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# Petroleum source rocks of the Silurian deposits on the Chernov swell (Timan-Pechora basin)

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Abstract. Silurian source rocks are among the least studied in the Timan-Pechora basin. This is mainly due to their occurrence at great depths (3.0–4.5 km) and the limited penetration of this stratigraphic interval by wells. Another source of information is the outcrops of the Silurian, which are known in the eastern and northeastern parts of the Timan-Pechora basin. The studied section of the Silurian deposits is exposed on the Padimeityvis River, located on the Chernov swell in the northeastern part of the basin. This article is devoted to the study of Silurian source rocks based on the results of lithological, coal petrographic studies and geochemistry of organic matter. The studied section is composed of carbonate and clay-carbonate deposits formed in shallow-water shelf conditions. Most of the section, composed of microcrystalline and microcrystalline with bioclasts limestones, is characterized by low concentrations of organic matter (TOC is generally less than 0.3 %). Elevated TOC contents (up to 1.16 %) are characteristic of clay-carbonate rock varieties, which make up about 20 % of the section. Sediments with increased concentrations of organic matter were formed in isolated and deepened areas of the bottom of the shallow-water basin as a whole. Assessment of the catagenetic transformation based on Rock-Eval pyrolysis data, coal petrographic studies, and conodont color indices showed that organic matter reached the conditions of the middle-end of the main oil generation zone (gradation MC<sub>2</sub>-MC<sub>3</sub>). The obtained geochemical characteristics (TOC, S<sub>2</sub>, HI), taking into account a certain level of organic matter maturity, indicate that the Silurian source rocks had an average hydrocarbon potential.

Keywords: Chernov swell, Silurian deposits, source rocks, organic matter, catagenesis, hydrocarbons

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## Introduction

Silurian deposits in the Middle Ordovician-Lower Devonian oil and gas bearing complex in the Timan-Pechora basin are considered as one of the sources for the generation of hydrocarbons (HC) (Bazhenova et al., 2008; Klimenko, Anischenko, 2010; Danilevskiy et al., 2003). Oil deposits in Silurian sediments have been established in the territories adjacent to the Chernov swell – the Chernyshev Ridge and the Varandey-Adzva structural zone. The presence of petroleum source rocks with geochemical parameters necessary for generation processes indicates the generation of hydrocarbons in the Silurian deposits. The assessment of the oil source properties in the Silurian deposits in the studied area of the Timan-Pechora basin is given in a few publications and on limited core material (Bazhenova

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et al., 2008, Danilov et al., 2011, Kotik et al., 2016, Pesetskaya, Pavlova, 1997). This is mainly due to their occurrence at great depths (3.0–4.5 km) and the limited penetration by wells of this stratigraphic interval. The lack of factual material can be compensated for by studying the Silurian deposits in outcrops, which are known at the Chernov swell. The study of the structure of the Silurian sedimentary section in outcrops, the identification of potential oil and gas-generating strata and the characteristics of organic matter (OM) are the goals of the lithological, organic geochemical and coalpetrographic studies, the results of which are discussed in this article.

#### Area and object of research

The study area is located in the northeast of the Timan-Pechora oil and gas bearing basin within the Chernov swell. The Chernov swell is a linear structure that separates the Korotaikha depression from the Varandey-Adzva structural zone and the Kosyu-Rogov depression (Timonin, Yudin, Belyaev, 2004) (Figure 1). The northwestern half of the swell (Vashutkino-Talota

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Fig. 1. Overview map of the studied area and the location of the studied section of the Silurian deposits. A – tectonic zoning map (Belonin et al., 2004), B – geological map (State Geological Map ..., 2007), C – photo of outcrops of Silurian deposits in the canyon of the Padimeityvis river.

thrust) in the form of monoclinal subsiding deposits has a simpler structure, and the southeastern half is complicated by back-thrasts, forming a wedge shape in the section.

The section of the Silurian deposits studied by us for about 500 meters is exposed in the canyon of the river Padimeityvis of the left tributary of the river Korotaikha. The bedding of the rocks is fairly consistent, with a general dip to the north at an angle of 60–65°. The exposed thickness of the section is about 460 m. In the age range, the Silurian deposits are represented here by the Wenlock, Ludlow, Pridoli stages (Chernov, 1972; Beznosova, 2008).

