

Geochemistry of Organic Matter in Permian Deposits in the Northeast of Korotaihinsky Depression

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Abstract. The article presents results of geochemical studies of Permian deposits in the northeastern part of Korotaihinsky depression. We show the distribution of organic carbon and bitumen in various lithological varieties of rocks. The smallest (0.04-0.7 %) concentrations of organic carbon are confined to the limestone and sandy-silty varieties; the maximum ones are set in the mudstone, carbonaceous mudstones (1.0-1.7 %) and coal (26 %). Deposits of Late Permian age are characterized by a high content of bitumen (0.018-0.293 %). The distribution of n-alkanes and isoprenoids in the hydrocarbon fraction of bitumen shows a significant proportion of sapropel organic matter with a small contribution of humic compounds. Permian bitumen is mixed – autochthonous with a dash of allochthonous hydrocarbons. Results of pyrolytic studies show low residual generating potential of rocks (HI < 65 mgHC/g Corg), due to the composition of organic matter and its catagenetic transformation.

Keywords: Permian sediments, organic matter, bitumen, n-alkanes

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Introduction

Korotaihinsky depression is one of the least studied structures in the geochemical aspect in the northeast of the Timan-Pechora Basin. Geochemical characteristics of organic matter (OM), its oil and gas generating potential in sedimentary complexes of the depression are provided in the few works on the basis of individual wells and natural exposures (Anischenko et al., 2004, Bazhenova et al., 2010, 2008; Kotik 2015; 2016). Therefore, conducting geochemical studies and obtaining new data will allow us to complement the information on the properties of oil and gas source rocks in the sedimentary cover of Korotaihinsky depression.

Area and object of the research

The area under study is located in the northeast of Korotaihinsky depression within the most dislocated part – Sabriyaginsky and Pestanshorsky fold-thrust zones. The main objects of our studies were the Permian clastic sediments that are exposed fragmentally in natural outcrops in the mean flow of the river Silovayaha (Fig. 1). Comprehensive geochemical study of rocks was conducted in three outcrops, which opened different stratigraphic intervals of the Permian: sezymiskian (P₁Sz) and goosinian (P₁gs) formations (outcrop 16), lekvorkutskian (P₁lv) formation (outcrop 15), sylovskian (P₂₋₃sl) formation (outcrop 13).

Complex of geochemical studies, including definition of the organic carbon content in the rock (TOC, %), extraction of chloroform bitumen A (CBA%), determination of the aliphatic hydrocarbons composition by gas chromatography (GC) was performed on the basis of Common Use Center “Geoscience” in the Institute of Geology of Komi of the R&D center of the Ural Branch of the Russian Academy of Sciences (Syktyvkar). Pyrolysis studies by Rock-Eval method were conducted in VNIGNI (Moscow).

The Permian section begins with limestone of Sezymiskian formation of Asselian-Sakmarian age that with a stratigraphic unconformity lie in the Middle Carboniferous deposits (Fig. 2). They are overlapped with clastic sediments of Artinskian ties (P₁gs-tl), represented by sandstones, siltstones and mudstones, in the upper part with predominance of sandstone and siltstone. Overlying sediments of Vorkutinskian series (P₁lv-in) of Kungurian-Ufimian are composed of cyclic alternation of sandstone, siltstone, mudstone, carbonaceous mudstone and coal. At the top of the series (Intinskian formation, P₁in) the content of coarse clastic rocks (sandstone grits, conglomerates) is increased up to 50% (Puhonto, 1998). Section of Pechora series (P₁₋₃pc) in the lower part (seidinskian formation, P₁₋₂sd) is composed mainly of argillites and siltstones interbedded with sandstones. The most significant upper part of the section (Seidinskian and Silovskian formations) composed of conglomerates, which are subject to silt-clay rocks containing coal seams (Puhonto, 1998). Permian sediments are overlapped with Triassic deposits, which are separated from them with basalts (Fig. 1).

