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BALTICA Volume 22 Number 2 December 2009 : 89-99

# Organic matter of Early Silurian succession – the potential source of unconventional gas in the Baltic Basin (Lithuania)

***Onytė Zdanavičiūtė, Jurga Lazauskienė***

Zdanavičiūtė, O., Lazauskienė, J. 2009. Organic matter of Early Silurian succession – the potential source of unconventional gas in the Baltic Basin (Lithuania). *Baltica, Vol. 22 (2)*, *89–98*. Vilnius. ISSN 0067–3064.

**Abstract** Increasing demand for alternative energy sources leads to an interest in unconventional hydrocarbons, e.g. natural shale gas. Based on initial evaluation, the Early Silurian graptolite shales are studied as prospective shale gas sources in the Baltic region. This paper addresses the occurrence, generation potential and the volume of unconventional gas in place. New organic geochemistry data and vitrinite like macerals reflectance measurements, incorporated with well logs and core data were used to reveal the potential for shale gas. The Early Silurian shales are organically rich, type II, oil–prone marine sediments. The organic matter content ranges from 0.7 up to 19.2%. Hydrocarbon generation potential ranges from 7 up to 113 kg HC/t rock, and the Hydrogen Index ranges from 136 up to 571 mg HC/g TOC. Maturity of the organic matter increases southwestwards from 0.6 up to 1.94% ($R_0$). The Early Silurian shales in Western Lithuania generated large amounts of hydrocarbons with an estimated volume of expelled hydrocarbons of about $13.75 \times 10^6$ kg. This mass of hydrocarbons is equivalent to $389 \times 10^5$ cubic meters of methane for a section of 1 $km^2$ and 150 m thickness.

***Keywords*** *Organic matter, graptolite shales, Early Silurian, Western Lithuania, shale gas potential.*

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## INTRODUCTION

The worldwide increasing of oil and natural gas consumption has given considerable interest in the new alternative energy sources. So–called unconventional natural gas that includes coal bed methane, shale gas and tight sand gas, is of great interest nowadays. Unconventional gas is the same substance as conventional natural gas, it just accumulates in different than sandstone or carbonate reservoirs. The shale gas is self–sourced thermogenic or biogenic methane, stored in free, adsorbed and dissolved states in reservoirs, predominantly composed of fine grained organic–rich low permeability matrix – mostly shales (Jarvie *et al*. 2007). The gas shales are often both the source rocks and the reservoir for the natural gas. The shale gas production in commercial quantities requires natural and artificial fractures to provide permeability, by applying the hydraulic fracturing technologies and specific low–cost horizontal drilling. The worldwide demand, high energy prices and recent advances in horizontal drilling has enabled shale gas production to become profitable (Horsfield, Schulz, GASH team 2008). Shale gas is exploited in the United States of America and in 2006 production reached 1.1 tcf/year of unconventional gas that comprises 5.9% of annual gas production (Jarvie *et al*. 2007). In that context, regions of Europe, usually considered as unperspective in terms of conventional fossil fuels, might contain targets for shale gas exploration (Horsfield, Schulz, GASH team 2008). Based on the preliminary evaluation of the shale gas potential in Europe, organic rich black shales of different age, e.g. Cambrian–Early Ordovician Alum shale, the Early Silurian Graptolite shale, Early Jurassic Posidonia shale, Carboniferous Namiurian and Early Cretaceous marine shales have been defined as the most perspective formations (Horsfield, Schulz, GASH team 2008).

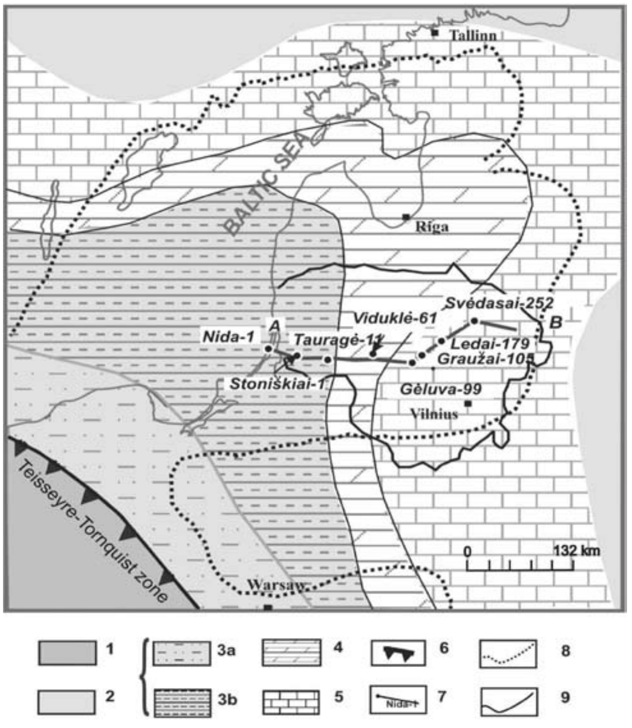


Fig. 1. Location of the Baltic Silurian Basin showing the distribution of Silurian lithofacies (modified after Lazauskiene *et al.* 2003). A–B – line of analyzed cross–section presented in Fig. 2. 1–North German–Polish Caledonides; 2–non–deposition craton area; 3–deep shelf facies: 3a–black graptolite shales; 3b–shaley facies; 4–open shelf facies (marlstones and limestones); 5–lagoonal facies (limestones, dolomites); 6–Caledonian deformation front; 7–location of cross–section A–B; 8–recent erosional limit of Silurian strata; 9–boundaries of facial zones.

The Early Palaeozoic organic rich Upper Cambrian–Tremadoc black shales (Alum shales) and the Early Silurian graptolite shales are considered as the most prospective for the shale gas potential in the Baltic Sea region. While the Cambrian–Tremadocian Alum shales occur mostly in Scandinavia (Buchardt, Lewan 1990), the Silurian shales are distributed in the territory of Lithuania (Figs 1, 2). Within the Silurian succession in Lithuania, the oil source rocks comprise the complex of Llandovery, Wenlock and the Early Ludlow shaley strata.