# Methods

The complex of studies included petrographic and chemical studies of the lithological composition of rocks, as well as coal petrographic and geochemical studies of dispersed OM.

Microscopic study of the OM of rocks was carried out in polished sections under simple reflected and ultraviolet light on a Leica DM-2500 microscope (Lomonosov Moscow State University, Moscow), as well as in thin sections in transmitted light on a MeF-2 microscope.

The content of organic carbon (TOC, %) in the rock was determined on an AN-7529 express analyzer by combustion in an oxygen stream of samples pretreated with 10% hydrochloric acid. The yield of bitumen in the rocks was determined by hot extraction with chloroform in Soxhlet apparatus. Gas chromatographic analysis of hydrocarbons in the composition of the saturated fraction (n-alkanes and isoprenoids) of chloroform extracts was carried out on a Kristall 2000M device. This set of studies was carried out at the Geoscience Center (Syktyvkar).

The pyrolytic characteristics of OM  $S_1$ ,  $S_2$ ,  $T_{max}$  were obtained on a Source Rock Analyzer (SR Analyzer, Humble Instruments) (IPGG SB RAS, Novosibirsk). To determine the influence of free hydrocarbons on the magnitude of the  $S_2$  peak and obtain more correct values of the parameter  $T_{max}$ , repeated pyrolysis of rock samples after extraction with chloroform was performed on a Rock-Eval 6 Standard (Vinci Technologies) device (VNIGNI, Moscow).

# **Results and discussion** *Lithological characteristics of the section*

In the Silurian period, the area under consideration was a marine epicontinental basin with settings of a typical shallow-water carbonate platform (Antoshkina et al., 2011, 2015). The facies conditions in the sedimentary basin changed repeatedly, which led to the accumulation of carbonate and clay-carbonate sediments of different material composition and structural-textural features. In the studied section of the Silurian deposits, according to the peculiarities of the lithological composition, 4 members are distinguished from bottom to top: claylimestone, limestone, clay-dolomite-limestone and limestone (Figure 2).

The first clay-limestone pack (160 m) is composed of limestones, dolomitic limestones with interlayers of clay limestones and marls (Figure 3, a-e). Limestones are represented by wavy-layered microbial-clotted,



Fig. 2. Lithological composition and distribution of geochemical parameters along the section. 1 - limestone, 2 - dolomitic limestone, 3 - clay limestone, 4 - stromatolitic limestone, 5 - limestone dolomite, 6 - clay limestone dolomite, 7 - marl, 8 - Rock-Eval pyrolysis data: <math>a - before extraction, b - after extraction.

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microcrystalline and microcrystalline with bioclasts varieties with spotty-banded and spotty textures. Limestones with the structure of mudstones and wackstones prevail, less often pack-wackstones (Figure 3, a, b). In the upper part, the proportion of clay-carbonate layers increases. The limestones are dominated by microcrystalline mudstones and peloid-ostracodic wackstones with small lithoclasts (Figure 3, c). The second limestone pack (161 m) is composed mainly of bioclastic and microcrystalline with bioclasts limestones, in structure by pack-wackstones, less often by mudstones (Figure 3, f, e). The lower and upper parts of the pack contain limestones with stromatolite biostromes. The third member (84 m) has a clay-dolomite-limestone composition. It is composed of limestones, dolomitic peloid-bioclastic limestones, and limestone clay dolomites (Figure 3, h-j). The structure is dominated by mudstones and wackstones. The section is completed by a limestone member (52 m), composed of limestone mudstones with rare bioclasts (Figure 3, k) and stromatolite limestones. The top of the pack contains bioclastic limestones with a packstone structure (Figure 3, 1).

### Facial conditions of OM accumulation

Consideration of the lithological composition in the studied section shows that the formation of Silurian deposits in the conditions of a shallow shelf did not contribute to the accumulation of petroleum source deposits with a consistent thickness and enriched OM (Figure 2). The accumulation of clay-carbonate deposits with increased TOC contents in the studied section is associated with individual deepened areas of the bottom of the shallow-water basin as a whole.

