Petrographic and pyrolysis-gas chromatography investigations of the Lower Palaeozoic organic matter of Lithuania

Onytė Zdanavičiūtė, Elźbieta Swadowska

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Investigations of dispersed organic matter in a polished rock section by means of polarised microscopy in white and blue light and data of kerogen studies by pyrolysis-gas chromatography (Py-GC) have been generalised. The major part of organic matter was found to be composed of liptinite (about 20%); fragments or well-preserved tasmanites are often observed; sporinite, cutinite or a matter generated from resins or wax are rarer. Py-GC data show Type II of kerogen rich in aliphatic hydrocarbons.

Keywords: Lithuania, organic matter, maturity, Cambrian, Ordovician, Silurian, chromatography, petrography

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Onytė Zdanavičiūtė. Institute of Geology and Geography, T. Ševčenkos 13, LT-2600 Vilnius, Lithuania. E-mail: zdanav@geologin.lt

Elźbieta Swadowska. Polish Geological Institute, Rakowiecka 4, PL 00-975 Warsaw, Poland

INTRODUCTION

The paper analyses data on petrographic investigations of organic matter and pyrolysis-gas chromatography (Py-GC) of kerogen (insoluble part of organic matter). According to its content in the rocks dispersed organic matter makes up a very small part and its maximum reaches only several percent. The total quantity of organic matter on Earth 1000 times exceeds the content of coal and oil in deposits (Tissot, Welte, 1984). Investigations of dispersed organic matter enable to solve many geochemical problems, including those of oil origin. As far back as early in the 20th century H. Potonie (1908) proposed to divide caustobioliths according to humites (mainly lignin-cellulose matter), liptobioliths (formed of resins, wax and spore integument, etc.) and sapropelites (composed of organic matter transformed by flora and fauna). The same types are distinguished also for organic matter. Humic organic matter of continental origin is a source of coal deposits and sapropelic organic matter of marine origin is a source for oil and gas fields.

METHODS

Generalised data on petrographic investigations of dispersed organic matter are given in the article with the aim to determine maturity (by light reflection measurements), as well as hydrocarbon composition and organic matter distribution in the Cambrian, Ordovician and Silurian oil source rocks.

The petrographic characteristic of dispersed organic matter is based on the studies of 11 borehole

cores at the Polish Institute of Geology, by carrying on a joint project (Modlinski et al., 1998). The investigations were performed in polished sections of rocks, using a polarised microscope of Axioscop type (Zeiss) in white and blue light. To describe petrographic compounds, the nomenclature and classification of International Coal Committee for Petrology (ICCP) was used (Stach, 1982). Measurement of reflected light parameters was done in monochromatic light, at 546 nm wavelength. This is measurement blend 0.16 mm wide. As a standard for comparison, optical glass with 1.0% reflectance was used (Polish standard PN-79/G-04525). The organic matter maturity was determined by measuring light reflection indices. The measurements were performed in syngenetic organic matter, bituminites and vitrinite-like particles. The data of the investigation are given in Table 1 and Fig. 1.

Kerogen (extracted from 16 rock samples taken in 13 wells) was analysed by the pyrolysis-gas chromatography method on a Hewlett-Packard 5890 chromatograph connected with Newtronic TP96 temperature control equipment. A Chrompack CP-Sil-8CB WCOT type 50 m long column, 0.22 mm in external diameter, and 0.12 μm internal diameter was used. Pyrolysis was performed at a temperature of 300–500 °C, increasing it gradually by 20 °C per minute. Helium gas was used, and liquid nitrogen was applied for retention of pyrolysis products. The chromatograms obtained were processed by applying HP-Chemstation software. The investigations were carried out at the geochemical laboratories of Norvegian Petroleum Research Institute within a joint project (Weiss et al., 1997). The data and pyrograms are given in Table 2 and Fig. 2.

DISCUSSION

The data of earlier investigations of organic matter (by Rock-Eval pyrolysis method) showed that in the Lithuanian area, like in the whole Baltic Syneclise, the source rocks contain sapropelic organic matter corresponding to Type II (classified after Espitalie et al., 1985) kerogen (Zdanavičiūtė, 1996).

