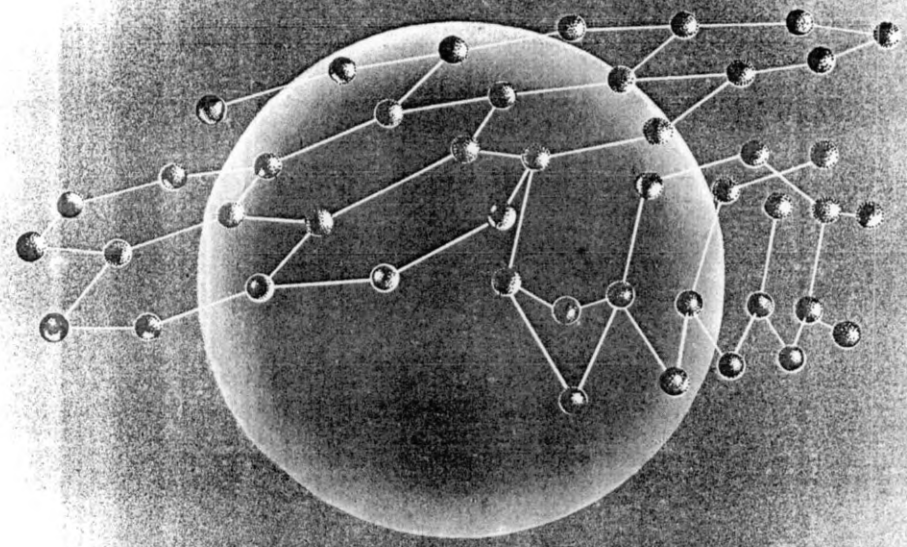
VOLUME 28 NUMBER 4
APRIL 1991

ISSN 0016-7029

geochemistry international



Published by SCRIPTA TECHNICA, INC.
A Wiley Company
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AMERICAN GEOLOGICAL INSTITUTE
and the
AMERICAN GEOPHYSICAL UNION

WILEY

ENGLISH EDITION PUBLISHED JUNE 1991

GEO028 04

UDC 550.42:546.027.26

THERMODYNAMICALLY ORDERED DISTRIBUTION OF CARBON ISOTOPES IN BIOGENIC GEOCHEMICAL SPECIMENS*

E. M. Galimov and V. B. Polyakov

Vernadskiy Institute of Geochemistry and Analytical Chemistry,
USSR Academy of Sciences

The isotope effect is examined in enzyme reactions occurring in several stages with microscopic reversibility. The effect can be represented as the sum of the thermodynamic and kinetic isotope effects. In stationary biochemical enzyme processes large-scale thermodynamic ordering in the isotope distribution occurs: ordering between groups linking compounds similar in molecular structure. Such thermodynamic carbon-isotope ordering in biogenic geochemical specimens is due to the large-scale ordering in biosystems. The reducing factor in front of the thermodynamic component is estimated by comparing the results of the theoretical study with the experimental data.

The ordered distribution of carbon isotopes in biogenic materials is of particular importance when carbon isotopes are applied to biogeochemistry and organic geochemistry [1, 2]. A thermodynamically ordered distribution of those isotopes is a major characteristic of biological isotope fractionation. This can occur at the intramolecular or intermolecular levels and also between major fractions of biogenic material [1-3].

A key role here is played by "large-scale" ordering, i.e., thermodynamic ordering between groups of organic materials that combine compounds similar in molecular structure [2, 4-6]. Microscopic reversibility of enzymatic reactions is the basic physical cause of that ordering [1, 3], which is the same at all levels, but the conditions of functioning of biosystems in which "large-scale" ordering occurs and the statistical laws applying to systems containing large numbers of objects may mean that the conditions are much less rigid than those for ordering between pure compounds.

Here we consider the "large-scale" ordering and its relation to isotope biogeochemistry and organic geochemistry via principles and models of biological isotope fractionation [1, 3].

ORIGINS OF THE ISOTOPE EFFECT IN ENZYME REACTIONS

Before we consider isotope effects in enzyme reaction chains, let us consider that in a single reaction. The treatment differs from [1] only in greater generality and rigor in the proofs without altering the essence of the basic concepts. No prior assumptions are made about the rate constants.

Calculation of the isotope effect in the stationary approximation is carried out on the basis of the following scheme:

*Translated from Geokhimiya, No. 9, pp. 1232-1240, 1990.

