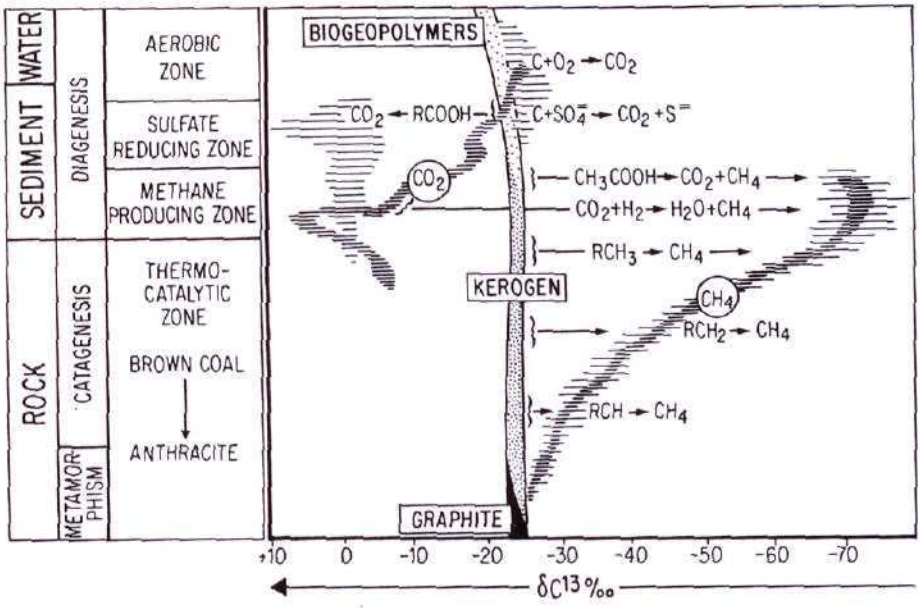


Fig. 9.10. — Relationship between carbon isotope composition of kerogen, CO_2 and CH_4 in different zones.

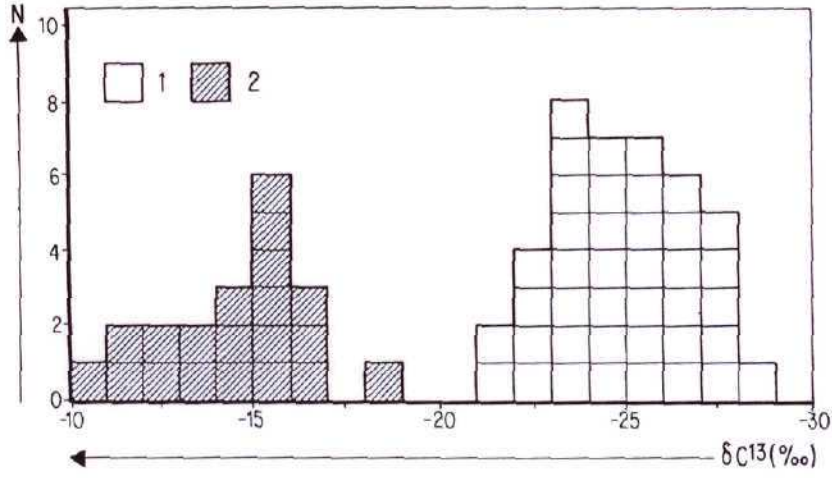


Fig. 9.11. — *Distribution of isotope composition of carbon of soil carbon dioxide:*

1. Location where predominantly grow C_3-plants [22]. 2. Locations where predominantly grow C_4- and CAM-plants [45].

Measurements of the carbon isotope composition of methane in anaerobic environments [58, 11, 82], as well as in laboratory experiments [51, 69, 36], reveal that microbiologically-produced methane is, on average, 30-50‰ richer in the C^{12}-isotope as compared with other OM (Fig. 9.10).