Results and discussion

The concentration of organic carbon in rocks ranges from 0.2 to 1.78%, reaching 26% in coal (Fig. 2). The lowest values of TOC (0.04-0.09 %) are set in the limestone of Sizimskian formation. In clastic rocks the increase of TOC occurs naturally in the sequence of: sandstone (0.23-0.26 %) – siltstone (0.47-0.72 %) – mudstone (1.01-1.78). Yield of chloroform bitumen from Lower Permian clay rocks is 0.006-0.012 %. Rocks of the Upper Permian interval contains the greatest concentration of chloroform bitumen (CB) 0.018-0.039 % – for clay varieties, and with a maximum of 0.293 % – for coal. Values of bitumoid rate (β_{CB}) are changed with the same tendency. In the Lower

Permian rocks β_{CB} is 0.3-1.6 %, rising to 2.4-2.6 % in the Upper Permian. These low values of the indicators β_{CB} characterize bitumens as the autochthonous, including residuals that gave its migration part.

Catagenetic transformation of OM in Permian complex in the area under study varies from the middle of mesocatagenesis to the beginning of apokatagenesis (Anischenko et al., 2004). Catagenesis of OM in Kazanian-Tatarian deposits are located on gradations MK₃-MK₅. In the mean flow of the river Silovayaha coal deposit of the same name is explored, where in Pechora series coals are of brand K (coking) and OS (lean caking) that matches the gradations MK₄-MK₅ (Coal Base of Russia, 2000). Catagenesis of OM of underlying Artinskian-Kungurian deposits reaches gradation MK₅-AK.

High maturity of OM is also confirmed by pyrolysis Rock-Eval.

In samples from Kungurian and Artinskian sediments, values of S₁ (content of free hydrocarbons) and S₂ (content of fixed hydrocarbons) are, respectively, 0.01 and 0.06-0.15 mgHC/g of rock. At such low values, indicators of T_{max} (maximum yield temperature of fixed hydrocarbons in the thermal degradation of kerogen) and HI (hydrogen index) are not defined. In samples of the Upper Permian interval higher values are recorded: S₁ – 0.03-0.73; S₂ – 0.45-18.64; HI – 27.65 mgHC/g of TOC. The residual hydrocarbon potential of OM from the Upper Permian rocks is characterized by very low values, due to the specific composition and the maturity degree of OM.

The proportion of saturated hydrocarbons in bitumen is not significant, on its concentration it is accounted from 3

to 34.78% of the total weight of CBA. Almost on the whole section Permian bitumen (except for samples of 15-04, 15-05 and 16-06) is characterized by a similar molecular weight distribution of low molecular normal alkanes of the composition C₁₃-C₁₈, the concentration of which varies from 67.33 to 76.17% (Table). Distribution histograms of alkane hydrocarbons have a unimodal distribution with a maximum at n-C₁₆ or n-C₁₇ except for sample 13-06 (coal), in which the distribution maximum is shifted to n-C₁₄ (Fig. 3a, b).

The concentration of alkanes C₁₉-C₂₄ varies from 11.51 to 18.06%. The samples are characterized by low background of macromolecular compounds in the n-C₂₅-C₃₅, their concentration is extremely low and the average is 1-3 %.

Among the examined samples coal (sample 13-06) has the highest content of high molecular weight alkanes normal structure – 8.93% and the lowest values of the ratio n-C₁₇/nC₂₅ – 5.34 and K_{odd}C₁₇ – 0.96.

Ratio of n-alkane sum in series C₁₄-C₂₀ to C₂₁-C₃₀ varies in a wide range from 5.37 to 11.58.

Odd ratio K_{odd}C₁₇ varies between 0.96-1.24.

The predominance of medium molecular odd n-alkanes (K_{odd}C₁₇ > 1) reflects the part of algal OM in the composition of the initial biomass (Hunt 1982; Tissot, Welte, 1984).

Value of even ratio K_{even}C₁₆ of 1.12-1.53 indicates on microbial material in the composition of source OM. In some samples there is a slight predominance of even compounds K_{odd}C₁₅-C₂₁ – 0.94-0.97 (Table). According to some researchers, the predominance of even compounds among C₁₄-C₂₂ is inherited from the fat of marine organisms (Tissot, Welte, 1984).