ISSN0016-7029/91/0004-0013$7.50/0

$$E + S \underset{K_{-1}}{\overset{K_{+1}}{\rightleftarrows}} ES_1 \underset{K_{-2}}{\overset{K_{+2}}{\rightleftarrows}} ES_2 \underset{K_{-3}}{\overset{K_{+3}}{\rightleftarrows}} \ldots ES_p \underset{K_{-(p+1)}}{\overset{K_{+(p+1)}}{\rightleftarrows}} \vdots$$
$$\vdots ES_{p+1} \underset{K_{-(p+2)}}{\overset{K_{+(p+2)}}{\rightleftarrows}} \ldots ES_{p+l} \underset{K_{-(p+l+1)}}{\overset{K_{+(p+l+1)}}{\rightleftarrows}} \vdots \ldots EP \underset{K_{-n}}{\overset{K_{+n}}{\rightleftarrows}} E + P, \quad (1)$$

in which E is the enzyme, ES_1 the enzyme-substrate complex, ES_i the intermediate states in that complex ($i=1, 2, \ldots, p, (p+1), \ldots (p+l), (p+l+1), \ldots n$), EP the final state of that complex (enzyme-product complex), and K_{+i} and K_{-i} the corresponding rate constants for the transitions between states.

An isotope effect is not apparent at all stages in an enzyme reaction. The isotope-sensitive stages are ones where the bonds to the isotopically substituted atom are altered [1, 7]. The isotope effects in the other stages are relatively small.

We will assume that the reaction occurs in n stages, with the effects small in the first $p + 1$ of them and the last $n—p—l—1$ of them; the sensitive stages are $p + 2$ and $p+l+1$, and possibly those intermediate between them. Thus all stages outside the vertical dotted lines have only minor isotope effects, and all the sensitive ones lie between them.

According to the stationary-concentration method [7, 8], two or more stages can be replaced in the stationary approximation by a single effective or observed rate constant, which can be expressed in terms of the true rate constants of all the replaced stages. We assume therefore that all the stages up to the first vertical bar in (1) are effectively one with the effective constants $\bar{K}_{+1} + \bar{K}_{-1}$, while all stages between the vertical bars in (1) represent a single stage with the effective constants K_a and K_b, and the remaining stages also are represented by a single stage having effective constants $\bar{K}_{+2}$ and $\bar{K}_{-2}$, which gives

$$E + S \underset{\bar{K}_{-1}}{\overset{\bar{K}_{+1}}{\rightleftarrows}} ES_p \underset{K_b}{\overset{K_a}{\rightleftarrows}} ES_{(p+l+1)} \underset{\bar{K}_{-2}}{\overset{\bar{K}_{+2}}{\rightleftarrows}} E + P. \quad (2)$$

The entire reaction is taken as being of effectively first order, so $\bar{K}_{+1}$ and $\bar{K}_{-2}$ are the products of the true rate constants and the substrate concentrations for $\bar{K}_{+1}$ and the product in the case of $\bar{K}_{-2}$. Let us also limit ourselves to the case in which the reverse combination of the enzyme and product has a negligible rate. That occurs if the reaction occurs under irreversible conditions [9]. This occurs under reversible conditions if we consider the initial instant of the reaction, when the concentration of P is small and therefore $\bar{K}_{-2}$ is known to be small. In what follows, we will consider the stationary case of irreversible conditions, where the isotope composition of the substrate can be taken as unchanged and

$$\bar{K}_{-2} \approx 0. \quad (3)$$

For the isotopically substituted form, (2) becomes

$$E + S^* \underset{\bar{K}_{-1}}{\overset{\bar{K}^*_{+1}}{\rightleftarrows}} ES^*_p \underset{K^*_b}{\overset{K^*_a}{\rightleftarrows}} ES_{(p+l+1)} \underset{\bar{K}^*_{-2}}{\overset{\bar{K}_{+2}}{\rightleftarrows}} E + P^*, \quad (2a)$$

in which the asterisk denotes a quantity that refers to the isotopic form and $\bar{K}^*_{+1} = j\bar{K}_{+1}$, $\bar{K}^*_{-2} = j\bar{K}_{-2}$, $j=[S^*]/[S]$, where $[S]$ is the substrate concentration. The substitution affects only K^*_a and K^*_b, while the isotope effect in the other stages is small.

