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## **Compositional Features of Hydrocarbons in Crude Oils from South Vietnam and West Siberia**

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*Nine crude basement oil samples from White Tiger field of Cuu Long basin (Vietnam) and from several oilfields of Western Siberian basin (Russia) were chosen for this study. The crude oils were fractionated by medium pressure liquid chromatography into saturated hydrocarbons, aromatic hydrocarbons and polar compounds. The saturated and aromatic hydrocarbons were determined by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). The results of evaluation suggest that oils from Paleozoic fields of Western Siberian basin and from fractured basement of White Tiger field were generated from mixture of marine and terrestrial origin.*

*Keywords: crude oil, basement, Paleozoic, hydrocarbons, biomarkers.*

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### **Introduction**

The present stage of development oil-gas exploration geology is characterized by the greater orientation on discovering non-traditional object. Such objects are natural reservoirs formed by fractured crystal rocks. The major part of hydrocarbon accumulations in such reservoirs is in buried ledges of the basement represented by fractured metasomatic of igneous rock, quartzite, granite, dolomites. The question of genesis of these oils remains debatable till now. Among variety of publications two ideas of hydrocarbon genesis in fractured basement can be emphasized [1]. The first, oil-gas generating systems are located above the basement or on slopes of ledges. The second, basement is considered as an independent oil-gas generating object, in structure of which various types oil-gas generating systems

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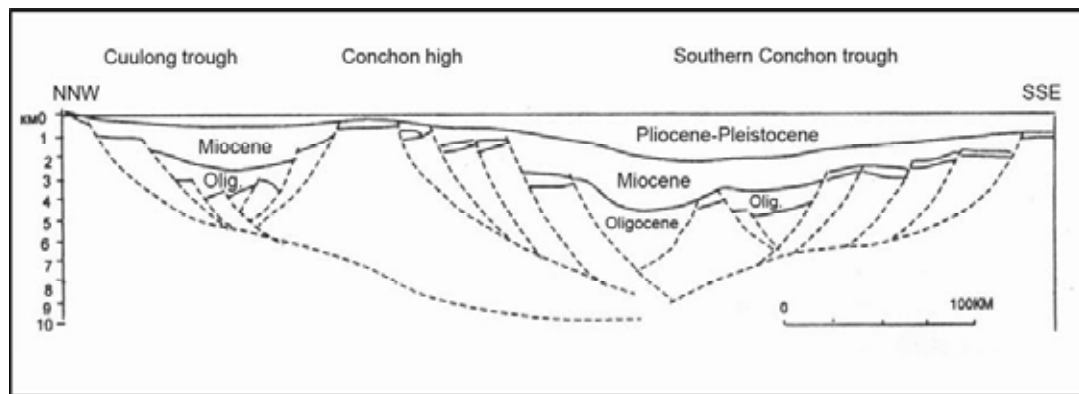


Fig. 1. Interpretation of the genesis of the Cuu Long and Conchon troughs from the standpoint of the listric faulting mechanism related to rifting

functioning under influence of deep factors are developed, in form of spontaneous, periodically shown deep ascending hydrocarbon streams.

In this paper we report the result of the analysis of molecular composition of basement oils from White Tiger field in the Cuu Long basin (South Vietnam) and from several oilfields in the West Siberia basin (Russia).

The Cuu Long basin is a tertiary rift basin locating at the Southern shelf of Vietnam. It covers an area of approximately 250 x 100km. The basin was formed during the rifting at Early Oligocene, Late Oligocene to Early Miocene inversion intensified the fractures of granite basement and made it become an excellent reservoir (Fig. 1). In spite of some discoveries in the Oligocene-Miocene layers and volcanic sections, fractured granite basement is still the main target of Cuu Long basin [2]. Tectonic activities play a key role in creating and enhancing the fractures in the basement. The basements are usually overlain directly by a prolific and pervasive Upper Oligocene source rocks. Geochemical data from many wells in the basin suggested that the oils found in the basin are of source rocks [3]. Fractured basement reservoirs are the unique characteristics of the Cuu Long basin, although there are other oil discoveries in the clastics and volcanics plays [4]. Oil was stored in the macro-fractures and micro-fractures. The matrix porosity of the magmatic body is negligible. From this basement five major oil fields are being predominantly produced: White Tiger, Rong, Rang Dong, Ruby and Su Tu Den fields. White Tiger field is a giant oil field in this basin.

