Oil & Gas Science and Technology – *Rev. IFP*, Vol. 63 (2008), No. 1, pp. 95-114
Copyright © 2008, Institut français du pétrole
DOI: 10.2516/ogst: 2007082

IFP International Conference
Rencontres Scientifiques de l'IFP

Molecular Structures of Heavy Oils and Coal Liquefaction Products
Structure moléculaire des huiles lourdes et produits de liquéfaction du charbon

Principal Regularities in Compositions and Structures of High-Molecular Compounds from Crude Oils and Natural Bitumens

A. Golovko, Yu. Golovko, L. Gorbunova, V. Kamyanov, G. Pevneva and T. Filimonova

Institute of Petroleum Chemistry, Siberian Branch of Russian Academy of Sciences
3, Academichesky av., 634021, Tomsk - Russia
e-mail: golovko@ipc.tsc.ru - julia_golovko@yahoo.com - lvg@ipc.tsc.ru - kamyanov@ipc.tsc.ru - pevneva@ipc.tsc.ru

Résumé — Caractéristiques fondamentales de la composition et de la structure des composés macromoléculaires du pétrole et des bitumes naturels — Les données expérimentales provenant de l'analyse des groupes structuraux et des composés macromoléculaires (résines et asphaltènes) de plus de 150 échantillons de pétroles extraits des gisements des provinces pétrolifères suivantes : Pannonskaïa (Serbie), Volgo-Ouralskaïa, Youjno-Kaspiïskaïa, des provinces de la Sibérie occidentale et du Kasakhstan occidental ainsi que des bassins pétrolifères de l'est et du sud-est de l'Asie sont regroupées dans cet article. Il est montré que le nombre d'atomes de carbone dans les alcanes de plus haut poids moléculaire peut atteindre des valeurs de 70-71 atomes pour les hydrocarbures du Cenozoique, mais seulement 35 à 40 atomes pour les huiles du Jurassique et du Paleozoïque. Les hydrocarbures pétroliers naphténo-aromatiques peuvent contenir jusqu'à six noyaux et 24 atomes de carbones présents dans les chaînes alkyles de la molécule. Les molécules de résines contiennent en moyenne 1-3 blocs structuraux, chacun constitué de 0 à 3 noyaux aromatiques et de 0 à 5 noyaux naphtèniques, de telle sorte que le nombre total des noyaux de chaque bloc ne dépasse pas 5 ou 6. Les masses moléculaires en poids des résines ne dépassent pas 1000-1500 g/mole. Les asphaltènes diffèrent des résines de même origine par :

- un nombre moyen de blocs structuraux constitués de molécules (jusqu'à 5) plus grand,
- majoritairement des ensembles tri- ou tetra-aromatiques,
- une moindre substition aliphatique des noyaux aromatiques,
- un nombre plus faible d'atomes de carbone dans les composés saturés.

D'après les données de cryoscopie dans le naphtalène, les masses moyennes des molécules d'asphaltènes ne dépassent pas 2500 g/mole. Suite aux interactions entre molécules, les composés de haut poids moléculaire (PHMC) peuvent former des agrégats et des particules poly-moléculaires, y compris des "paquets" quasi cristallins, eux-mêmes s'associant à leur tour, en particulier en ce qui concerne les asphaltènes. En raison de la désagrégation spontanée et de la formation de telles particules, les pétroles constituent un système polydispersé en équilibre dynamique. Les variations de composition et de structure des composés de haut poids moléculaires (PHMC) ont été étudiées en fonction de la profondeur à laquelle ils se situent dans le gisement, en fonction de l'âge et de la composition lithologique des sédiments du gisement. Bien que l'histoire thermique des composés ne soit pas considérée dans cet article, des constances peuvent être établies. Les composés macromoléculaires du pétrole (PHMC), constitués de matières hétéro-organiques chimiquement labiles, sont soumis, sous différentes conditions du gisement, à des transformations de composition et de structure chimiques rapides et importantes.

Abstract — Principal Regularities in Compositions and Structures of High-Molecular Compounds from Crude Oils and Natural Bitumens — *Experimental data on structural group composition and macro-structural characteristics of hydrocarbons and petroleum high-molecular compounds (PHMC) – resins and asphaltenes – from more than 150 samples of crude oil samples extracted on the oil-fields of Pannonian (Serbia), Volgo-Ural, South-Caspian, West-Kazakhstanian, West-Siberian, and several East- and Southeast Asian oil-bearing basins are summarized. It was shown that the number of carbon atoms in the highest n-alkane molecules reaches up to 70-71 in Cenozoic, but only 35-40 in Jurassic and Paleozoic oils. Petroleum hybrid naphtheno-aromatic hydrocarbons are compounds with up to six rings to 24 C-atoms in alkyl fragments of molecules. Resin molecules contain, on a mass weighted average, 1-3 structural blocks each consisting of 0-3 aromatic and 0-5 naphthenic rings in such combinations that the total number of cycles in each block does not exceed 5-6. The weight of average molecular masses of resins does not exceed 1000-1500 g/mole. Asphaltenes differ from resins from the same source by larger average numbers of structural blocks in molecules (up to 5), by the predominantly tri- and/or tetracycloaromatic nature of these blocks, by lesser substitution factors of aromatic nuclei and lesser proportions of C-atoms in saturated fragments. The weight of average masses of asphaltene molecules measured by cryoscopy in naphthalene does not exceed 2500 g/mole. Owing to strong intermolecular interactions, PHMC molecules form various associated structures and poly-molecular particles, including quasicrystalline "batches" and multi-batch aggregates, especially in asphaltenes. Through spontaneous decay and formation of such particles the oils have the character of dynamically equilibrium poly-disperse systems. Compositional and structural variations of PHMC were studied depending on the depths at which they occurred, age and lithological composition of oil-bearing sediments. Although thermal histories are not considered here, clear regularities are established. PHMC, consisting of chemically labile hetero-organic substances, under any bedded conditions are subjected to compositional and structural transformations which are more rapid and substantial as compared with petroleum hydrocarbons.*

INTRODUCTION

The fast development of world economics routinely increases the demand for energy. An increase in energy requirements by 50% within the next few years is predicted. It is widely believed that oil and natural gas will remain the main energy sources for a very long time in the future [1].

To date, about 160 billion tons of crude oil has already been produced in the world. Approximately the same volumes of residual oil resources (162 billion tons) are proved to be extractable, more than 10% of them being heavy high-viscous crude oils with density above 885 kg/m^3 and viscosity above 50 MPa s at 20°C. Geologically proved resources of such oils are fivefold greater (≈ 810 billion tons) [2]. Average heavy oil production is now about 12% of total world oil production.

Until the end of the XX century the oil-refining industry was mainly oriented to light crude oil refining, but heavier kinds of raw materials will become the main objects of refining at refineries of the future. Catalytic cracking has remained a basic process of petroleum residue refining for a long time. However, catalytic processes cannot provide a quite satisfactory technical and economic balance by refining of the heaviest kinds of petrochemical raw materials. Because of the present high level of the crude oil price the interest in non-traditional hydrocarbon sources has rekindled, in such materials which should serve as a raw stock for existing or modernized oil refineries. The heavy residual oils and natural bitumens as organic components of tar sands are the most attractive kinds of such raw materials.

Today the low and medium density oils are the most relevant, but due to the development of new technologies for middle density synthetic oil production from heavy residual oils and natural bitumens. The role of the latter in the total world recovery of hydrocarbon raw materials will grow. It calls not only for the construction of new modern catalytic units, but for the development of fundamentally new methods for deep conversion of carbonaceous raw materials into high-quality oil products.

High wax content, as well as tarry-asphaltenic matter content, are specific features of heavy carbonaceous raw materials. The lack of information on compositional and structural characteristics of these components, as well as on their role in formation of oil dispersal systems, is one of the main causes of low efficiency of existing industrial technological schemes of heavy oil refining, which restrains the development of new methods. Because of their negative influence on the activity of catalysts and quality of final marketable oil products, high-molecular petroleum components call for further investigation.

1 OBJECTS OF STUDY

This report presents the new experimental data obtained at the Institute of Petroleum Chemistry SB RAS. The data on the chemical nature of relatively insufficiently known heavy oil components such as waxes, naphthenoarenic hydrocarbons, resins and asphaltenes are discussed.

1.1 Waxes

Oil waxes are high-molecular hydrocarbons including normal and branched alkanes, alkylcyclanes and small amount of alkylarenes which are heavier than C_{18} and with long linear aliphatic chain in molecules. Oil waxes are subdivided into macrocrystalline paraffins and microcrystalline ceresins [3]. The macrocrystalline paraffins contain predominantly n-alkanes C_{18}-C_{30} with a fusion temperature up to 56°C, and the group of microcrystalline ceresins consists of n-alkanes above C_{40} and some quantity of branched and cyclic hydrocarbons with a fusion temperature above 60°C.

1.2 Hybrid Naphthenoarenic Hydrocarbons

Data on the composition of petroleum alkanes, polycyclanes (steranes and triterpanes) and alkylaromatic hydrocarbons (HCs) are widely in use in geochemistry to recognize initial oil-generated organic matter and estimate its thermal maturity degree. The compounds with hybrid structure which contain simultaneously both naphthenic and aromatic rings are investigated much less. They are very difficult to isolate from crude oil and to separate into narrow fractions of chemically similar substances because of lack of information on these compounds.

Data on oil steroids and triterpenoids with from one to three aromatic cycles in molecules are given in the literature [4-7]. The variety of these oil components is caused by transformations of biological steroids and terpenoids during diagenetic processes of their aromatization and fragmentation [5, 8-10]. As a result, the wide set of polycyclanes, naphthenomono-, naphthenobi- and naphthenotriarenes with steroid and pentacyclic triterpenoid molecular skeletons is formed. Extending the variety of oil HC types, the destruction of the initial biologically synthesized molecules leads to the appearance of bi-, tri- and tetracyclic compounds of other somewhat different modified types.

Besides partly aromatized steranes and terpanes, high-molecular naphthenoaromatic HCs with up to 8 cycles in molecules occur in crude oils [11]. The presence of fragments identical to those typical for bio-molecules and transformed organic matter in the structure of such HCs also suggests a relationship between polycyclic oil hybrid HCs and the initial biosynthetic material.

1.3 High-Molecular Hetero-Atomic Compounds

1.3.1 Petroleum Resins

By the procedure of their isolation from crude oil (precipitation of asphaltenes with large hexane excess, further adsorption of maltenes on ASK silica gel, elution of HC fractions with hexane and final desorption of resins with 1:1 benzene-ethanol mixture [12]) all sufficiently well-adsorbable hetero-atomic and aromatic compounds should be accumulated in resinous fractions, both low- and high-molecular ones [13, 14].

Average molecular of oil resins reach up to 1500 g/mol. Resin molecules consist on average of one-three structural units (blocks), *i.e.* contain from one to three mainly bi- or triarenic nuclei framed with branched aliphatic and alicyclic fragments, providing the solubility of resins in lower alkanes [14].

1.3.2 Petroleum Asphaltenes

Asphaltenes are the most high-molecular oil components. Their cryoscopically measured average molecular in naphthalene can reach up to several thousand mass units. Asphaltene molecules consist of three-five aromatic structural units, mainly based on tri- and tetracyclic nuclei which, on average, are larger than in resin molecules. The saturated fragments of the frame are distinctly less branched, so the average asphaltene aromaticity can reach up to 40-45% instead of 30-35% for resins [14].

