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Carbon isotopy of individual aromatic compounds of petroleum for their geochemistry understanding

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The article analyzes published and original data related to the carbon isotopic composition of individual aromatic compounds of fossil organic matter and oil. It has been shown that there is reliable evidence of the intramolecular isotopic heterogeneity of a number of molecules. For example the isotopically depleted carbon of the methyl group of alkylnaphthalenes and the terminal methyl of *n*-alkanes. The $\delta^{13}C$ inheritance from the biochemical precursor during the aromatization is also well documented in the example of diterpenes in the series *abietic acid – dehydroabietane – simonellite – retene*, as well as in the other terpene and steroid series. At the same time, there is evidence of carbon isotopic fractionation during the formation of several aromatic compounds from a single precursor. The increasing aromatization of the prebuild polycyclic structure does not change the $\delta^{13}C$ value of the molecule, and the formation of aromatic compounds with different numbers of aromatic rings in competing reactions leads to isotope differentiation in accordance with the thermodynamically determined distribution of carbon isotopes. If the suggestion is correct, it is the key to the understanding of specific petroleum aromatic hydrocarbons formation mechanism. It is possible that a comparison of $\delta^{13}C$ values for pairs of compounds formed during the transformation of one precursor will also provide information on the temperature conditions for the occurrence of the corresponding reactions.

Keywords: *aromatization isotope effect, carbon isotopes of aromatic hydrocarbons, isotopic bond numbers.*

Изотопия углерода индивидуальных ароматических соединений нефти для понимания их геохимии

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В статье проанализированы опубликованные и оригинальные данные, относящиеся к изотопному составу углерода индивидуальных ароматических соединений ископаемого органического вещества. Имеются надёжные свидетельства внутримолекулярной изотопной неоднородности ряда молекул, например изотопно лёгкого углерода метильной группы алкилнафталинов и концевого метила *н*-алканов. Наследование изотопного состава углерода от биохимического предшественника при ароматизации полициклической структуры хорошо документировано на примере дитерпеноидных структур в ряду *абиетиновая кислота – дегидроабиетан – симонеллит – ретен*, а также в рядах других терпеноидных и стероидных структур. При этом имеются свидетельства изотопной дифференциации углерода при образовании нескольких ароматических соединений из единого ациклического предшественника. Нарастающая ароматизация уже имеющейся полициклической структуры не изменяет значение $\delta^{13}C$ молекулы, а образование ароматических соединений с различным числом ароматических циклов в конкурирующих реакциях ведёт к изотопной дифференциации в соответствии с термодинамически обусловленным распределением изотопов углерода, что потенциально является ключом к расшифровке механизма формирования ароматических углеводородов ископаемого органического вещества и нефтей. Возможно, что сопоставление значений $\delta^{13}C$ для пар соединений, образованных при трансформации одного предшественника, даст информацию и о температурных условиях протекания соответствующих реакций.

Ключевые слова: *изотопный эффект ароматизации, изотопы углерода ароматических углеводородов, изотопические числа связи.*

Introduction

Carbon investigations are powerful instruments for studying organic matter of oils and oil source rocks. Fractionation of carbon isotopes at the stage of photosynthesis and subsequent biochemical and geochemical transformations lead to the formation of the observed $^{13}C/^{12}C$ isotopic ratio of fossil molecules. A number of molecules are directly inherited by fossil organic matter from the biosphere. Others are undergoing significant changes, including the formation of new aliphatic and aromatic cycles.

Intramolecular isotopic heterogeneity

The isotopic composition of carbon atoms in nonequivalent positions of the hydrocarbon molecule is not the same. This is due to both kinetic and equilibrium isotopic fractionations. The theory of intramolecular isotopic effects was elaborated by E. M. Galimov [3, 4, 18].

Le Métayer et al., [7] proved that the carbon of the methyl group of alkylnaphthalenes was isotopically lighter than the carbon of the aromatic system. Certain variability was observed in alkylnaphthalenes from different oil samples of different maturation, but the overall trend was

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unchanged [7]. We calculated carbon β-factors[1] for different alkylnaphthalenes using Galimov's additivity principles [3, 4, 18]. Our calculations showed a negative correlation between carbon β-factor of the alkylnaphthalene and a number of methyl groups in its molecular unit. This correlation relating to equilibrium state agreed with the trend observed in natural samples [7].