The content of organic matter in the Lower Palaeozoic rocks is greatly varying, but petrographically, according to distribution regularity and maturity, its differentiation is rather low. The samples studied are notable for syngenetic, sapropelic, marine organic matter prevalence, as well as the vitrinite-like particles, and there are abundant charred remains of fauna. Among mineral components, fine detritic sapropel is seen greatly scattered in the form of lenses or nests (Fig. 1). Rocks, especially those rich in organics, contain sapropel variously mixed with clay minerals forming a bulk of the rocks. Homoge-

Photo 1

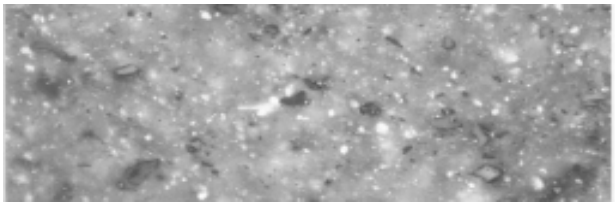

Photo 2

Photo 3

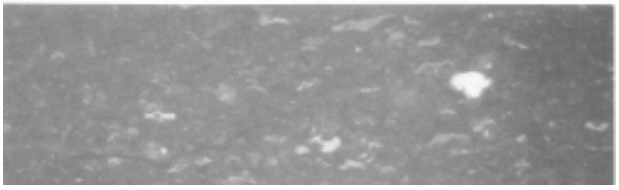

Photo 4

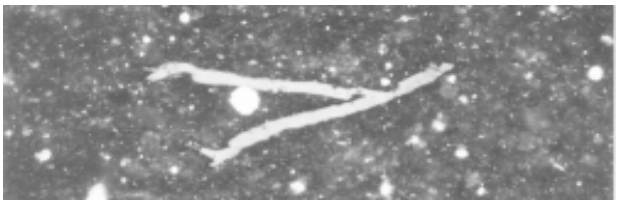

Fig. 1. Micrographs of scattered organic mater (blue and white fluorescent light).
1 pav. Dispersinės organinės medžiagos fotografijos (žydroje ir baltoje fluorescentinėje šviesoje)
Photo 1. Geniai-1 well, (Cm_1), 1709.3–1914.5 m. Liptodetrinite (orange); blue light. 1 cm = 20 μm.
1 fotografija. Genių-1 gręž. (Cm_1), 1709,3–1914,5 m. Liptodetrinitas. 1 cm = 20 μm
Photo 2. Mikoliškės-1 well, (Cm_2) 2187.8–2199.2 m. Bituminous impregnation (brownish), lamalginite (yellow) in the middle of the photo; blue light. 1 cm = 20 μm.
2 fotografija. Mikoliškių-1 gręž. (Cm_2) 2187,8–2199,2 m. Uoliena prisotinta bitumoidu, fotografijos centre – lamalginitas, 1 cm = 20 μm
Photo 3. Lauksargiai-3 well, (O_2), 1721.7–1737.1 m. Fragments of graptolite (light grey) in the organo-mineral groundmass sapropelic type (black); white light. 1 cm = = 20 μm.
3 fotografija. Lauksargių-3 gręž. (O_2), 1721,7–1737,1 m. Graptolito fragmentai organinėse-mineralinėse sapropelinio tipo nuosėdose. 1 cm = 20 μm
Photo 4. Vainutas-3 well, (S_1), 1905.5–1911.1 m. Liptodetrinite (oragnge–brownish) and alginite (light–yellow); blue light. 1 cm = 20 μm.
4 fotografija. Vainuto-3 gręž. (S_1), 1905,5–1911,1 m. Liptodetrinitas ir alginitas (gelsvas). 1 cm = 20 μm

nous bituminite genetically related to fine detrital sapropel makes up pieces smaller than 1 μm and fine veins to 20 μm. In white light, bituminite is characterised by a dark brown colour in slightly catagenically changed rocks; the colour ranges to light brown in the rocks changed more catagenically. Under blue light the rocks that changed slightly catagenically, bituminite fluoresces in brown colour. In organic matter often vitrinite-like particles prevail. The forms of their distribution in the rocks differ greatly. The most frequent form is that of plates, from several tens of microns, sometimes shaped like well-polished grains or small bricks. Often vitrinite-like macerals have the morphologic features showing that these are charred faunal remains (graptolites). Liptinite makes a large part of organic matter, its content is equal to or exceeds 20% (Table 1). Liptinite particles together with dispersive liptodentrite occur most often in sapropel and rarer among mineral components. Fragments and well-preserved tasmanites are frequent, they are typical components of sapropelic marine sediments. Sporinite, cutinite or a matter originated from resins or wax is rarer. Liptinite particles fluoresce rather intensively from bright yellow to orange, red or brown tint.

