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Distribution Patterns of Main Structural-Group Parameters of Crude Oils from North Caucasus Oil-and-Gas Basin According to ^{1}H NMR Data

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Received June 1, 2021; revised July 13, 2021; accepted December 29, 2021

Abstract—Using the ^{1}H NMR examination of a representative set of crude oils (86 samples, 54 oil fields and exploration areas) from the North Caucasus oil-and-gas basin, we obtained, for the first time, the structural-group composition of crude oils over the entire basin. Distribution density plots were presented for all the composition parameters measured. It was demonstrated that, because none of the parameters obeys normal distribution, nonparametric statistical analysis is needed for the data processing. In particular, medians and median confidence intervals (the latter being determined by signed-rank test), rather than means or root-mean-square deviations, should be relied upon. The North Caucasus oils were found to have a markedly lower content of aromatics (both monocyclic and bi-/polycyclic) than the crude oils from Western Siberia and Volga–Urals. Compared with the Eastern Siberia basin, the North Caucasus oils are distinguished by a slightly higher presence of bicyclic and polycyclic aromatics. At the same time, the North Caucasus oils exhibit the highest content of normal and monomethylated alkanes among the four basins under consideration. The North Caucasus oils were classified into three stratigraphic groups according to their oil composition. The first group consists of Triassic and Jurassic reservoirs. These crude oils have the lowest content of aromatics and the highest content of normal and monomethylated alkanes. The second group is the Cretaceous sediments, and the third group includes Paleogenic and Neogenic deposits. The content of aromatics increases consistently from the bottom to the top of the section.

Keywords: North Caucasus crude oils, structural-group parameters, crude oil composition, ^{1}H NMR

DOI: 10.1134/S0965544122060020

The present study continues a series of publications on the analysis of the composition of crude oils of major oil-and-gas basins (OGBs) in Russia and neighboring countries based on ^{1}H and ^{13}C NMR examination [1–7]. The ultimate goal of this series is to correctly identify the generalized composition of crude oils in, at least, North Eurasia. Moreover, given the diversity of the OGBs to be analyzed, these data could further be extrapolated, with an acceptable approximation, to all crude oils on earth. It should be noted, in this context, that a misconception has prevailed in the modern petroleum geochemistry as to the appropriate methods for describing the composition of a set of crude oils. Researchers typically rely on the mean, highest, and lowest values of parameters, as well as (sometimes) on their root-mean-square deviations (e.g., [8]). However, the mathematical statistics principles with regard to data processing [9, 10] dictate that, for a fairly large set of oils, a composition parameter cannot be considered identified properly unless either a distribution function or distribution density function has been determined for this parameter. To date, such data have only been published for the sulfur content in crude oils [11]. Thus, within the scope of our works, the distribution density functions were first obtained for all the OGBs under study [1, 3, 6, 7].

This study focused on crude oils from the North Caucasus OGB. This basin differs substantially [12] from those previously explored [1–7]. Its commercial oil and gas occurrence has been proven in a section from Lower Triassic to Neogene [12]. The reservoir occurrence depth range is very wide: from several hundred to six thousand meters. The range of reservoir temperatures is also broad: 20–180°C. In particular, the highest oil reservoir temperatures in Russia have been recorded in this OGB [12]. The region's source rocks have been studied, at least, since the early 1960s. A comprehensive study on this subject by Bazhenova et al. [13], which includes a brief review of prior relevant publications, showed that these rocks range from the Lower Triassic to Oligocene–Miocene age. It was demonstrated that most of these formations consist of mixed type (II + III) kerogene and some are type II and type III. The paper further notes some presence of terrigenous components (in various concentrations) in the precursor organic matter (OM) of almost all the source rocks [13].

We have found only one prior study dedicated to the analysis of the composition of Ciscaucasian crude oils by advanced methods [14]. The referenced paper reports data on the types of the source rocks and precursor OM that were derived from assessing the compositions of a number of cyclic biomarkers in 50 crude oil samples from 33 oil fields. The assessment covered all major stratigraphic plays of the region from Triassic to Neogene. These crude oils were shown to be of marine origin, with significant terrigenous admixtures in some deposits.

EXPERIMENTAL

We tested crude oil samples from the TIPS RAS collection gathered in the 1960s, 70s, and 80s. According to the adopted sample preparation procedure [1], total C_{8+} or C_{9+} fractions were selected as objects of structural-group analysis for this study. The reasons for this decision are detailed in reference [1].