For the evaluation of the shale gas potential the key issues are to predict the volume of gas in place and reservoir qualities of shaley layers. Gas generation potential of gas shales is mostly controlled by the TOC content, type and maturity of the organic matter and the reser-

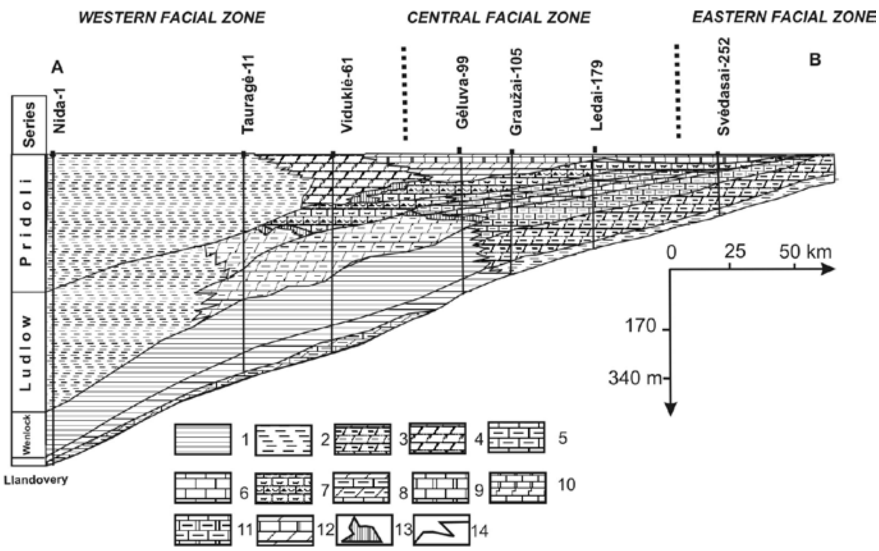


Fig. 2. Lithofacial cross–section throughout the Silurian succession in Lithuania. Line of cross–section A–B is shown in Fig. 1. 1–black shales with graptolites; 2–carbonaceous claystones; 3–clayey marlstones; 4–carbonaceous marlstones; 5–clayey limestones; 6–limestones; 7–organogenicdetrital limestones; 8–clayey limestones and marlstones; 9–dolomites; 10–dolomites and gypsum; 11–clayey dolomites; 12–dolomites interbedded with marlstones; 13–reefogenic buildups; 14–boundaries of Silurian stages and/or formations.

voir properties (determined by porosity, permeability, fracturing and adsorption potential) of the shales.

As a result of recent hydrocarbon exploration activities, the Early Silurian succession in Lithuania has been quite intensively studied, but only in terms of conventional source rocks potential, mostly focusing on the lithofacies and diagenetic aspects, reservoir properties of the succession (Lapinskas 1996, 2000; Musteikis 1993; Paškevičius 1997; Lazauskiene *et al*. 2002, 2003; Zdanaviciute, Lazauskiene 2004, 2007). Until now no studies have been carried on of the Early Silurian succession in terms of the distribution, generation potential and the prospectivity of shale gas (neither on any of the other unconventional hydrocarbon types).

Thus, this paper brings forward an analysis of the Early Silurian shaley succession in the Western Lithuania with aims to predict the generation, occurrence and the most probable potential of the shale gas. Evaluation of the vertical and lateral occurrence including heterogeneities in content and composition of the organic mater together with estimation of the methane gas volume generated throughout evolution of the Baltic Sedimentary Basin (as a function of maturity and organic mater type) and prediction of the shale gas resources will also be dealt within in this study.

The distribution of shales, prospective in terms of shale gas, is determined based on existing well log, core and seismic data, while the evaluation of the generation potential and volumes of the methane gas is based on the results of the analytic studies of the organic matter and vitrinite reflectance.

## GEOLOGICAL SETTING

The Baltic Sedimentary Basin (BSB) developed as a passive margin basin during the latest Precambrian–Middle Ordovician (Poprawa *et al.* 1999). The change to convergent margin setting related to the collision processes along the south–western rim of the Baltica tectonic plate is recorded during the Late Ordovician–Early Silurian (Lazauskiene *et al.* 2002). The western and central parts of the basin have subsided throughout the Silurian time, while the easternmost part shows the gradual uplift since the Late Silurian. The sedimentary evolution of the BSB during the Silurian is recorded in a more than 1 km thick succession of shales and carbonates in the Lithuania offshore (Lapinskas 2000; Lazauskiene *et* a*l.* 2003) and thins eastwards to 50–100 m (Fig. 2). The structural evolution of the area has had a significant impact on formation of the petroleum play of the BSB. Western Lithuania area is strongly dissected by faults, penetrating the crystalline basement and the Early Palaeozoic succession. The faults, dissecting the sedimentary cover are oriented N–S, W–E, NW–SE and NE–SW predominantly. Two major systems of late Caledonian reverse faults, oriented WSW–ENE and SSW–NNE prevail in the studied area (Fig. 3; Sliaupa *et al.* 2002). The local uplifts are confined to SSW–NNE trending faults, showing rather regular spacing. The Silurian strata deepen south–westward: in the east the depth is ~200 m whereas in the west – 2050 m (Fig. 3). The thickness of the Early Silurian strata varies in a range of 40 meters, the thinnest section of 120 m recorded in the central and south–westernmost part of the area (adjacent to wells Ramučiai–1, Vabalai–1), whereas the thickness increases towards the north and southwest (adjacent to wells Mikoliškės–1) or show the locally restricted increase in thickness adjacent to some wells (e.g. Stoniškiai–1; Fig. 4).

The facial composition of the Silurian succession in the BSB shows considerable heterogeneity, being related to changes in basin architecture during the Silurian and different sedimentary palaeoenvironments. Mostly terrigenous facies (graptolite shales and claystones) dominate in the western and central parts of the Lithuania, grading into marlstones in the transitional zone and to the limestone and dolomite facies, forming the carbonate platform in the East (Figs 1, 2). The Early Llandovery terrigenous–calcareous succession was formed in response to the major sea level fall at the Ordovician–Silurian boundary. Up to 40 m thick Early Llandovery basal shallow water organogenic–detrital carbonates, accumulated in the eastern marginal zone, pass to the south–west into greenish dark claystones and shales (Lapinskas 2000; Lazauskiene *et al.* 2003). Middle–Late Llandovery in the Western Lithuania is predominantly composed of thin laminated black and dark grey graptolite shales, cyclically interbedded with grey and red–colored claystones and marlstones (see Fig. 2). High percentage of mudstones presented within the Llandovery section indicates that they were presumably deposited within a deep–shelf setting under dysaerobic to anaerobic conditions (Lapinskas 2000; Lazauskiene *et al.* 2003). The Early Silurian transgression reached a maximum at the end of Llandovery and the deposition of Early Wenlock dark graptolite shales occurred within the generally regressive sea–level mode. The Wenlock section in the western part is represented by dark grey graptolite shales and clayey marlstones with rare interlayers of clayey limestones, deposited within the deep–marine environments, while dolomitic marlstones with very fine–grained and organogenic–detrital limestones prevail in the eastern and central facial zones. Early Ludlow dolomitic marlstones of eastern part pass westwards into dark grey and black claystones,