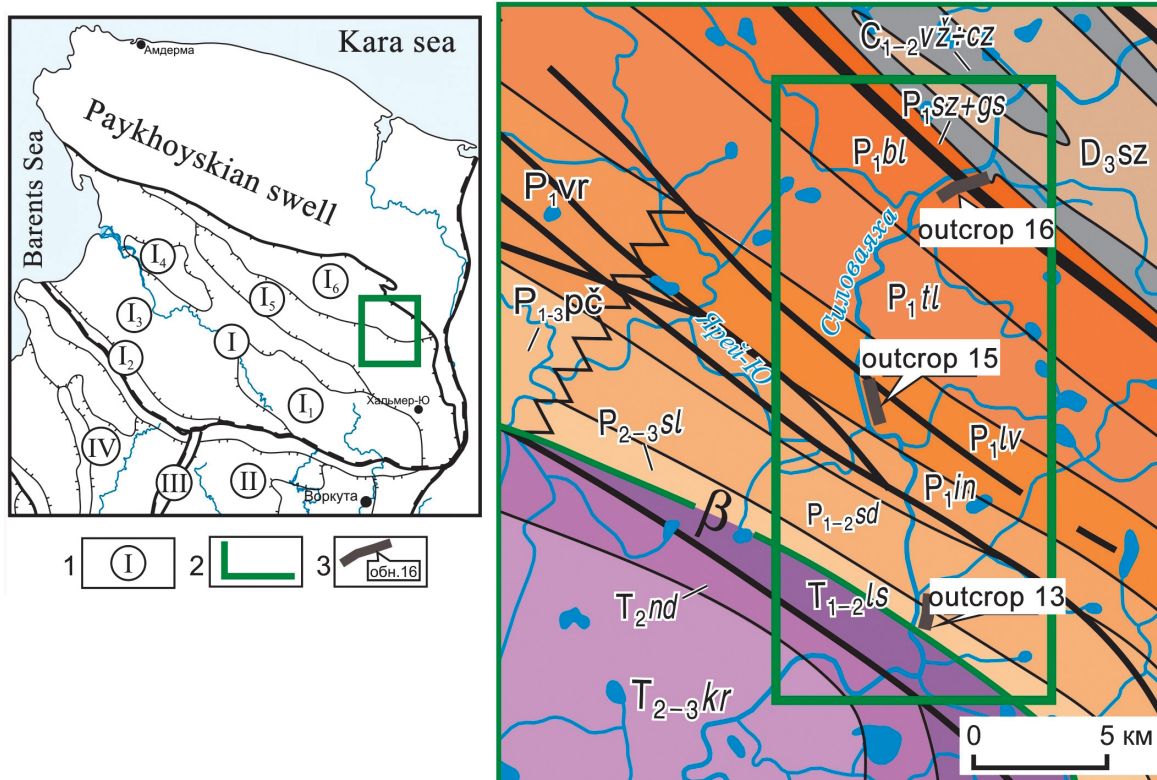


Fig. 1. Geological map of the area under study (Shishkin et al., 2012). 1 – numbers of tectonic elements, 2 – boundary of investigations region, 3 – studied outcrops and their numbers. Tectonic elements: I – Korotaihinsky depression, II – Verhnevorkutinsky dislocation zone, I₅ – Vashutkino-Talotinsky thrust, I₃ – Labogeytsky ledge, I₄ – Odindoksky anticlinal zone, I₅-I₆ – fold-thrust zones (I₅ – Pestanshorskyy, I₆ – Sabriyaginsky); II – Vorkutinsky cross uplift; III – Chernyshev ridge; IV – Varandey-Adzvinzky structural zone.