^1H NMR spectra of 250–350 mg/mL oil solutions in $CDCl_3$ (400 MHz) were recorded at 313 K on a DRX-400 spectrometer (Bruker, Germany) equipped with a 5-mm probe without sample spinning. The spectrum record modes were as follows: data acquisition time 4 s, relaxation delay 3 s, pulse width 55°, 128–256 scans. The correction factors for all analytical groups of signals, taking into account their saturation, were measured with an error of ±1% by comparing the integral signal intensities in the spectra obtained both without saturation (relaxation delay 20 s, pulse width 70°) and with saturation (12 samples, three spectra in each mode for each sample). The correction factors were determined separately for gas condensates and light oils, for "conventional" oils, and for oils with significant broadening of ^1H NMR signals. Chemical shifts against a tetramethyl silane standard are known to strongly depend on the concentration of the fraction in the solution, the composition of the fraction, and the recording temperature. Therefore, the most intense signal, which corresponded to the CH_2 resonance in the middle of alkyl chains, was taken as a reference point for measuring the chemical shifts. For this signal, we assumed: $\delta = 1.280$ ppm.

RESULTS AND DISCUSSION

We examined 86 samples of crude oils from 54 fields and exploration areas (Table 1) that cover, in total, the entire basin area. The samples represent all the productive plays, from Lower Triassic to Neogene, and major tectonic structures (Table 1) [1]. The occurrence depth and the reservoir temperatures (T_{res}) ranged from 300 to 5800 m and from 20 to 180°C, respectively. The distributions of depths and temperatures for the tested oil samples (Fig. 1) are reasonably consistent with their frequency of occurrence in the OGB [12].

The following structural-group parameters were measured for all the samples:

H_γ—hydrogen of CH_3 groups separated by at least three C–C bonds from aromatic rings, carbonyl groups, or heteroatoms;

H_β—hydrogen of $-CH_2-$ and $-CH<$ groups, in β- and more distant positions to the same structural units;

H_α—hydrogen of CH_3-, $-CH_2-$, and $-CH<$ groups in α-position to the same structural units;

H_{ar}—hydrogen in aromatic rings, further divided into two ranges:

$H_{\mathrm{ar,1}}$—hydrogen predominantly in monoaromatic structures; and

$H_{\mathrm{ar,2+}}$—hydrogen predominantly in bi- and polycyclic aromatic structures; and

H_{dbl}—hydrogen in isolated double bonds.

In addition, the values of $H_{\mathrm{ar,2+}}/H_{\mathrm{ar,1}}$ and H_α/H_{ar} [1] were calculated.

For all parameters, the average characteristics of distribution were calculated, namely: mean; median; root-mean-square deviation (RMSD); and median confidence interval (Table 2). We also evaluated the simplest criteria to distinguish a distribution from normal: the ratio of the average absolute deviation (AAD) around the mean to the RMSD; eccentricity; and excess kurtosis [10, 15].

Table 1. Oil fields represented in tested samples

No.	Oil field	Well no.	Depth, m	Age, stage, series	Horizon, formation, bed	T_{res}, °C
Indolo-Kuban foredeep						
1	Anastas'evsko-Troitskoye		N/A	N_1	Hor. IV	64
2	Akhtyrsko-Bugundyrskoye	228	1368–1419	Pg_3	Hor. IV, Maikop	45
3	Akhtyrsko-Bugundyrskoye	380	1044–1070	Pg_3	Hor. II, Maikop	30
4	Akhtyrsko-Bugundyrskoye	411	N/A	Pg_1	Hor. VI, Il'sk	N/A
5	Praskoveiskoye	71	2598–2622	Pg_{1-2}	Cherkessk	N/A
Adygei salient						
6	Bezvodnenskoye	27	3475–3480	J_2	Bed I, Velichayevskoye	N/A
Kuma uplift zone						
7	Vostochno-Bezvodnenskoye	66	3103–3107	K_{1a}	Bed VIII	130
8	Vostochno-Bezvodnenskoye	230	3154–3157	K_{1a}	Bed IX	125
9	Vostochno-Sukhokumskoye	6	4832–4842	T_2		152
10	Kultaiskoye	3	3341–3346	$J_{\underline{2}}$		140
11	Kukhumskoye	6	4818–4822	$T_{\underline{1o}}$		N/A
12	Kurgan-Amurskoye	16	3468–3475	$J_{\underline{2}}$	Bed II	N/A
13	Kurgan-Amurskoye	17	3395–3402	K_{1a}	Bed XIII	140
14	Kurgan-Amurskoye	3	2720–2723	K_{1al}	Bed I	134
15	Maiskoye	5	3752–3788	J_2	Bed II	148
16	Ozek-Suat	51	3187–3183	K_{1a}	Bed XIII	143
17	Prigranichnoye	3	3330–3335	J_2	Bed I	146
18	Prigranichnoye	2	3158–3160	K_1	Bed IX	130
19	Pushkarskoye	4	3641–3658	T_{1o}		N/A
20	Tyubinskoye	3	3877–3880	J_2	Bed VI	155
21	Urozhainenskoye	50	3578–3597	$J_{2bt\text{-}b}$		150
22	Velichayevskoye	13	3510–3520	P–T		145
23	Zimnyaya Stavka	41	3493–3514	T		145
24	Zimnyaya Stavka	37	3037–3095	K_1		130
25	Levanevskoye	6	3269–3274	K_1	Bed IX	133
26	Povarkovskoye	1	3087–3090	K_1	Bed VIII	130
27	Solonchakovoye	37	4397–4421	T_1		155
28	Yubileinoye	18	4487–4492	T_{1o}	Olenek	N/A
29	South Area	1	3365–3368	J_2		N/A
30	South Area	3	3228–3233	K_1	Bed IX	147
31	Kamyshovoye	8	3271–3276	J_2	Bed V	140
32	Velichayevo-Kolodeznoye	205	2849–2852	K_1	Bed IV	128
33	Velichayevo-Kolodeznoye	212	2904–2909	K_1	Bed V	128
34	Velichayevo-Kolodeznoye	106	3068–3076	K_1	Bed VIIIa	130
35	Russky Khutor Severny	90	3487–3491	J_2		130
36	Russky Khutor Severny	57	3182–3186	K_1	Bed IX	126
Tersk-Caspian foredeep. Sunzhensk anticlinal zone						
37	Andreyevskoe	1007	5730–5800	K_{2km}		180
38	Benoiskoe	43	2390–2410	K_2		120
39	Karabulak-Achalukskoye	93	2431–2449	K_{1a}		90
40	Karabulak-Achalukskoye	89	1819–1834	K_2		85
41	Oktyabr'skoye	57	3614–3666	N_1	Chokrak	N/A
42	Oktyabr'skoye	217	1970–1972	K_2		N/A
43	Oktyabr'skoye	231	4545–4578	K_2		168