OM-enriched clay limestones and dolomites, which mainly compose packs I and III, were formed under sublittoral conditions. Microcrystalline structure, bedding character, rare traces of bioturbation, poor faunal remains indicate the relative isolation of the sedimentation basin (Figure 4, a). In the deeper areas of the sublittoral, during the periods of maximum sea level, the most OM enriched marls were formed (Figure 4b). In both cases, the sedimentation environment favored the relative accumulation of organic material and its conservation. This is due to the fact that the limited circulation of water prevents free oxygen exchange and decomposition of OM by aerobic heterotrophic organisms. The presence of terrigenous admixtures in the sediments also favors the accumulation of OM. The adsorption of dissolved OM on the surface of mineral particles promotes faster deposition through the water column and increases its protection from destruction by bacteria (Bazhenova et al., 2000).

The OM poverty in bioclastic and peloid-bioclastic limestones characteristic of packs II and IV is due to their



Fig. 3. The main lithological types of rocks of the Silurian deposits composing the identified units. Pack I: a - microcrystalline limestone, mudstone, sample 6-1, b - microcrystalline limestone with bioclasts, wackstone, sample 17-2, c - peloid-ostracod limestone, wackstone, sample 23-3, d - clay limestone, mudstone, sample 13-1, e - marl, sample 26-1; Pack II: f - bioclastic limestone, packstone, sample 30-2, g - microcrystalline limestone with bioclasts, wackstone, sample 31-5, pack III: h - limestone dolomite, mudstone, sample 36-5, i - peloid-bioclastic dolomite, mudstone, sample 51-1; pack IV: k - microcrystalline limestone, mudstone, sample 51-1; pack IV: k - microcrystalline limestone, mudstone, sample 65-1, l - bioclastic limestone, packstone, sample 68-5.

accumulation in the littoral-sublittoral zone with active hydrodynamics of the aquatic environment and the vital activity of benthic organisms that did not contribute to the retention and concentration of OM (Figure 4b). Active circulation in the water column provided constant oxygen replenishment, which was spent on the decomposition of OM. Bioturbation of sediments by benthic organisms provided additional aeration of sediments and degradation of OM (Demaison, Moore, 1980).

#### Content, HC potential and catagenesis of OM

The TOC concentrations in the studied rocks vary from 0.02 to 1.16% and depend on their lithological composition (Figure 2). Bioclastic, peloid-bioclastic, microcrystalline and microcrystalline with bioclasts limestones are characterized by low TOC contents, generally not exceeding 0.30%. In clay limestones and dolomites (IRR – insoluble rock residue – 9–21%), the TOC concentration rises to 0.74%. The maximum contents up to 0.83–1.16% are found in carbonateargillaceous rocks with an increased clay component



Fig. 4. Model of accumulation of OM-enriched Silurian sediments in isolated (lagoon) (a) and open sea (sublittoral) (b) conditions. 1 - phyto- and zooplactone; 2 - organic matter; 3 - bioturbation; 4 - benthic fauna.

(IRR - 43–55%). In general, clay-carbonate deposits with an increased OM content are mainly distributed in members I and III, with a total thickness of about 110 m, which is about 20% of the section (Figure 2).

The values of the parameters  $S_1$  and  $S_2$  obtained during the Rock-Eval pyrolysis for the studied samples are 0.10–0.68 mg HC/g rock and 0.21–2.76 mg HC/g rock, respectively (Table 1, Figure 2). The hydrogen index (HI) varies within the range of 122–363 mg HC/g TOC. The generation potential ( $S_1 + S_2$ ), like the TOC content, depends on the lithology of the rocks. The highest values are found in clay limestones and dolomites -1.06-2.86 mg HC/g rock. For bioclastic limestones, the S<sub>1</sub> + S<sub>2</sub> value is the lowest -0.31-0.37 mg HC/g rock.