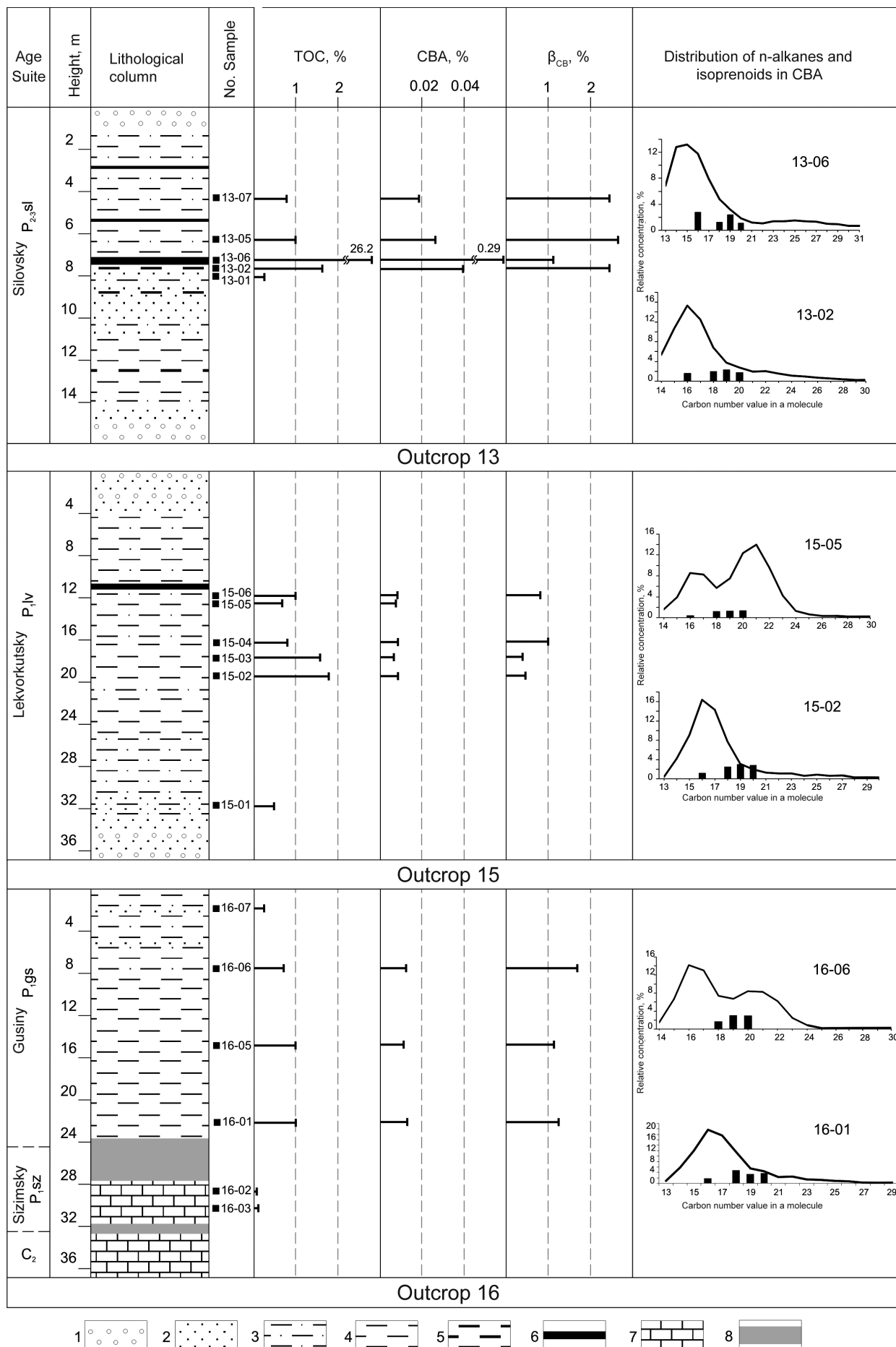


Fig. 2. Lithological-geochemical section of the Permian sediments along the river Silovayaha. 1 – conglomerate, gravelite; 2 – sandstone; 3 – siltstone; 4 – mudstone, 5 – carbonaceous mudstone; 6 – coal; 7 – limestone; 8 – interval without outcrops.

Age	P _{2-3sl}				P _{1lv}					P _{1gs}		
Sample	13-02	13-05	13-06	13-07	15-02	15-03	15-04	15-05	15-06	16-01	16-05	16-06
Catagenesis gradation	MK ₃ –MK ₅				MK ₅					AK		
C ₁₃ –C ₁₈	68,85	76,17	69,91	67,80	71,46	73,96	57,28	33,93	71,85	67,33	70,06	51,38
C ₁₉ –C ₂₄	17,56	14,79	12,04	18,06	12,67	11,51	29,27	59,44	15,17	17,46	16,15	39,48
>C ₂₅	3,28	0,94	8,93	2,53	2,88	0,99	4,82	1,52	0,87	1,55	0,00	0,00
∑i-alkanes	10,31	8,10	9,11	11,61	12,99	13,54	8,62	5,11	12,11	13,65	13,79	9,14
$\frac{\sum H(C_{14}-C_{20})}{\sum H(C_{21}-C_{30})}$	6,44	11,58	5,37	8,94	9,04	11,84	2,85	1,58	10,15	8,41	10,82	3,26
K _{HЧ} C ₁₅ –C ₂₁	1,02	1,03	1,06	1,06	0,97	0,95	0,94	1,06	0,95	0,94	1,00	1,03
*K _Ч C ₁₆	1,32	1,32	1,12	1,20	1,40	1,53	1,46	1,40	1,53	1,34	1,42	1,44
**K _{HЧ} C ₁₇	1,13	1,24	0,96	1,24	1,19	1,16	1,24	1,17	1,15	1,12	1,09	1,21
<i>h</i> -C ₁₇ / <i>h</i> -C ₂₅	14,01	22,20	5,34	18,42	17,52	20,82	6,25	13,80	23,18	20,59	–	–
Pr/Ph	1,36	1,03	2,15	0,94	1,06	1,12	1,04	0,94	1,09	0,89	1,09	1,02
Pr/ <i>h</i> -C ₁₇	0,19	0,14	0,30	0,18	0,21	0,21	0,17	0,15	0,19	0,19	0,25	0,23
Ph/ <i>h</i> -C ₁₈	0,25	0,26	0,23	0,31	0,37	0,39	0,31	0,24	0,35	0,33	0,42	0,40
Pr+Ph/ H _Ч C ₁₇ +H _Ч C ₁₈	0,21	0,18	0,28	0,23	0,26	0,27	0,22	0,19	0,24	0,24	0,31	0,29