Asphaltenes form complicated mycellar macro-particles in hydrocarbon media, including crude oils and petroleum residues. Properly asphaltene molecules form lamellar quasi-crystalline batches of four-six layers or strata in these macro-particles. The layers (strata) are flat, condensed polyarenic nuclei, framed with saturated structural fragments [14-16]. Paramagnetic properties peculiar to these petroleum asphaltenes favor strengthening of these batches.

Similar batch micro-particles can be formed in resin solutions too, but the toughness of batches is less in resins and, accordingly, the proportion of spatially organized molecules in resins is less than in asphaltenes because of the lesser average dimensions of aromatic nuclei.

Structural units in oil resins and asphaltenes are similar in their carbon skeletons to molecules of HCs and hetero-atomic compounds occurring in HC oil fractions. The differences consist of different quantitative parts of components capable of intermolecular association and batch spatial organization, and rising from HCs to resins, and further to asphaltenes.

2 METHODS OF INVESTIGATION

2.1 Isolation of Waxes

The solutions of initial crude oil or bitumen in hot isooctane were mixed with aluminum oxide, then the mixture was fed into a Soxhlet apparatus: HCs were extracted further by isooctane in 48 hours. The concentrate obtained after solvent distillation was dissolved in ligarine, then a precipitator (acetone) was added by small doses to the system under continuous stirring. The system was further sustained at – 21°C for two hours and precipitated waxes were filtered [17].

Gas Chromatographic analysis of waxes was performed using a chromatograph GC 800 (Carlo Erba, Italia), equipped with a packed capillary column (25 m length, 0.32 mm internal diameter) and filled with polyphenylsiloxane-car-borane phase HT-5 (particles of 0.1 μm in diameter); flame-ionization detector; helium as carrier-gas; linear increase in column temperature from 40 up to 370°C with a rate of 4°C/min; and maintenance of final temperature for 37 minutes. The xylene solutions of waxes were injected into the column.

2.2 Isolation of Naphthenoarenes

The fractions of mono- and biaromatic HCs were isolated from oily (hydrocarbon) parts of crude oils via column liquid-adsorption chromatography on neutral aluminum oxide with activity of grade II by Brockman. The mobile phase used as eluent was n-hexane. According to Rf values for authentic individual compounds as well as UV spectra of substances recorded on Specord UV-VIS, the eluates obtained were combined in homogeneous groups.

Alkyl- and naphthenoarenes were separated by methanol extraction [18]. To the share of naphtheno-benzenes fell 15.1-39.6 mass percent of monoarenes, whereas to the share of naphthenonaphthalenes fell – 20-54.0 mass percent of biarenes in different crude oils.

Mass-spectrometric analysis of naphthenoarenes was performed using the MKH-1310 instrument (Russia) with direct injection of the sample into the ionization chamber at 250°C; the energy of ionizing electrons being about 12 eV. The spectra obtained as well as group compositions and molecular-mass distributions for members of all isobar-homologue series of HCs were calculated by the procedures described in [19].

2.3 Isolation of Asphaltenes and Resins

To prevent any discrepancies possible because of the significant dependence of yields and properties of high-molecular oil components on the experimental conditions, all operations for their isolation from raw materials were performed only by unified procedures. These procedures involve precipitation of asphaltenes with the hexane excess (40:1 by volume) followed by separation of resins and hydrocarbons (oils) by Soxhlet's method with ASK grade silica gel as adsorbent, hexane and 1:1 benzene-ethanol mixture for elution of oils and resins as solvents [12, 14].

Analysis of resins and asphaltenes

IR and UV spectra of the products were obtained in their chloroform solutions using «Specord M-80» and «Specord UV-VIS» spectrometers, respectively.

NMR spectra were recorded on an «AVANCE» AV-300 Fourier-spectrometer with deuterochloroform as solvent and hexametyldisiloxane as internal standard at 60°. The concentrations of substances in their solutions varied from 2 to10 wt.%. To eliminate the mistakes caused by association and spatial organization of molecules, the results of spectra integration were extrapolated to infinite dilution [22]. As a result, the parts of protons in aromatic structures (H_a), in CH, CH_2 and CH_3-groups as well as directly associated with aromatic C-atom (H_α) protons, and protons in CH_3 (H_γ), and CH_2 (H_β) groups which occur at other structural positions in saturated molecular fragments were determined.

The information on molecular weights, elemental compositions and distributions of protons between different structures in molecules determined by NMR spectrometry were used for integral structural group analysis (SGA) of substances by methods described in [14].

3 DISCUSSION OF RESULTS

3.1 Waxes

The behavior of hydrocarbon systems in many respects depends on the content and composition of waxes. These characteristics determine in particular the scale of paraffin, resin and asphaltene sedimentation by oil production, transportation and storage [23]. The information on composition and distribution of waxes is necessary to develop effective technologies for paraffin crude oil extraction from bearing deposits.

The genesis of high-molecular HCs is related mainly to lipids occurring in compositions of plants, animals, microorganisms and to waxes of insects [3]. Biosynthetic precursors of petroleum waxes may be fatty acids, esters and carotenoids which contain up to 50 carbon atoms in molecules, as well as tricyclic terpenoids, polyisoprenoid alcohols above C_{100} [23-25]. It is very likely that the formation of high-molecular waxes resulted from the destruction of kerogenes at high temperatures and pressures [26].

It is important that high-molecular HCs are weakly subjected to microbial degradation: they more easily retain the native characteristics of initial organic matter [27] and therefore they are of great importance in studies of biodegradable oils. Data on the distribution of higher n-alkanes in these oils are the principal source of information on the type of organic matter participating in the formation of hydrocarbon accumulations.

We separated and analyzed by high-temperature gas chromatography the waxes from more than 50 oil samples of Western Siberian, Sakhalin, Volga-Ural, Timano-Pechora, Northern Caucasian, Mongolian and Chinese oil fields. These oils are of different geological ages from Pliocene to upper Devonian. They are deposited at different depths from 210 to 3200 m beneath the surface, lithology being terrigenous in Cenozoic and Mesozoic sediments but carbonate or mixed carbonate-terrigenous in Paleozoic ones *(see Table 1)*.

Although in other deposits of a similar depth and age compositional variations in the oils may vary due to different thermal histories, the study of the structural properties of high-molecular weight oil compounds which are presently deposited in these geological structures are of major interest for oil processing and prediction of oil composition.

Though a proportion of high-molecular HCs may be precipitated in reservoirs, pipelines and other elements of field equipment, and so dropped out of analytic sight the data obtained for waxes are satisfactorily correlated with the results of oil alkane content and composition determination as a whole. The oil alkanes containing no more than 35 C-atoms in molecules here are conventionally referred to as low-molecular ones.

In the majority of oils the low-molecular n-alkanes prevail over high-molecular ones (waxes). The wax content in crude oils varies within a very wide range from 0.5 up to 47.4 wt.%. Their group composition is also very inconstant. The crude oils of some Sakhalin and Western Siberian fields are characterized by considerable predominance of n-alkanes over branched and cyclic HCs. The wax concentrations in these crude oils are enhanced mainly due to the increase in the proportion of higher n-alkanes. Branched and cyclic HCs dominate in waxes from the rest of the studied oils *(Table 1, Fig. 1)*.

The studied crude oils differ substantially by the molecular-mass distributions (MMD) of the n-alkanes. These MMDs are usually unimodal in methano-naphthenic oils. One group of such oils contains the highest concentrations of HCs C_{13}-C_{15} *(Fig. 2a)*, whereas another group is characterized by the broad maximum in the C_{17}-C_{24} region *(Fig. 2b)*.

Biodegraded naphthenic *(Fig. 2c)* and naphthenomethanic *(Fig. 2d)* oils are also presented in our collection. The former are characterized by the great predominance of cyclic HCs, while the latter contain isoalkanes and especially isoprenanes as the main components.

The investigated oils also differ by the width of n-alkanes' MMDs, *i.e.* by the number of carbon atoms in the molecule of the highest member of the C_{max} series *(Table 1, Fig. 2)*. Waxes from sharply naphthenic oils are practically devoid of low-molecular n-alkanes. Cenosoic Sakhalin oils contain, however, n-HCs with up to 71 C-atoms in molecules. C_{max} values reach 65 and 57 in Mesosoic oils of West Siberia and Mongolia, respectively, while C_{max} values in Paleozoic crude oils of Volga-Ural and Timan-Pechora provinces are not greater than 51. Still lower values of $C_{max} \leq 35$-40 were often found for deeply buried Jurassic and Paleozoic oils in West Siberia *(Table 1)*.

A similar tendency for a decrease in MMDs (max values) with a simultaneous increase in age and occurrence depth of oil-bearing deposits were observed earlier by mass spectral data for homological series of alkyl monocyclanes and alkylbenzenes of the same oils [19].

These changes obviously testify that due to subsurface catagenetic transformations of hydrocarbon systems, the high-molecular compounds are more easily dissociated under the conditions of thermal destruction (cracking) than the low-molecular members of the same series. The same processes account for the shift of the maximum positions in MMDs of n-alkanes to lower molecular weights with an increase in age and occurrence depth of oil-bearing deposits [4, 28].

It is significant that approximately 0.5 wt.% of high-molecular microbiologically stable n-alkanes are presented in the "biodegraded" Sakhalin oil, which contains only isoprenanes in its low-molecular non-waxed part.

3.2 Naphthenoarenes

Hybrid naphthenoaromatic HCs were investigated using crude oils of Western Siberia, Sakhalin and Serbia. Brief geological characteristics of the hydrocarbon accumulations under study are given in Table 2.

3.2.1 Naphthenomonoarenes

Analysis by mass spectrometry revealed the presence in crude oils of napthenobenzenes (benzocyclanes) of six homological series containing from one to six naphthenic cycles in molecules in amounts decreasing with the increase in the number of rings. The authors of [4, 29-35] reported the presence of individual compounds of these structural types in crude oils, shale oils and dispersed organic matter (OM) of rocks.

The mass-spectral data show that naphthenomonoarenes contain up to 24 carbon atoms in alkyl frames of polycyclic nuclei compounds. Note that compounds containing 1-3 C-atoms in alkyl groups dominate in each homological series. Characteristics of naphthenobenzenes in crude oils of different genetic nature are shown in Figure 3.