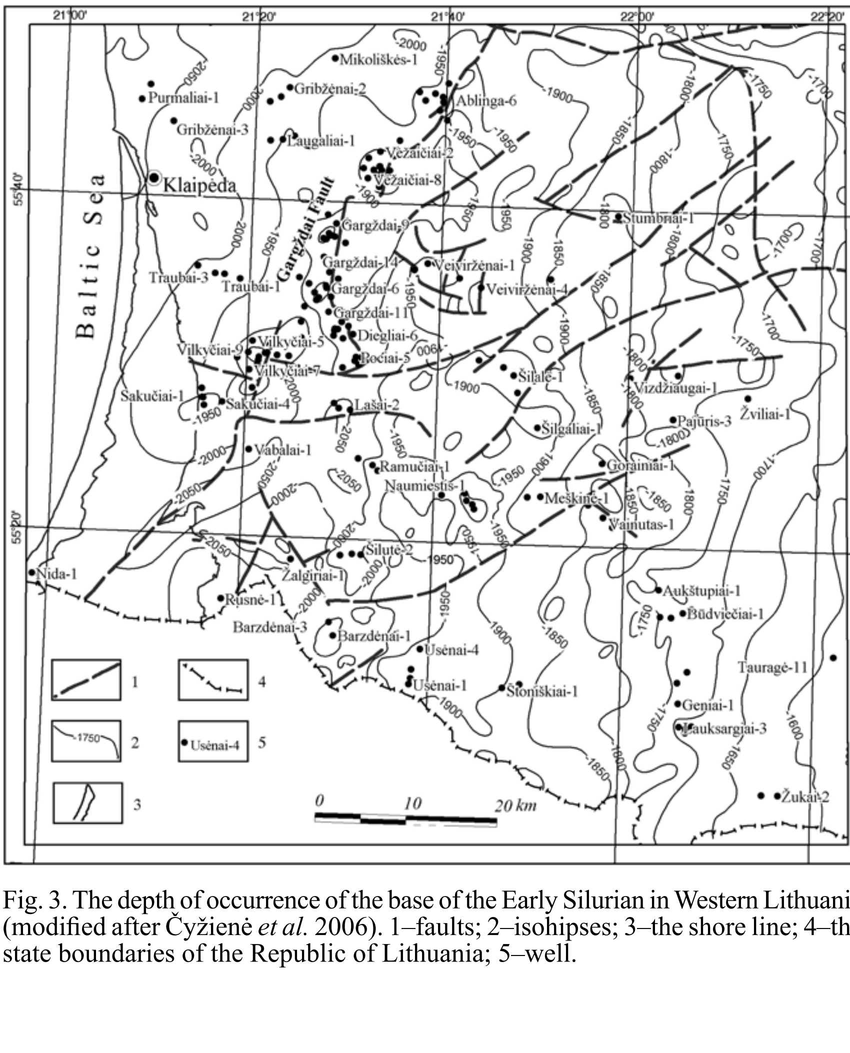


Fig. 3. The depth of occurrence of the base of the Early Silurian in Western Lithuania (modified after Čyžienė *et al.* 2006). 1–faults; 2–isohipses; 3–the shore line; 4–the state boundaries of the Republic of Lithuania; 5–well.

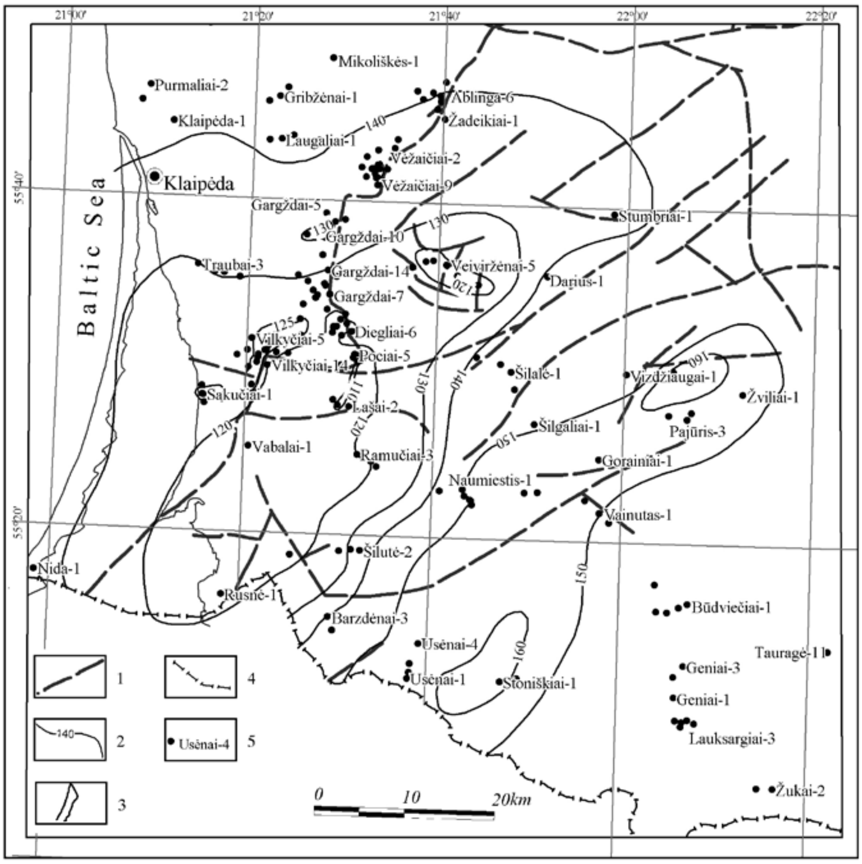


Fig. 4. Thicknesses of the Early Silurian in Western Lithuania. 1–faults; 2–isopahs; 3–the shore line; 4–the state boundaries of the Republic of Lithuania; 5–wells.

deposited within the regressive environments. Late Ludlow is represented by grey calcareous marlstones interbedded with light organogenic–detrital limestones in the west and organogenic–detrital limestones and dolomites in the eastern and central parts of the basin (Lazauskiene *et al.* 2003). The Pridolian sedimentation has been marked by the general transgressive trend – tidal flat and lagoonal dolomites, dolomitic marlstones and fragmental limestones gave way to open shelf biomicritic marlstones in the central part and, to the west, to deeper water shales in the Early Pridolian section. Light grey limestones with marlstone interbeds comprise the Late Pridoli in the east, passing westwards into grey marlstones and calcareous claystones (Fig. 2; Lazauskiene *et al.* 2003).

## MATERIAL AND METHODS

The data describing the general structure, occurrence and composition of the Silurian sequence came from well, core, well log, seismic data and results of analytic studies. The analytic studies were performed on selected samples of organic matter dispersed in the clayey–muddy Silurian deposits. In total 80 core samples from of 20 boreholes from the Western Lithuania were analyzed. Part of the data has previously been published by the senior author (Zdanaviciute, Lazauskiene 2004, 2007) with emphasis of the petroleum potential.