The West Siberia basin is the largest oil and gas bearing basin in Russia. There are three large stratigraphic complexes in Western Siberia (Fig. 2): a Pre-Cambrian and Lower Paleozoic basement complex; a Late Paleozoic-Permian-Triassic transit complex; a complex of Mesozoic and Cenozoic sediments [5]. The complex geological structure and poorly understood geodynamic evolution of the Western Siberian basin have caused contradicting views on the tectonic evolution of the basin [6, 7, 8]. Traditional interpretation of the pre-Mesozoic basement show schemes of Pre-Jurassic tectonic divisions with zones of karelikes, baikalides, salarides, median solid plate tectonics show a large number of micro-plates represented by accretion prism complex and various portable zones between them [9].

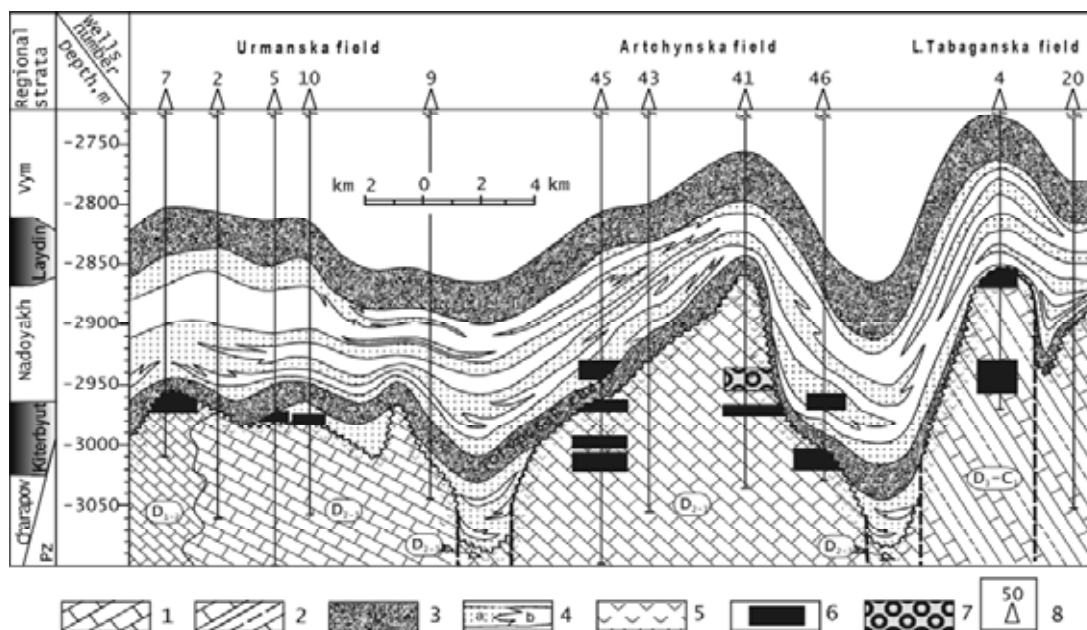


Fig. 2. Schematic north-south structural-stratigraphic cross-section through the Urmanska, Artchynska and L. Tabaganska fields, showing the contact between the Jurassic succession and the underlying pre-Jurassic basement. Key: 1 – Paleozoic carbonates; 2 – Paleozoic carbonates and siliciclastics; 3 – claystones; 4 – sandstones (a) and siltstones (b); 5 – weathered zone; 6 – oil reservoir zone; 7 – gas reservoir zone; 8 – well and number

### Material and methods

The present work attempts to evaluate the geochemical relationships between the oils recovered from some oil fields in various regions and investigate oil characterization, maturation, source depositional environments and oil families. This target was achieved through analytical results of gas chromatography and gas chromatography-mass spectrometry analysis (GC-MS) for 5 crude oils from White Tiger fields in Cuu Long basin (South Vietnam): WT-1, WT-2, WT-3, WT-4, WT-5 and for 4 crude oils from several fields in Western Siberian (WS) basin: WS-ML (Maloitcheska field), WS-Ar (Archinska field), WS-Urm (Urmanska field) and WS-Ost (Ostaninska field).