It is clear that naphthenobenzenes with one or two saturated cycles in molecules prevail in crude oils of marine and mixed types. Concentrations of investigated HCs from

TABLE 1
Brief geologic and geochemical characteristics of studied crude oils

Oil field	Perforation interval (m)	Age of sediments	Content (wt.%), of		C_{max}*
			waxes	n-alkanes	
1	2	3	4	5	6
Sakhalin					
East Ekhabi	210-228	Cenozoic, myocene, N_1	2.2	0.01	71
Ekhabi	491-538	Cenozoic, myocene, N_1	7.4	0.92	53
East Ekhabi	683-906	Cenozoic, myocene, N_1	1.4	0.06	52
Paromay	936-977	Cenozoic, myocene, N_1	1.1	0.02	45
Kolendo	1484-1495	Cenozoic, myocene, N_1	0.5	traces	51
Lower Dagi	2835-2847	Cenozoic, myocene, N_1	10.6	1.53	35
Western Siberia					
Van-Eganskoe	976-978	Upper Cretaceous, Cr_2	11.3	0.00	70
Nivagalskoe	1840-1847	Lower Cretaceous, Cr_1	1.2	0.08	50
Tagrinskoe	2182-2187	Lower Cretaceous, Cr_1	7.9	0.92	35
Pravdinskoe	2322-2326	Lower Cretaceous, Cr_1	8.1	3.78	54
Yershovoe	2435-2445	Lower Cretaceous, Cr_1	2.8	0.29	48
Severnoe	2134-2144	Upper Jurassic, J_3	1.7	0.19	61
Gorstovoe	2208-2312	Upper Jurassic, J_3	47.4	10.27	35
Yershovoe	2536-2541	Upper Jurassic, J_3	2.0	0.17	50
Nivagalskoe	2728-2736	Upper Jurassic, J_3	0.2	0.01	65
Vakhskoe	2452-2462	Middle Jurassic, J_2	10.4	1.20	53
Western Ostaninskoe	2800-2814	Middle Jurassic, J_2	2.9	0.35	46
Gerasimovskoe	2820-2842	Middle Jurassic, J_2	18.8	2.10	51
East. Gerasimovskoe	2836-2844	Middle Jurassic, J_2	7.5	0.71	61
Shirotnoe-1	3033-3052	Lower Jurassic, J_1	9.9	1.00	58
Shirotnoe-2	3060-3067	Lower Jurassic, J_1	16.8	1.59	49
Tolparovskoe	3216-3227	Lower Jurassic, J_1	9.1	1.74	35
Prikoltogorskoe	3280-3292	Lower Jurassic, J_1	22.9	6.17	55
Kalinovoe	2314-2372	Paleozoic	10.6	5.54	54
Stupenchatoe	2900-2912	Paleozoic	20.6	2.96	39
Northern Kalinovoe	3031-3044	Paleozoic	26.5	2.27	57
Urmanskoe	3086-3089	Paleozoic	14.3	6.29	52
Southern Urmanskoe	3154-3203	Paleozoic	14.6	2.42	50
Volga-Ural province					
Allagulovskoe	1133-1145	Carbonaceous, C_2	7.2	1.72	48
Allagulovskoe	1138-1150	Carbonaceous, C_2	9.2	3.28	49
Allagulovskoe	1140-1158	Carbonaceous, C_2	3.7	1.53	53
Mordovoozerskoe	1141-1151	Carbonaceous, C_2	10.5	4.39	50
Mordovoozerskoe	1155-1188	Carbonaceous, C_2	7.5	2.84	50

Oil field	Perforation interval (m)	Age of sediments	Content (wt.%), of		C_{max}*
			waxes	n-alkanes	
Continuation of Table 1					
1	2	3	4	5	6
Chernushkinskoe	1488-1501	Carbonaceous, C_1	3.5	0.17	46
Novobesovskoe	1671-1680	Carbonaceous, C_1	15.6	4.12	49
Novolabitovskoe	1938-1992	Upper Devonian, D_3	15.1	4.45	50
Novolabitovskoe	1981-1992	Upper Devonian, D_3	4.7	2.18	51
Timan-Pechora province					
Yaregskoe	150-200	Upper Devonian, D_3	4.1		
Upper Omrinskoe	942	Upper Devonian, D_3	10.8		
Lower Omrinskoe	950	Upper Devonian, D_3	14.1	4.30	51
Lys'venskoe	1077-1187	Upper Devonian, D_3	16.2		
Western Tebukskoe	1365	Upper Devonian, D_3	4.8	1.41	50
Usinskoe	3080-3144	Upper Devonian, D_3	5.2		
Northern Caucasia					
Starogroznenskoe	4469	Cenosoic, N_1	18.0		
Northeastern China					
Southern Sun'Yan	420-430	Cenosoic, N_1	34.3	0.00	
Fularty	480	Cenosoic, N_1	40.6	0.00	
Pannonian basin (Serbia)					
Velebit, well 1	749-751	Cenosoic, N_1	8.6		
Velebit, well 8	758-763	Cenosoic, N_1	8.1		
Velebit, well 19	783-785	Cenosoic, N_1	3.5		

* a number of carbon atoms in the "highest member" of n-alkane homologous series.

benzomono- to benzotetracyclanes are very similar in continental oils.

The authors of [5, 36-37] report a certain relation between crude oils rich in benzopolycyclanes and OM of humus or mixed humus-sapropelic types. This suggests that a higher content of polynaphthenes in crude oils of continental type results from the significant contribution of humus components of the initial organic matter to the composition of these HCs.

Significantly larger amounts of benzomono- and benzobicyclanes in the other oils are due to the higher contribution of sapropelic OM. It was shown in [38] that under elevated temperatures and pressures OM of this type produces monoarenes that are most likely alkyl- or naphtheno-substituted ones.

3.2.2 Naphthenobiarenes

According to mass-spectrometry data, naphthenobiarenes (naphtobicyclanes) are present in crude oils in compounds containing up to 6 saturated cycles and up to 20 C-atoms in alkyl frames of nuclei. The content of naphthenobiarenes in sufficiently deeply buried oils decreases fast with an increase in the number of rings in molecules.

Distributions of naphthenobiarenes in oils of different genesis are quite unusual too. Naphthomonocyclanes predominate in continental oils. Concentrations of naphthotetracyclanes are also higher in oils formed from OM of marine type *(Fig. 4)*. Naphthomono- and naphthotetracyclanes were also found in higher amounts in oils of mixed, humus-sapropelic genesis.

The authors of [39] reported comparatively large contents of mono- and dinaphthenoaromatic compounds in crude oils

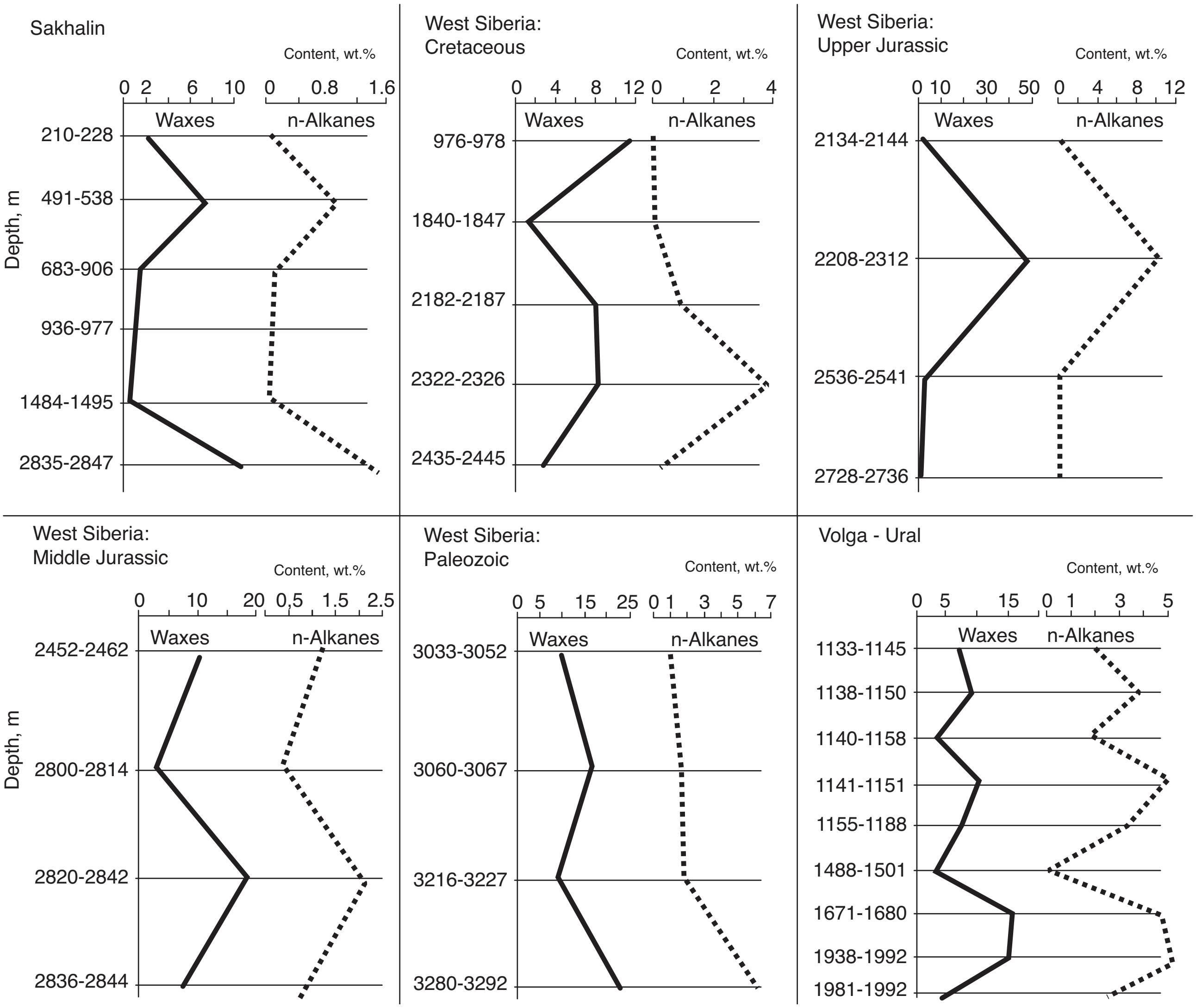

Figure 1

Content of waxes and low-molecular n-alkanes in crude oils from different provinces.

generated in lagoon carbonate rocks, as well as in young, immature crude oils.

According to [4, 40], benzo- and naphthocyclanes are intermediates in the transformation of initial polycyclanes into more dehydroaromatized compounds. Significant discrepancies in concentrations and distributions of these HCs in the different crude oils mentioned above are due to different degrees of their catagenetic conversion. Using Serbian crude oils as an example, we found that these discrepancies virtually disappear in the case of naphthenotriarenes, and their distributions are very similar in oils from different fields *(Fig. 5)*.

It is obvious that the data on complex hybrid compounds containing saturated and aromatic cycles could also be a source of information about the origin of natural hydrocarbon accumulations.