Direct measurements of the intramolecular distribution of carbon isotopes in relation to *n*-alkanes, performed by the NMR method [5] showed that the carbon of the terminal methyl group was isotopically different from the rest of the carbon of the molecule. Thus terminal methyl is depleted in ^{13}C up to 13 ‰. Following results confirmed above mentioned data [9]. Thus terminal methyl of heptane depleted up to 11 ‰ ^{13}C compared to neighboring carbon atom [9]. Our calculation of the isotopic difference by thermodynamically determined β_i factors [3] gives the $\delta^{13}C$ difference of the terminal methyl and methylene units of about 16 ‰.

These examples, which confirm agreement between observed the intramolecular carbon isotope heterogeneity in hydrocarbons and that calculated based on the appropriate β_i-factors, can be considered as argument in favor of the applicability of the β_i-factor approach to predictions of intramolecular isotopic effects in natural hydrocarbons. Note that at present the method of E.M. Galimov is recognized as quite workable with the understanding of its not too high accuracy for structures containing various functional groups [6], which is not the case of the hydrocarbons we are discussing.

Aromatization of saturated cycles in the course of geological evolution

Consider some literature data on hydrocarbons with varying degrees of aromaticity, which supposedly have common precursor. One of the first works by Freeman et al. [2] was carried out on the material of the Eocene Messel clays (Germany). The carbon isotopic composition of hydrocarbons of several series, structurally related to oleanane, was investigated. There are no pronounced changes in the isotopic composition of carbon with an increase in aromatization for individual series of compounds selected for analysis; the isotope effect during aromatization is unreliable. It is important to emphasize that Freeman et al. [2] investigated aromatization occurring in diagenesis and used a series of compounds which had polycyclic structure initially.

Recently Schaeffer et al. [13] studied hydrocarbons in fossil wood of different species of the Quaternary age. They studied products of the transformation of abietic acid, as well as triterpenoids. No carbon isotope trend was recorded (figure). As previously Freeman et al. [2], Schaeffer et al. [13] investigated aromatic hydrocarbons and their oxygen-containing analogs formed from a ready-made polycyclic system in diagenesis. Data from [10] also indicate the absence of the carbon isotope difference in the dehydroabietane-simonellite-retene series.

Liao et al. [8] reported data on the carbon isotopic composition of hopanes with different numbers of aromatic rings along with the same data on monoaromatic steranes and diasteranes from Estonian kukersite. For hopanes, Liao et al., found that hopane aromatization led to the carbon enrichment in ^{13}C isotope up to 2—4 ‰, whereas monoaromatic steranes and diasteranes were found to be indistinguishable [8]. The difference in the carbon isotopic composition between hopane structures hydrocarbons was explained by various sources of the hopanes [8]. In particular, they can be derived from bacteriohopantetrol and diploptene.

Cyclization, aromatization and carbon isotope effects

Previously Bushnev et al. [15] established a negative carbon isotopic shift between *n*-alkylbenzene (AB) and *n*-alkylnaphtalene (AN) representing oil aromatic hydrocarbons with a different number of cycles – and having a common C_{21} precursor. The 2.7 ‰ enrichment of C_{21} *n*-alkylnaphthalene in heavy carbon ^{13}C isotope with respect to C_{21} *n*-alkylbenzene is observed for a number of oils from the Upper Devonian reservoirs of the Timan-Pechora basin (Tabl. 1). We compared the enrichment observed in natural samples with appropriate equilibrium carbon isotopic shift, calculated by Galimov's method of isotopic bond numbers [3, 4, 18].

According to this method, the β-factor for a $^{13}C/^{12}C$ single isotopolgue substituted in the *i*-th position can be calculated by the following equation [3, 4, 18]:

$$\beta_i = 1 + \sum_j L_j + \sum_k l_k$$

where β_i is the β-factor for a $^{13}C/^{12}C$ single isotopolgue substituted in the *i*-th position; L_j is the increment (isotopic bond number) to the β-factor from the *j*-th chemical bond of the carbon atom under isotope substitution; and l_k is the increment to the β-factor from *k*-th chemical bond of the second surrounding. Values of the increments L_j and l_k were found and tabulated by E. M. Galimov (see the final version in Table. 2, in [3]). The β-factor of the chemical compound containing n carbon atomsis as following.

$$\beta = \frac{1}{n}\sum_i \beta_i$$

where β is the β-factor of the compound as a whole.