Table 1. (Contd.)

No.	Oil field	Well no.	Depth, m	Age, stage, series	Horizon, formation, bed	T_{res}, °C
			Tersk-Caspian foredeep. Sunzhensk anticlinal zone			
44	Oktyabr'skoye	147	903–904	N_1		50
45	Khayankortskoye	35	3250–3372	K_2		148
46	Zamankulskoye	66	3754–3778	J_{3o}		130
47	Zamankulskoye	50	2985–3003	K_{1br-a}	Hor. VII	119
			Tersk-Caspian foredeep. Tersk anticlinal zone			
48	Akhlovskoe	813	3076–3095	K_{2km}	Bench II	123
49	Bragunskoye	34	4302–4334	K_2		160
50	Zapadno-Gudermesskoye	206	4855–4900	K_2		175
51	Malgobek-Gorskoye	128	2900–2920	Pg_1		115
52	Malgobek Area	51/1	1181–1220	N_{1kr}	Bed XII–XIII	45
53	Mineral'noye	1	4808–5052	K_2		187
54	Sernovodskoye	12	2830–2860	K_2	Bench II	100
55	Chervlenoye	9	5291–5391	K_2		185
56	Eldarovskoye	50	4146–4159	K_2	Bench V	160
57	Starogroznenskoye	359	319–324	N_1	Chokrak	24
58	Starogroznenskoye	721	4449–4522	K_1		155
59	Starogroznenskoye	488	1847–1852	N_1	Chokrak	70
60	Starogroznenskoye	691	3831–3912	K_2		143
61	Yastrebinoye	110	4884–4950	K_{1a}		N/A
62	Goryacheistochenskoye	112	5108–5165	K_1		174
63	Goryacheistochenskoye	114	4513–4590	K_2		160
			Eastern Karpinsk Ridge			
64	Olenekovskoe	104	959–961	K_{1al}	Bed VIII	56
65	Tengutinskoye	178	1132–1133	K_{1a}		56
66	Kaspiiskoye	100	2240–2278	J_{2b}		114
67	Kaspiiskoye	67	2283–2309	J_{2b}		112
68	Kaspiiskoye	70	2289–2294	J_{2b}		115
69	Kaspiiskoye	72	2297–2298	J_{2b}		108.5
70	Kaspiiskoye	73	2381	J_{2b}		100
71	Komsomol'skoye	1	2800–2804	J_{2b}		130
72	Sostinskoye	8	1824–1828	K_{1a}		90
73	Sostinskoye	9	1848–1850	K_{1a}		90
74	Sostinskoye	3	1852–1854	K_{1a}		90
75	Bairskoye	3	1965–1972	K_{1a}		98–103
76	Bairskoye	7	1967–1975	K_{1a}		98–103
77	Bairskoye	5	1968–1976	K_{1a}		98–103
78	Kurgannoye	406	2012–2015	K_{1a}		108
79	Kurgannoye	379	2018–2025	K_{1a}		108
80	Kurgannoye	336	2052–2052	K_{1nc}		120
81	Yekaterininskoye	115	2218–2235	K_{1nc}		115
82	Nadezhdinskoye	127	2226–2239	K_{1a}		120
83	Dorozhnoye	50	2244–2248	K_{1a}		115
84	Ulan-Kholskoye	65	2162–2164	K_{1nc}		116–118
			Unknown			
85	Stalskoe	8	3807–3815	J_{2bt-b}	Bed II	N/A
86	Zakum Area	1	3600–3625	T_{2a}		N/A