3.3 High-molecular hetero-atomic compounds

Having processed the analytical data on ≈ 1300 crude oils described in the literature and investigated by our group, we found that the average content of high-molecular hetero-atomic compounds (HMHC) in crude oils decreases

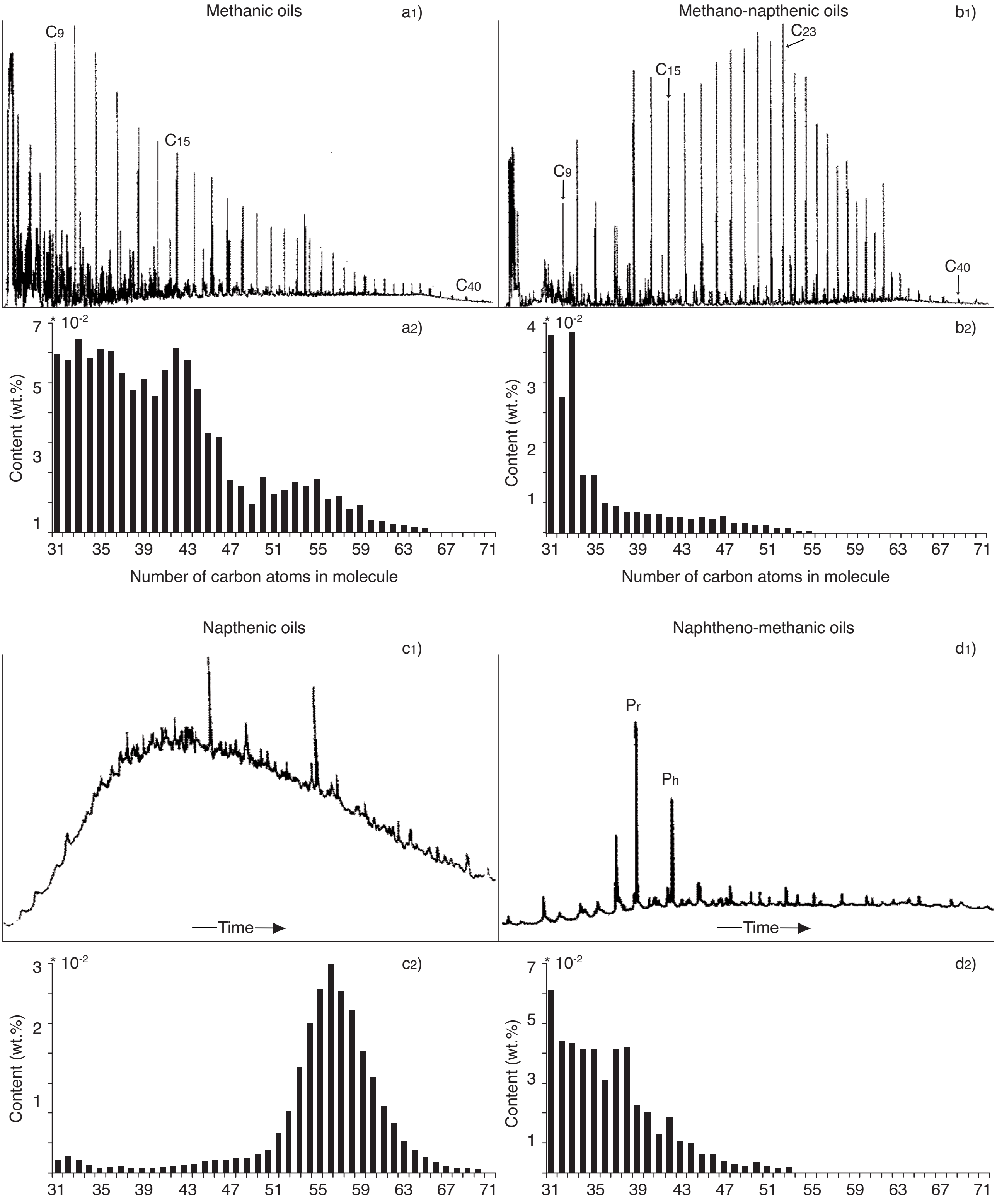

Figure 2

Typical chromatograms (a_1, b_1, c_1, d_1) and MMDs of higher n-alkanes (a_2, b_2, c_2, d_2) in different crude oils.

TABLE 2

Conditions of occurrence of investigated crude oils

Oil-field	Well number	Perforation interval (m)	Age of sediments
Western Siberia			
Nivagalskoe	P-105	1840-1847	Lower Cretaceous, Cr_1
Tagrinskoe	P-72	2182-2187	Lower Cretaceous, Cr_1
Yershovoe	P-138	2435-2445	Lower Cretaceous, Cr_1
Severnoe	424	2134-2144	Upper Jurassic, J_3
Yershovoe	P-184	2536-2541	Upper Jurassic, J_3
Nivagalskoe	P-124	2728-2736	Upper Jurassic, J_3
Gerasimovskoe	14/3	2820-2842	Middle Jurassic, J_2
Tolparovskoe	1	3216-3227	Lower Jurassic, J_1
Stupenchatoe	5	2900-2912	Paleozoic
Northern Kalinovoe	25	3031-3044	Paleozoic
Southern Urmanskoe	1	3154-3203	Paleozoic
Sakhalin			
Eastern Ekhabi	206	210-228	Cenozoic, myocene, N_1
Ekhabi	363	491-538	Cenozoic, myocene, N_1
Eastern Ekhabi	303	683-906	Cenozoic, myocene, N_1
Paromai	82	936-977	Cenozoic, myocene, N_1
Kolendo	157	1484-1495	Cenozoic, myocene, N_1
Lower Dagi	75	2835-2847	Cenozoic, myocene, N_1
Pannonian basin (Serbia)			
Sirakovo	19	1429-1436	Cenozoic, myocene, N_1
Sirakovo	20	1440-1444	Cenozoic, myocene, N_1
Sirakovo	18	1544-1548	Cenozoic, myocene, N_1
Sirakovo	2	1701-1704	Cenozoic, myocene, N_1
Sirakovo	1	1778-1782	Cenozoic, myocene, N_1
Bradarats-Malyurevats	10	1804-1808	Cenozoic, myocene, N_1
Bradarats-Malyurevats	5	1985-1989	Cenozoic, myocene, N_1
Bradarats-Malyurevats	4	2156-2170	Cenozoic, myocene, N_1

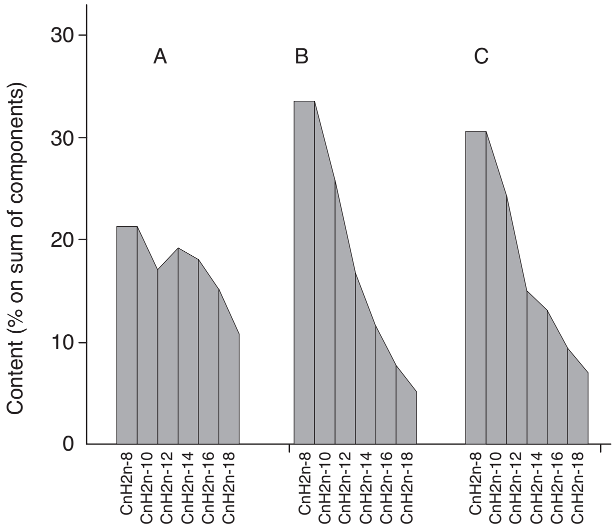

Figure 3

Distribution of naphthenomonoarenes in crude oils of different genesis. A: continental, B: marine, C: mixed type.

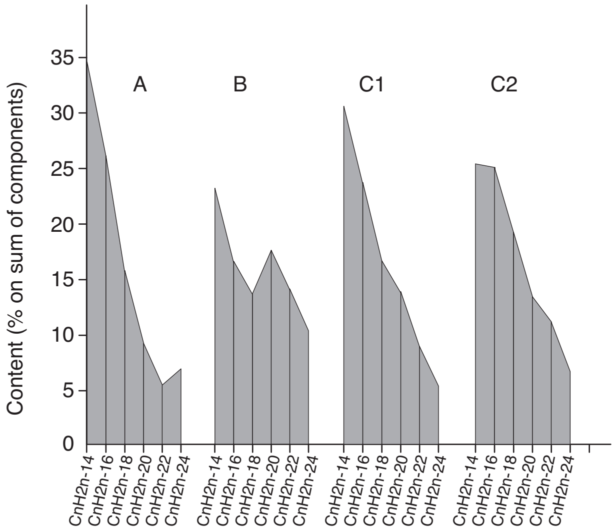

Figure 4

Distributions of naphthobicyclanes in crude oils of different genesis. A: Continental type; B: marine type; C_1: mixed type (Western Siberia); C_2: mixed type (Sakhalin).

TABLE 3

Average content of HMHC in crude oils as a function of geological and geochemical characteristics of oil-bearing deposits

Age of oil-bearing sediments	Depth of occurrence (m)	Content (wt.%)			Resin-to-asphaltene ratio
		Resins	Asphaltenes	Total HMHC	
Cenozoic	0-1000	10.1	0.96	11.1	12.0
	1000-2000	9.7	0.94	10.6	10.3
	2000-3000	8.9	1.17	10.1	7.6
	3000-4000	8.7	1.30	10.0	6.7
Mesozoic	0-1000	14.7	1.96	16.8	7.3
	1000-2000	9.6	1.24	10.8	7.7
	2000-3000	6.3	0.77	7.1	8.2
	3000-4000	4.6	0.54	5.1	8.5
Paleozoic, terrigenous sediments, except Cambrian	0-1000	29.4	3.68	33.1	8.2
	1000-2000	15.7	2.88	18.6	5.5
	2000-2500	9.6	1.89	11.5	5.1
	2500-3000	8.1	1.32	9.4	6.1
	3000-3500	6.1	0.86	7.0	7.1
	3500-4000	4.8	0.63	5.4	7.6
	> 4000	4.2	0.47	4.7	8.9
Paleozoic, carbonate sediments, except Cambrian	0-1000	16.7	6.94	23.6	2.4
	1000-1500	14.9	5.02	19.1	3.0
	1500-2000	10.7	2.63	13.3	4.1
	2000-2500	8.8	1.79	10.5	4.9
	2500-3000	8.0	1.20	9.2	6.7
Cambrian	1500-2000	4.5	0.73	5.2	6.2
	2000-2500	3.3	0.19	3.5	17.4
	> 2500	0.4	traces	0.4	_

with the burial depth, this happening especially abruptly in more ancient Paleozoic horizons *(Table 3)*.

The fraction of resins in Cenosoic (predominantly in Neogenic) oils decreases with the burial depth, while that of asphaltenes increases, which results in lower resin-to-asphaltene ratios in more deeply occurring beds. In oils from Mesozoic and Paleozoic deposits, the concentrations of both resins and asphaltenes decrease with the depth in such a way that the resin-to-asphaltene ratios increase.

The relation of the total HMHC concentrations in crude oils to the depth of deposition, *i.e.*, to thermobaric conditions, is most evidently observed in oils from Paleozoic deposits, at small depths bearing the most highly resinous oils containing maximum amounts of asphaltenes. On average, the lowest concentrations of HMHC and the highest values of the resin-to-asphaltene ratios were observed in the most ancient Cambrian oils.

In general, these results are consistent with those reported by the authors of [41] on transformations of oil components in the subsurface reserves and, in addition to that, show that the scales of asphaltenes formed in the early stages of catagenesis could exceed the concurrent losses in the amounts of resins. In the course of degradation of resins, which becomes faster with the depth, the contribution from the products of their transformation into asphaltenes becomes smaller, and under sufficiently severe thermobaric conditions it no longer compensates for the asphaltene losses due to their thermal destruction and carbonization. That is one of the principal reasons of a decrease in asphaltene concentrations in extensively metamorphized Cambrian oils.