The compositions of oil samples were determined by the method of liquid-adsorption chromatography of the deasphalted oil. The asphaltenes were removed by precipitation, using dry hexane in forty-fold excess (by volume) relative to the crude oil sample. The analysis was carried out on a column packed with two sorbents: SiO<sub>2</sub> (upper part) and Al<sub>2</sub>O<sub>3</sub> (2nd degree of activity; lower part) in the ratio of 2:1. The elution of saturated hydrocarbons, aromatic hydrocarbons and resins was carried on using hexane, hexane-benzene (2:1) and benzene-methanol mixture in the volume ratio of 1:1. The saturated and aromatic hydrocarbons were analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS).

GC analysis of the saturate and aromatic hydrocarbons fractions was achieved by HP-6890. Oven temperature was programmed from 80°C to 300°C at 4°C/min and final time 60 min. The column is capillary CBP-1 with 25m length, inner diameter 0.25mm and with a film thickness of approximately 0.22µm or SPB-1 (the column length 30m, inner diameter 0.32mm, film thickness of fixed phase 0.25µm). GC/MS used a 50m x 0.25mm fused silica capillary column HPMS-6890 from Hewlett

Packard. Analysis mode: SIM (Selected Ion Monitoring). Ions are monitored as follows ( $m/z$ ): 85, 191, 217, 218, 231, 128, 142, 156, 170, 184, 178, 192, 206.

### Results and discussion

Total content of saturate and aromatic hydrocarbons of crude oils varies from 86.7 up to 96.7 % wt.; it is maximum (90.5–96.7 % wt.) in oils from White Tiger field. The concentration of resin and asphaltenes varies from 3.3 to up 13.3 % wt. The crude oils from White Tiger field are low concentration of asphaltenes (1.0–2.0 % wt.); it is maximum (4.3 % wt.) in oil from WS-ML well (Table 1).

The distribution of n-alkanes in crude oils can be used to indicate the organic matter source [10, 11]. Distribution of n-alkanes of crude oils from several oilfields of Western Siberian basin shows that the studied oils appear to be mature, based on the abundance of n-alkanes in the range  $n\text{-C}_{15}$  to  $n\text{-C}_{20}$ , slightly even carbon preference and moderately to low concentration of heavy normal alkanes (Fig. 3). The increase in the  $n\text{-C}_{15}$  to  $n\text{-C}_{20}$ , suggests marine organic matters with contribution to the biomass from algae and plankton [12] (Fig. 4). The striking molecular feature of oils is that all characterized by uniformity in n-alkanes distribution patterns, suggesting that they are related and have undergone similar histories, with no signs of water washing or biodegradation [13].

Distribution of n-alkanes of crude oils from White Tiger field shows high molecular-weight normal of paraffin components and maximum concentration in the  $n\text{-C}_{15}$ ,  $n\text{-C}_{20}$  and  $n\text{-C}_{26}$  (Fig. 3). Thus marine organic matters of crude oils from this field suggest from wrack and terrestrial plant (Fig. 4)

The carbon preference index (CPI-1) of all studied oils ranging from 1.0 to 1.1 (Table 1) generally shows no even or odd carbon preference, indicate mature samples [14].