The location map of the distribution of the sediments, that could be considered as „black shales" and the lithological profile are shown in Fig. 2. In this paper results of such the geochemical studies are summarized: vitrinite reflectance data, total organic carbon (TOC) analysis data, Rock Eval pyrolysis, determination of the composition of saturated hydrocarbons by means of gas chromatography (GC–12 samples in total), and biomarker analysis by means of gas chromatography–mass spectrometry (GC–MS–12 samples in total). The analyses were carried out at the laboratories of Polish Geological Institute, Denmark and Greenland Geological Survey and SINTEF Petroleum Research Institute (Norway).

Preliminary information about content of total organic carbon (TOC) in the rocks was determined by combustion LECO IR212 induction furnace after elimination of carbonates and silicates by solving them in hydrochloric acid. Information about the type of organic matter and degree of the maturity was obtained adopting a relatively simple, inexpensive and efficient method of pyrolysis – so–called Rock Eval analysis, performed using a Delsi Model II Rock Eval instrument.

The gas chromatography was performed on Hewlett–Packard 5890 gas chromatographers. Gas chromatography and mass spectrometry of saturated hydrocarbons were performed with the HP5971A spectrometer coupled to an above mentioned gas chromatographer.

The maturity of the organic matter was determined by measuring reflectance indices of vitrinite like macerals. The measurements were performed on polished thin sections (1–2 mm) or on concentrated indigenous kerogen (isolated from rock matrix) by means of polarised microscope of Aksioskop type (Zeiss). Measurements were performed in monochromatic light at a wavelength 546 nm through immersion oil. The mean reflectance value ($R_o$%) has been derived for the every thin section to average the measurements of the different vitrinite like macerals.

All these standard geochemical methods and equipment are described in detail in the previous publications, related to the geochemical studies of the organic matter and petroleum potential in the Baltic Sedimentary Basin (Zdanaviciute, Lazauskiene 2004, 2007).

In order to unravel the occurrence, the structural framework and the thickness distribution of the Early

Silurian shales, a wide set of well, 2D reflection seismic and core data from nearly 200 wells, located in the Western Lithuania, have been employed (Figs 2, 3, 4).

## KEROGEN TYPE, ORGANIC RICHNESS AND THERMAL MATURITY

The most favourable conditions for the accumulation of the organic matter in the Baltic Sedimentary Basin during Silurian time were in the deep–shelf setting. Here successions of black and dark–grey–colored graptolite shales, interbedded with claystones, marlstones and dark–colored microcristaline limestones were formed. The organic matter content within the sediments of this complex can reach up to 9–16.5% or more (Kadūnienė 2001). This organic rich complex comprises the Middle Llandovery–Early Ludlow strata, and is regarded as one of three major source rock intervals within the Baltic Sedimentary Basin (Zdanaviciute, Lazauskiene 2004, 2007). The thickness of the Middle Llandovery–Early Ludlow succession reaches up to 360 m in the southwestern part of Lithuania. The content of the organic matter within the section varies quite considerably both vertically and laterally – the most organic rich rocks are recorded in the lowermost part of the interval (within the Middle Llandovery shaley strata) and gradually decrease upwards. The average content of the organic matter ($C_{org}$) in the Middle Llandoverian graptolite shales reaches up to 1.6%, in the Wenlock section the $C_{org}$ values is 1.2% and decreases to 0.8% in the Early Ludlow shales and claystones (Kadūnienė 2001). Still, taking into account the lithological composition of the Early Silurian shale strata only the Middle Llandovery–Wenlock organic rich graptolite shales would be considered in terms of the „black shales" in this paper.

The results of the analysis showed the syngenetic, sapropelic, marine origin organic matter together with the vitrinite like macerals and abundant charred remains prevailing. Liptinite comprises the major part of the studied organic matter; its content reaches or even exceeds 20%. Liptinite and dispersed liptodentrite particles have been found in sapropelic organic matter and, more rarely, as the scattered particles. Fragments and well–preserved particles of tasmanites, quite particular for the sapropelic marine sediments, were also frequently observed. Sporinite, cutinite and the organic mater originated from resins or wax, are quite rare (Zdanavičiūtė, Swadowska 2002).

Based on RockEval screening pyrolysis data, the organic matter has been attributed to sapropelic organic matter of type II kerogen, as classified by Espitalie *et al.*, 1985. Type II kerogen originates from mixed phytoplankton, zooplankton, and bacterial debris usually in marine sediments (Peters *et al.* 2005). Thus, the organic matter of type II comprises the major source rocks' levels in Lithuania and Baltic Sedimentary Basin (Zdanavičiūtė, Bojesen-Koefoed 1997).

The total organic carbon (TOC) ranges up to 19.2% (wt.) with the highest values recorded predominantly in black shales of the Early Silurian (Table 1). Hydrogen Index (HI) and Production Index (PI) are parameters that describe the hydrogen content of the organic matter

Table 1. Rock Eval analyses data (selected samples with TOC >1%) and calculated „vitrinite" reflectance data ($R_o$) for Lower Silurian deposits.