The samples investigated locally contain epigenetic organic matter that appears due to migration of bitumens. Bitumens are nearly invisible in white light, but they are well-distinguished in blue light; they fluoresce from yellow to orange tint of different intensity. In Lithuania, a bitumens are widely spread in the wells of Mikoliškės-1, Sakučiai-2 and Žalgiris-1. Their average content is determined in the wells of Lauksargiai-2 and Lašai-2. Bitumens are first of all related to terrigenous and rarer to calcareous rocks, which fill up pore voids or are concentrated in microfissures.

Table 1. **Data on petrographic composition of organic matter and R_o**
1 lentelė. **Organinės medžiagos petrografinės sudėties ir R_o duomenys**

Well, No	Depth, (m)	Rock age	Lithology	Composition of the organc matter (%)					R_o (%)
				V*	L*	Sap*	Bt*	Bm*	
Geniai-1	1907.3–1914.5	$Є_1$	Argillite	10	40	50	–	+	–
Gorainiai-1	2103.6–2111.3	$Є_1$	Argillite	60	10	30	–	–	Roll = 1.23
Sakučiai-2	2157.1–2162.5	$Є_1$	Argillite	70	30	–	–	+	–
Mikališkės-1	2187.8–2199.2	$Є_2$	Argillite	60	10	30	–	+	Roll = 0.92
Stumbriai-1	2006.2–2013.3	$Є_2$	Argillite	20	20	20	40	–	Rol = 0.35 Roll = 0.69
Vainutas-2	1965.0–1968.2	$Є_2$	Sandstone	25	35	40	–	–	Roll = 1.23
Žalgiriai-1	2101.6–2106.5	$Є_2$	Argillite	10	20	70	–	+	Roll= 1.06
Baubliai-4	1951.7–1964.1	O_2	Argillite	50	20	30	–	–	Roll = 1.15
Lauksargiai-3	1721.7–1737.1	O_2	Argillite	20	20	40	20	–	Rol = 0.44 Roll = 0.98
Sakučiai-2	1961.6–1969.6	O_3	Argillite	–	–	–	–	+	–
Aukštupiai-1	1775.0–1790.0	S_1	Argillite	50	20	20	10	–	Roll = 1.00
Gorainiai-1	1915.0–1923.5	S_1	Marl	35	15	30	20	–	Roll = 1.20
Lauksargiai-2	1695.0–1707.6	S_1	Argillite	30	20	30	20	+	Rol = 0.43 Roll = 0.93
Lašai-2	1971.9–1985.0	S_1	Argillite	–	100	–	–	+	–
Vainutas-3	1905.5–1911.1	S_1	Argillite	40	10	30	20	–	Roll = 1.15

*V – vitrinite-like macerals; L – liptinite; Sap – organomineral association of sapropel type; Bt – bituminite; Bm – bitumen; Rol – bituminite reflectance; Roll – vitrinite reflectance.

Organic matter maturity is determined from light reflectance by bituminite and vitrinite-like particles. Variations in catagenesis degree depend mainly on rock occurrence depth; the R_o index shows its increase from NE to SW.

The reflection index R_o for vitrinite-like particles indicates organic matter maturity and generation phase of hydrocarbons (Robert, 1985). Organic matter in the samples studied was from immature to oil generation or dry gas generation phase. The temperature ranges corresponding to the R_o value according to Epstein (1977) are very wide – from 40–60 to 400 °C.

There is a large difference (measurements were done in the same sample) between R_o measured for bituminite and vitrinite-like particles, which were formed mainly of charred graptolite remains. This seems to be related to the fact that bituminites in the early stage of the rock diagenesis show a lower reflectance than vitrinite (Robert, 1985), whereas reflectance of charred graptolite as a rule grows more rapidly than that of vitrinite (Link, Bustin, Goodarzi, 1990).

In Lithuania, Cambrian rocks occurring at the depths of 1907.3–2199.2 m contain bituminite with the R_o equal to 0.35% (Stumbriai-1 well), while R_o vitrinite-like particles range from 0.69% (Stumbriai-1 well) to 1.23% (Gorainiai-1 well). A similar maturity was found in younger rocks as well. Ordovician rocks lying at a depth of 1721.7–1964.1 m contain bituminite with R_o equal to 0.44% (Lauksargiai-3 well), vitrinite-like particles with R_o 0.98% (Lauksargiai-3 well) and 1.15% (Baubliai-4 well). Bituminite R_o for Silurian rocks, within the interval of 1695.0–1923.5 m is 0.43% (Lauksargiai-2 well) for vitrinite-like particles R_o ranges from 0.93% (Lauksargiai-2 well) to 1.20% (Gorainiai-1 well).