Pyrolysis studies of samples after hot extraction, partially freed from HC and resinous-asphaltene components, show a reduction in peaks  $S_1$  and  $S_2$ . Parameter  $S_1$  significantly decreases and levels out, amounting to 0.01–0.05 mg HC/g rock (Figure 2, Table 1).  $S_2$  is reduced by 15–79%. A decrease in the  $S_2$  peak leads, respectively, to a decrease in the HI

| Samp. | Rock                   | IRR<br>% | TOC,<br>% | TOC <sup>ex</sup> ,<br>% | S <sub>1</sub> ,<br>mg HC/g<br>rock | S <sub>2</sub> , mg HC/g rock | S <sub>1</sub> <sup>ex</sup> ,<br>mg HC/g<br>rock | S2 <sup>ex</sup> ,<br>mg HC/g<br>rock | HI,<br>mg HC/g<br>TOC | HI <sup>ex</sup> ,<br>mg HC/g<br>TOC | T <sub>max</sub> <sup>ex</sup> ,<br>⁰C | PI <sup>ex</sup> |
|-------|------------------------|----------|-----------|--------------------------|-------------------------------------|-------------------------------|---|---------------------------------------|-----------------------|--------------------------------------|--|------------------|
| 1-3   | clay limestone         | 12       | 0.70      | 0.66                     | 0.21                                | 0.85                          | 0.03  | 0.62                                  | 122                   | 73                                   | 441                                    | 0.05             |
| 1-6   | limestone              | 9        | 0.34      | 0.30                     | 0.10                                | 0.51                          | 0.05  | 0.30                                  | 148                   | 71                                   | 438                                    | 0.14             |
| 13-1  | clay limestone         | 21       | 0.62      | 0.57                     | 0.24                                | 1.06                          | 0.02  | 0.68                                  | 170                   | 110                                  | 452                                    | 0.02             |
| 15-1  | marl                   | 43       | 1.10      | 1.06                     | 0.18                                | 1.35                          | 0.03  | 1.15                                  | 123                   | 111                                  | 448                                    | 0.02             |
| 21-1  | marl                   | 48       | 1.16      | 1.13                     | 0.10                                | 2.76                          | 0.01  | 1.70                                  | 238                   | 168                                  | 440                                    | 0.01             |
| 26-1  | marl                   | 44       | 0.83      | 0.77                     | 0.23                                | 1.03                          | 0.02  | 0.49                                  | 124                   | 67                                   | 438                                    | 0.03             |
| 30-3  | bioclasts<br>limestone | 7        | 0.15      | 0.12                     | 0.10                                | 0.21                          | 0.02  | 0.05                                  | 144                   | 56                                   | 421                                    | 0.30             |
| 34-1  | bioclasts<br>limestone | 5        | 0.19      | 0.16                     | 0.10                                | 0.27                          | 0.02  | 0.11                                  | 140                   | 52                                   | 429                                    | 0.18             |
| 36-1  | clay dolomite          | 15       | 0.44      |                          | 0.19                                | 0.95                          |   |                                       | 217                   |                                      |  |                  |
| 36-4  | limestone<br>dolomite  | 11       | 0.31      | 0.28                     | 0.10                                | 0.67                          | 0.01  | 0.52                                  | 215                   | 162                                  | 446                                    | 0.02             |
| 51-2  | marl                   | 55       | 0.98      | 0.91                     | 0.25                                | 1.81                          | 0.03  | 1.89                                  | 184                   | 172                                  | 440                                    | 0.02             |
| 65-2  | clay limestone         | 10       | 0.55      | 0.48                     | 0.68                                | 1.98                          | 0.02  | 0.41                                  | 363                   | 76                                   | 435                                    | 0.05             |

Table 1. Data from pyrolysis studies (Rock-Eval). IRR – insoluble rock residue; TOC – organic carbon content; TOC<sup>ex</sup>, – organic carbon content after extraction; HI – 100\*S<sub>2</sub>/TOC; S<sub>1</sub><sup>ex</sup>, S<sub>2</sub><sup>ex</sup>, HI<sup>ex</sup>, T<sub>max</sub><sup>ex</sup>, PI<sup>ex</sup> – S<sub>1</sub><sup>ex</sup> / S<sub>1</sub><sup>ex</sup>, – results of pyrolysis of samples after extraction

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The degree of catagenetic transformation of OM was determined on the basis of pyrolysis data, coal petrographic studies, and conodont color alteration index (CAI).

The level of catagenetic transformation of OM according to the results of pyrolysis was assessed by two parameters – the  $T_{max}$  value and the values of the productivity index (PI). The  $T_{max}$  value varies in the range 421–452 °C. The PI index values for most of the samples vary in the range of 0.02–0.14 (Table 1, Figure 5). The high PI values of 0.18–0.30 observed for samples 30-3 and 34-1 at low values of  $T_{max}$  421–429 reflect the effect of the presence of migratory bitumen in the rocks (Lopatin, Emets, 1987) (Figure 5). In general, the obtained  $T_{max}$  and PI data indicate the OM maturity level corresponding to the middle-end of the main oil generation zone (MC<sub>2</sub> – MC<sub>3</sub>).