Our calculation of the equilibrium carbon isotope shift between C_{21} *n*-alkylnaphtalene and C_{21} *n*-alkylbenzene, by Galimov's method of isotope bond numbers gives 2.59 ‰ at 300 K and agrees well with 2.6 ‰ observed in natural samples (Table 2).

New data on the carbon isotopic composition of C_{21} and C_{23} *n*-alkylbenzene and *n*-alkylnaphthalene oil from wells 76-Laboganskaya (D_1l, Timan-Pechora basin) [17]

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[1] The β-factor or the reduced isotopic partition function ratio is the main concept of the stable isotope fractionation theory [1]. In equilibrium, the isotope fractionation factor between two compounds A and B ($\alpha_{A/B}$) is expressed in terms of their β-factors as follows: $\alpha_{A/B} = \beta_A / \beta_B$. Based on the general equations: $\delta^{13}C_A - \delta^{13}C_B \approx (\alpha_{A/B} - 1) \times 1000 = \Delta_{A/B} \times 1000$ (where $\Delta_{A/B} = \alpha_{A/B} - 1$ is the isotopic shift), the following equation holds in equilibrium: $\delta^{13}C_A - \delta^{13}C_B \approx (\beta_A / \beta_B - 1) \times 1000$.
In equilibrium difference in $\alpha^{13}C$ of two compounds is directly expressed in terms of their β-factors.

Table 1. $\delta^{13}C$ of specific aromatic hydrocarbons, ‰

Таблица 1. $\delta^{13}C$ конкретных ароматических углеводородов, ‰

Oilfield	$C_{21}AB$	$C_{21}AN$	difference	$C_{23}AB$	$C_{23}AN$	difference
Syurkharatinskaya / Сюрхаратинская	−30.2 ± 0.4	−26.9 ± 0.7	−3.3			
Verkne-Kolvinskaya / Верхнеколвинская	−31.4 ± 0.5	−29.1 ± 0.4	−2.3			
Yanemdeyskaya / Янемдейская	−31.1 ± 0.2	−27.8 ± 0.1	−3.3			
Medynskaya / Медынская	−34.6 ± 0.4	−32.0 ± 0.3	−2.6			
Myadseyskaya / Мядсейская	−35.1 ± 0.6	−33.0 ± 0.2	−2.1			
Laboganskoe / Лабоганское	−35.1 ± 0.4	−32.6 ± 1.0	−2.5	−34.0 ± 0.3	−32.0 ±0.5	−2.0
Severj-Domanichevskaya Северо-Доманичевская	−36.9 ± 0.2	−35.0 ± 0.4	−1.9			

Note. Rows 1—5 were published [15], rows 6, 7 — new data.
Примечание. Данные строк 1—5 были опубликованы [15], строки 6, 7 — новые данные.

Table 2. The values of the difference in the isotopic composition of carbon of C_{21} *n*-alkylbenzene and 1-*n*-alkylnaphthalene determined experimentally and calculated in different ways

Таблица 2. Значения разницы изотопного состава углерода *н*-алкилбензола и 1-*н*-алкилнафталина состава C_{21}, определённые экспериментально и вычисленные разными способами

Definition method / Способ определения	$\delta^{13}C_{AB} - \delta^{13}C_{AN}$, ‰
Average value for 7 oils samples, for each hydrocarbon of each oil sample at least 3 measurements Среднее значение для 7 образцов нефтей, для каждого углеводорода каждого образца нефти не менее 3 измерений	−2.57
Calculation according to E. M. Galimov isotopic bond numbers method [3]. Temperature 300 K Расчёт методом изотопических чисел связей по Э. М. Галимову [3]. Температура 300 K	−2.59
Calculation based on Polyakov and Horita's [11] data. The temperature of 290 K — is the probable temperature of early diagenesis Расчёт на основе данных Полякова и Хориты [11]. Температура 290 K — вероятная температура раннего диагенеза	−1.83
Calculation based on Polyakov and Horita's [11] data. The temperature of 423 K — is the probable temperature of oil window peak Расчёт на основе данных Полякова и Хориты [11]. Температура 423 K — вероятная температура главной фазы нефтеобразования	−0.91