TABLE 4

Average characteristics of investigated Cenozoic oils

Age of sediments, range of depths of occurrence (H), m	H_{av} (m)	Content (wt.%)				f_a*	f_p / f_n**
		Paraffin	Sulfur	Resins	Asphaltenes		
Pliocene, N_2, 200-950 m (5)	567	0.1	0.21	9.1	0.1	20.4	0.65
Pliocene, N_2 (1)	2850	13.6	0.32	9.4	0.2	23.0	1.32
Pliocene, N_2, 3680-3850 m (2)	3762	4.5	0.31	8.6	0.5	22.8	1.12
Miocene, N_1, 290-820 m (5)	537	0.1	0.21	12.3	0.9	15.4	0.67
Miocene, N_1, 1210-1440 m (3)	1310	0.0	0.24	7.9	0.4	17.7	0.45
Miocene, N_1, 1430-1550 m (3)	1473	3.0	0.15	4.4	0.3	6.0	1.93
Miocene, N_1, 1700-1810 m (3)	1763	2.0	0.10	6.5	0.7	10.7	2.15
Miocene, N_1, 1990-2305 m (5)	2093	0.1	0.26	7.1	0.3	10.1	1.95
Miocene, N_1 (1)	2305	0.0	0.10	2.6	0.0	8.0	2.58
Miocene, N_1 (1)	3150	4.3	0.15	5.1	1.1	23.2	1.18
Miocene, N_1 (1)	4469	6.3	0.00	1.6	0.0	2.6	1.72
Paleogene (carbonates) (1)	1200	0.0	6.39	32.8	2.0	16.7	0.63
Paleogene (carbonates) (1)	4030	8.0	0.61	6.2	7.1	22.7	1.10
Paleogene (granitoids) (1)	4364	17.7	0.04	4.1	1.8	7.6	1.42

* f_a: Fraction of carbon atoms in aromatic fragments of molecules.

** f_p: Fraction of carbon atoms in paraffin fragments of molecules; f_n: Fraction of carbon atoms in naphthenic fragments of molecules.

Today, advanced analytical tools permit us to describe structural features of high-boiling and residual petroleum components using a wide set of parameters calculated on the basis of radiospectroscopic analysis and information on the average molecular weights and the functional compositions of the substances under study.

Using the method of an integral structural analysis (ISA) developed at the Institute of Petroleum Chemistry SB RAS [14], we have established the values of the average structural parameters of nearly 180 samples of oils and natural bitumens from different oil-producing provinces of Eurasia (Serbia, Northern Caucasia, Transcuacasia, Volga-Ural province, Western Siberia, Kazakhstan, Turkmenia, Sakhalin, Mongolia, China and Vietnam). The data set contains information on the oils from Fanerozoic bearing rocks of different lithological compositions occurring in a wide range of depths from several (Kazakhstanian natural bitumens) up to 4400 meters *(Tables 4-7)*. The number of the investigated samples is given in parentheses in all of these tables. The designations of parameters in these Tables are the same as in [14], and the most significant ones will be explained below.

Out of a large number of calculated parameters only the fractions of C-atoms in aromatic structures (aromaticity) f_a and proportions of C-atoms in paraffin (f_p) and

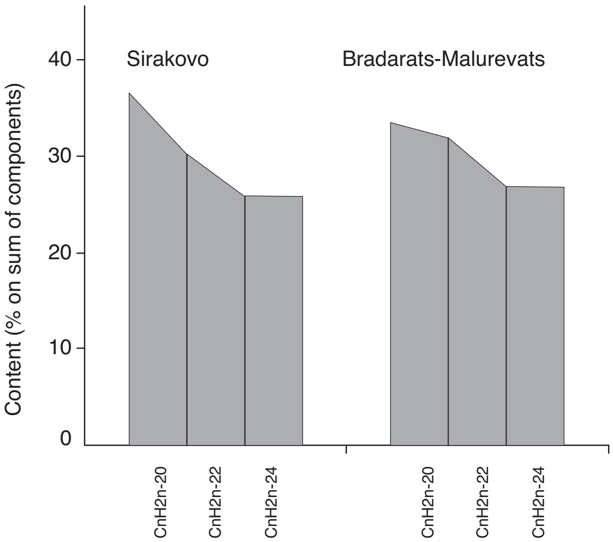

Figure 5

Distributions of naphthotricyclanes in Serbian crude oils.

TABLE 5

Average characteristics of West-Siberian oils

Age of sediments, range of depths of occurrence (H), m	H_{av} (m)	Content (wt.%)				f_a	f_p / f_n
		Paraffin	Sulfur	Resins	Asphaltenes		
Senomanian, Cr_2 (6)	905	0.0	0.76	10.4	1.1	21.4	0.65
Albian, Cr_1 (3)	1396	1.0	0.40	6.9	1.1	20.3	0.93
Aptian, Cr_1 (3)	1697	4.4	1.04	7.6	0.5	21.6	1.71
Barremian, Cr_1, 1660-1830 m (12)	1762	3.7	1.08	7.2	0.6	18.5	1.82
Barremian, Cr_1, 1920-2050 m (3)	1984	2.8	0.75	6.0	0.4	15.5	1.86
Hoterivian, Cr_1, 1750-1860 m (2)	1809	3.6	1.10	6.7	0.9	15.2	1.01
Barremian, Cr_1, 1960-2040 m (6)	1998	4.8	0.74	4.0	0.3	15.2	1.87
Barremian, Cr_1, 2180-2500 m (3)	2312	4.0	0.90	7.4	0.5	14.1	1.75
Valanginian, Cr_1, 1770-1910 m (3)	1827	0.1	0.78	7.7	1.3	21.5	1.62
Valanginian, Cr_1, 2008-2200 m (10)	2130	2.1	0.72	6.3	0.6	16.5	1.75
Valanginian, Cr_1, 2300-2600 m (5)	2394	2.0	0.77	8.4	0.7	20.8	1.80
Berriasian, Cr_1, (1)	2685	4.2	1.88	7.1	0.61	22.6	1.80
Upper Jurassic, J_3^0, 2770-2920 m (6)	2800	4.2	1.29	7.6	0.78	17.7	2.11
Upper Jurassic, J_3^1, 2200-2440, (4)	2350	3.2	0.82	6.6	0.62	15.9	1.68
Upper Jurassic, J_3^1, 2500-2670, (8)	2605	3.6	0.90	5.8	0.39	15.8	1.84
Middle Jurassic, J_2^v, 2000-2500 m (2)	2256	4.4	0.83	5.5	0.71	15.2	1.05
Middle Jurassic, J_2^v, 2700-2920 m (15)	2817	4.4	0.88	5.4	0.41	14.3	0.67
Middle Jurassic, J_2^m, 2200-2370 m (2)	2286	—	0.02	—	—	8.9	5.66
Middle Jurassic, J_2^m, 2460-2540 m (4)	2501	—	0.89	11.1	7.1	14.5	2.45
Middle Jurassic, J_2^m, 2680-2740 m (6)	2705	—	1.15	11.2	6.6	11.7	1.65
Middle Jurassic, J_2^m, 2870-2950 m (2)	2912	—	1.01	10.7	4.1	11.0	1.30
Middle Jurassic, J_2^m, (1)	3735	—	0.11	—	0.0	13.3	6.74
Paleozoic, M, 2800-2900 m (2)	2850	13.8	0.74	6.2	0.54	13.7	2.40
Paleozoic, M, 3030-3150 m (2)	3082	13.5	0.89	4.6	0.40	18.2	3.05

naphthenic (f_n) structures are given in Tables 4-7, *i.e.*, the values necessary to determine hydrocarbon types of oils according to [42].

It is clear that the ISA results of the total oils, in fact, characterize all of their main hydrocarbon components (oily fractions).

The data obtained confirm the well-known increase in the paraffinic content of all of the oil components in each stratigraphic complex investigated in this work, which is manifested in an increase in the f_p / f_n values and, therefore, in transformation of oil from naphthenic ($f_p / f_n < 0.5$) or naphtheno-methanic type ($0.5 < f_p / f_n < 1.0$) into methano-naphthenic ($1.0 < f_p / f_n < 2.0$) or even methanic type $f_p / f_n > 2.0$).

The same ISA method was used when studying the chemical nature of oil HMHC. The results are generalized in Tables 8-13. Only West-Siberian oils, presented by an extensive number of samples, are treated as Mesozoic objects.

The data obtained indicate unambiguously that skeletons of molecular fragments (structural units) in oil HMHC by their structures are identical and completely cover all multiple types of hydrocarbons (HC) and hetero-atomic compounds (HAC) found in distillate oil fractions [4, 13].

According to the adsorption principle of their isolation, in addition to the above-mentioned single-block HAC molecules oil resins contain molecules built by two or possibly more structural units. The fraction of the poly-block molecules is comparatively small, as the average number of blocks (m_a) in resins is most frequently less than two and exceeds this value only in a few Paleozoic objects.

TABLE 6

Characteristics of studied Mesozoic crude oils and natural bitumens from other (except West Siberia) oil-producing provinces of Eurasia

Oil-field (province)	Age of Deposits	H_{av} (m)	Content (wt.%)				f_a	f_p / f_n
			Paraffin	Sulfur	Resins	Asphaltenes		
Kara-Murat (Kazakhstan)	Cr_2	<10	0.0	0.10	42.5	17.6	23.2	0.52
Mortuk (Kazakhstan)	Cr_1^{alb}	<7	0.0	0.28	31.8	3.2	22.3	0.53
Mortuk (Kazakhstan)	Cr_1^{nkm}	202	0.0	0.30	43.9	9.4	22.6	0.53
Mortuk (Kazakhstan)	Cr_1^{nkm}	282	0.0	0.29	39.1	9.0	18.4	0.52
Dongeleksor (Kazakhstan)	$Cr_1^{apt+nkm}$	<12	0.0	0.19	30.1	6.7	22.5	0.58
Kara-Arna (Kazakhstan)	Cr_1	1054	1.0	4.19	19.1	8.1	23.7	0.54
Karazhanbas (Kazakhstan)	J	288	1.5	2.15	23.8	4.1	17.0	0.59
Northern Buzachi (Kazakhstan)	J	328	1.6	1.78	20.0	2.8	18.8	0.65
Kalamkas (Kazakhstan)	J	852	3.2	2.17	12.0	3,0	20.1	0.68
Northern Sun'Uan (China)	Cr_1	1540	20.6	0.12	7.6	0.2	10.5	2.44
Zoonbaian (Mongolia)	Cr_1	1125	16.8	0.13	15.7	0.3	15.2	3.63
Tamsagbulag (Mongolia)	J_3	2450	17.8	0.20	5.3	1.0	12.6	1.29

TABLE 7

Average characteristics of studied Paleozoic crude oils from Volga-Ural province

Age of and occurring depth of oil-bearing deposits (H), m	H_{av} (m)	Content (wt.%)				f_a*	f_p / f_n**
		Paraffin	Sulfur	Resins	Asphaltenes		
Permian (1)	1132	9.0	0.34	3.2	0.3	37.5	0.55
Permian (1)	4296	1.2	0.30	5.8	0.99	22.0	2.30
Upper Carbonaceous, C_2^v (2)	1159	8.0	4.26	12.2	5.9	22.6	1.06
Upper Carbonaceous, C_2^b (3)	1144	6.3	4.04	9.4	4.3	23.2	1.43
Lower Carbonaceous, C_1^c (2)	1374	7.1	3.29	9.6	3.2	20.9	0.72
Lower Carbonaceous, C_1^c (1)	3115	6.8	3.59	11.9	2.3	17.7	1.00
Lower Carbonaceous, C_1^c (1)	1676	5.7	4.76	14.2	10.1	22.1	1.30
Lower Carbonaceous, C_1 (1)	3796	1.4	0.35	4.1	0.59	21.4	2.97
Upper Devonian D_3^{fr}, 940-1000 m (2)	970	8.4	0.97	9.5	0.7	9.6	1.20
Upper Devonian D_3^{fr}, (1)	1369	4.2	0.99	21.1	4.0	16.7	0.40
Upper Devonian D_3^{fr}, 1940-2010 m (4)	1975	8.8	4.88	12.5	5.8	20.6	1.30

The basic structural units of molecular blocks of all oil HMHC – both resins and asphaltenes – are polycyclic nuclei containing aromatic and/or naphthenic rings in such amounts that their total number in each block, K_o*, does not exceed five.