The above-described values of R_o for bituminite range from 0.35 to 0.44% and show that in Lithuania the organic matter contained in Cambrian, Ordovician and Silurian rocks is not sufficiently mature for oil generation. R_o values for vitrinite-like particles range from 0.69 to 1.23% and show that these rocks are mature to generate liquid hydrocarbons (a stage of "oil window"). Palaeotemperatures during transformation of organic matter ranged from 50 to 150 °C.

Based on petrographic studies of organic matter in the Lower Palaeozoic rock complex, the following source rock criteria that correspond to generation phases of liquid and gas hydrocarbons can be distinguished in Lithuania's area: Cambrian – 2006.2–2013.3 m deep in Stumbriai-1 well and 1965.0–1968.2 m in Vainutas-2 well; Ordovician – 1721.7–1737.1 m in Lauksargiai-3 well; Silurian – 1775.0–1790.0 m, Aukštupiai-1 well; 1915.0–1923.5 m in Gorainiai-1 well; 1695.0–1707.6 m in Lauksargiai-2 well, and 1905.5–1911.1 m in Vainutas-3 well.

Epigenetic bitumens indicating local reservoirs are determined in the Cambrian rocks of Geniai-1 (1907.3–1914.5), Sakučiai-2 (2157.1–2162.5), Mikoliškės-1 (2187.8–2199.2) and Žalgiriai-1 (2101.6–2106.5 m) wells. In the Ordovician sequences, epigenetic bitumens have been determined in the rocks of Sakučiai-2 (1961.6–1969.6 m) well, in Silurian rocks – Lašai-1 (1971.9–1985.0 m) and Vainutas-1 (1905.5–1911.1 m) wells.

Pyrolysis-chromatogtraphy data define the composition of kerogen and are often used for determination of organic matter catagenesis degree. The higher maturity of organic matter is indicated by a lower content of aromatic and isoprenoid hydrocarbons and higher amounts of aliphatic n-alkane homologs (Van Graas et al., 1981).

The pyrograms (Fig. 2) and data in Table 2 show that all samples are rich in paraffin pyrolysates, having in their chain connecting normal alkanes with 25 or more carbon atoms. This indicates high amounts of aliphatic structures in organic matter (Larter, 1984).

In the central and western parts of the Baltic Syneclise, Cambrian-Tremadoc rocks are formed mostly of dark grey and black argillite reaching 20 m in thickness and rich in organic matter, with total organic carbon (TOC) making up to 12% (by weight). These are perfect oil source rocks – the Alum Shale equivalent of a high maturity corresponding to the "peak" or "late oil" stage. Unfortunately, they are eroded east of the line Kaliningrad – North Öland. East of this line there are dark grey and black clayey rocks containing less than 1% of TOC and only sometimes reaching 6.1%.

In Lithuania, as in the whole eastern part of the Baltic Syneclise, source rocks can be considered to be represented by Middle and Lower Cambrian argillite and aleurolite, with their joint thickness in the Baltic Sea reaching even 140 m. Organic matter content in these rocks ranges from 0.05 to 3.1%, but as a rule it is lower than 1%. The oil and gas generation potential (S1+S2, according to Rock-Eval analyses) reaches 9 kg HC/t_{rock}. Hydrogen Index is lower than 450. The maximum pyrolysis temperature ranges from 433 to 450 °C, indicating maturity of organic matter as corresponding to the "early oil" generation phase (Zdanavičiūtė, 1996; 2000). This conclusion is confirmed by pyrolysis-gas chromatography data obtained during investigations of argillite kerogen from Laužai-1 well (2085.4 m). This chromatogram is dominated by peaks representing aliphatic compounds ((m+p)-xylene/n-octene = 0.71), and the n-alkene/n-alkane doublets extend to C_{25}. Such distribution suggests a significant liquid hydrocarbon generation potential (Weiss et al., 1997).