Table. Geochemical parameters of saturated hydrocarbons in Permian deposits in the northeast of Korotaihinsky depression (river Silovayaha).

* – $2 * C_{16} / (C_{15} + C_{17})$ ** – $2 * C_{17} / (C_{16} + C_{18})$.

The distribution of n-alkanes reflects the predominance of sapropel base in the OM, but with a small admixture of humus component, more manifested in coal. Despite the formation of the considered coal in marsh environments, a large proportion of light hydrocarbons characterize allochthonous bitumen, which once again confirms the increased sorption capacity of carbonaceous rocks.

A number of bitumen samples are characterized by a

different distribution of saturated hydrocarbons (Fig. 2). In samples of 15-04, 15-05 and 16-06, where the proportion of low molecular weight alkanes of n-C₁₃–C₁₈ falls from 33.93 to 57.28%, and content of medium n-alkanes increased to 29.27–59.44 % (Table), the chromatograms clearly show bimodal distribution with n-alkane peaks at n-C₁₆, n-C₁₇ and n-C₂₁ (Fig. 3 c,d). These samples have the lowest ratios $\Sigma n(C_{14}-C_{20}) / \Sigma n(C_{21}-C_{30})$ – 1.58–2.36. This character of the

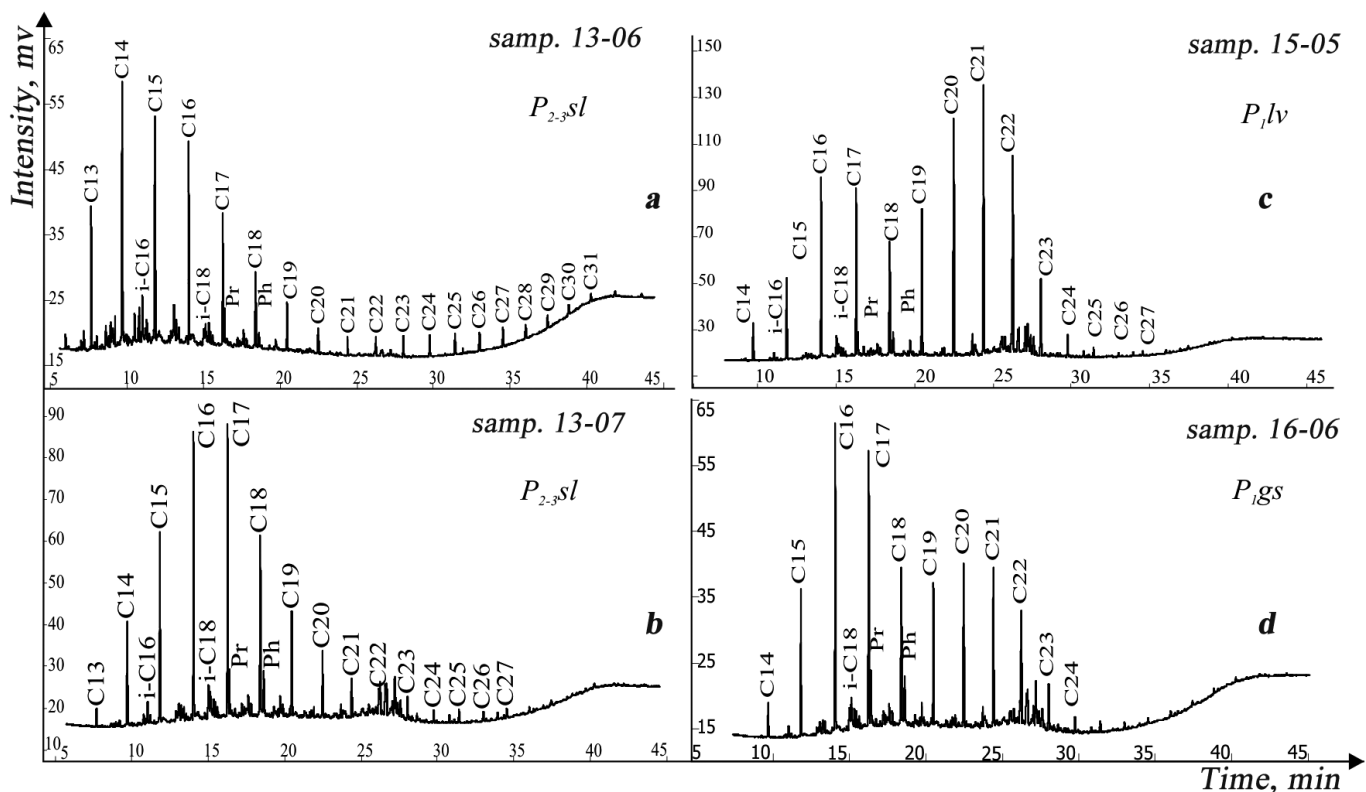


Fig. 3. Chromatograms of the molecular weight distribution of normal and isoprenoid alkanes in bitumens.

molecular weight distribution in bitumen indicates of different initial composition of OM.

All isoprenoid samples studied (where we could identify $i\text{-C}_{16}\text{-C}_{20}$) are characterized by low concentrations. They accounted from 5.11 to 13.79%. It is believed that the ratio of pristane ($i\text{-C}_{19}$) to phytane ($i\text{-C}_{20}$) (Pr/Ph) is indicative of redox conditions in diagenesis for the initial OM (Hunt 1982; Tissot, Welte, 1984; Peters, Moldowan, 1993). In most of the samples there is slight predominance of pristane-phytane ratio. The ratio of Pr/Ph ranges from 0.94 to 1.36, and only for one sample it is increased to 2.15 (Table). This may indicate that the accumulation of the initial OM proceeded in sub-oxidizing environment.