Structural units in resin molecules generally contain mainly condensed bi- and triarenic nuclei framed by alicyclic and aliphatic fragments developed in a different fashion, depending on the oil's nature, but the total number of C-atoms in a block rarely lies beyond the range of C* = 24-35. The number of C-atoms bonded directly to aromatic nuclei, C_α*, in most cases is more than four; indicating that aromatic and naphthenic cycles in structural units are, as a rule, condensed with each other.

The average number of C-atoms in paraffin fragments of resin molecules, C_p*, most often significantly exceeds the amount of terminal methyl groups in saturated molecular structures, $C\gamma$*; indicating a mainly linear or weakly branched character of the aliphatic chains.

TABLE 8

Average structural parameters of resins from Cenozoic petroleums

Age of deposits, average depth (m)	m_a	K_o*	K_a*	K_{sat}*	C*	Cp*	C_α*	C_γ*	σ_α
N_2, 365 (3)	1.70	5.98	2.28	3.70	32.4	7.3	4.8	3.0	0.62
N_2, 2850 (1)	2.07	6.10	2.65	3.45	35.5	9.6	4.5	3.9	0.55
N_2, 3762 (2)	1.48	4.78	2.05	2.73	30.6	10.6	3.9	2.7	0.54
N_2, on average, 1911 (6)	*1.69*	*5.60*	*2.26*	*3.34*	*32.3*	*8.8*	*4.5*	*3.1*	*0.58*
N_1, 538 (4)	1.84	4.95	2.86	2.09	36.0	18.4	5.2	4.1	0.47
N_1, 1220 (3)	1.48	4.75	2.70	2.05	31.1	9.8	4.5	3.0	0.48
N_1, 1474 (3)	1.88	5.24	2.48	2.76	32.0	10.0	4.3	2.3	0.54
N_1, 1806 (1)	1.59	5.03	2.14	2.89	30.2	8.9	3.6	3.1	0.50
N_1, 2088 (5)	1.88	6.06	2.59	3.47	32.2	9.8	4.2	3.0	0.47
N_1, 2582 (1)	1.44	5.85	1.87	3.98	28.9	10.8	4.8	2.7	0.69
N_1, 3150 (1)	1.73	4.33	2.38	1.95	29.5	11.7	3.1	4.2	0.40
N_1, 4469 (1)	1.58	4.58	2.13	2.45	25.5	6.06	3.95	1.89	0.54
N_1, on average, 1748 (19)	*1.75*	*5.26*	*2.55*	*2.71*	*32.0*	*11.5*	*4.4*	*3.1*	*0.50*
Pg, granitoids, 4364 (1)	1.30	4.92	2.75	2.17	38.9	18.5	3.8	5.5	0.72

m_a: number of structural units (blocks) in an average molecule; K_o*: total number of cycles; K_a*: number of aromatic cycles; K_{sat}*: number of saturated (naphthenic) cycles; C*: total number of C-atoms in an average molecule; Cp*: number of C-atoms in alkyl moieties of an average molecule; Ca*: number of C-atoms in α-position to aromatic nuclei and hetero-functional groups; C_γ*: number of C-atoms in CH_3-groups not connected with aromatic nuclei and hetero-functions; σ_a: substitution degree of peripheral C-atoms of aromatic nuclei.

TABLE 9

Average structural parameters of asphaltenes from Cenozoic oils

Age of deposits, average depth (m)	m_a	K_o*	K_a*	K_{sat}*	C*	Cp*	C_α*	C_γ*	σ_α
N_2, 365 (1)	2.21	5.57	2.71	2.86	30.8	7.8	5.3	2.3	0.62
N_2, 2850 (1)	2.04	6.79	2.71	4.08	29.8	2.8	3.8	2.8	0.44
N_2, 3762 (2)	2.10	3.96	2.62	1.34	28.8	11.2	5.0	2.3	0.60
N_2, on average, 1911 (4)	*2.11*	*5.07*	*2.66*	*2.41*	*29.6*	*8.2*	*4.8*	*2.4*	*0.56*
N_1, 293 (1)	2.11	5.92	2.71	3.21	27.7	4.7	4.8	2.2	0.56
N_1, 1225 (1)	3.18	7.72	2.76	4.96	26.9	1.4	4.2	1.4	0.49
N_1, 1980 (1)	3.03	6.96	3.61	3.35	30.4	1.6	3.7	1.6	0.36
N_1, 3150 (1)	3.36	3.68	3.55	0.13	29.4	13.9	4.5	1.7	0.45
N_1, on average, 1662 (4)	*2.92*	*6.07*	*3.16*	*2.91*	*28.6*	*5.4*	*4.3*	*1.7*	*0.46*
Pg, carbonates, 1200 (1)	2.31	9.21	2.87	6.34	49.7	14.2	3.1	5.5	0.41
Pg, carbonates, 4030 (1)	2.64	6.48	3.18	3.30	32.0	4.7	4.9	2.2	0.51
Pg, granitoids, 4364 (1)	2.10	4.25	2.64	1.61	36.8	18.8	3.2	4.0	0.49

Asphaltene molecules differ in their structure from those of resins only in a larger number of blocks in an "average" molecule" (generally up to 5), larger average dimensions of condensed polyarenic nuclei (on average, tri- and tetracyclic) that underlie their structural blocks, and smaller fractions of C-atoms in naphthenic fragments connected directly to aromatic cycles and, therefore, sterically preventing the latter from tightening into macro-particle "batches".

The literature reports cases of oil resin and asphaltene samples containing an extraordinarily large number of naphthenic cycles in an average structural block, K_{sat}*, ≥ 5. We

TABLE 10

Average structural parameters of resins from West-Siberian crude oils

Age of deposits, average depth (m)	m_a	K_o*	K_a*	K_{sat}*	C*	Cp*	C_α*	C_γ*	σ_α
Senomanian, Cr_2, 905 (6)	1.85	4.56	2.40	2.16	30.5	11.3	4.4	2.4	0.56
Albian, Cr_1, 1396 (3)	1.87	4.89	2.61	2.28	28.9	8.1	4.5	2.2	0.55
Aptian, Cr_1, 1697 (3)	1.68	3.62	2.30	1.32	27.0	11.8	3.5	2.4	0.47
Barremian, Cr_1, 1762 (12)	1.56	3.80	2.13	1.67	26.5	10.6	3.7	2.0	0.51
Barremian, Cr_1, 1984 (2)	1.75	4.15	2.38	1.77	25.6	8.7	3.6	2.0	0.47
Barremian, Cr_1, 1794 (14)	1.59	3.85	2.17	1.68	26.4	10.3	3.7	2.0	0.50
Hoterivian, Cr_1, 1809 (2)	1.65	4.08	2.52	1.56	30.4	13.7	3.4	2.2	0.42
Hoterivian, Cr_1, 1998 (6)	1.56	4.35	2.18	2.17	25.4	7.0	4.0	1.7	0.51
Hoterivian, Cr_1, 2497 (1)	1.49	3.38	1.99	1.39	30.3	15.8	3.8	2.1	0.55
Hoterivian, Cr_1, 2011 (9)	1.57	4.18	2.23	1.95	27.1	8.4	3.8	1.9	0.49
Valanginian, Cr_1, 2130 (9)	1.70	4.20	2.32	1.88	25.7	8.3	3.7	2.1	0.49
Valanginian, Cr_1, 2421 (3)	1.60	3.22	2.09	1.13	26.4	12.7	3.5	2.5	0.48
Valanginian, Cr_1, 2203 (12)	1.68	3.96	2.26	1.70	25.9	9.4	3.7	2.2	0.49
Berriasian, Cr_1, 2685 (1)	1.77	5.13	2.44	2.69	30.4	8.9	4.0	3.1	0.49
Lower Cretaceous, Cr_1, 1943 (42)	1.64	4.04	2.26	1.78	26.7	9.6	3.8	2.1	0.50
Upper Jurassic, J_3^0, 2800 (5)	1.65	2.88	2.02	0.86	24.4	9.8	3.4	2.1	0.53
Upper Jurassic, J_3^1, 2350 (4)	1.68	4.26	2.33	1.83	28.5	11.0	3.4	2.6	0.46
Upper Jurassic, J_3^1, 2605 (8)	1.71	3.83	2.36	1.47	29.5	13.5	4.8	2.1	0.60
Upper Jurassic, J_3^1, 2520 (17)	1.68	3.65	2.20	1.45	27.8	11.8	4.1	2.2	0.55
Middle Jurassic, J_2^v, 2256 (2)	1.89	4.22	2.43	1.79	27.8	9.8	4.3	2.3	0.55
Middle Jurassic, J_2^v, 2817 (14)	1.92	4.22	2.50	1.72	30.1	12.3	4.3	3.4	0.53
Middle Jurassic, J_2^v, 2747 (16)	1.91	4.22	2.49	1.73	29.8	12.0	4.3	3.3	0.53
Middle Jurassic, J_2^m, 2501 (2)	1.95	6.34	2.50	3.84	34.0	7.2	5.0	3.0	0.62
Middle Jurassic, J_2^m, 2685 (8)	1.92	5.32	2.45	2.87	33.2	10.7	5.0	3.3	0.63
Middle Jurassic, J_2^m, 2706 (5)	1.95	5.00	2.46	2.54	33.8	12.6	5.0	3.5	0.63
Middle Jurassic, J_2^m, 2950 (1)	1.73	4.92	2.28	2.64	29.0	8.1	5.0	2.8	0.65
Middle Jurassic, J_2, 2726 (24)	1.91	4.59	2.48	2.11	30.9	11.6	4.5	3.3	0.56
Paleozoic, M, 2850 (2)	1.68	4.87	2.18	2.69	30.5	10.0	4.0	2.5	0.58
Paleozoic, M, 3082 (2)	1.80	4.39	2.35	2.04	29.5	10.8	4.3	2.9	0.55
Paleozoic, M, 2966 (4)	1.74	4.63	2.26	2.37	30.0	10.4	4.2	2.7	0.56

believe that these substances contain large (tetra- and/or isolated pentacyclic) saturated blocks with no aromatic nucleus [14, 43]. This hypothesis was confirmed when analyzing low-temperature thermal destruction products of asphaltenes from different crude oils [44].

Summarizing the results of structural-group analyses of oil HMHC, we found that the character of their interrelations with the composition of hydrocarbon (oily) components of the same oils sharply changes, depending on the age of oil-bearing or, strictly speaking, oil-forming rocks.