and C_{21} composition in oil from well 27-North-Domanovichskaya (D_3fm, Belarus) are listed in Table 1. These data confirm depletion of *n*-alkylbenzene in ^{13}C compared to *n*-alkylnaphthalene. It should be emphasized that $\delta^{13}C$ data for C_{23} *n*-alkylbenzene and *n*-alkylnaphthalene have not been previously reported. Averaging the new data with previously published data [15] gives $\delta^{13}C_{AN} - \delta^{13}C_{AB} = 2.6$ ‰.

Polyakov and Horita [11] calculated carbon β-factors for 67 hydrocarbons (alkanes, alkenes, alkynes, cycloalkanes, and aromatics) including their 267 single-substituted isotopomers in temperature range 200—800 K using the harmonic oscillator — rigid rotator model and the Urey/Bigeleisen-Mayer approach. They expressed the temperature dependence of the logarithm of the β-factor as a fifth-order polynomial of the inverse absolute temperature square. Coefficients of the fifth-order polynomial all 267 single-substituted isotopomers were tabulated in Supplement to their paper [11]. Unfortunately, β-factors for alkylnaphthalene derivatives were not calculated by Polyakov and Horita [11]. Therefore, the calculations of β-factors for $C_{21}AN$ using Polyakov and Horita's [11] data were performed with some degree of convention, since we used the polynomial coefficients for appropriate carbon in aromatic ring in *o*-divinylbenzene for the calculation of the β-factor for the bridgehead carbon atoms of alkylnaphthalene. By this method, one can estimate the temperature dependence of the equilibrium isotopic shift between alkylnaphthalene and alkylbenzene with temperature. We have estimated it at temperatures, which are typical for early diagenesis and oil window peak. We have accepted the temperature at the bottom of the shelf basin in the

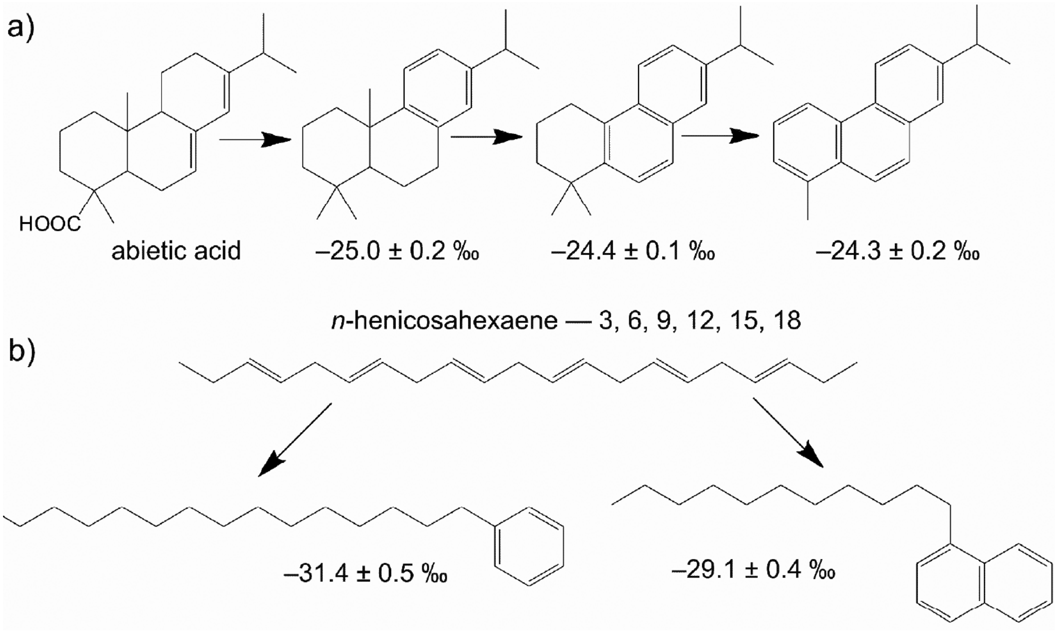

Fig. 1. a — the carbon isotope data of abietic acid transformation products — dehydroabietane, simonellite, and retene isolated from buried pine wood (SE France) according to [13]; b — the carbon isotope composition of C_{21} *n*-alkylbenzene and 1-*n*-alkylnaphtalene from Verkhnekolvinskaya-65 oil according [15] and their proposal formation pathway according to [16]