Enrichment of methane in C^{12} is usually explained by the kinetic isotope effect. Nevertheless, it is logical to assume (keeping in mind the essential role of the thermodynamic isotope effects in biological systems) that the enrichment in C^{12} of the microbiological methane has a thermodynamic basis. In other words, the effect is due to isotope exchange in the CO_2—CH_4-system used by bacteria for methane formation. The calculated values for thermodynamic isotope effects in CO_2—CH_4-systems, at 20-40° C, are in good agreement with the isotope fractionation observed [24].

There are several CO_2 sources in sediments and rocks, two of which are of biological origin. The first results from the oxidation of OM while the second results from its decomposition:

$$\text{(a)}\quad C_xH_yO_z + O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

$$\text{(b)}\quad C_xH_yO_z \rightarrow C_{x-1}H_yO_{z-2} + CO_2$$

Carbon dioxide, resulting from the oxidation of OM, has an isotopic composition related to the average carbon isotopic composition of the OM. This is obviously true for both sediments and soils. δC^{13}-values for soil carbon dioxide range from − 23 to − 28‰ [22] with the exception of that which is isotopically heavier [47] from sites occupied by C_4-plants or CAM-type (1) plants (Fig. 9.11).

In anaerobic environments, carbon dioxide may be produced from oxygen-containing groups (e.g. carboxyl, formyl) depleted in the C^{12}-isotope. The balance of these types of carbon dioxide, and that of carbonate origin, determines the carbon isotope composition of the CO_2 in sediments (Fig. 9.10).

Carbon dioxide may be noticeably depleted in the C^{12}-isotope in the zone where methane-producing bacteria occur, as a result of the reaction:

$$CO_2 + H_2 \rightarrow CH_4 + H_2O$$

This was shown in experiments with the microorganism *Methanobacterium thermoautotrophicum* [36].

The isotopic composition of the CO_2 and CH_4 is determined by isotope redistribution in the CO_2—CH_4-system. Therefore carbon isotope fractionation in the course of gas-formation should not markedly affect the carbon isotope composition of kerogen.

VI. δC^{13} OF KEROGEN DURING CATAGENESIS

A. Sediments.

In the upper part of marine sediments a trend favouring an increase in the light carbon isotope, with depth of burial of the OM, is sometimes observed [46, 18, 77]. This may be due

(1) CAM-type plant = plant with the crassulacean acid metabolism.

to changes in the isotopic composition of the OM during diagenesis. However, in many cases the alteration is not systematic. To date, information is available on δC^{13}-variations in OM buried to several hundred metres in deep-sea sedimentary successions [9, 21, 67]. These variations seem to reflect alterations in the sedimentary environment, the temperature of the basin and the carbon source rather than process related to kerogen transformation.

Thus, on the strength of all the evidence, one may conclude that the isotopic composition of the kerogen is reached at an early stage of diagenesis, evidently after the humic carbon has entered the kerogen structure.