| Well name | Depth, m | Lithology | TOC | $T_{max}$ | $S_1$ | $S_2$ | HI | PP | PI | $R_o$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Akmenė 71 | 1367 | Claystone | 7.34 | 432 | 1.46 | 37.35 | 509 | 38.81 | 0.04 | 0.616 |
| Baubliai 1 | 1813 | Claystone | 19.2 | 442 | 10.06 | 103.76 | 540 | 113.82 | 0.09 | 0.796 |
| Geniai 1 | 1754 | Claystone | 6.72 | 443 | 2.88 | 19.77 | 294 | 22.65 | 0.13 | 0.814 |
| Girdžiai 48 | 1373.5 | Claystone | 3.74 | 437 | 0.82 | 15.61 | 417 | 16.43 | 0.05 | 0.706 |
| Klaipėda 1 | 2040.3 | Claystone | 5.58 | 448 | 3.69 | 16.24 | 291 | 19.93 | 0.19 | 0.904 |
| Kuliai 1 | 2031.6 | Claystone | 3.78 | 442 | 3.02 | 15.11 | 400 | 18.13 | 0.17 | 0.796 |
| Lauksargiai 1 | 1671.1 | Claystone | 17.2 | 442 | 6.98 | 76.17 | 443 | 83.15 | 0.08 | 0.796 |
| Lauksargiai 3 | 1688.8 | Claystone | 3.52 | 446 | 3.87 | 14.3 | 406 | 18.17 | 0.21 | 0.868 |
| Laužai 1 | 1962.5 | Claystone | 9.03 | 445 | 3.07 | 41.03 | 454 | 44.1 | 0.07 | 0.85 |
| Malukai 1 | 1612 | Claystone | 9.72 | 425 | 2.25 | 55.53 | 571 | 57.78 | 0.04 | 0.49 |
| Mamiai 1 | 1686.2 | Claystone | 1.16 | 443 | 0.17 | 1.65 | 142 | 1.82 | 0.09 | 0.814 |
| Mikoliškės 1 | 2031 | Claystone | 11.19 | 442 | 4.58 | 37.57 | 336 | 42.15 | 0.11 | 0.796 |
| Nida 1 | 2044.2 | Claystone | 11.1 | 443 | 4.38 | 42.52 | 383 | 46.9 | 0.09 | 0.814 |
| Paluknė 1 | 1662 | Claystone | 2.03 | 437 | 0.33 | 6.38 | 315 | 6.71 | 0.05 | 0.708 |
| Pociai 3 | 1891 | Claystone | 6.87 | 443 | 3.64 | 19.75 | 287 | 23.39 | 0.16 | 0.814 |
| Ramučiai 1 | 2009.1 | Claystone | 4.49 | 446 | 3.89 | 6.01 | 134 | 9.9 | 0.39 | 0.868 |
| Rukai 1 | 1894.1 | Claystone | 10.8 | 440 | 5.64 | 35.23 | 326 | 40.87 | 0.14 | 0.76 |
| Šatrija 1 | 1727.6 | Claystone | 14.1 | 440 | 6.27 | 68.82 | 488 | 75.09 | 0.08 | 0.76 |
| Vilkaviškis-131 | 1192 | Claystone | 4.07 | 429 | 0.7 | 13.75 | 338 | 14.45 | 0.05 | 0.562 |

TOC – total organic carbon (weight %); $T_{max}$ – max temperature of pyrolysis, °C; $S_1$ – amount of free hydrocarbons (kg HC/t rock); $S_2$ – amount of pyrolizable hydrocarbons (kg HC/t rock); HI – Hydrogen Index ($100 \times S_2$/TOC); PP – petroleum potential $S_1+S_2$ (kg HC/t rock); PI – Production Index ($S_1 / S_1+S_2$); $R_o$ – „vitrinite" reflectance data calculated from $T_{max}$.

Table 2. The organic matter composition of hydrocarbons and biomarker parameters of thermal maturity for Lower Silurian (selected samples).

| Well name | Asphaltene, % | Saturate, % | Aromatic, % | Polar, % | CPI | Pr/ $n$-$C_{17}$ | Ph/ $n$-$C_{18}$ | Pr/Ph | Hopane/ sterane | Hopane/ moretane | Homohopane izom. ratio | Sterane izom. ratio |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Akmenė-71 | 50.9 | 7.6 | 6.8 | 85.6 | 1.00 | 0.93 | 0.47 | 1.74 | 0.94 | 0.85 | 0.54 | 0.23 |
| Baubliai-1 | 37.6 | 9.4 | 21.6 | 69.0 | 1.00 | 0.52 | 0.27 | 2.42 | 1.93 | 0.83 | 0.56 | 0.35 |
| Geniai-1 | 14.6 | 30.8 | 13.3 | 55.9 | 1.10 | 0.76 | 0.51 | 1.89 | 1.03 | 0.89 | 0.61 | 0.49 |
| Geniai-1 | 11.3 | 34.1 | 15.0 | 50.9 | 1.10 | 0.68 | 0.39 | 2.23 | 0.98 | 0.89 | 0.60 | 0.46 |
| Mikoliškės-1 | 18.9 | 31.7 | 14.6 | 53.7 | 1.02 | 0.42 | 0.28 | 2.06 | 1.0 | 0.88 | 0.58 | 0.49 |
| Ramučiai-1 | 4.13 | 77.8 | 5.8 | 16.4 | 1.02 | 0.19 | 0.18 | 1.24 | bd | bd | bd | bd |

CPI – Carbon Preference Index calculated as 2×sum ($n$-$C_{23–31}$)/2×sum ($n$-$C_{24–30}$) + $n$-$C_{22}$ + $n$-$C_{32}$ v; Pr/$n$-$C_{17}$ – pristane/$n$-heptadecane ratio; Ph/$n$-$C_{18}$ – phytane/$n$-octodecane ratio; Pr/Ph – pristane/phytane ratio; bd – component is below detection.

and the amount of hydrocarbons generated from the organic matter. The highest HI values of 540 mg HC/g TOC are were recorded in the Baubliai–1 well. The majority of the organic rich samples (TOC > 1.0%) have HI values of 300–400 mg HC/g TOC.

The thermal maturity of the organic matter in the studied area was defined integrating a wide set of data – Rock Eval $T_{max}$ and production index data (Table 1); the reflectance measurements obtained from vitrinite like macerals and the biomarker analysis data obtained from indigenous rock extracts (Table 2).

Rock Eval $T_{max}$ values of the Early Silurian shales in Western Lithuania range from 425 to 448$^{o}$C, gradually increasing with depth (Table 1, Fig. 5). PI values have been defined in a range of 0.04–0.39. The distribution of $T_{max}$ values imply that the maturity of the organic matter increases to the west. The peak oil generation („oil window") was recorded in SouthWestern Lithuania. It is worthwhile to mention that the extremely high maturity values are locally recorded within the area adjacent to Ramučiai and Rukai wells (Fig. 6).

The values of $T_{max}$ and PI also are partly dependant on the type of the organic matter. Thus, $T_{max}$ can not be regarded as a direct indicator of thermal maturity for

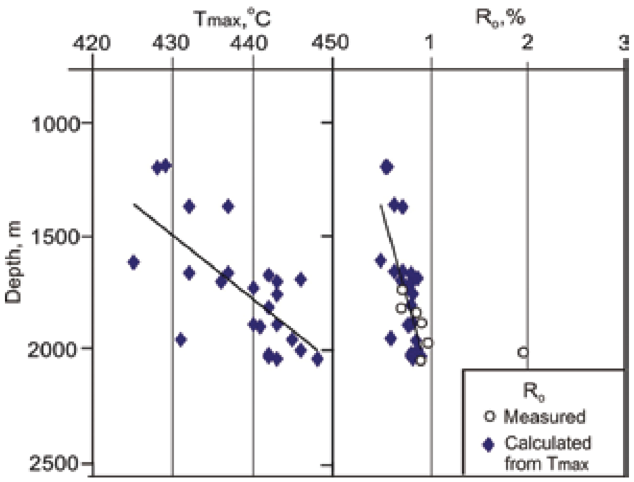


Fig. 5. $T_{max}$ and „vitrinite" reflectance (measured and calculated from $T_{max}$) versus depth.

the Silurian shales that contain predominantly marine, algal–derived organic matter in the Baltic Silurian Basin. $T_{max}$ has been compared with other thermal maturity data, e.g. vitrinite reflectance and biomarker data.