Рис. 1. а — данные по изотопному составу углерода продуктов трансформации абиетиновой кислоты — дегидроабиетана, симонеллита и ретена, выделенных из ископаемой древесины сосны (ЮВ Франция) по [13]; b — изотопный состав углерода C_{21} *н*-алкилбензола и 1-*н*-алкилнафталина из нефти Верхнеколвинская-65 [15] и их пути формирования [16]

equatorial region of the Atlantic equal to 17 °C (290 K, [12]) as the average temperature of early diagenesis. The calculated equilibrium isotopic shift $\delta^{13}C_{AB} - \delta^{13}C_{AN}$ is equal to −1.83 ‰ at this temperature (table 2). At the temperature of oil window peak (150 °C or 423 K according to [14]) the equilibrium $\delta^{13}C_{AB} - \delta^{13}C_{AN}$ is −0.91 ‰ (table 2). The former value relating to early diagenesis temperature is closer to the data observed in natural samples (*cf.* table 1). Accordingly, discovered proximity of the carbon isotopic shift between alkylbenzenes and alkylnaphthalenes observed in natural samples to the equilibrium value allows us to determine under what conditions and at what stages of maturation of organic matter the processes of cyclization and aromatization of polyene chains occur.

Conclusion

The negative carbon isotopic shift between C_{21} *n*-alkylbenzene and C_{21} *n*-alkylnaphtalene having a common biochemical precursor is discovered in natural samples of oils from different stratigraphic levels in Timan-Pechora Basin in Russia and Upper Devonian oil from Belarus. The same regularity was also observed for C_{23} *n*-alkylbenzene and C_{23} *n*-alkylnaphtalene.

The observed carbon isotopic shift between C_{21} *n*-alkylbenzene and C_{21} *n*-alkylnaphtalene is coincide with the equilibrium carbon isotopic shift between those compounds at 300 K calculated by Galimov's method of isotopic bond numbers.

It has been shown that the thesis of an equilibrium carbon shift between C_{21} alkylbenzene and C_{21} alkylnaphthalene allows determining under what conditions and at what stages of maturation of fossil organic matter the aromatization and cyclization processes occur.

Comparison of published isotopic data with the C_{21}AB and C_{21}AN results allows formulating the following hypothesis to be proven. If fossil hydrocarbons increasing in aromaticity were based on initially polycyclic system, they should be isotopically undistinguishable. If hydrocarbons were formed during cyclization and aromatization by competing reactions, they have different carbon isotopic compositions. Possibly this is the key to aromatics formation understanding.

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References

1. Bigeleisen J., Mayer M. G. Calculation of equilibrium constants for isotope exchange reactions. J. Chem. Phys., 1947, 15, pp. 261—267.

2. Freeman K. H., Boreham R. E., Summons R. E. and Hayes J. M. The effect of aromatization on the isotopic compositions of hydrocarbons during early diagenesis. Org. Geochem., 1994, 21 (10—11), pp. 1037—1049. https://doi.org/10.1016/0146-6380(94)90067-1

3. Galimov E. M. Isotope organic geochemistry. Org. Geochem., 2006, 37, pp. 1200—1262. https://doi.org/10.1016/j.orggeochem.2006.04.009

4. Galimov, E. M. Carbon Isotopes in Oil and Gas Geology. Moscow: Nedra, NASA, p. 384. Translation, F-682, Washington, D. C., 1975.