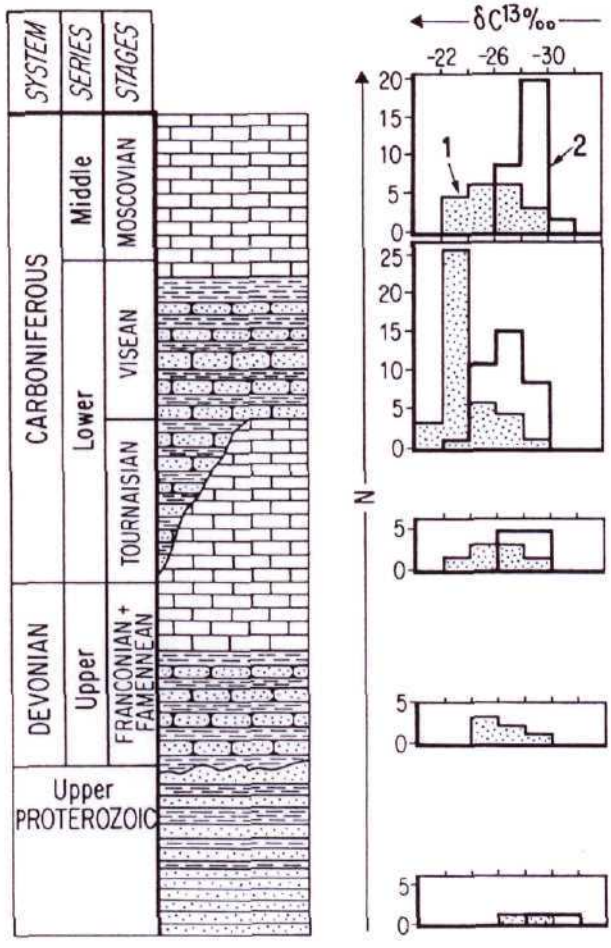


Fig. 9.12. — Distribution of isotope composition of carbon of kerogen [1] and chloroform-extracted bitumen [2] based on stratigraphic profiles of the Permian-Ural Area [24].

B. Ancient rocks.

Data on the carbon isotope composition of kerogens in Paleozoic deposits of the Volga-Ural area (the Russian Platform) are shown in Fig. 9.12. Some of the data are taken from previous work [24] but the rest are new and are listed in Table 9.5. As can be seen, the

TABLEAU 9.5
CARBON ISOTOPIC COMPOSITION OF KEROGENS AND BITUMENS(1)
FROM PALEOZOIC DEPOSITS OF THE PERMIAN URAL AREA

Stratigraphic complex	Area, borehole (No)	Sampling (depth : m)	Rock	Content in the rock (weight%)		δC^{13} (‰)	
				Kerogen	Bitumen	Kerogen	Bitumen
C_2vr Moscovian stage, Verejskyi horizon	Durinskaya, 12(2)	1 918	lm (3)	0.20	0.625	− 26.7	− 30.0
	Nozhovskaya, 36	1 117	lm	0.21	0.001	− 25.7	− 27.8
	Tartinskaya, 31	1 082	lm	0.54	0.313	− 23.8	− 27.5
	Andreevskaya, 23	1 163	sh (3)	0.36	0.003	− 25.9	− 26.8
	Tartinskaya, 31	1 115	sh	1.56	0.015	− 23.9	− 28.6
C_2b Bashkirskyi stage	Tazovskaya, 45	1 609	sh	0.71	0.080	− 23.5	− 27.0
	Tartinskaya, 19	1 151	lm	0.06	0.003	− 27.9	− 30.
C_1tl Visean stage, Tulskiy horizon	Tukachevskaya, 7	1 718	lm	0.43	0.010	− 26.3	− 29.1
	Tukachevskaya, 7	1 724	sh	0.56	0.010	− 24.8	− 26.8
	Tukachevskaya, 7	1 735	sh	1.35	0.010	− 27.3	− 29.6
	Romanshorskaya, 1	1 772	sh	0.57	0.060	− 24.5	− 27.9
	Vidrjanskaya, 39	1 998	sh	0.71	0.080	− 23.4	− 27.2
	Yayvinskaya, 4	2 327	lm	0.23	0.113	− 23.3	− 25.2
	Tazovskaya, 45	2 014	sh	0.85	0.080	− 22.9	− 24.7
	Tazovskaya, 45	2 014	sh	0.64	0.118	− 22.8	− 25.4
	Koltskovskaya, 1	1 463	sh	0.96	0.040	− 23.2	− 26.6
	Andreevskaya, 23	1 603	sh	1.09	0.010	− 22.8	− 24.9
	Gondyrevskay, 60	1 405	sh	1.04	0.020	− 24.1	− 26.2
	Gondyrevskaya, 60	1 409	sh	0.80	0.001	− 22.4	− 26.7
	Tartinskaya, 31	1 479	sh	1.60	0.015	− 22.9	− 27.3
	Tartinskaya, 31	1 512	sh	1.11	0.010	− 21.5	− 27.1
	Dmitrievskaya, 5	1 774	sh	13.23	0.080	− 22.5	− 24.0
C_1bb Visean stage, Bobrikovskyi horizon	Gondyrevskaya, 60	1 440	sh	2.19	0.080	− 25.6	− 29.2
	Olkhovskaya, 86	1 870	sh	3.00	0.080	− 23.5	− 24.7
	Yayvinskaya, 4	2 499	sh	0.82	0.030	− 23.7	− 27.5
	Nozhovskaya, 36	1 499	lm	0.23	0.010	− 28.2	− 29.2
	Tartinskaya, 19	1 531	sh	0.73	0.010	− 22.3	− 25.9
C_1mn Tournaisian stage	Dmitrievskaya	1 788	sh	1.09	0.040	− 24.5	− 27.2
	Dmitrievskaya, 5	1 809	sh	1.13	0.060	− 23.2	− 26.4
	Nozhovskaya, 36	1 527	lm	0.65	0.010	− 25.4	− 27.3
C_1t	Andreevskaya, 23	1 818	lm	0.50	0.010	− 26.6	− 28.0
	Koltsovskaya, 1	1 515	sh	0.64	0.040	− 27.4	− 29.1