The system of kinetic equations in that approximation, corresponding to (2)

and (2a), have on the basis of (3) the form

$$\begin{gathered}
K_{+1}C_0 + K_bC_2 - (K_{-1} + K_a)C_1 = 0,\\
K_b^*C_2^* - \overline{K}_{-1}C_1^* - K_a^*C_1^* + \overline{K}_{+1}^*C_0 = 0,\\
\overline{K}_{-1}(C_1 + C_1^*) + \overline{K}_{+2}(C_2 + C_2^*) - (\overline{K}_{+1} + \overline{K}_{+1}^*)C_0 = 0,\\
K_aC_1 - (K_b + \overline{K}_{+2})C_2 = 0,\\
K_a^*C_1^* - (K_b^* + \overline{K}_{+2})C_2 = 0.
\end{gathered} \tag{4}$$

Here C_0 is the free-enzyme concentration, C_1 the enzyme concentration in the ES_p state, and C_2 that in the $ES_{(p+1)}$ state. Only four of these five homogeneous equations in five unknowns are independent.

The isotope composition of the atoms of the product that occupy a particular position is

$$\frac{[P]}{[P^*]} = \frac{\overline{K}_{+2}C_2}{\overline{K}_{+2}C_2^*} = \frac{C_2}{C_2^*}. \tag{5}$$

This is derived from (4). Let us express C_1 via C_2 from the fourth equation in (4) and substitute that into the first equation:

$$K_{+1}C_0 = \frac{K_b\overline{K}_{+1} + K_a\overline{K}_{+2} + \overline{K}_{+2}\overline{K}_{-1}}{K_a^*}C_2, \tag{6}$$

and similarly from the fifth and second equations in (4):

$$\overline{K}_{+1}^*C_0 = \frac{K_b^*\overline{K}_{-1} + K_a^*\overline{K}_{+2} + \overline{K}_{+2}K_{-1}}{K_a^*}C_2. \tag{7}$$

We divide (7) by (6) to get from (5) that

$$\frac{[P^*]}{[P]} = \frac{K_a^*(K_b\overline{K}_{-1} + K_a\overline{K}_{+2} + \overline{K}_{+2}\overline{K}_{-1})}{K_a(K_b^*\overline{K}_{-1} + K_a^*\overline{K}_{+2} + \overline{K}_{+2}\overline{K}_{-1})}. \tag{8}$$

The ratio of those isotopes in the substrate is $-j$, so the partition coefficient is*

$$\alpha_{S/P} = \frac{K_a(K_b^*\overline{K}_{-1} + K_a^*\overline{K}_{+2} + \overline{K}_{+2}\overline{K}_{-1})}{K_a^*(K_b\overline{K}_{-1} + K_a\overline{K}_{+2} + K_{+2}K_{-1})}. \tag{9}$$

Let us perform elementary transformations on (9) with $\alpha_a = K_a^*/K_a$ and $\alpha_b = K_b^*/K_b$:

*Ivlev [10] obtained the expression

$$\alpha_{S/P} = \frac{K_2}{K_2^*}\frac{K_1}{K_1^*}\frac{K_a}{K_a^*}\frac{K_b^*K_{-1}^* + K_a^*K_{+2}^* + K_{+2}^*K_{-1}^*}{K_bK_{-1} + K_aK_{+2} + K_{+2}K_{-1}}$$

without incorporating the conditions $K_2 = K_2^*$, $K_1 = K_1^*$, $K_{-1} = K_{-1}^*$. When these conditions are used, we get our (9) and then (12), so his assertion that his expression for the isotope effect in an enzyme reaction cannot be reduced to that obtained in [1], namely, equation (5.40) on p. 172, is incorrect.

$$\alpha_{S/P} = \frac{K_a\left(1+\frac{K_b^*}{\overline{K}_{+2}}+\frac{K_a^*}{\overline{K}_{-1}}\right)}{K_a^*\left(1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{K_{-1}}\right)} = \frac{\alpha_a+\frac{K_b}{\overline{K}_{+2}}\frac{\alpha_b}{\alpha_a}+\frac{K_a}{\overline{K}_{-1}}}{1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}} = \tag{10}$$

$$= \frac{(\alpha_a-1)+\frac{K_b}{\overline{K}_{+2}}\left(\frac{\alpha_b}{\alpha_a}-1\right)+\left(1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}\right)}{1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}}$$