The average structural parameters of HMHC from geologically the youngest, most immature Cenozoic oils change with the age and depth of occurrence of oil-bearing horizons symbatically with respect to the changes in their structural-group composition, *i.e.*, they are also subjected to an increase in the paraffinic content of all of the oil components with depth. In particular, on average, the maximal number of naphthenetic cycles, K_{sat}*, = 3.34 (up to 3.70 in some cases) and the minimum number of paraffinic carbon atoms, C_p*, = 8.8 are typical for the resin oil components in shallow Pliocene reservoirs, which in their hydrocarbon composition are sharply naphthenetic. Note that the values of K_{sat}* values decrease to 2.7 in resins of mainly naphthenomethanic Miocene oils and to 2.2 for resins of methanic oils occurring in Paleogene rocks as the depth of occurrence is increased; while the values of C_p* are simultaneously increased in the same direction up to 11.5 and 18.5, respectively *(Table 8)*.

Different, exactly opposite behavior is characteristic of HMHC present in crude oils from more ancient Mesozoic and Paleozoic horizons. For instance, structural units of resin molecules from naphthenic, non-paraffin Senomanian West-Siberian oils contain, on average, 2.16 saturated cycles and

TABLE 11

Average structural parameters of asphaltenes from West-Siberian crude oils

Age of deposits, average depth (m)	m_a	K_o*	K_a*	K_{sat}*	C*	Cp*	C_α*	C_γ*	σ_α
Senomanian, Cr_2, 905 (6)	3.08	6.49	3.13	3.36	29.8	2.7	4.5	2.1	0.50
Albian, Cr_1, *1600 (2)*	*3.25*	*6.38*	*3.40*	*2.98*	*34.9*	*8.0*	*5.0*	*2.8*	*0.49*
Aptian, Cr_1, *1697 (3)*	*3.16*	*6.11*	*3.54*	*2.58*	*31.2*	*6.0*	*4.4*	*2.3*	*0.44*
Barremian, Cr_1, 1762 (12)	3.41	6.22	3.40	2.82	31.8	6.0	4.6	2.3	0.49
Barremian, Cr_1, 1984 (2)	3.70	6.70	3.69	3.01	32.6	5.0	4.6	2.1	0.49
Barremian, Cr_1, 1794 (14)	3.45	6.29	3.44	2.85	31.9	5.9	4.6	2.3	0.49
Hoterivian, Cr_1, 1809 (2)	3.68	6.44	3.72	2.72	32.3	5.7	4.1	2.1	0.40
Hoterivian, Cr_1, 1990 (3)	4.04	6.47	3.74	2.73	32.6	6.4	5.1	2.6	0.51
Hoterivian, Cr_1, 2497 (1)	2.84	5.99	3.33	2.66	32.0	7.8	4.9	2.1	0.53
Hoterivian, Cr_1, *2014 (6)*	*3.72*	*6.38*	*3.67*	*2.71*	*32.4*	*6.4*	*4.7*	*2.4*	*0.48*
Valanginian, Cr_1, 2130 (9)	3.11	6.24	3.39	2.85	31.3	5.4	4.4	2.0	0.45
Valanginian, Cr_1, 2421 (3)	3.12	5.89	3.47	2.42	30.1	5.8	4.6	2.1	0.47
Valanginian, Cr_1, cp., 2203 (12)	3.11	6.15	3.41	2.74	31.0	5.5	4.5	2.0	0.46
Berriasian, 2685 (1)	3.32	6.48	3.55	2.93	31.7	4.6	4.9	2.0	0.46
Lower Cretaceous, 1963 (38)	3.27	6.26	3.37	2.89	31.8	5.9	4.6	2.2	0.47
Upper Jurassic, J_3^0, 2769 (3)	2.38	4.81	2.98	1.83	27.5	8.0	4.9	1.9	0.54
Upper Jurassic, J_3^1, 2350 (4)	3.29	6.38	3.54	2.84	31.6	5.3	4.5	2.2	0.44
Upper Jurassic, J_3^1, 2605 (8)	3.37	5.57	3.44	2.13	31.1	8.2	4.8	2.1	0.50
Upper Jurassic, J_3, 2570 (15)	3.15	5.63	3.37	2.26	30.5	7.4	4.7	2.1	0.49
Middle Jurassic, J_2^v, 2256 (2)	3.14	6.48	3.42	3.06	31.5	5.7	4.8	2.5	0.48
Middle Jurassic, J_2^v, 2796 (11)	2.97	6.05	3.25	2.80	34.2	8.1	4.9	3.5	0.52
Middle Jurassic, J_2^v, 2713 (13)	3.00	6.14	3.33	2.81	33.8	7.7	4.9	3.3	0.51
Middle Jurassic, J_2^m, 2501 (2)	2.73	9.61	3.06	6.55	36.3	3.5	5.2	3.5	0.56
Middle Jurassic, J_2^m, 2706 (4)	3.10	9.53	3.24	6.29	37.8	3.9	5.2	3.9	0.56
Middle Jurassic, J_2^m, 2950 (1)	2.99	10.35	3.22	7.13	37.2	3.7	5.2	3.7	0.55
Middle Jurassic, J_2^m, 2685 (7)	2.98	9.67	3.19	6.60	37.3	3.8	5.2	3.8	0.56
Middle Jurassic, J_2, 2703 (20)	2.99	7.38	3.28	4.10	35.0	6.3	5.0	3.5	0.53
Paleozoic, M, 2901 (1)	3.43	6.64	3.28	3.36	33.8	6.8	5.1	2.7	0.53
Paleozoic, M, 3082 (2)	2.48	5.88	3.20	2.68	31.7	7.0	4.6	2.5	0.50
Paleozoic, M, 2966 (3)	2.96	6.26	3.24	3.02	32.8	6.9	4.8	2.6	0.52

TABLE 12

Structural parameters of resins from Paleozoic crude oils

Age of deposits, average depth (m)	m_a	K_o*	K_a*	K_{sat}*	C*	Cp*	C_α*	C_γ*	σ_α
P, 1132 (1)*	1.89	3.70	2.70	1.00	22.9	7.9	3.1	1.8	0.40
P, 4296 (1)	1.64	3.24	2.46	0.78	25.5	14.3	2.0	2.9	0.23
C_2^v, 1159 (2)	2.05	4.75	2.60	2.15	29.8	10.6	5.0	2.5	0.68
C_2^b, 1144 (3)	2.07	3.79	2.62	1.17	28.6	13.4	5.3	2.2	0.70
C_2, 1150 (5)	2.06	4.17	2.61	1.56	29.1	12.3	5.2	2.3	0.69
C_1^c, 1374 (2)	1.67	4.41	2.25	2.16	28.9	10.2	3.9	2.9	0.55
C_1^c, 3115 (1)	1.67	4.35	2.26	2.09	27.9	9.5	4.0	2.7	0.56
C_1^b, 1676 (1)	2.13	3.99	2.77	1.22	34.0	18.1	3.6	4.0	0.47
C_1, 3796 (1)	1.77	2.68	2.68	0.00	27.5	15.8	1.7	3.1	0.19
D_3^{fr}, 970 (2)	1.95	4.65	2.48	2.17	29.7	10.2	5.3	2.0	0.67
D_3^{fr}, 1369 (1)	2.15	1.39	1.04	0.35	25.8	17.4	5.5	2.1	0.62
D_3^{fr}, 1975 (3)	1.84	3.27	2.43	0.84	29.3	16.4	4.5	3.1	0.64
D_3^{fr}, 1539 (6)	1.93	3.42	2.22	1.20	28.9	14.5	4.9	2.6	0.65
Pz, M, 2850 (2)	1.68	4.87	2.18	2.69	30.5	10.0	4.0	2.5	0.58
Pz, M, 3082 (2)	1.80	4.39	2.35	2.04	29.5	10.8	4.3	2.9	0.55
Pz, M, 2966 (4)	1.74	4.63	2.26	2.37	30.0	10.4	4.2	2.7	0.56

* Crude oil of Lys'venskoye field.

11.3 carbon atoms in alkyl chains *(Table 7)*. Note that in methano-naphthenic Upper Jurassic objects these indices change to 1.45 and 11.8, respectively, reflecting the phenomena of an ordinary increase in the paraffinic content of all of the oil components, while in resins from still more deeply occurring, methanic in hydrocarbon composition Middle Jurassic, Lower Jurassic and Paleozoic oils the role of naphthenic structures is somewhat increased again (K_{sat}* values increase up to 2.37) and the average dimensions of paraffin chains decrease to C_p* = 10.4.

Similar antisymbatic changes in structural-group characteristics of hydrocarbons and resin-asphaltene components were clearly observed in Paleozoic oils of Volga-Ural and Kazakhstan provinces.

The reasons for these differences have not been revealed so far. They might have been caused by lithologic factors, namely, the occurrence of only terrigenous sediments in Cenozoic horizons described in this work (Serbia, Southern Caspian depression and Sakhalin) and by essential contributions from organic matter generated in carbonate rocks into the composition of hydrocarbon accumulations formed in deeply buried Mesozoic and Paleozoic deposits.

CONCLUSION

The data obtained in the investigations performed in this work point out obvious interrelations between the concentrations and compositions of petroleum high-molecular hydrocarbons and hetero-atomic compounds – resins and asphaltenes – and the conditions under which these natural organic systems were formed, as well as the degrees of their catagenetic transformations.

Hydrocarbons with long non-branched aliphatic chains in their molecules, namely: n-alkanes, their monomethyl-substituted isomers, alkylmonocyclanes and alkylbenzenes, form in crude oils wide homological series, whose length (upper bound) changes regularly depending on the age and depth of occurrence of the bearing rocks, *i.e.*, in fact, on the degree of catagenetic transformation of the system. The longest series of these HCs, reaching up to C_{max} = 70-72, are frequently observed in naphthenic and naphtheno-methanic oils from Cenozoic deposits occurring at depths as low as 1500-2000 m. In more ancient – Jurassic and Paleozoic – deposits, the upper bound of the same series falls to C_{max} = 35-40 with a simultaneous increase in the total content of these HCs in crude oil (increase in the paraffinic content of all of the oil components).

A regular decrease in concentrations of high-molecular hetero-organic compounds, especially those of resins, is

TABLE 13

Structural parameters of asphaltenes from Paleozoic crude oils

Age of deposits, average depth (m)	m_a	K_o*	K_a*	K_{sat}*	C*	Cp*	C_α*	C_γ*	σ_α
P, 1132 (1)*	2.12	4.52	3.08	1.44	21.5	3.2	3.4	1.0	0.40
P, 4296 (1)	2.12	5.47	3.19	2.28	26.3	4.2	2.5	2.4	0.25
C_2^v, 1159 (2)	3.10	6.81	3.25	3.56	32.2	5.5	5.7	2.3	0.71
C_2^B, 1144 (3)	2.91	8.30	3.13	5.17	31.6	2.3	5.9	2.0	0.74
C_2, cp., 1150 (5)	*2.99*	*7.70*	*3.18*	*4.52*	*31.8*	*3.6*	*5.8*	*2.1*	*0.73*
C_1^c, 1374 (2)	3.08	5.67	3.43	2.24	30.2	7.2	4.6	2.6	0.50
C_1^c, 3115 (1)	2.55	5.52	3.22	2.30	27.9	6.0	3.9	2.3	0.46
C_1^b, 1676 (1)	3.39	6.62	3.31	3.31	33.5	7.1	6.2	2.1	0.73
C_1, 3796 (1)	1.82	5.78	3.80	1.98	32.4	9.9	2.5	2.3	0.23
D_3^{fr}, 1975 (3)	3.14	5.80	3.36	2.44	32.1	8.1	5.4	2.4	0.63
Pz, M, 2850 (2)	3.43	6.64	3.28	3.36	33.8	6.8	5.1	2.7	0.53
Pz, M, 3082 (2)	2.48	5.88	3.20	2.68	31.7	7.0	4.6	2.5	0.50
Pz, M, 2966 (4)	*2.96*	*6.26*	*3.24*	*3.02*	*32.8*	*6.9*	*4.8*	*2.6*	*0.52*

* Crude oil of Lys'venskoye field.

observed in all stratigraphic complexes of deposits. Occasional disturbances of this pattern might have been caused by the presence of carbonate layers in the succession of sedimentary rocks.