(1) Chloroform extract
(2) Situation of the fields is pointed elsewhere [24]
(3) lm : limestone
sh : shales and sandstones

carbon isotope composition of kerogens in ancient deposits varies in the same range as in recent sediments. Obviously, no essential change in the isotope composition of kerogen occurs during catagenesis. This conclusion is confirmed from investigations of coals which show that their isotope composition is unrelated to their rank, or degree of metamorphism [13, 37, 83, 23].

Artificial coalification experiments reveal a small (0.5-1‰) enrichment in the heavy isotope as the degree of coalification increases [3, 38] but this effect has not been observed in nature.

C. Kerogens and bitumens.

During the catagenic maturation of OM, hydrocarbons and other compounds of low polarity are liberated. These compounds which can be extracted with organic solvents (bitumen fraction) are usually isotopically lighter than the kerogen carbon of the same sample. This difference is almost certainly from the biological source. Extractable carbon derives predominantly from kerogen moieties rich in C—H-linkages which contain relatively light carbon because of the thermodynamically ordered isotope distribution in biological precursors. Lipids are richest in C—H-linkages and are considered to be the most probable precursor of oil hydrocarbons [77].

The isotopic compositions of kerogens and associated bitumens have been investigated and the correlation shown (Fig. 9.13) indicates their genetic relationship.

The isotopic composition of oil does not always correlate with that of the kerogen from associated beds (Fig. 9.14). This is understandable, since, before its accumulation, oil

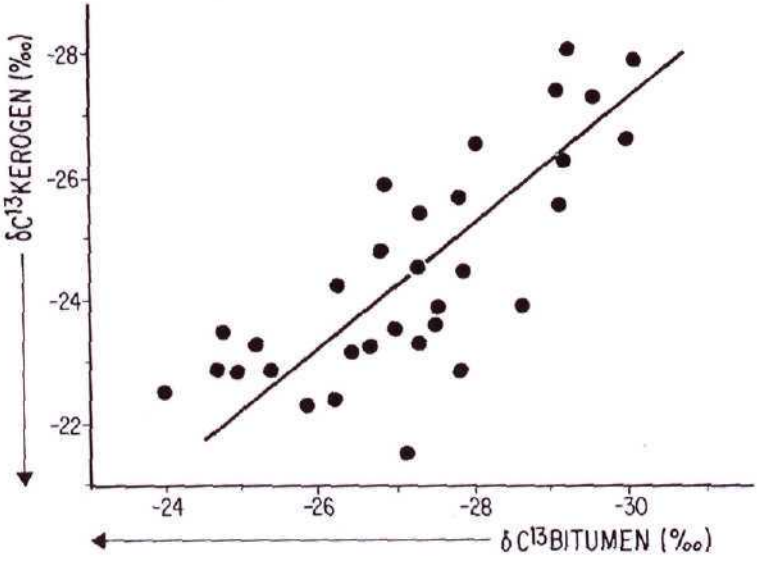


Fig. 9.13. — Relationship of carbon isotopic composition in kerogen and bitumen from the same core in Permian-Ural Area.