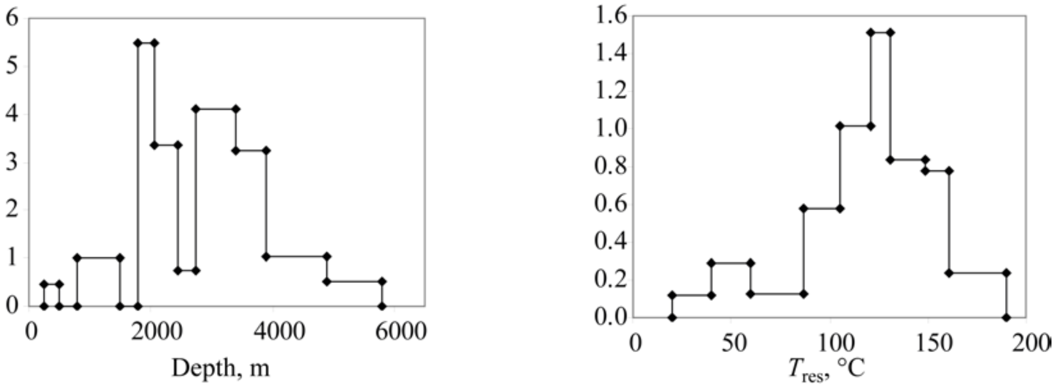

Fig. 1. Distribution density of occurrence depth and reservoir temperature for crude oil samples under study.

In contrast to the previously investigated basins, the content of unsaturated compounds in the majority (46 out of 86) of the North Caucasus crude oil samples proved to be below the detection limit (0.002% H_{dbl} with respect to the total hydrogen in the sample). This finding corroborates our previous data obtained by high pressure liquid chromatography in combination with ozonolysis [16]. This explains the incompleteness of the H_{dbl} data in Table 2.

The data in Table 2 are suitable for estimating a deviation of the distribution of the composition parameters from normal. In this regard, the table shows that none of the measured parameters obeys the normal distribution law. The distribution density plots presented

Table 2. Distribution characteristics of composition parameters for North Caucasus crude oils[a]

Parameter		H_{ar}	H_{dbl}	H_{α}	H_{β}	H_{γ}	$H_{ar,2+}$	$H_{ar,1}$	$H_{ar,2+}/H_{ar,1}$	H_{α}/H_{ar}
Mean		2.37		4.22	67.97	25.44	1.41	0.96	1.49	1.79
Median (M)		2.25		3.79	67.17	25.50	1.35	0.94	1.46	1.76
RMSD		0.95		1.75	4.92	3.31	0.59	0.39	0.29	0.20
M confidence interval (0.05)	From	2.10		3.59	66.1	24.2	1.22	0.85	1.38	1.74
	To	2.37		4.23	69.9	26.1	1.50	1.04	1.54	1.78
Eccentricity		***0.52***		**0.67**	***–0.52***	**2.66**	***0.61***	0.29	–0.34	**2.87**
Excess kurtosis		0.32		–0.10	***0.87***	**27.40**	**1.35**	**–1.22**	**6.57**	**26.98**
Spread/RMSD		4.96		4.49	5.04	7.54	5.33	4.45	7.14	7.71
AAD/RMSD[a]		0.78		0.80	0.83	**0.69**	0.76	0.82	**0.73**	**0.62**
50%	From (a)	1.75	<0.002	3.16	64.29	23.42	1.06	065	1.30	1.70
	To (b)	2.96	<0.002	5.30	72.31	27.14	1.74	1.24	1.65	1.83
80%	From (c)	1.20		1.93	62.74	21.91	0.69	0.47	1.23	1.61
	To (d)	3.61		6.85	73.53	28.36	2.20	1.46	1.86	1.99
90%	From	0.92		1.83	61.32	21.47	0.48	0.39	1.12	1.56
	To	3.94		7.68	75.18	29.57	2.41	1.57	1.98	2.06
Lowest		0.67	<0.002	1.45	51.42	20.50	0.25	0.28	0.24	1.43
Highest		5.40	0.006	9.32	76.22	45.44	3.40	2.00	2.32	2.98
Ratios	b/a	1.69		1.68	1.12	1.16	1.64	1.92	1.27	1.08
	d/c	3.02		3.55	1.17	1.29	3.18	3.10	1.51	1.23
Differences	b–a	1.21		2.14	8.02	3.73	0.68	0.59	0.35	0.14
	d–c	2.41		4.92	10.79	6.45	1.50	0.99	0.63	0.38

[a] Bold figures indicate values that differ from normal distribution with a significance level below 0.01. Bold underlined italics: values that correspond to a significance level of 0.01 to 0.05.