The pristane/phytane (Pr/Ph) ratio is one of the most commonly used geochemical parameters and has been used as an indicator of depositional environment with low specificity due to the interferences by thermal maturity and source inputs. Ten Haven et al. stressed that high Pr/Ph ( $>3$ )

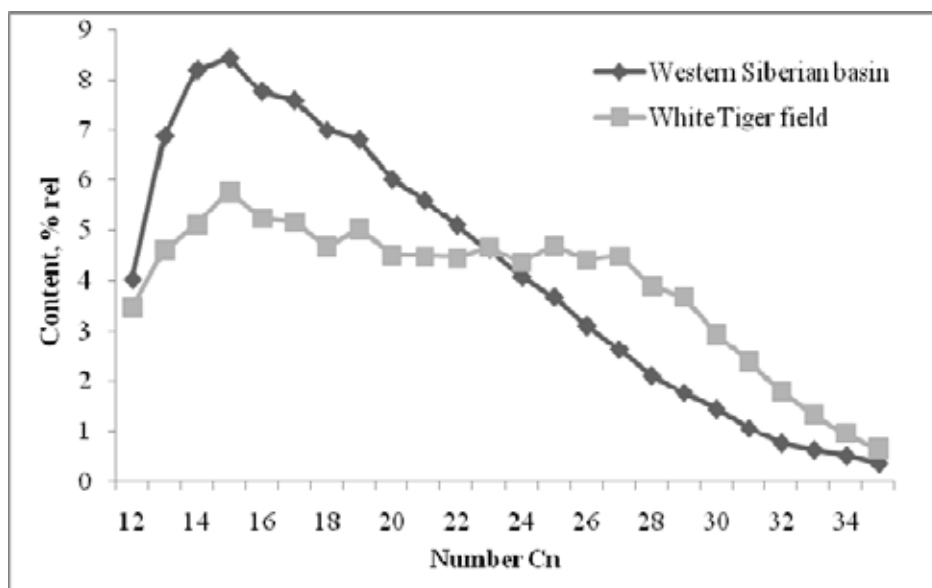


Fig. 3. Typical distribution of n-alkanes in crude oils

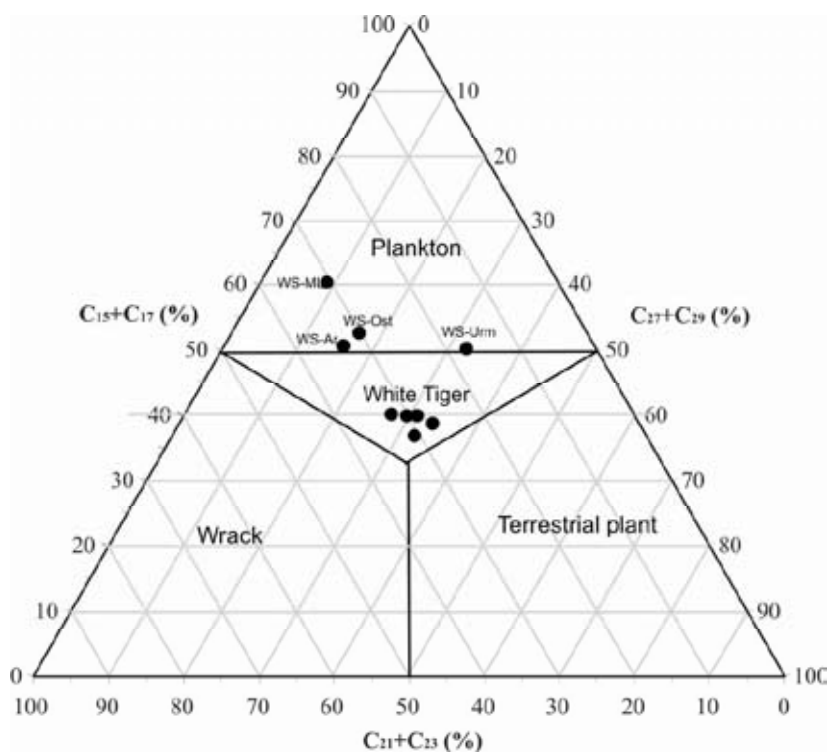


Fig. 4. Relative content of n-alkanes of various origins in crude oils

indicates terrigenous input under oxic conditions and low Pr/Ph ( $<0.8$ ) indicates anoxic/ hyper saline or carbonate environments [15].