5. Gilbert A., Yamada K. and Yoshida N. Exploration of intramolecular ^{13}C isotope distribution in long chain *n*-alkanes (C11–C31) using isotopic ^{13}C NMR. Org Geochem.,

2013, 62, pp. 56—61. https://doi.org/10.1016/j.orggeochem.2013.07.004

6. He Y., Bao H., Liu Y. Predicting equilibrium intramolecular isotope distribution within a large organic molecule by the cutoff calculation. Geochim. et Cosmochim. Acta, 2020, 269, pp. 292—302. https://doi.org/10.1016/j.gca.2019.10.032

7. Le Métayer P., Grice K., Chow C. N., Caccetta L., Maslen E., Dawson D., and Fusetti L. The effect of origin and genetic processes of low molecular weight aromatic hydrocarbons in petroleum on their stable carbon isotopic compositions. Org. Geochem., 2014, 72, pp. 23—33. https://doi.org/10.1016/j.orggeochem.2014.04.008

8. Liao J., Lu H., Sheng G., Peng P., and Hsu C. S. Monoaromatic, diaromatic, triaromatic, and tetraaromatic hopanes in kukersite shale and their stable carbon isotopic composition. Energy Fuels, 2015, 29, pp. 3573—3583. https://doi.org/10.1021/acs.energyfuels.5b00106

9. Liu C., McGovern G. P., Liu P., Zhao H., Horita J. Position-specific carbon and hydrogen isotopic compositions of propane from natural gases with quantitative NMR. Chemical Geology, 2018, 491, pp. 14—26. https://doi.org/10.1016/j.chemgeo.2018.05.011

10. Marynowski L., Smolarek J., Bechtel A., Philippe M., Kurkiewicz S., Simoneit B.R.T. Perylene as an indicator of conifer fossil wood degradation by wood-degrading fungi. Org. Geochem., 2013, 59, pp. 143—151. https://doi.org/10.1016/j.orggeochem.2013.04.006

11. Polyakov V. B., Horita J. Equilibrium carbon isotope fractionation factors of hydrocarbons: Semi-empirical force-field method. Chemical Geology 559, 2021, 119948. DOI: 10.1016/j.chemgeo.2020.119948

12. Richards F. A. and Vaccaro R. F. The Cariaco Trench, an anaerobic basin in the Caribbean Sea. Deep-Sea Research, 1956, 8, pp. 214—228. DOI: 10.1016/0146-6313(56)90005-3

13. Schaeffer P., Bailly L., Motsch E., Adam P. The effects of diagenetic aromatization on the carbon and hydrogen isotopic composition of higher plant di- and triterpenoids: Evidence from buried wood. Organic Geochemistry 136, 2019, 103889. https://doi.org/10.1016/j.orggeochem.2019.06.010

14. Tissot, B. P., Welte, D. H., 1984. Petroleum Formation and Occurrence. Springer-Verlag, New York, 699 p.

15. Bushnev D.A., Burdelnaya N. S., Valyaeva O. V. *N-alkilbenzol i 1-n-alkilnaftalin sostava* S_{21} *v neftyakh: izotopnyy effekt pri tsiklizatsii/aromatizatsii?* (C_{21} *n*-alkylbenzene and 1-*n*-alklylnaphthalene in Oils: Isotope Effect during Cyclization/Aromatization?). Geochemistry International, 2020, 58 (1), pp. 61—65. DOI: 10.1134/S0016702920010036

16. Bushnev D. A. and Valyaeva O. V. *N-alkilbenzoly i 1-n-alkilnaftaliny v ryade neftey pozdnedevonskogo vozrasta Timano-Pechorskoy provintsii* (N-alkylbenzene and 1-*n*-alkylnaphthalene in series of Late Devonian oils of the Timan-Pechora province). Vestnik of Institute of geology Komi SC UB RAS, 2015, No. 10, pp. 17—20. DOI: 10.19110/2221-1381-2015-10-17-20

17. Valyaeva O. V., Ryabinkina N. N., Bushnev D. A. *Uglevodorody-biomarkery neftey Labaganskogo mestorozhdeniya Timano-Pechorskoy neftegazonosnoy provintsii* (Biomarker hydrocarbons of oils from the Labagan field of the Timan-Pechora oil and gas province). Georesursy (Georesources), 2020, 22 (1), pp. 46—54. DOI https://doi.org/10.18599/grs.2020.1.46-54

18. Galimov E. M. *Printsip additivnosti v izotopnoy termodinamike* (Principles of additivity in isotope thermodynamics). *Geokhimiya*, 1982, No. 6, pp. 767—783.

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