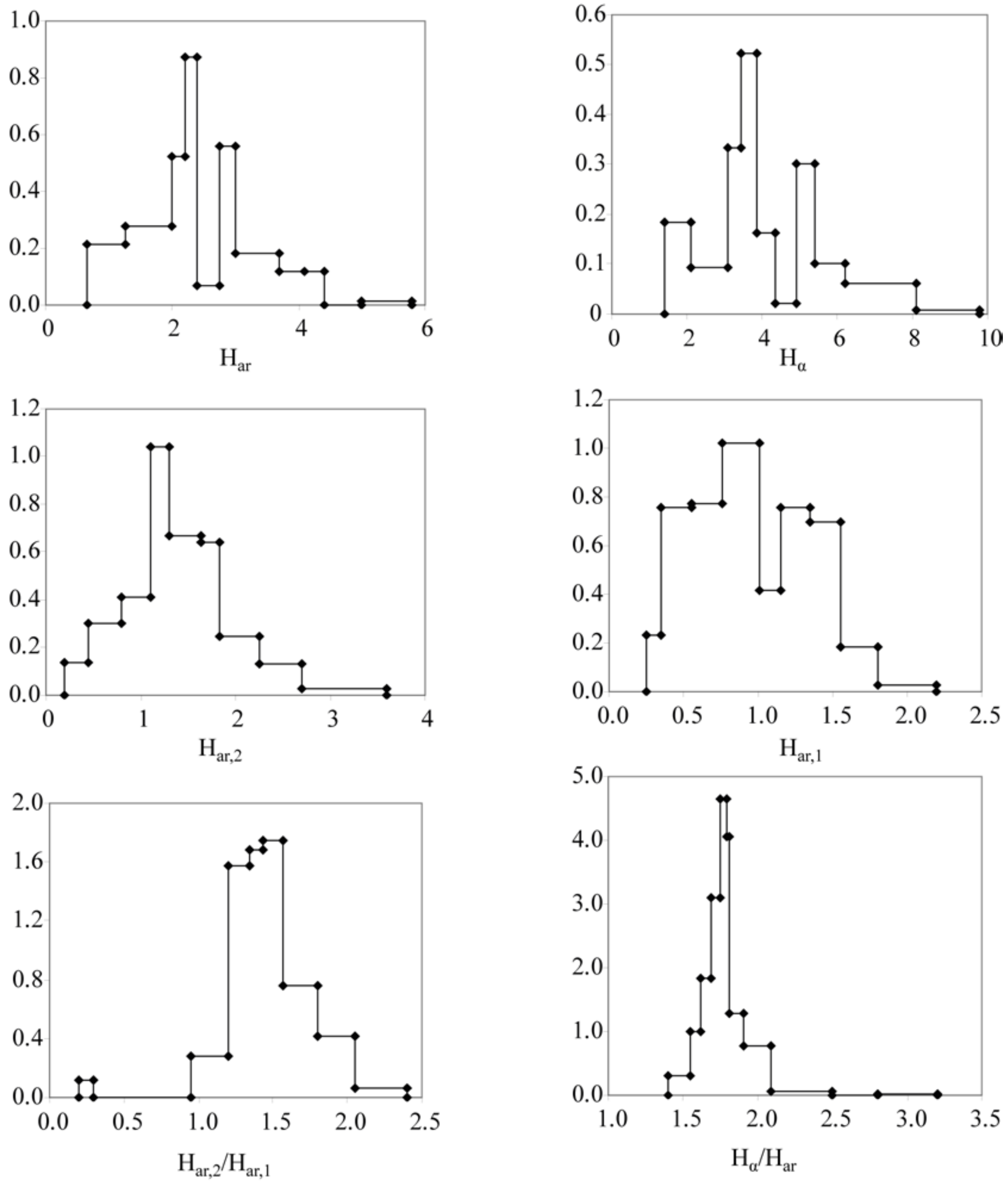

Fig. 2. Distribution density of parameters describing aromatic components in crude oils.

in Figs. 2 and 3 provide a detailed picture of the respective distributions. These plots, combined with Table 2, clearly indicate that many distributions are bimodal and almost all are asymmetric. Consequently, these oil composition data can only be processed by non-parametric statistical methods. In particular, medians and median confidence intervals determined by signed-rank test [9, 10], rather than means and RMSDs, are informative (see Table 2).