Considering that in these symbols

$$\alpha_b/\alpha_a \approx \beta_S/\beta_P,$$

where β_s and β_p are the β factors for the substrate and product correspondingly, and performing termwise division for (10), we get

$$\alpha_{S/P} = 1+\frac{\frac{K_b}{\overline{K}_{+2}}\left(\frac{\beta_S}{\beta_P}-1\right)}{1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}}+\frac{\alpha_a-1}{1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}}, \tag{11}$$

and for the isotope shift

$$\Delta_{S/P} = \frac{\frac{K_b}{\overline{K}_{+2}}}{1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}}\Delta_e+\frac{1}{1+\frac{K_b}{\overline{K}_{+2}}+\frac{K_a}{\overline{K}_{-1}}}\Delta_c. \tag{12}$$

Here we have used $\Delta_e \equiv \left(\frac{\beta_S}{\beta_P}-1\right)$ is the isotope shift in the case where equilibrium is attained and $\Delta_c \equiv (\alpha_a-1)$ is that for a purely kinetic effect. This agrees with the analogous expression in [1] for a simple enzyme mechanism at a low substrate concentration ($[S] \ll K_M$, with K_M the Michaelis constant) on the basis that the corresponding constants of the single-stage processes are replaced by the effective ones for the multistage kinetics.

Thus the isotope effect in an enzyme reaction is the sum of the reduced thermodynamic and kinetic effects [1]. If $K_b/K_{+2} \gg 1$, the thermodynamic component predominates and one gets an ordered distribution in the absence of equilibrium. Otherwise, the isotope effect is kinetic.

ISOTOPE EFFECTS IN DIRECT-CHAIN STATIONARY ENZYMATIC PROCESSES

In what follows, we do not assume *a priori* that the thermodynamic component exceeds the kinetic one, and represent (11) for convenience as

$$\alpha_{S/P}-1 = \varkappa\left(\frac{\beta_S}{\beta_P}-1\right)+\lambda\Delta_c. \tag{13}$$

Let us consider a chain of unbranched enzyme reactions under stationary conditions:

$$\ldots \xrightarrow{\kappa_i} S_i \xrightarrow{\kappa_{i+1}} S_{i+1} \xrightarrow{\kappa_{i+2}} \ldots .$$

Under stationary conditions, the concentrations of the substrates S_i are constant over time. This means that there is no accumulation, so the flux ought to be identical between substrates in the chain of reactions. All of this also applies to the isotopic-substitution flux I^*, so

$$I = K_i S_i,$$
$$I^* = K_i^* S_i^*, \tag{14}$$

in which S_i is the concentration of substrate i from (14) it follows that

$$\left(\frac{S_i^*}{S_i}\right) \Big/ \left(\frac{I^*}{I}\right) = \frac{K_i}{K_i^*}. \tag{15}$$

We put $S_i^*/S_i = R_i$ and $I^*/I = R_I$ to get $R_i/R_I = K_i/K_i^*$, and from (13) we get for the ratio of the rates that

$$\frac{R_i}{R_I} = 1 + \varkappa_i \left(\frac{\beta_{S_i}}{\beta_{S_{i+1}}} - 1\right) + \lambda_i \Delta_{ci}. \tag{16}$$

The subscript i in (16) differs from that in (13) in enumerating the substrates and corresponding reactions, while β_{S_i} is the β factor for substrate i. In terms of the isotope shifts $\Delta_{i/I} = R_i/R_i - 1$, (16) gives

$$\Delta_{i/I} = \varkappa_i \left(\frac{\beta_{S_i}}{\beta_{S_{i+1}}} - 1\right) + \lambda_i \Delta_{ci}, \quad i = 1, 2, \ldots p \ldots. \tag{17}$$

The isotope effects are for carbon and the β_i do not differ greatly from 1, so we neglect the terms quadratic in $\beta - 1$ to get

$$\Delta_{i/I} = \varkappa_i (\beta_{S_i} - \beta_{S_{i+1}}) + \lambda_i \Delta_{ci}. \tag{18}$$

Expression (18) can be split into two terms, one dependent on the β factor for substrate i and the other independent of it:

$$\Delta_{i/I} = \varkappa_i \beta_{S_i} + (-\varkappa_i \beta_{S_{i+1}} + \lambda_i \Delta_{ci}), \; i = 1, 2, \ldots p \ldots.$$