The results of determining the OM maturity from the pyrolysis data are consistent with the earlier assessment of catagenesis based on the CAI data (Kotik et al., 2017). The color change of conodont elements is used as an approximate estimate of the degree of thermal transformation of the host rocks and, accordingly, the OM contained in them. The obtained CAI values for the Silurian deposits are 1.5-2 (Figure 6), which indicates the intensity of heating of the enclosing strata up to 140 °C (Epstein, Epstein, Harris, 1977). This level of thermal impact corresponds to the conditions of catagenesis at the MC<sub>2</sub> gradation of the main zone of oil generation (Handbook..., 1998).

Coal petrographic studies did not allow assessing the catagenetic transformation of OM due to the lack of macerals suitable for measuring the reflection index. However, the presence of qualitative features such as a weak glow in ultraviolet light or its complete absence,



Fig. 5. Catagenesis of OM according to the values of pyrolysis parameters  $T_{max}$  and productivity index (PI)

Earlier studies by D.A. Bushnev, N.S. Burdel'naya (2012) for samples of Silurian deposits of the Padimeityvis river and its tributary Bezymanny, a higher catagenetic maturity of OM was established. According to the distribution of polycyclic HCs of the sterane and hopane series, OM catagenesis reaches the  $MC_2 - MC_3$  gradations and possibly higher values (Bushnev, Burdel'naya, 2012).

Thus, the totality of the available data indicates the level of OM catagenetic transformation corresponding to the middle-end of the main oil generation zone. The obtained geochemical characteristics (TOC,  $S_2$ , HI), taking into account a certain level of OM maturity, indicate that the studied petroleum source rocks of the Silurian deposits had an average HC potential.

## Composition and type of OM

The study of samples of clay-carbonate rocks (samples 21-1, 26-1, 51-2), the most enriched in OM by coal-petrographic methods, did not reveal the content of such macerals as bituminite (pre-mature, mature) and "hard bitumen" (post-mature) (Taylor, Liu, Teichmüller, 1991). All organic components are bitumen, which are the end products of the transformation of algogenic OM. In rocks, bitumen is present in the form of films between mineral grains and deposits, which gives it a brownish tint in simple reflected light (Figure 7, a-c). The most distinct distribution of bitumen in the rock is observed in ultraviolet light, where they form extended layers and separate isolated inclusions (Figure 7, d-f).



Fig. 6. Changes in the catagenetic transformation of OM along the section



Fig. 7. Micrographs of bitumen in reflected (a-f) and transmitted (g-i) light. a-c - reflected white light, oil immersion, x 50: a-sample 21-1, b-sample 26-1, c-sample 51-2; d-f-ultraviolet light, oil immersion, x 50: d-sample 21-1, e-sample 21-1, f-sample 51-2. b-bitumen. Black mark in the center of the frame 5x5  $\mu$ m. g-i-transmitted light: g-sample 35-3, h-sample 29-1, i-sample 23-3.

In carbonate rocks, which are a kind of reservoirs for hydrocarbons, bituminous content is manifested in a different way. Bitumen fill in the rock stylolite seams, cracks and voids, which indicates their partial or significant movement relative to the source rock (Figure 7, g-i). The carbonate rocks are also characterized by an increased content of bitumen against a background of low concentrations of TOC, the bitumen coefficient ( $\beta_{CB}$ ) is 14–34% (Table 2). High  $\beta_{CB}$  values also indicate the allochthonous nature of bitumen in the host rocks. The study of HC composition of the saturated fraction of bitumen extracted from rocks was carried out according to the data of gas chromatography analysis. The previously studied features of the hydrocarbon composition of bitumen in the Silurian deposits of the Chernov swell showed differences in the nature of the molecular weight distribution of n-alkanes and isoprenoids (Kotik et al., 2017). Studies have shown that the nature of HC distribution depends on the lithological composition of the sediments (carbonate/clay content).