To compare the composition of the North Caucasus oil samples with the previously explored crude oils (from the Volga–Urals, Western Siberia, and Eastern Siberia OGBs) [1, 3, 6], a non-parametric Mann–Whitney test (MWT) was used. This test is designed to indicate the equality probability of two distributions (and to show which of them is shifted upwards) [9, 10]. The results are presented in Table 3. To visualize shifts between the distributions at different significance levels (SL) of the

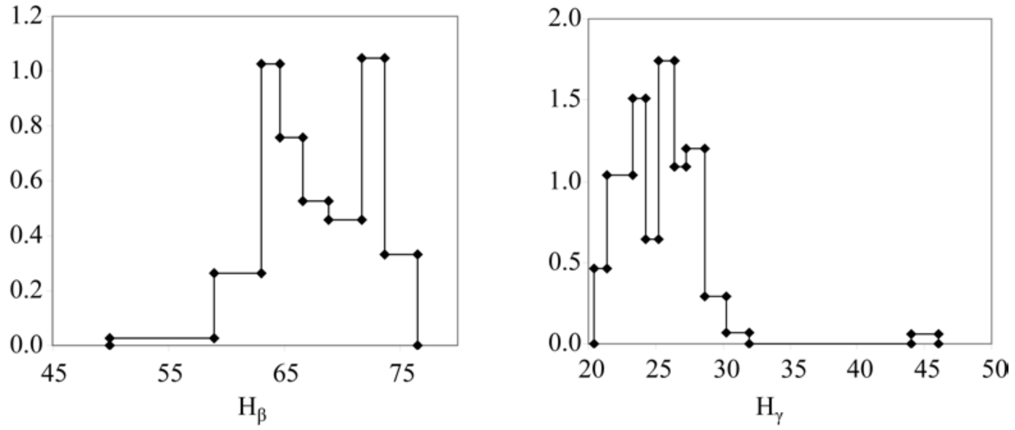

Fig. 3. Distribution density of H_β and H_γ.

respective MWT values, Fig. 4 shows the distribution density plots for three pairs of parameters in which the differences (MWT values) had SL on the order of 10^{-6}, 10^{-12}, and 10^{-21}.

Table 3 indicates that the difference of the North Caucasus crude oils from the Volga-Urals and Western Siberia is primarily in the content of aromatics. The North Caucasus oils exhibit markedly lower concentrations both of monocyclic and bi-/polycyclic aromatics. Moreover, in terms of $H_{ar,2+}/H_{ar,1}$ ratio, the North Caucasus oils stand out from the other three OGBs with a reliably higher proportion of bi-/polycyclic aromatics in the total aromatics. Based on the H_α/H_{ar} shift—a value primarily indicative of the degree of substitution of aromatic cycles—the amount of the substituents of these cycles in the North Caucasus oils is lower. There is no substantial difference in the total aromatics between the Eastern Siberia and North Caucasus crude oils. On the other hand, the content of bi-/polycyclic aromatics is reliably lower in the Eastern Siberia oils. This is likely explained by the fairly high presence of gas condensates in the Eastern Siberia fluids tested, whereas the North Caucasus samples were essentially free of gas condensate.

When comparing the parameters that describe saturated moieties (H_β and H_γ), the North Caucasus oils also exhibit a significant difference from the other OGBs. The only exception is the H_γ distribution similarity to the Western Siberia oils. A higher H_β with a lower H_γ is typical of crude oils that have a large proportion of normal and monomethylated alkanes.

Three groups of crude oils were previously identified in the North Caucasus [14]. The first group was revealed in the Triassic, Jurassic, and Lower Cretaceous deposits. These oils are characterized by high catagenetic maturity; they were generated in clays from shallow marine OM with a potential presence (up to 20%) of terrigenous

Table 3. Comparison of composition parameters of crude oils from North Caucasus vs. previously explored OGBs [1, 3, 6] using MWT [10][a]

OGB		H_{ar}	H_α	H_β	H_γ	$H_{ar,2+}$	$H_{ar,1}$	$H_{ar,2+}/H_{ar,1}$	H_α/H_{ar}
Western Siberia	U[b]	**1208**	**1041**	1096	**3051**	**1665**	**833**	1033	**1859**
	SL[c]	**2.5×10^{-1}**	**7.3×10^{-12}**	3.2×10^{-12}	**0.26**	**6.4×10^{-8}**	**2.1×10^{-14}**	1.0×10^{-12}	**1.3×10^{-6}**
Volga–Urals	U	**1358**	**677**	976	**5075**	**2440**	**608**	1376	**1152**
	SL[c]	**6.6×10^{-22}**	**6.0×10^{-26}**	37×10^{-24}	**1.6×10^{-4}**	**7.6×10^{-16}**	**2.3×10^{-26}**	8.5×10^{-22}	**4.1×10^{-23}**
Eastern Siberia	U	3342	**3047**	1878	**1246**	2638	**3888**	863	**212**
	SL[c]	0.012	**0.001**	50×10^{-10}	**2.0×10^{-14}**	1.4×10^{-5}	**0.31**	2.7×10^{-17}	**2.0×10^{-22}**

[a] Bold figures indicate cases where the value for the North Caucasus crude oils is lower.