migrates, sometimes over long distances, both horizontally and vertically. For example, in the Permian region of the Volga-Ural Basin, the oil of the jasnopoljanskiy horizon (Lower Carboniferous) is one of the isotopically lightest in the section whereas the kerogen, in corresponding deposits, is isotopically heavier than in other intervals of the section [24]. On the other hand sometimes there is a positive correlation between the isotopic correlation of kerogen, bitumens and oil [87].

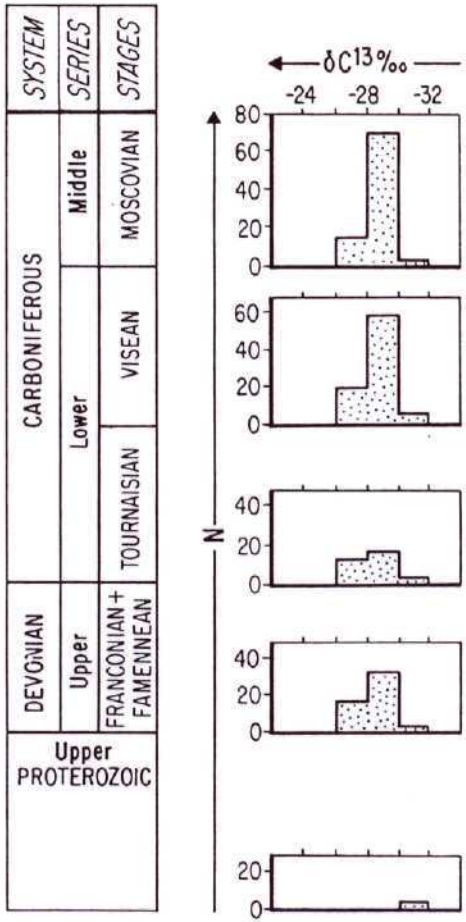


Fig. 9.14. — Distribution of isotopic composition of carbon of oils based on stratigraphic profiles of the Permian-Ural Area [24].

Obviously the correlation (or lack of it) in the isotopic composition of kerogen and oil, in certain sections, may serve as a basis for reconstructing the picture of oil migration within the formation.

D. Kerogen and natural gas.

Kerogen is the source of methane and other gaseous hydrocarbons in sedimentary rocks. The gases are formed by radical or thermocatalytic fragmentations which involve several types of isotope effects; these are reviewed in detail elsewhere [24]. Here all that we need to note is the relationship that exists between the isotopic composition of the gas and the intramolecular isotopic distribution in the kerogen. Methane forms by hydrogen disproportionation of the kerogen structure. The peripheral groups, rich in C—H-linkages such as CH_3-groups, appear to be cleaved first. As the CH_3-groups are exhausted structures less rich in C—H-linkages become the source of the methane carbon. Because of the thermodynamically ordered isotope distribution, methane formed from CH_3-groups ($\beta_{CH_3} = 1.131$) is isotopically lighter than methane formed from CH_2-moieties ($\beta_{CH_2} = 1.149$), CH-moieties ($\beta_{CH} = 1.168$) and so on. Thus, the intramolecular carbon isotope distribution in the kerogen determines carbon isotope composition of the methane (Fig. 9.10). A number of regularities in the isotopic distribution in gases result from this dependence, for instance the decrease in the C^{12} content of methane, with depth, [28, 71], the correlation between the carbon isotope composition of methane and vitrinite reflectance [80], and the occurrence of isotopically heavy methane (-15 to $-25‰$) in anthracites [12, 83]. A method identifying gas migration pathways was developed on this basis [24, 33].