In the petroleum source rocks of clay-carbonate composition, bitumen of heavier hydrocarbon composition with an increased content of medium and high molecular weight n-alkanes are almost everywhere (Figure 8, a, b). Two types of distribution of normal and isoalkanes have been established. Bitumens of the first group (samples 15-1, 21-1, 26-1, 51-2) are characterized by the maximum distribution of n-alkanes in the  $n-C_{13}$ - $C_{20}$  range and the highest n- $C_{17}$ /n- $C_{27}$  ratio – 1.26–2.84 (Table 2, Figure 8, a). The lighter composition of the HC fraction is confirmed by the presence of light HC accumulations in the rocks (Figure 7, f). For the second group of samples (1-3, 1-6, 10-1), the maximum of the distribution of n-alkanes is shifted to the highmolecular range > n-C<sub>20</sub>, the values of the n-C<sub>17</sub>/n-C<sub>27</sub> ratio for them are the lowest -0.36-1.42 (Table 2, Figure 8, b). In such rocks, there is a greater amount of clay-bituminous interlayers and streaks of bitumen with an increased content of resinous-asphaltene components, without visible luminescence. The ratio of isoprenoid and n-alkanes such as Pr/n-C<sub>17</sub>, Ph/n-C<sub>18</sub>, Pr+Ph/C<sub>17</sub>+C<sub>18</sub> (isoprenoid coefficient, Ki) and Pr/Ph for the studied samples is also determined by the type

| No. | Samp. | TOC,% | TOC <sup>ex</sup> , % | CEB,%  | $\beta_{CB},\%$ | $\beta_{CB}^{ex}$ , % | <i>н</i> -С <sub>17</sub> / | Pr /                      | Ph /              | Pr+Ph/              | Pr / Ph | CPI  |
|-----|-------|-------|-----------------------|--------|-----------------|-----------------------|-----------------------------|---------------------------|-------------------|---------------------|---------|------|
|     |       |       |                       |        |                 |                       | <i>н</i> -С <sub>27</sub>   | <i>н</i> -С <sub>17</sub> | н-С <sub>18</sub> | $H-C_{17}+H-C_{18}$ |         |      |
| 1   | 1-3   | 0.70  | 0.66                  | 0.0527 | 8               | 8                     | 0.81                        | 0.51                      | 0.83              | 0.66                | 0.71    | 1.02 |
| 2   | 1-6   | 0.34  | 0.30                  | 0.0468 | 14              | 15                    | 0.67                        | 0.45                      | 0.69              | 0.57                | 0.68    | 0.97 |
| 3   | 10-1  | 0.50  | 0.45                  | 0.0593 | 12              | 13                    | 0.91                        | 0.26                      | 0.45              | 0.34                | 0.80    | 0.99 |
| 4   | 13-2  | 0.28  | 0.22                  | 0.0414 | 15              | 17                    | 1.17                        | 0.22                      | 0.31              | 0.27                | 0.78    | 0.95 |
| 5   | 15-1  | 1.10  | 1.06                  | 0.0551 | 5               | 5                     | 3.43                        | 0.16                      | 0.18              | 0.17                | 1.39    | 0.96 |
| 6   | 20-1  | 0.46  | 0.37                  | 0.1079 | 23              | 29                    | 0.64                        | 0.20                      | 0.28              | 0.24                | 0.76    | 0.97 |
| 7   | 21-1  | 1.16  | 1.13                  | 0.0386 | 3               | 3                     | 1.26                        | 0.08                      | 0.08              | 0.08                | 1.15    | 0.97 |
| 8   | 23-3  | 0.18  | 0.15                  | 0.0383 | 21              | 26                    | 1.06                        | 0.10                      | 0.12              | 0.11                | 0.85    | 0.99 |
| 9   | 26-1  | 0.83  | 0.77                  | 0.0748 | 9               | 10                    | 2.49                        | 0.15                      | 0.18              | 0.16                | 1.26    | 0.97 |
| 10  | 29-1  | 0.18  | 0.16                  | 0.0298 | 17              | 19                    | 1.13                        | 0.12                      | 0.13              | 0.12                | 1.08    | 0.98 |
| 11  | 30-3  | 0.15  | 0.12                  | 0.0375 | 25              | 31                    | 2.84                        | 0.06                      | 0.09              | 0.08                | 1.04    | 0.95 |
| 12  | 34-1  | 0.19  | 0.16                  | 0.0420 | 22              | 27                    | 1.74                        | 0.12                      | 0.25              | 0.17                | 0.87    | 0.95 |
| 13  | 35-3  | 0.15  | 0.11                  | 0.0504 | 34              | 46                    | 0.36                        | 0.15                      | 0.16              | 0.15                | 1.02    | 0.99 |
| 14  | 36-4  | 0.31  | 0.28                  | 0.0415 | 13              | 15                    | 0.97                        | 0.10                      | 0.25              | 0.16                | 0.67    | 0.97 |
| 15  | 42-1  | 0.08  | 0.06                  | 0.0272 | 34              | 47                    | 1.42                        | 0.18                      | 0.37              | 0.25                | 0.87    | 0.98 |
| 16  | 51-2  | 0.98  | 0.91                  | 0.0891 | 9               | 10                    | 1.81                        | 0.26                      | 0.40              | 0.31                | 1.03    | 1.01 |
| 17  | 65-1  | 0.25  | 0.21                  | 0.0440 | 18              | 20                    | 2.63                        | 0.14                      | 0.35              | 0.20                | 0.98    | 0.96 |