Results of katagenesis modeling (Koopmans et al., 1998; Bushnev et al., 2004) suggest a possible increase in the value of this ratio in the range 0.6-1.5 only due to the growth of the thermal transformation of OM. In general, considered bitumens differ in the composition of the original OM, its accumulation conditions and maturity. OM is very mature, as evidenced by geochemical parameters, namely the maturity coefficient $K_1 = (\text{Pr} + \text{Ph}) / (\text{C}_{17} + \text{C}_{18}) < 0,3$ (it is known that increasing catagenesis of OM leads to a decrease in this ratio (Connan, Cassow, 1980)), as well as the ratio of pristane to heptadecane (Pr/n- C_{17}) and phytane to n-oktadecane (Ph/n- C_{18}), the values of which are generally less 0.4.

The above patterns of molecular weight distribution of iso- and n-alkanes indicate the presence of similar biological markers in bitumens formed in different depositional conditions. The main source of HC generation was sapropel OM, but there was a mixed substance with various impurities of humus component. Bitumens of considered deposits are also mixed (residual autochthonous and allochthonous), in which there are one or other allochthonous fractions of hydrocarbons. Similar features in the composition of bitumen are also noted in the surrounding areas of Korotaihinsky and Kosyu-Rogovsky depressions, where Permian deposits contain genetically heterogeneous mixed bitumens (Anishchenko et al., 2004; Bazhenova et al., 2008; Kotik, 2015; 2016).

Conclusion

The content of organic carbon in the Permian sediments increases regularly in clay-carbonaceous rocks at higher bitumen content in the Upper Permian part of the section. The distribution of n-alkanes and isoprenoids in bitumens indicates a mixed nature with their significant contribution to the sapropel component of OM and the presence of migration of light hydrocarbons.

The values of geochemical and pyrolytic data characterize the Permian deposits as primarily gas-source with low and middle generating potential. The high maturity degree of OM and implementation of its hydrocarbon potential is confirmed by pyrolytic, coal-petrographic and bitumen research methods.

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