VII. δC^{13}-VARIATIONS IN KEROGEN THROUGH GEOLOGICAL TIME

A gradual decrease in the enrichment in the C^{12}-isotope in passing from ancient to recent Phanerozoic kerogens has been noted [40,85]. Better data may result however by studying the alteration in the isotopic composition of kerogens in a regional Phanerozoic sequence, as was carried out for the Russian Platform [32]. Representative samples of each geological age of the sedimentary section were prepared by mixing several hundred specimens from different areas. The isotopic compositions of the bitumens and kerogens were determined separately. The δC^{13}-variation of organic carbon is shown in Fig. 9.15. Variations of certain other parameters, characterizing the sedimentary environment throughout the Phanerozoic of the Russian Platform, are shown in Fig. 9.16. There does not appear to be any distinct dependence of the organic carbon isotope composition on the lithofacies, sedimentation rate, concentration of organic carbon and so on. Variations in the isotopic composition of organic and carbonate carbon do not correlate, but the agreement between the carbonate values and other geochemical parameters is better than that of the organic carbon.

Two interesting features concerning the δC^{13}-variation of the organic carbon with geological time are:

(a) There is a sharp depletion in the C^{12}-isotope in the kerogens and bitumens in the Carboniferous and,

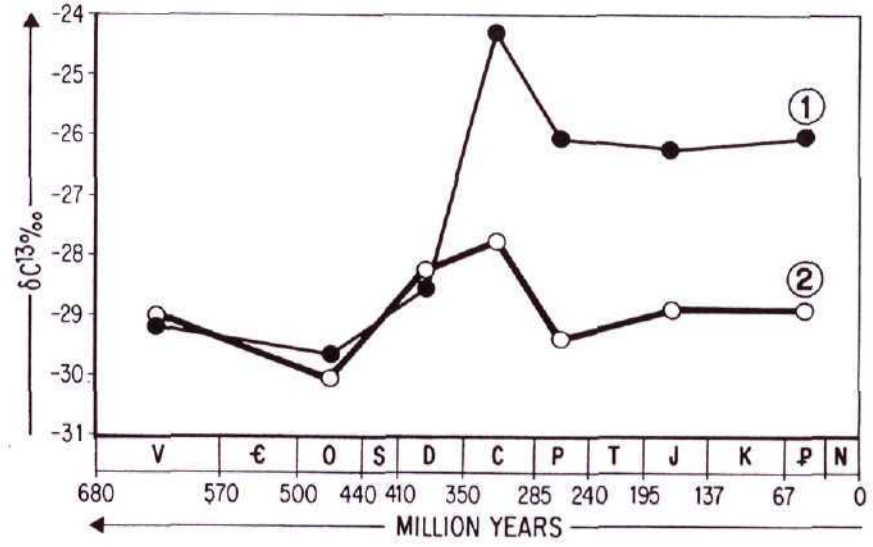


Fig. 9.15. — Dependence of the mean isotopic composition of carbon in:

1. Kerogen. 2. Chloroform-extracted bitumen on geologic age of rocks in the Phanerozoic sequence of the Russian Platform [32].