The reflectance of vitrinite is one of the standard optical thermal maturity indices. The vitrinite comprises macerals derived from land plants and is one of the primary components of most types of kerogens (Peters *et al.* 2005). However, the majority of the succession of the Early and Middle Palaeozoic age does not contain vitrinite marcels, as the land–plants had not yet evolved in pre–Devonian times. Therefore, in order to determine the thermal evolution for the Early and Middle Palaeozoic sediments often are used the reflectance of the vitrinite like macerals. Buchardt and Lewan (1990) suggested that vitrinite like macerals from the Middle Cambrian to Lower Ordovician Alum Shales section in South Scandinavia respond to heating in a similar way to that of what they call „suppressed vitrinite" in shales of the younger age (in contrast to „coal vitrinite"). The authors described this for natural samples and thermally immature samples which were artificially matured using hydrous pyrolysis.

The measured data of vitrinite like macerals reflectance and data of $T_{max}$, converted to vitrinte reflectance equivalent, are presented in Table 1 and Fig. 5. For the conversion the following equation has been adopted:

$$R_o \text{ (calculated from } T_{max}) = 0.0180 \times T_{max} - 7.16$$

As the Early Palaeozoic oils in the Baltic basin are described as low–sulphur (Zdanaviciute, Lazauskiene, 2004, 2007), such a conversion is applicable also for shales containing low–sulfur type II and type III kerogen (Jarvie *et al.* 2001), thus, could be successfully adopted to study the Early Palaeozoic succession on Lithuania. Still, the equation is of limited use to analyze samples with very low maturity (where $T_{max}$ is < 420$^{o}$C) or extremely high maturity, where $S_2$ (second peak of Rock Eval pyrogram) is less than 0.50 mg HC/g rock (Peters *et al.* 2005).

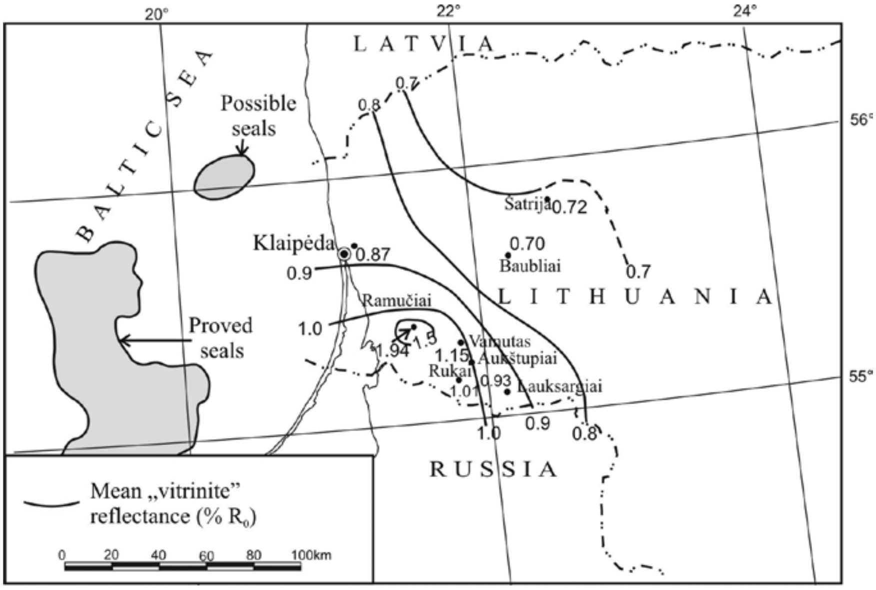


Fig. 6. Sketch map of the distribution of mean „vitrinite" reflectance values in the Silurian source rocks in Lithuania (modified after Zdanaviciute, Lazauskiene 2007).

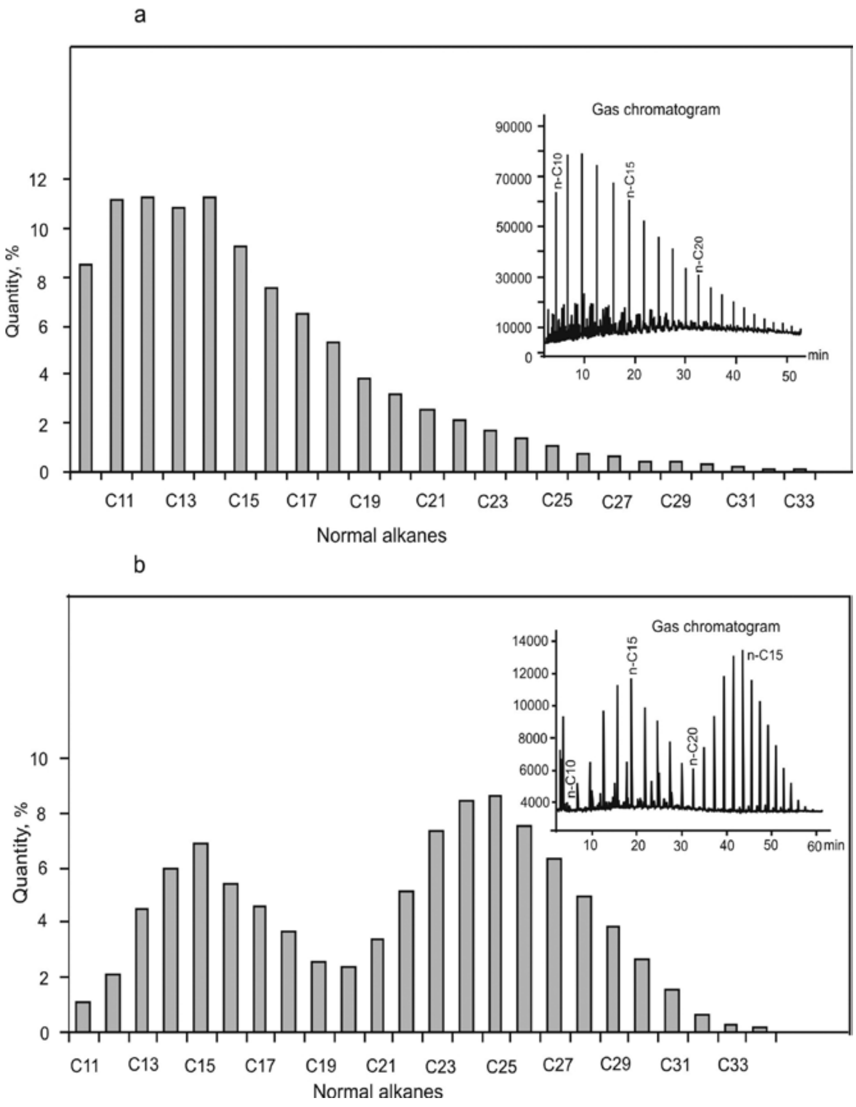


Fig. 7. Plot of the distribution of *n*-alkanes in the Early Silurian organic matter. (a)–well Ramučiai–1, depth 2009.1 m; (b)–well Nida–1, depth 2044.2 m.