The expression in parentheses is denoted by A_i to get

$$\Delta_{i/I} = \varkappa_i \beta_{S_i} + A_i.$$

If we introduce the means $\varkappa$ and A over the entire set of substrates for the quantities independent of β_{S_i}, then

$$\Delta_{i/I} = (\bar{\varkappa} + \Delta\varkappa_i)\beta_{S_i} + \bar{A} + \Delta A_i, \tag{19}$$

in which

$$\Delta\varkappa_i = \varkappa_i - \bar{\varkappa}; \; \Delta A_i = A_i - \bar{A}.$$

Let us split up the substrates into groups by β factor. Then on averaging with respect to isotope composition for each group, we get

$$\Delta_{\mu/I} = (\bar{\varkappa} + \Delta\varkappa_\mu)\beta^\mu + \bar{A} + \Delta A_\mu, \tag{20}$$

where the subscript μ enumerates the groups; ΔA_μ and $\Delta\varkappa_\mu$ are the mean values of $\Delta\varkappa_i$ and ΔA_i, for group μ. A_i and μ_i are independent of β_{S_i}, so the set of A_i and $\varkappa_i$ in a given group can be considered as a random sample from the entire set of A_i and $\varkappa_i$ in the chain. If the number of substrates in a group is large, the mean A_i and $\varkappa_i$ for it will differ little from the $\overline{\varkappa}$ and $\overline{A}$ for the entire chain on account of the law of large numbers, i.e., if the number of substrates is large enough in a given group, $\Delta\varkappa_\mu$ and ΔA_μ will be small. Then (20) gives the isotope shift between groups μ and ν as

$$\Delta_{\mu/\nu} = \overline{\varkappa}(\beta^\mu - \beta^\nu) + \Delta\varkappa_\mu\beta^\mu - \Delta\varkappa_\nu\beta^\nu + \Delta A_\mu - \Delta A_\nu,$$

where all the terms are small by comparison with the first. We combine them into a single term denoted by $\Delta A'_{\mu\nu}$, to get

$$\Delta_{\mu/\nu} = \overline{\varkappa}(\beta^\mu - \beta^\nu) + \Delta A'_{\mu\nu}. \tag{21}$$

In a chain of irreversible enzyme reactions under stationary conditions, one gets large-scale thermodynamic ordering: the isotope shifts for large substrate groups with similar β are proportional to the latter.

ISOTOPE EFFECTS IN BRANCHED-CHAIN ENZYME REACTIONS

Biosynthesis in an organism is not a straight-chain process. Intersecting and divergent paths arise [11]. In a photosynthetic organism, those paths may be taken as divergent (with intersections and branching) from a single initial flux I_0. The flux from one branch to the next will be called a branch. Branches are numbered by superscripts, e.g., S_i^k denotes substrate i in branch k. For branch k we have

$$\Delta^k_{I/I_0} = \Delta^k_{I/I_0} + \varkappa_i^k\beta_{S_i} + A_i^k. \tag{22}$$

Here k enumerates the branch and by definition

$$\Delta^k_{I/I_0} = \frac{I_k^*/I_k}{I_0^*/I_0} - 1, \tag{23}$$

in which I_k is the flux in branch k.

We group together substrates with similar β on the assumption that each group combines a large number of branches, so

$$\Delta_{\mu/I_0} = \overline{\varkappa}\beta^\mu + \overline{A} + \Delta^\mu_{I/I_0} + \Delta A_\mu + \Delta\varkappa_\mu\beta^\mu. \tag{24}$$

Δ^μ_{I/I_0} is the mean value of Δ^k_{I/I_0} for group μ and is independent of the β factor for S_i^μ. Each group contains numerous branches, so the quantities in group μ independent of the β factor represent a random sample of large volume from the entire set of values for those quantities in the organism, and in accordance with the law of large numbers, the differences in them from the mean for the entire organism is small. Thus from (24) for the isotope shift of groups μ and ν we get

$$\Delta_{\mu/\nu} = \overline{\varkappa}(\beta^\mu - \beta^\nu) + \Delta A'_{\mu\nu}, \tag{25}$$

in which $\Delta A'_{\mu\nu}$ denotes the small contribution from quantities independent of the β factors for groups μ and ν.

Ordering can thus arise: the isotope compositions are proportional to the β factors for large groups of substrates with similar β-factors in irreversible stationary processes. The only constraint above is that the processes are stationary, which is closely so in most cases [11]. "Large-scale" thermodynamic

ordering does not necessarily require the thermodynamic component to predominate in the isotope effect for an individual reaction. It is merely necessary that it predominates over the deviation of the mean value of the kinetic component of the given group from its mean for the entire organism. The formulas apply not only for groups that gather together individual compounds but also for ones involving parts of molecules if their β factors are similar.