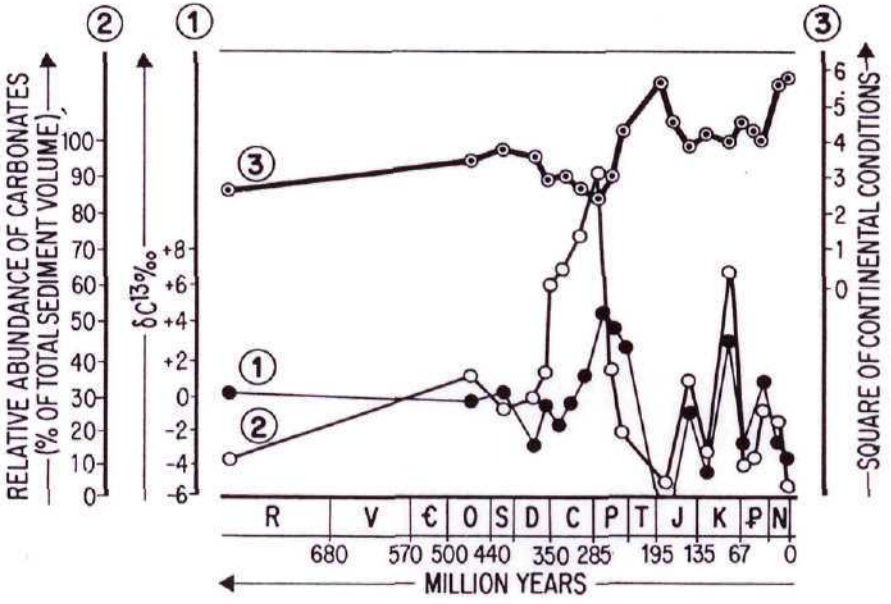


Fig. 9.16. — Comparison of variations of the carbon isotope composition of phanerozoic carbonates with the carbonate distribution in the deposits of each geological age and with the existence of terrestrial environment within the Russian Platform.

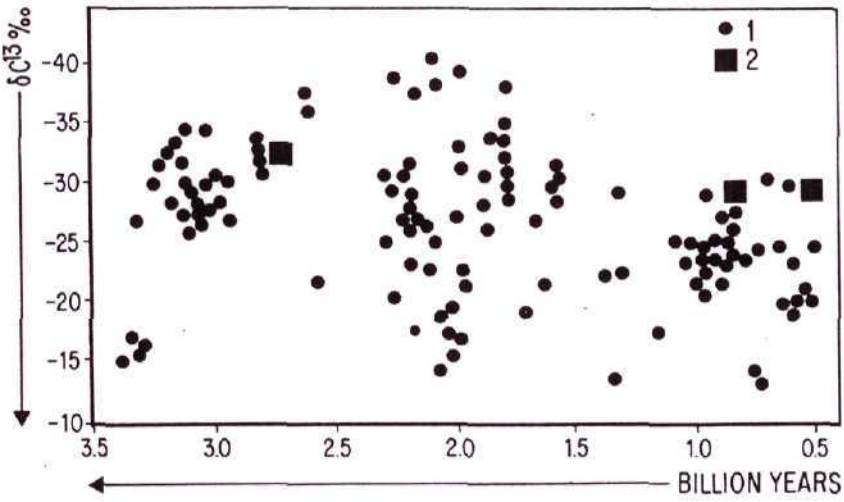


Fig. 9.17. — Carbon isotope composition of Precambrian kerogens:

●: denote results of separate measurements [40, 59, 19]. ■: mean-values [32].

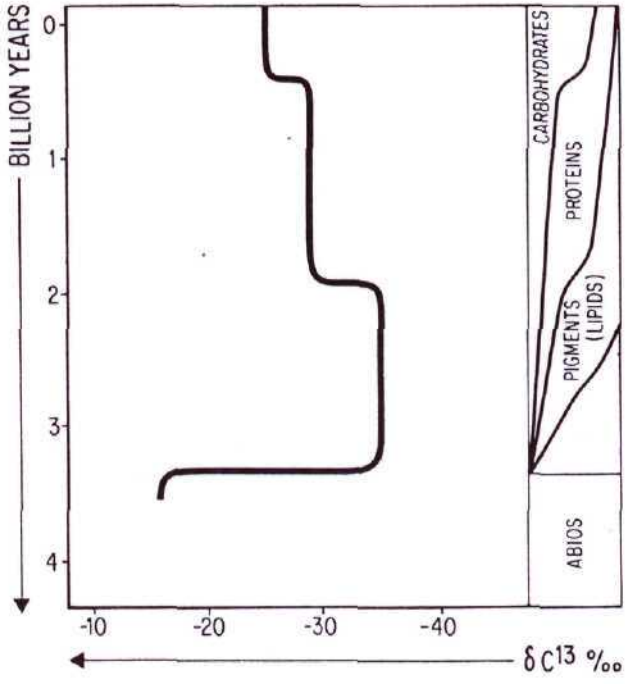


Fig. 9.18. — Generalized curve of alteration of isotope composition of organic carbon through geologic time on the ground of supposed evolution of the biochemical composition of living organisms.