The data, presented in Fig 6, show the mean reflectance values ranging from 0.6 to 0.7% $R_o$ in the north–eastern part of Lithuania and gradually increasing to 0.8–0.9%$R_o$ in the southwestern, the deepest buried part of the basin. The reflectance values, implying thermal maturities beyond the peak of liquid hydrocarbons generation were recorded in Klaipėda–1 (0.87% $R_o$) and Rukai–1 (1.01% $R_o$) wells. The measurements in Ramučiai–1 well show extremely high mean reflectance values of 1.94% $R_o$, implying the late gas generation phase. Such a locally increased thermal maturity of the organic matter can probably be explained in terms of magmatic intrusions in this area (Kepežinskas *et al*. 1996), or geothermal anomalies of different origin, rather than by the depth of occurrence of sediments. Such a palaeothermal anomalies also are supported by diabase intrusions identified by well, seismic, gravity and magnetic data in the Late Silurian and, rarely, in the Cambrian–Early Silurian succession in the Baltic Sea (Motuza *et al*. 1994; Sliaupa *et al*. 2002). Moreover, the radiogenic heating, related to the emplacement of anarogenic granites that contain increased amounts of K, U, Th, also must be considered (Sliaupa *et al*. 2005).

## THE COMPOSITION OF THE ORGANIC MATTER

The group composition of the extractable organic matter (mostly depending on the biological origin of the organic matter) indicates the polar (S+N+O) and saturated hydrocarbons dominating over the aromatic hydrocarbons. Polar hydrocarbons prevail in the composition of the organic matter, usually comprising from 16.4 up to 85.6% of the total amount, while the content of asphaltenes varies in the rage of 11.3–50.9% (Table 2).

The depositional environments and the level of the thermal maturity of the organic matter have been assessed by the analysis of the saturate hydrocarbon fractions by gas chromatography–mass spectrometry methods, with the use of different biomarker parameters that are commonly applied in the geochemical studies. Analysis of GC chromatograms shows that most of saturate fractions compounds are dominated by *n*–alkanes in the range from *n*–$C_{11}$ to *n*–$C_{18}$ carbon atoms in the molecule with one maximum (Fig. 7a) Therefore, the results of the analysis of the shale extract from well Nida–1 (2044.2 m depth) showed a bimodal, smooth *n*–alkane distribution with modes at *n*–$C_{15}$ and *n*–$C_{25}$, as well as moderate amount of acyclic isoprenoids (Fig. 7b). It could be tentatively suggested that hydrocarbons from this sample were derived from two different sources, one of which had relatively „waxy" composition. Presumably, the shales with the high $C_{20+}$ *n*–alkanes content in extractable organic matter (such *n*–alkanes distribution is recorded in the Early Silurian samples of Western Lithuania) will show lower gas–to–oil ratio (GOR) values that is consistent with the oil maturity window; whereas samples with low $C_{20+}$ hydrocarbons content (< 5%) will have higher GOR values (Jarvie *et al*. 2007).

The pristane/phytane (Pr/Ph) ratio in the Early Silurian shales varies in the range from 1.24 to 2.42. This parameter, commonly indicating the oxicity of the depositional environments, however, is also maturity dependant (Peters *et al*. 2005). The ratio of odd–to–even *n*–alkanes – Carbon Preference Index (CPI), calculated for the $C_{23}$–$C_{32}$ *n*–alkanes, shows the values close to 1.0 for all the samples analyzed. Since CPI ratio values are maturity dependant and decrease with increasing thermal maturity of the organic matter (Tissot, Welte 1984), values about 1.0 indicate high maturity of studied organic matter.

The analysis of the fractions of the saturated hydrocarbons of high molecular weight and content of steranes and triterpanes for the shaley strata with shallow depth of occurrence would allow more accurate assessment of the degree of catagenesis. However, the organic matter of the Early Paleozoic succession comprises low content of the saturated hydrocarbons of high molecular weight. As the maturity of the organic matter of source rocks is directly related to the depth of occurrence, the maximum of the maturity is recorded in the southwestern part of Lithuania. The samples from this area typically are characterized by high hopane/moretane ratio (mostly is > 0.8), high homohopane isomerisation ratio (0.54–0.61) and moderate to high sterane isomerisation ratio (0.23–0.49). Moreover, relatively high content of the $C_{30}$ diahopane was recorded in some of wells in the western part of Lithuania. The organic matter in well Ramučiai–1 is over mature, thus, it was not possible to estimate the maturity in this well by using biomarker of saturate hydrocarbon parameters.

## ORGANIC MATTER TRANSFORMATION AND VOLUMES OF HYDROCARBONS GENERATED

The generation potential of hydrocarbons strongly depends on the original quantity (original total organic carbon $TOC_o$) and quality (original hydrogen index $HI_o$) of the organic matter in thermally immature source rocks (Peters *et al*. 2005). The assessment of the hydrocarbon generation potential of the Early Silurian shales in the Western Lithuania is based mostly on available Rock Eval data (see Table 1). Using the equations, proposed by of G. E. Claypool (Peters *et al*. 2006), the extent of the organic matter conversion to petroleum (so–called fractional conversion) was determined. By making some assumptions, the fractional conversion (f), original $TOC_o$, amount of expelled hydrocarbons ($SI_{expelled}$) and expulsion efficiency (ExEf) were derived from the change in original hydrogen index ($HI_o$) and original production index ($PI_o$) to present day values of these indexes ($HI_p$ and $PI_p$; Peters *et al*. 2005).

The extent of the organic matter conversion (fractional conversion) to the liquid and gaseous hydrocarbons (f) could be assessed by adopting the equation:

$$f = 1 - \frac{HIp\ \{1200 - [HIo / (1 - PIo)]\}}{HIo\ \{1200 - [HIp / (1 - PIp)]\}} \quad (1);$$

here $PI_p$ – the present day production index (measured by means of Rock Eval pyrolysis $PI_p=S_1/(S_1+S_2)$, that indicate the amount of generated hydrocarbons); we assume that $HI_o$ – the original hydrogen index and $PI_o$ – the original production index for the most of immature source rocks are equal to 500 and 0.02 respectively (Peters *et al*. 2005); 1200 – the maximal amount of hydrocarbons that could be formed assuming, that organic carbon comprises 83.33% of total hydrocarbon composition (Peters *et al*. 2005).