According to Lijmbach G.W. low values ( $Pr/Ph < 2$ ) indicate aquatic depositional environments including marine, fresh and brackish water (reducing conditions), intermediate values (2–4) indicate fluviomarine and coastal swamp environments [16]. The most of studied oil samples are characterized by pristane/phytane ratio ranging from 1.1 to 1.95 (Table 1), confirming that these oils have been originated from marine organic source deposited reducing conditions. Except well WS-Ost ( $Pr/Ph = 2.22$ ) from fluviomarine and coastal swamp environments.

In the studied oil samples, plot of  $Pr/n-C_{17}$  and  $Ph/n-C_{18}$  displays all oils produced from source rock which failed into mixed organic matter zone and deposited in transitional zone (Estuarine/shoreline). Biomarker parameters are used to determine information concerning about quality and type of organic matter based on the presence of marker compounds of C<sub>15</sub>+ saturated and aromatic hydrocarbons.

Steranes were one of the first groups of biomarkers to be used extensively in petroleum geochemistry. Predominance of C<sub>27</sub> steranes in an oil or rock extract would signify an algal or marine input whereas C<sub>29</sub> steranes signified the presence of higher plant or terrestrial input. As a whole in the crude oils, in C<sub>27</sub>–C<sub>29</sub> ( $m/z = 217$ ) steranes C<sub>27</sub> (41.56–56.27 %) prevails as compared with C<sub>28</sub> and C<sub>29</sub> steranes (except for oil from WS-Urm field) (Table 2). It indicates that these oils were formed in open marine and delta source zones [17].

C<sub>30</sub>-4-methyl steranes: the components identified on  $m/z$  217 and  $m/z$  231. The 4-methyl steranes are found in both freshwater lacustrine and marine sediments. The crude oils from White Tiger field

Table 1. Geochemical parameters of studied oil samples derived from GC and GC-MS analyses

Well name	WS-ML	WS-Ar	WS-Urm	WS-Ost	WT-1	WT-2	WT-3	WT-4	WT-5
Depth, m	2865	3104	3096	2708	3712	3455	3910	4203	4368
Saturate HCs, % wt.	72.6	73.7	79.6	82.8	90.0	82.5	89.3	89.9	91.2
Aromatic HCs, % wt.	14.1	13.4	9.9	8.0	6.6	8.0	6.4	6.6	5.5
Total hydrocarbons, % wt.	86.7	87.1	89.6	90.8	96.6	90.5	95.7	96.5	96.7
Resins, % wt.	9.0	8.8	8.5	7.9	2.3	8.5	2.3	2.5	1.8
Asphaltenes, % wt.	4.3	4.1	1.9	1.4	1.1	1.1	2.0	1.0	1.5
Total polar products, % wt.	13.3	12.9	10.4	9.2	3.4	9.5	4.3	3.5	3.3
Pristane/Phytane	1.11	1.10	1.42	2.22	1.89	1.95	1.89	1.85	1.84
Pristane/n-C <sub>17</sub>	0.29	0.18	0.30	0.47	0.43	0.44	0.43	0.42	0.43
Phytane/n-C <sub>18</sub>	0.29	0.17	0.23	0.23	0.25	0.25	0.25	0.25	0.25
CPI-1(C <sub>20</sub> -C <sub>28</sub> )	1.0	1.0	1.0	1.0	1.1	1.0	1.1	1.1	1.1
n-C <sub>15</sub> +n-C <sub>17</sub> , % rel.*	56.13	51.06	48.27	53.4	37.57	39.84	39.99	39.06	37.21
n-C <sub>21</sub> +n-C <sub>23</sub> , % rel.*	30.55	34.21	33.81	34.76	32.03	32.57	32.39	32.21	32.53
n-C <sub>27</sub> +n-C <sub>29</sub> , % rel.*	13.32	14.73	17.92	11.84	30.40	27.59	27.62	28.73	30.26
<i>Note:</i> *—Content of mixture of homologues n-alkanes: C <sub>15</sub> , C <sub>17</sub> , C <sub>21</sub> , C <sub>23</sub> , C <sub>27</sub> and C <sub>29</sub>									