[b] U is the MWT value.

[c] SL is the significance level of the difference between distributions.

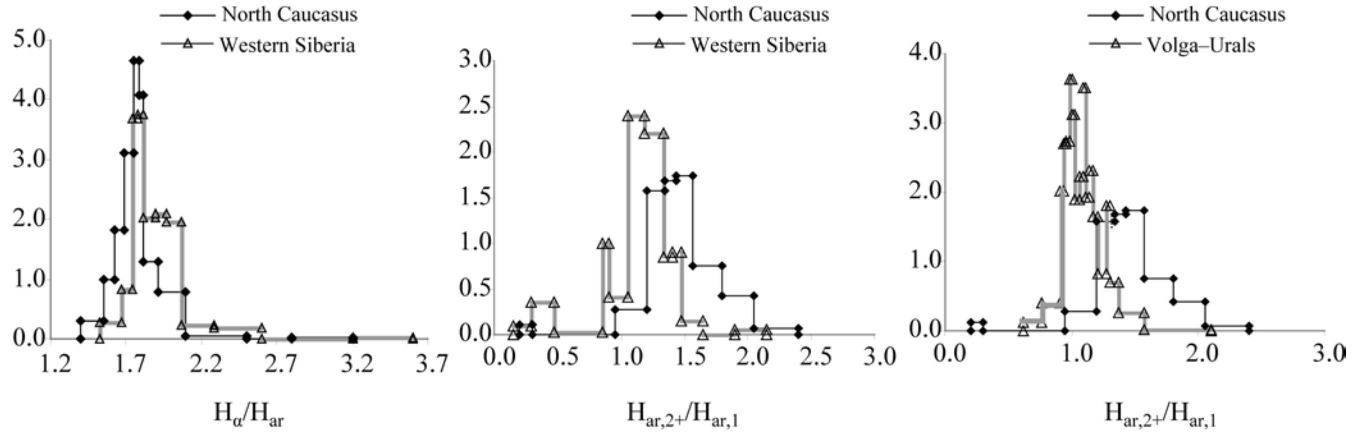

Fig. 4. Comparison of distribution density for three pairs of parameters between which the significance level of MWT values was on the order of 10^{-6}, 10^{-12}, and 10^{-21} (see Table 3).

OM. The second group consists of Upper Cretaceous oils and crude oils from the Cenozoic sediments of the Tersk–Sunzhensk zone. They are catagenetically mature, and “typically marine, generated in clays” [14]. The third group is the Cenozoic oils from the West Kuban Trough. They are also marine oils generated in clays, although catagenically less mature. Thus, the principal difference between the oil groups identified in the referenced study concerned their catagenetic maturity degrees. On the other hand, this paper provides no solid evidence that the crude oils under consideration can be distinctly classified into these groups.

Our data assessment produced a different classification of the crude oils according to their content of aromatics and alkanes (both normal and monomethylated). We were able to expressly distinguish three groups: the oils from

Table 4. Comparative composition of crude oils in reservoirs belonging to three different age ranges[a]

Age[b]	Parameter		H_{ar}	H_{α}	H_{β}	H_{γ}	$H_{ar,2+}$	$H_{ar,1}$	$H_{ar,2+}/H_{ar,1}$	H_{α}/H_{ar}
T–J (26)	Mean		1.52	2.69	73.0	22.8	0.93	0.59	1.56	1.83
	Median (M)		1.33	2.49	73.0	22.7	0.84	0.51	1.52	1.77
	M confidence	From	**1.12**	**1.90**	**72.3**	**22.0**	**0.68**	**0.45**	1.36	1.66
	interval (0.05)	To	**1.76**	**3.21**	**73.6**	**23.8**	**1.12**	**0.66**	1.73	1.88
	Lowest		0.67	1.45	64.2	20.5	0.35	0.28	0.97	1.44
	Highest		4.36	7.71	76.2	25.4	2.58	1.78	2.04	2.98
K (49)	Mean		2.50	4.38	66.6	26.6	1.46	1.04	1.43	1.75
	Median (M)		2.34	4.06	66.2	26.5	1.43	0.99	1.38	1.75
	M confidence	From	**2.22**	**3.78**	**65.4**	**25.7**	**1.28**	**0.94**	1.32	**1.71**
	interval (0.05)	To	**2.78**	**4.92**	**67.7**	**27.2**	**1.55**	**1.16**	1.50	**1.76**
	Lowest		1.29	1.85	51.4	20.9	0.25	0.52	0.24	1.43
	Highest		3.89	7.39	74.7	45.4	2.43	1.49	2.32	2.06
Pg–N (11)	Mean		3.83	7.13	62.4	26.7	2.33	1.50	1.55	1.87
	Median (M)		3.81	6.92	63.5	26.0	2.23	1.50	1.52	1.83
	M confidence	From	**3.08**	**5.8**	**59.9**	25.3	**1.79**	**1.29**	1.41	**1.76**
	interval (0.05)	To	**4.33**	**8.0**	**64.5**	27.3	**2.62**	**1.61**	1.58	**1.98**
	Lowest		2.79	5.07	53.9	25.0	1.67	1.12	1.39	1.73
	Highest		5.40	9.32	67.2	31.3	3.40	2.00	1.87	2.02

[a] Bold figures indicate confidence intervals that do not overlap with those for reservoirs of other ages.