(b) The differences between the isotopic composition of the kerogens and bitumens appears first in the Carboniferous.

These facts are apparently related, in some way, to the appearance of land vegetation.

Investigations of Precambrian kerogens have revealed that their carbon is enriched in the light isotope to nearly normal "biological" levels. This fact, together with the ubiquity of reduced carbon in the Precambrian [76] indicates an early formation of the biosphere. Data on the isotopic composition of Precambrian kerogens are summarized in Fig. 9.17. Isotope distributions in Precambrian organic carbon shows two characteristic features.

The first is the relative enrichment of Precambrian kerogen in the C^{12}-isotope. δC^{13}-values of kerogens older than 2 billion years range from -28 to $-38‰$, whereas for Phanerozoic kerogen these values range from -23 to $-30‰$; this was first noted by Hoering[40].

The second consists in the anomalous C^{12}-isotope depletion in the most ancient sediments. Shopf *et al.*[60] showed that kerogen from the Theespruit formation (Onverwacht, Swaziland, South Africa; $3.5 \times 10^9 yr$) was characterized by δC^{13}-values of about $-16‰$. These authors believe that this anomaly may record the transition from abiogenic to biogenic carbon, or the time at which the mechanism of biological isotope fractionation first appeared.

Several assumptions have been made regarding the C^{12}-isotope enrichment value of early Proterozoic kerogens. Epstein [20] assumed that it was related to the low abundance of biogenic carbon at that time which led to a corresponding displacement of the isotope balance in favour of a C^{12}-rich atmospheric CO_2. Degens [14] suggested that isotopically light organic carbon in the Precambrian might be related to a Precambrian sea characterized by lower pH-values and higher CO_2-concentrations. Pardue *et al.* showed, [61], from blue-green algal studies, that under certain conditions, (specifically a decreased cell concentration in the medium) the isotopic fractionation increased; this, they supposed, could account for isotopically light Precambrian carbon.

Schidlowski and cowokers [19, 43] note, and discuss, the enrichment in the C^{12}-isotopic composition of early Proterozoic kerogens as well as the C^{13}-isotopic enrichment of ancient Archean kerogens. They consider that the δC^{13}-variations of Precambrian organic carbon are, in general, in the range characteristic of Phanerozoic OM and that they are related to variations in the ratio of carbonate to organic carbon through geological time. However, this explanation requires synchronous δC^{13}-variations for carbonate and organic carbon; this does not seem to have been so. Variations in the isotopic composition of Precambrian carbonates have been found to correlate well with major tectonic events in the Earth's history [26, 32], but for organic carbon no such correlation has been found.

Nevertheless, in our view, variations in the δC^{13}-values of organic carbon throughout geological time are not random and reflect turning-points in the evolution of the biosphere. Variations in this value throughout the Precambrian and Phanerozoic are shown schematically in Fig. 9.18, with sudden changes at 3.5 billion, 2 billion and 0.4 billion years. The last corresponds to the appearance of land vegetation and a raising of the O_2-concentration in the atmosphere to present levels. The second abrupt change coincides with changes in the sulphur isotope composition and possibly corresponds to the appearance of sulphate-reducing bacteria. Fig. 9.18 also attempts to convey the idea that the changes may be related to milestones in the historical evolution of the principal biochemical constituents of organisms; discussion of this problem, however, is out with the framework of this paper.

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