 $\begin{array}{l} \mbox{Table 2. Geochemical parameters of bitumen of the Silurian deposits. CEB- chloroform extracted bitumen. $\beta_{CB}$- CEB/TOC*100; $\beta_{CB}^{ex}$- CEB/TOC^{ex}$100; CPI-\frac{1}{2}*(C_{25}+C_{27}+C_{29}+C_{31}+C_{32})/(C_{26}+C_{28}+C_{30}+C_{32}+C_{34})+(C_{25}+C_{27}+C_{29}+C_{31})/(C_{24}+C_{26}+C_{28}+C_{30}+C_{32})$ \\ \end{array}$ 



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Fig. 8. Chromatograms of the distribution of n-alkanes and isoprenoids in the saturated fraction of bitumen

of molecular weight distribution of hydrocarbons (Table 2). For bitumens with increased concentrations of high molecular weight n-alkanes (Figure 8, b), the values of  $Pr/n-C_{17}$ ,  $Ph/n-C_{18}$ , Ki are higher and phytane predominates (Pr/Ph - 0.67 - 1.08) (Table 2).

In carbonate rocks containing a fraction of displaced bitumen, two types of distribution of n-alkanes are mainly observed. In the first type, the HC maximum is in a wide molecular range  $C_{17}$ – $C_{30}$  (Fig. 8, c). The second type is characterized by a bimodal distribution of n-alkanes with maxima at  $C_{15}$ – $C_{17}$  and  $C_{24}$ – $C_{27}$  (Figure 8, d). For rocks containing bitumen with a bimodal distribution, stylolite seams with bitumen are almost everywhere (Figure 7, g-i). In carbonate rocks, all bitumen are similar to the first group of bitumen of clay-carbonate rocks in terms of variations in the values of the geochemical parameters  $Pr/n-C_{17}$ ,  $Ph/n-C_{18}$ , Ki (Table 2). This allows us to classify them as parautochthonous bitumoids.

Despite the differences in hydrocarbon distribution, common to all studied bitumen is the predominance of odd n-alkanes of the composition  $C_{15}$ ,  $C_{17}$ ,  $C_{19}$  in the middle molecular part, which is a characteristic biomarker of marine OM (Petrov, 1984).

# Conclusion

1. Studies have shown that the Silurian deposits contain petroleum source rocks that had an average HC potential. Clay-carbonate packs with increased generation potential make up about 20% of the sedimentary section.

2. The initial organic material was marine planktonic OM. The accumulation of sediments enriched in organic

matter took place in low energy and deep areas of the bottom of the shallow-water basin as a whole.

3. Evaluation of the degree of catagenetic transformation according to pyrolysis data, conodont color indices and coal petrography indicates that the OM of rocks has reached the conditions of the middle-end of the main oil generation zone.

4. Correspondence of hydrocarbons to the composition of bitumen of carbonate and clay-carbonate sediments indicates the emigration and redistribution of hydrocarbons from petroleum source rocks into more permeable carbonate rocks.

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