DISCUSSION AND COMPARISON WITH EXPERIMENT

Geochemically speaking, we have to consider how these arguments apply to fossil organic matter. Diagenetic geopolymers derive from numerous compounds, and one cannot state a particular precursor for a given part of the polymer. The components of fossil organic matter that are similar in molecular structure thus constitute the group of the biochemical precursors and/or their fragments. The conditions are met for "large-scale" ordering. Those conditions are also met by fractions of increasing polarity isolated from oils, sediments, and bitumoids, since each fraction includes a large number of compounds. "Large-scale" ordering may make itself felt in the organic matter also at the level of individual compounds, since in most cases (apart from certain biomarkers) they derive from various biochemical compounds and their fragments. A condition favorable to "large-scale" ordering is the fact that a multitude of species and individuals is involved in the formation of a sediment, so the individual features are extinguished [1]. Our method of distinguishing biogenic and abiogenic substances in geological specimens on the basis of the thermodynamically ordered distribution of carbon isotopes in them [1] thus has a direct relationship to the "large-scale" thermodynamic ordering.

The thermodynamic ordering of the distribution of carbon isotopes in organic matter can be disrupted during diagenesis and catagenesis, when kinetic isotope effects disrupt the original thermodynamically ordered isotope distribution [1]. The changes can provide valuable information on the processes [4].

Numerous data exist on the "large-scale" ordering [1, 2, 4-6, 12]. This applies particularly to the sublinear nature of the isotope distribution in fossil organic matter taken over fractions with increasing polarities. The β factors of organic compounds increase with the polarity [1, 2]. When diagenesis does not disrupt this distribution, it can be used to compare experimental data with the conclusions of theory. However, there are difficulties in estimating the exact β for each group, so quantitative discussion is difficult. Correlations can be based on experimental data [2, 13] using the isotope composition of the various structural groups in petroleum hydrocarbons (Fig. 1). The coefficient of proportionality between the β factors and isotope compositions of oils from various deposits is ~ 0.5, so the mean reducing factor in (25) is 0.5. Equating that value to the expression for the reducing factor from (12), we get

$$\frac{K_b/\bar{K}_{+2}}{1+\frac{K_b}{\bar{K}_{+2}}+\frac{K_a}{\bar{K}_{-1}}}\approx 0.5. \qquad (26)$$

This can be so only if

$$\frac{K_b}{\bar{K}_{+2}}\geqslant 1. \qquad (27)$$

However, then that factor for the thermodynamic component should be larger than the corresponding factor for the kinetic component (where the equality occurring for the particular case $(K_a/K_{-1}=0)$, so the thermodynamic component contributes more to the isotope effect, which applies of course to the mean values for those effects. This has not been assumed *a priori*, so it confirms that view, as pointed out previously [1].

CONCLUSIONS

1. In a stationary enzyme process, there is thermodynamic isotope ordering between large groups of substances similar in molecular structure.

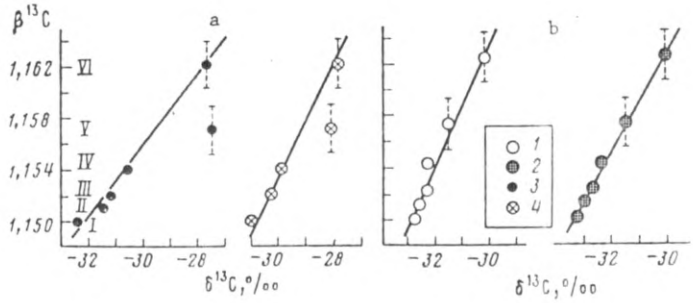

Fig. 1. Correlation of the isotope composition of oil structural groups with β factors [13]: a) Perm Kama area; b) West Siberian plate; deposits: 1) East Surgut; 2) Samotlor; 3) Kustov; 4) Kokuy; I) *n*-alkanes; II) monomethyl alkanes; III) isoprenoids; IV) naphthenes; V) aromatic hydrocarbons; VI) porphyrins.

2. Stationary behavior is the sole constraint on the ordering in biogenic material at all levels, so that ordering of the distribution of carbon isotopes provides a universal approach to the study of geochemical specimens of biological origin.

3. Comparison with experiment shows that the thermodynamic component makes a larger contribution than the kinetic one as regards the mean values.

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