The extent of fractional conversion of the Early Silurian shales has been calculated based on data from well Ramučiai–1 (Table 1).

$$f = 1 - \frac{136\ \{1200 - [500 / (1 - 0.02)]\}}{500\ \{1200 - [136 / (1 - 0.4)]\}} = 0.832;$$

Therefore, 83% of the hydrocarbon generation process in the area of the Western Lithuania adjacent to well Ramučiai–1 has been completed.

The original total organic carbon ($TOC_o$) content in the source rocks before they get matured, could be calculated adopting the mass balance equation:

$$TOC_o = \frac{83.33 \times HIp \times TOCp}{[HIo \times (1 - f) \times (83.33 - TOCp) + HIp \times TOCp]} \quad (2)$$

Thus, the original content of TOC for the area adjacent to well Ramučiai–1 is calculated as:

$$TOC_o = \frac{83.33 \times 136 \times 4.5}{[500 \times (1 - 0.832) \times (83.33 - 4.5) + 136 \times 4.5]} = 7.06 \text{ wt.\%;}$$

The estimated value implies that the mature Early Silurian shales in well Ramučiai–1 contain high amount of organic matter (4.5 wt%). Moreover, before the maturation sediments in this well contained excellent quantities of the organic matter– 7.06 wt%.

The amount of the expelled hydrocarbons ($SI_{expelled}$) and expulsion efficiency (ExEf) could be calculated accordingly:

$$SI_{expelled} = 1 - \frac{1000(TOCo - TOCp)}{83.33 - TOCp} \quad (3);$$

$$ExEf = 1 - \frac{(1 - f)[PIp/(1 - PIp)]}{f + [PIo/(1 - PIo)]} \times 100 \quad (4);$$

here $TOC_p$ is the present day content of the total organic carbon.

Thus, the amount of hydrocarbons, expelled in the Early Silurian shaley succession in Western Lithuania equals to:

$$SI_{expelled} = \frac{1000 \times (7.06 - 4.5)}{83.33 - 4.5} = 32.47 \text{ mg HC/g rock}$$

Assuming that oil and shale densities equals respectively to 850 mg/cm$^3$ and 2.4 g/cm$^3$, the average thickness of the Early Silurian black shale strata is 150 m (Fig. 3) and the area of one square kilometer, the estimated volume of expelled hydrocarbons (SI) equals to 13.75 $\times$ 10$^6$ kg. This mass of hydrocarbons is roughly equivalent to 389 $\times$ 10$^5$ cubic meters of methane (the calculations presented below). The graph of J. W. Schmoker (1994) was used for conversation of mass hydrocarbons to methane.

$$SI = \frac{32.47 \times 2400}{850} \times 10^6 \times 150 = 13.75 \times 10^6 \text{ kg HC} = 389 \times 10^5 \text{ m}^3 \text{ of methane.}$$

Based on parameters estimated above, the expulsion efficiency (ExEf) is calculated:

$$ExEf = 1 - \frac{(1 - 0.832) \times [0.4 / (1 - 0.4)]}{0.832 + [0.02 / (1 - 0.02)]} \times 100 = 86.9\%$$

Thus, the numbers presented above clearly indicate the very high expulsion efficiency of the Early Silurian black shales in Western Lithuania. Obviously, these are only tentative values, as only the measurements from the area, described by very high maturity, were used for calculations. As some of the input parameters for the calculations have not been determined analytically, adopting some derivative values instead, the accuracy of the total estimated volumes should be considered assuming quite high errors. Though, it is well known that only very small amount of hydrocarbons generated (usually only few percent) may have been preserved and be latter on extracted. Only in very rare cases, up to 10% of the total estimated volumes of hydrocarbons might be produced. Furthermore, for the more accurate assessment of the shale gas generation potential, a wide range of the additional parameters, such as mineralogical composition and the reservoir properties of the Early Silurian shales, gas storage capacity, formation pressure and temperature etc. are required.

Whereas the Early Silurian succession overlies Cambrian and Ordovician oil bearing complexes in the Baltic Sedimentary Basin, the Silurian shaley sediments could both adsorb and absorb hydrocarbons, generated also from Cambrian and Ordovician source rocks.

## CONCLUSIONS

The Early Silurian organic rich graptolite shales in Western Lithuania, described by high content (total organic carbon > 1%) and the maturity (vitrinite like macerals reflectance index $R_o$ ~ 0.9–1.0%) of the organic matter, could be considered in terms of shale gas prospective „black shales". The depth of the occurrence of the base of the Early Silurian increases to the southwest, ranging from 200 m in the east to nearly 2,050 m in the westernmost part of Lithuania. Two major systems of WSW–ENE and SSW–NNE trending faults dissect the Silurian succession. The thickness of the Early Silurian strata within the shale gas prospective area varies in a range of 40 meters, the thinnest section of ~ 120 m recorded in the central part, whereas the thicknesses increases (up to 160 m) towards the north and southwest or carries out rather local character in some wells.

The Early Silurian strata are an organic–rich, containing kerogen type II, oil–prone shales of marine origin. Correlation of biomarker parameters, Rock Eval results and vitrinite like macerals reflectance data allowed to determine the regional trend in the distribution of the thermal maturity of the organic matter, implying that the thermal maturity gradually increases to southwest and reaches the „early oil" and „oil peak phase" in the south–westernmost part of Lithuania. A max reflectance value of 1.94% $R_o$, recorded in the sample from Ramučiai–1, shows the late gas generation phase. Such a sharp, but locally restricted, increase in the maturity of the organic matter could be explained in terms of the temporal variations in the heat flow related to magmatic intrusion or the thermal events of the different origin.

The Early Silurian shales in Western Lithuania might have had generate a large volumes of methane gas within the limits of „black shale" productive area, due to a number of favourable conditions, such as excellent original organic richness of sediments, sufficient thermal maturity and generation potential. The expulsion efficiency, computed for the Early Silurian strata in Western Lithuania, is very high. The estimated volume of expelled hydrocarbons might have been as high as $13.75 \times 10^6$ kg or $389 \times 10^5$ cubic meters of methane (in the section of one sq. km and ~ 150 m thickness of shale strata). As the Cambrian and Ordovician oil bearing complexes also show a good hydrocarbon generation potential, the Early Silurian shale source rocks could also adsorb hydrocarbons diffused from Cambrian and Ordovician source rocks.


### Acknowledgements

The authors thank the reviewers Dr. Anatoly I. Khoubldikov (Kaliningrad, Russia) and Dr. Niels H. Schovsbo (Copenhagen, Denmark) for constructive comments that helped to improve the manuscript. Also we thank the Lithuanian Geological Survey under the Ministry of Environment and Geological Museum of Lithuania for their assistance in providing the access to samples and archive data.


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