[b] Figures in parentheses indicate the number of samples in the group.

Triassic and Jurassic reservoirs; the oils from Cretaceous (both Upper and Lower) deposits; and the Cenozoic oils. This classification considered the medians of the measured composition parameters, with due regard to the median confidence intervals determined by signed-rank test (Table 4).

Table 4 shows that the three groups are only similar in the $H_{ar,2+}/H_{ar,1}$ value; in addition, the Cretaceous and Cenozoic oils are similar in H_γ, and the Cretaceous and Triassic/Jurassic oils are similar in H_α/H_{ar}. The aromatic content grows monotonically as the reservoir age decreases, such that the difference between the medians of total aromatics (nearly proportional to the difference in H_{ar}) in the groups at the age extremes is about three-fold. There is an important similarity in the Pg–N to T–J ratios for the H_{ar}, $H_{ar,2+}$, and $H_{ar,1}$ medians (2.8, 2.7, and 3.0, respectively). The table clearly indicates a higher content of normal and monomethylated alkanes (H_β and H_γ) in the Triassic/Jurassic oils. To the best of our knowledge, such a pattern of differences in the oil compositions has never been reported in prior studies.

The low content of normal and monomethylated alkanes in the Cenozoic oils is due to biodegradation, as noted in [14] and confirmed by our chromatography/mass spectrometry data. However, the high content of these alkanes in the Triassic/Jurassic oils remains unexplained (especially taking into account that, after discarding one crude oil sample with a unique composition, the highest H_β in the Western Siberia and Volga–Urals oils is below the lower confidence interval of the median for the Triassic/Jurassic oils). We suggest that in actuality the presence of terrigenous precursor OM may be appreciably higher than “up to 20%” as specified in [14].

Regarding the potential causes for the difference in the aromatic content (both among the OGBs being compared and among the stratigraphic plays within the North Caucasus), we can only make generalized hypotheses. One possible explanation is the difference in the precursor OM, with the specific magnitude of this difference remaining unknown. Alternatively, we may hypothesize a difference in the oil generation conditions (for example, a difference in the hydrogen available in the rocks to ensure hydrogenation or preclude dehydrogenation). Presently, given the paucity of research on the potential pathways for aromatics formation in crude oils, a more definite rationale cannot be proposed. Particularly, there are serious doubts about the conventional concept of the dehydrogenation of saturated analogs as a major pathway for aromatics formation because no consistency between, for instance, naphthalenes and decalines in crude oils has ever been identified.

CONCLUSIONS

Using the ^{1}H NMR examination of a representative set of crude oils (86 samples, 54 oil fields and exploration areas) from the North Caucasus oil-and-gas basin, we obtained, for the first time, the structural-group composition of crude oils over the entire basin. Distribution density plots were presented for all the composition parameters measured. It was demonstrated that, because none of the parameters obeys normal distribution, non-parametric statistical analysis is needed for the data processing. In particular, medians and median confidence intervals (the latter being determined by signed-rank test [9, 10]), rather than means or root-mean-square deviations, should be relied upon. The North Caucasus oils were found to have a markedly lower content of aromatics (both monocyclic and bi-/polycyclic) than the crude oils from Western Siberia and Volga–Urals. Compared with the Eastern Siberia basin, the North Caucasus oils are distinguished by a slightly higher presence of bicyclic and polycyclic aromatics. At the same time, the North Caucasus oils exhibit the highest content of normal and monomethylated alkanes among the four basins under consideration [1, 3, 7]. The North Caucasus oils were classified into three stratigraphic groups according to their oil composition. The first group consists of Triassic and Jurassic reservoirs. These crude oils have the lowest content of aromatics and the highest content of normal and monomethylated alkanes. The second group is the Cretaceous sediments, and the third group includes Paleogenic and Neogenic deposits. The content of aromatics increases consistently from the bottom to the top of the section.

ACKNOWLEDGMENTS

This work was carried out within the State Program of TIPS RAS. The authors are grateful to Mr. Gordadze, Dr. Sci. in Geology and Mineralogy, Professor of the Gubkin Russian State University of Oil and Gas, for his kind cooperation.

CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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