contain very high concentrations of C<sub>30</sub>-4-methyl steranes (S8= 0.3–1.28), relating to dinoflagellates which particularly appearing dominant in the salinity/low salinity/freshwater settings [17]. On the contrary, the crude oils from Western Siberian basin contain very low concentrations of C<sub>30</sub>-4-methyl steranes (S8=0.02–0.06) (Table 2).

In the crude oils from White Tiger fields, isomers of C<sub>29</sub>ααα regular steranes observed on m/z 217 and S1 values ranging from 0.4–0.55 determine high mature stage of organic-rich mater producing oil again. On the contrary, in the crude oils from Western Siberian basin, S1 low values ranging from 0.08–0.25 (Table 2).

Together with steranes, triterpanes belong to the most important petroleum hydrocarbons that retain the characteristic structure of the original biological compounds. Tricyclic, tetracyclic terpanes, hopanes and other compounds contribute to the terpane fingerprint mass chromatogram (m/z=191).

Tricyclic terpanes are often associated with oils from lacustrine origin and sometimes-marine origin, but appear absent in higher plant. Relative high concentrations of C<sub>23</sub> tricyclic terpanes in comparison with C<sub>30</sub> hopanes of the most studied oil samples (H11=0.92–3.58) (except for oil from WST-Urm and WST-Ost, H11=0.15–0.23) indicate that the oils related to materials of lacustrine and shoreline origins [17].

The presence of pentacyclic terpanes is measured by T<sub>s</sub>/(T<sub>s</sub>+T<sub>m</sub>) ratio and often used for assessing thermal maturity. H6=0.49–0.68 in these oils give evidence of high maturity of organic mater producing oil (Table 2).

Hopane/sterane ratio: hopanes are derived from precursors in bacterial membranes. In the White Tiger field high ratios of C<sub>30</sub> hopane and steranes calculated by M4 parameter ranging from 0.81–0.89 are more indicative of bacterial and/or algal materials in lacustrine environment and characterized for

Table 2. Biomaker parameters of studied oil samples

Code	Parameter description	Well name								
		WS-ML	WS-Ar	WS-Urm	WS-Ost	WT-1	WT-2	WT-3	WT-4	WT-5
H11	C <sub>23</sub> Tricyclic/C <sub>30</sub> Hopane	1.72	0.92	0.15	0.23	1.24	3.58	1.09	1.38	1.19
H15	Oleanane / Hopane	0.017	0.04	0.06	0.04	0.11	0.09	0.12	0.14	0.12
S1	C <sub>29</sub> Steranes $\alpha\alpha\alpha$ 20S/(20S+20R), m/z 217	0.25	0.17	0.08	0.08	0.55	0.40	0.54	0.52	0.53
S3_1	Steranes $\alpha\alpha\alpha$ C <sub>27</sub> , % rel.(m/z 217)	46.42	44.74	19.67	41.56	54.79	48.55	55.84	56.27	53.98
S3_2	Steranes $\alpha\alpha\alpha$ C <sub>28</sub> , % rel. (m/z 217)	25.02	16.20	29.03	16.40	17.20	25.53	18.42	16.66	16.94
S3_3	Steranes $\alpha\alpha\alpha$ C <sub>29</sub> , % rel. (m/z 217)	28.56	39.06	51.30	42.04	28.01	25.92	25.74	27.07	29.08
S4_1	Steranes $\alpha\beta\beta$ C <sub>27</sub> , % rel. (m/z 218)	37.11	31.13	16.12	30.88	39.75	42.52	38.10	41.07	40.06
S4_2	Steranes $\alpha\beta\beta$ C <sub>28</sub> , % rel. (m/z 218)	16.31	13.99	29.49	23.24	21.71	23.49	23.76	20.68	20.19
S4_3	Steranes $\alpha\beta\beta$ C <sub>29</sub> , % rel.(m/z 218)	46.58	54.88	54.39	45.88	38.54	33.99	38.14	38.25	39.75
S5	Diasteranes Index {C <sub>27</sub> $\beta\alpha$ Diasterane/(Same+C <sub>27</sub> Steranes)}.	0.19	0.17	0.16	0.25	0.16	0.14	0.15	0.17	0.18
S8	C <sub>30</sub> 4 – Methyl Sterane of C <sub>29</sub> 20 $\alpha\alpha\alpha$ R (m/z 231: m/z 217)	0.04	0.06	0.02	0.04	1.18	0.3	1.28	1.01	1
M4	C <sub>30</sub> Hopane/(C <sub>30</sub> Hopane +Sum C <sub>29</sub> Sterane )	0.67	0.76	0.73	0.75	0.83	0.89	0.82	0.81	0.82
H6	C <sub>27</sub> Hopanes Ts/ (Ts+Tm)	0.55	0.55	0.49	0.56	0.68	0.58	0.68	0.68	0.56