Multi-block molecules of petroleum resins and asphaltenes are built of structural units (blocks), whose carbon skeletons and functional compositions are identical to HCs and hetero-atomic compounds occurring in distillate oil fractions, and cover all multiple types of these low-molecular oil components. The principal differences between resins and asphaltenes consist of a larger number of structural units (condensed aromatic nuclei) in asphaltene molecules, larger average dimensions of these nuclei (blocks), and a higher degree of their spatial batch organization.

The data presented clearly indicate that the crude oils were formed and evolved as united multi-component polydisperse systems, all components of which being allied structurally and genetically interrelated. Although this article has not been concerned with the area of geochemistry, correlation with thermal histories would certainly help to generalize the conclusions presented here.

REFERENCES

1 International Energy Outlook (2006) Energy International Administration of the DDE, Washington, DC.

2 Dorokhin V.P., Paliy A.O. (2004) Sostoaynye i perspektivy dobychy tayzelykh i bituminoznykh neftei i mire, *Neftepromyslovoye delo* (Rus.) **5**, 47-50.

3 Hsieh M., Philp R.P. (2001) Ubiquitous occurrence of high molecular weight hydrocarbons in crude oils, *Org. Geochem.* **32**, 8, 955-967.

4 Petrov Al.A. (1984) *Uglevodorody nefti* (*Petroleum hydrocarbons*), Nauka, Moscow.

5 Tissot B.P., Welte D.H. (1981) *Petroleum Formation & Occurence*, Mir, Moscow

6 Wakeman S.G., Schaffner C., Giger W. (1980) Polycyclic aromatic hydrocarbons in Recent lake sediments.-II. Compounds derived from biogenic precursors during early diagenesis, *Geochim. Cosmochim. Ac.* **44**, 415-429.

7 Rullkotter T., Peakman T.M., ten Haven H.L. (1994) Early diagenesis of terrigenous triterpenoids and its implications for petroleum geochemistry, *Org. Geochem.* **3**, 215-233.

8 Chaffee A.L., Johns R.B. (1983) Polycyclic aromatic hydrocarbons in Australian Coals.-I. Angulary fused pentacyclic tri and tetraaromatic components of Victorian brown coal, *Geochim. Cosmochim. Ac.* **47,** 2141-2155.

9 Moldowan J.M., Fago F.I. (1988) Structure and significance of novel rearranged monoaromatic steroid hydrocarbon in petroleum, *Geochim. Cosmochim. Ac.* **52**, 1145-1154.

10 Zubenko V.G., Gordadze G.N., Petrov Al.A. (1979) Vysokokipyatchshie aromaticheskie uglevodorody anastasjevskoy nefty, *Neftekhimiy*a (Rus.) **19**, 6, 833-838.

11 Ostroukhov S.B., Aref'ev O.A., Petrov Al.A. (1983) Heksacyclicheskie monoaromaticheskye uglevodorody nefty, *Neftekhimiya* (Rus.) **23**, 2, 152-159.

12 Bogomolov A.I., Temyanko M.B., Khotyntseva L.I. (1984) *Sovremennye metody issledovaniy*a *neftei* (*Modern methods of petroleum investigations*), Nedra, Leningrad.

13 Kamyanov V.F., Aksenov V.S., Titov V.I. (1983) *Geteroatomnye komponenty neftei* (*Heteroatomic petroleum components*), Nauka, Novosibirsk.

14 Kamyanov V.F., Filimonova T.A., Gorbunova L.V. *et al.* (1988) Neftyanye smoly i asfal'teny (Petroleum resins and asphaltenes), in *Khimicheskiy sostav neftei Zapadnoi Sibiri* (*Chemical composition of west-Siberian crude oils*), Nauka, Novosibirsk.

15 Yen T.F., Erdman J.G., Pollack S.S. (1961) Investigation of structure of petroleum asphaltenes by X-ray diffraction, *Anal. Chem.* **33**, 1587-1594.

16 Dickie J.P., Haller M.N., Yen T.F. (1969) *J. Colloid Interf. Sci.* **29**, 475.

17 Thanh N.X., Hsieh M., Philp R.P. (1999) Waxes and asphaltenes in crude oils, *Org. Geochem.* **30**, 2/3, 119-132.

18 Golovko Yu., Voronetskaya N.G., Pevneva G.S., Golovko A.K. (2006) Petroleum Napthenomono- and napthenobiarenes, *Petrol. Chem.* **46**, 2, 73-83.

19 Kamyanov V.F., Golovko A.K., Gorbunova L.V. (2007) Hydrocarbon composition of oils as basis of their chemical classification, *Neftekhimiya* (Rus.) **47**, 3, 3-13.

20 Houben-Weyl (1953) *Methoden der organischen chemie. B.II. Analytishe methoden*, Verlag Georg Tieme, Stuttgart, 1032 s.

21 Klimova V.A. (1975) *Osnovnye mikrometody analiza organicheskikh coedineniy* (*Principal micromethods of organic compounds' analysis*), Khimiya, Moscow, 207 s.

22 Rezvukhin A.I., Ogorodnikov V.D., Polethshuk O.H. *et al.* (1983) Contchentratsionnay i temperaturnaya zavisimosti spektrov PMR smolisto-asphaltovykh komponentov neftey, *Doklady AN SSSR* (Rus) **268**, 5, 1135-1138.

23 Philp R.P., Bishop A.N. (1995) Exploration and reservoir geochemistry: concepts, applications, and results, *Proceedings of First International Petroleum Conf.: Petrochem95, Technology Trends in Petrol. Industry*, 57-79.

24 Del Rio J.C., Philp R.P. (1992) High molecular weight hydrocarbons: a new frontier in organic geochemistry, *Trends Analytical Chem.* **11**, 187-193.

25 Del Rio J.C., Philp R.P. (1992) Oligomerization of fatty acids as possible source for high molecular weight hydrocarbons and sulfur-containing conpounds in sediments, *Org. Geochem.* **18**, 869-880.

26 Del Rio J.C., Philp R.P., Allen J. (1992) Nature and geochemistry of high molecular weight hydrocarbons (above C40) in oils and solid bitumens, *Org. Geochem.* **18**, 541-555.

27 Heath D.J., Lewis C.A., Rowland S.J. (1997) *Org. Geochem.* **26**, 11-12, 769-776.

28 Solodkov V.K., Galkina G.A., Dragunskaya V.S., Kamyanov V.A. (1977) O geokhimyi alkanov nefty Izvestiya AN Turkm. SSR, Ser. Phys.-Techn., *Chem. Geol. Nauk.* **4**, 57-60.

29 Ishiwatari Ri., Fukushima K. (1979) Generation of unsaturated and aromatic hydrocarbons by thermal alteration of young kerogen, *Geochim. Cosmochim. Ac.* **43**, 8, 1343-1349.

30 van Aarssen B.G.K., Cox H.C., Hoogendoorn P., de Leeuw J.W. (1990) A cadinene biopolymer in fossil and extant dammar resins as a source for cadinanes and bicadinanes in crude oils from South East Asia, *Geochim. Cosmochim Ac.* **54**, 11, 3021-3031.

31 Simoneit B.R.T., Grimalt J.O., Wang T.G., Cox R.E., Hatcher P.J., Nissenbaum A. (1986) Cyclic terpenoids of contemporary resinous plant detritus and of fossil woods, ambers and coals, *Org. Geochem.* **10**, 877-889.

32 Philp R.P. (1985) *Fossil Fuel Biomarkers*, Elsevier, Amsterdam.

33 Poinsot J., Adam P., Trendel J.M., Connan J., Albrecht P. (1995) Diagenesis of higher plant triterpenes in evaporitic sediments, *Geochim. Cosmochim. Ac.* **59**, 22, 4653-4461.

34 Simoneit B.R.T. (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance, *Geochim. Cosmochim. Ac.* **41**, 4, 463-476.

35 Heidy M.E., Kaam-Peters V. (1998) A high resolution biomarker study of different lithofacies of organic sulfur-rich carbonate rocks of a Kimmerigian lagoon, *Org. Geochem.* **28**, 3/4, 151-177.

36 Starobinets I.S., Kul'babayeva A.G., Nurmukhamedova M.A. (1980) O raspredelenyy individualnykh monocyclicheskykh aromatycheskykh uglevodorodov v neftyakh i o prochesakh ikh nakoplenya, *Geologiya nefti i gasa* (Rus.) **10**, 32-37.

37 Glebovskaya E.A., Meltsanskaya T.N., Surova N.Z. (1974) *Organicheskoye vechshestvo covremennykh I iskopaemykh osadkov* (*Organic matter of modern and fossil sediments*), Nedra, Moscow.

38 Chetverikova O.P., Dubovik V.I., Pentina T.Yu. (1976) *Issledovaniye organicheskogo vechshestva sovremennykh I iskopaemykh osadkov* (*Investigation of organic matter from modern and fossil sediments*), Nedra, Moscow.

39 Bendoraitis J.G. (1974) *Hydrocarbons of biogenic origin in petroleum-aromatic triterpenes and bicyclic sesquiterpenes. Adv. Org. Geochem.*, Edition Technip., Paris, pp. 209-224.

40 ten Haven H.L., de Leeuw J.W., Sinnighe Damste J.S. *et al.* (1988) Applications of bilogical markers in the recognition of palaeohypersaline environment, *GSSP* **40**, 123-130.

41 Dobryansky A.F. (1948) *Geokhimiya Nefti* (*Petroleum geochemidtry*), Gostoptekhizdat, Leningrad, 476 p.

42 Kamyanov V.F., Gorbunova L.V., Ogorodnikov V.D. (1999) Novyi podkhod k classifikatsii kaustobiolitov, *Neftekhimiya* (Moskow) **39**, 2, 134-143.

43 Filimonova T.A., Gorbunova L.V., Kamyanov V.F. (1984) Izuchenye khimicheskoi prirody vysokomoleculayrnykh komponentov nefty mestorozdenya Russkoye, *Neftekhimiya* (Moskow) **24**, 1, 3-10.

44 Aref'ev O.A., Zabrodina M.N., Norenkova I.K. *et al.* (1978) *Izvestiya AN SSSR Ser. Geol.* **9**, 134.

Final manuscript received in September 2007