organic producing oil of organic matters of terrestrial origin. But in the studied oilfield of Western Siberian basin this parameter ranging from 0.67–0.76 are more characterized for organic producing oil of organic matters of plankton [17].

18 $\alpha$ (H)-Oleanane: the component on m/z 191 and identified by oleanane/C<sub>30</sub> hopane ratio named as H15. Oleanane is thought to be derived from precursors originating in higher plant and evolved in Late Cretaceous to recent [17]. The presence of oleanane with low concentration in the oils (H15=0.017–0.14) indicates a small amount of higher plant in original materials.

Compounds of naphthalene and phenanthrene types are indentified in bi – and tricyclic aromatic hydrocarbons of investigated crude oils. Tri-aromatic hydrocarbons (phenanthrenes) are predominating in the major part of aromatic fraction of the most of investigated oils (Table 3).

The content of appropriate naphthalenes in all crude oils is growing up while the quantity of methyl groups in side substituents of aromatic rings is increasing. Naphthalenes with tri atoms of C in

Table 3. Content of aromatic hydrocarbons in the investigated crude oils

Well name	Naphthalenes*	Content of naphthalenes homologues in mixture, % relative				MNR	ENR	DNR	Phenanthrenes*	Content of phenanthrenes homologues in mixture, % relative			Rc
		MN	EN	DMN	TMN					P	MP	DMP	
WS-ML	61.76	1.99	11.79	14.50	71.72	1.47	1.87	2.05	38.24	23.05	44.84	32.11	0.75
WS-Ar	65.02	2.60	15.34	13.78	68.29	1.32	1.66	2.08	34.98	23.34	47.59	29.07	0.76
WS-Urm	19.84	2.03	12.50	15.09	70.39	1.65	2.19	1.39	80.16	17.45	45.93	36.62	0.82
WS-Ost	33.69	2.59	2.59	3.39	91.44	1.32	1.32	1.88	63.31	24.46	48.01	27.53	0.76
WT-1	6.04	0.00	0.00	2.94	97.06	–	–	2.15	93.96	11.32	47.31	41.36	0.99
WT-2	42.81	1.39	8.59	14.34	75.68	5.51	7.23	1.77	57.19	28.87	44.92	26.21	0.79
WT-3	1.05	0.00	0.00	0.00	100.00	–	–	–	98.95	10.99	45.53	43.48	1.00
WT-4	8.07	0.00	0.00	9.84	90.16	–	–	1.61	91.93	10.12	44.22	45.66	1.02
WT-5	6.04	0.00	0.00	6.65	93.35	–	–	1.61	93.96	10.69	44.31	45.00	1.02

Note:

\* – total content of appropriate group in a mixture of identified aromatic compounds, MN-methylnaphthalen, EN-ethylnaphthalen, DMN-dimethylnaphthalen, TMN-trimethylnaphthalen, P-Phenanthrene, MP-methylphenanthrene, DMP-dimethylphenanthrene  
–MNR=2-methylnaphthalen/1-methylnaphthalen  
–ENR=2-ethylnaphthalen/1-ethylnaphthalen  
–DNR=(2,6-+2,7-dimethylnaphthalen)/(1,6-dimethylnaphthalen).



side alkyl chain (TMN) are in the maximum concentration and naphthalene without substituents was not identified in these oils. Except in the crude oils from WT-3, WT-4, WT-5 methyl-naphthalenes were not identified. By indices of maturity, which were calculated by the isomers of naphthalene present the following results. Ratio 2-methylnaphthalen/1-methylnaphthalen (MNR) in the crude oils from oilfields of Western Siberian basin varies from 1.32 to 1.65; it shows the most mature oils. Maximum ratio (7.23) 2-ethylnaphthalen/1-ethylnaphthalen (ENR) is crude oil from WT-2. By index DNR which was calculated by the dimethylnaphthalenes, the most transformed are crude oils from oilfields of Western Siberian basin [17].

Phenanthrene and its alkyl-substituted homologues with 1-2 atoms of C were identified in oils by the mass-spectrometric technique; they are the most usual representatives of tri-cyclic aromatic hydrocarbons in oils. The concentration of phenanthrenes in mixture of identified aromatic compounds in investigated crude oils is changing from 38.24 to 98.95% rel. In the most crude oils compounds with one methyl group in the side chains (MP) are predominating among all homologues of phenanthrene (except oils from wells WT-4 and WT-5). Their concentrations in mixture of phenanthrenes homologues are changing from 44.22 to 48.01 % rel. The minimum concentrations of homologues of phenanthrenes is phenanthrene (its content is changing from 10.12 to 28.87 % rel.) (Table 3).

Special parameter Rc (vitrinite reflectivity) was calculated as ratio between the content of some isomers of methylphenanthrenes in a mixture and the content of phenanthrene; its value is the characteristic of oil thermal maturity [18]:

$$Rc = 0.6 * 1.5 * (2-MP + 3-MP) / (P + 9-MP + 1-MP) + 0.4$$

Calculated for crude oils from oilfields of Western Siberian basin parameter is changing from 0.75 to 0.82. Thus the maturity of these oils is katagenesis MK2. For crude oils from White Tiger field it is changing from 0.79 to 1.02.

### Conclusions

On the basis of the studied data for five oils in the White Tiger field and four oils in the Western Siberian basin, some comments drawn out as follows:

Oils from Paleozoic fields of Western Siberian basin and from fractured basement of White Tiger field were generated from mixture of marine and terrestrial origin. Greater contribution of terrestrial material in the source rock of White Tiger field leads to higher contents of paraffin  $C_{n > 22}$ , oleanan, steranes  $C_{29}$  in these crude oils. Oil from White Tiger field has more thermally mature, which is possible due to the higher temperature of reservoir (140°C), compared with Paleozoic deposits of Western Siberian basin. This may explain the contradictions of the results of determining level of thermal maturity were derived from various parameters.

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## **Особенности состава углеводородов нефтей Южного Вьетнама и Западной Сибири**

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*Девять образцов нефтей фундамента Южного Вьетнама и палеозоя Западной Сибири были выбраны для исследования. Нефти были разделены методом жидкостной адсорбционной хроматографии на насыщенные углеводороды, ароматические углеводороды и полярные компоненты. Состав насыщенных и ароматических углеводородов нефтей анализировали с помощью методов газовой хроматографии (ГХ) и хромато-масс-спектрометрии (ГХ-МС). Результаты исследования показали, что нефти из отложений палеозоя Западной Сибири и триасового фундамента месторождения «Белый Тигр» генерированы из смеси морских и терригенных фаций.*

*Ключевые слова: нефть, фундамент, палеозой, углеводороды, биомаркеры.*

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