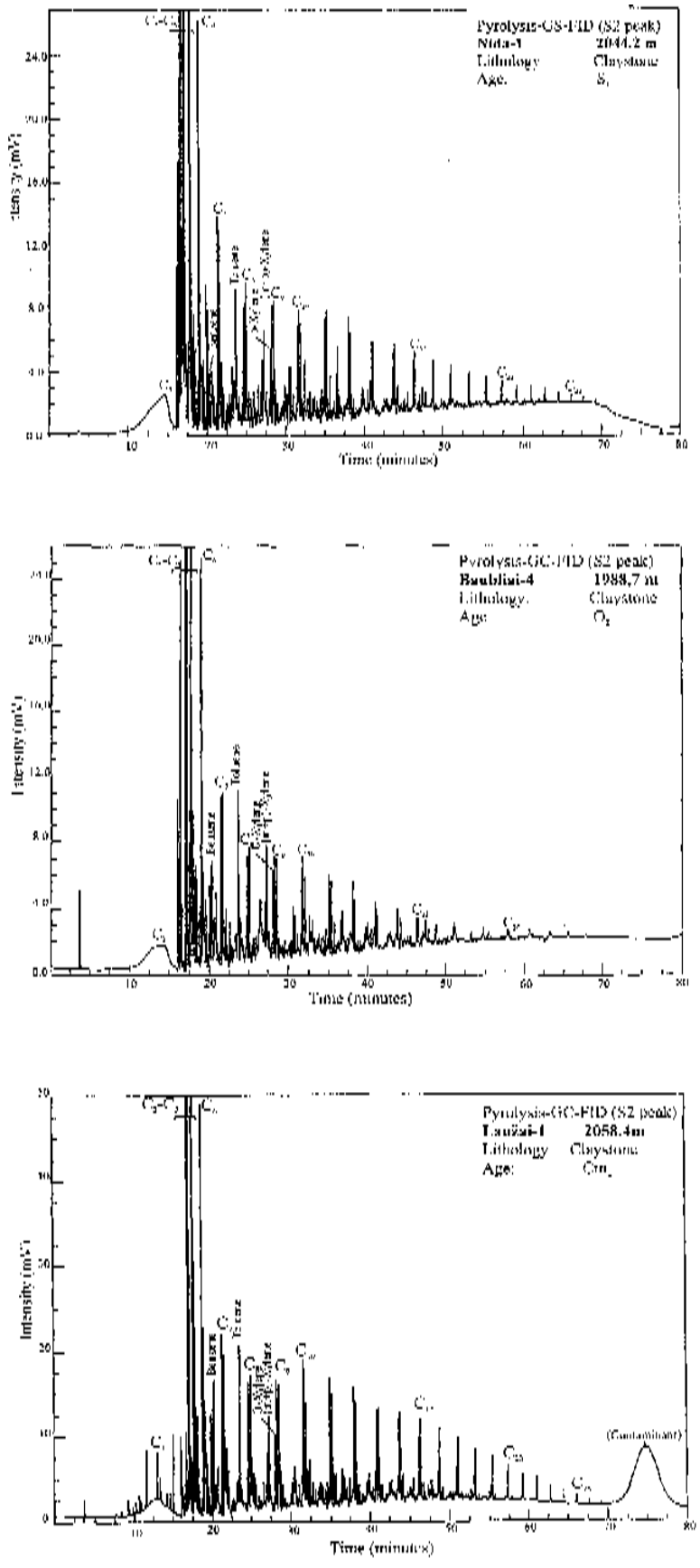

Fig. 2. Pyrolysis-gas chromatograms of typical kerogen examples from Cambrian, Ordovician and Silurian source rocks
2 pav. Kambro, ordoviko ir silūro uolienų kerogeno tipinės pirogramos

In the Ordovician section oil-generating rocks are represented by dark grey and black argillite belonging to Fjäcka and Mössen formations, with a rather small thickness reaching only 5–10 m. Organic matter content ranges from 0.9 to 10%, sometimes reaches 15%. The oil and gas generation potential is 22 kg HC/t_{rock} on average, but can reach 55–70 kg HC/t_{rock} at Hydrogen Index of 521. Organic matter maturity increases south-westwards from 0.4 to 0.8% (R_o). All this shows perfect source rock characteristics. The TOC average ranges from 4.7 to 8.9%, Hydrogen Index from 190 to 620 mg/g TOC, implying the presence of Type II kerogen.

Pyrolysis-gas chromatograms show that the dominating n-alkene/n-alkane doublets extend to C_{25}. Aromatics are present but not significant, as (m+p)-xylene/n-octene ratios indicated, typically they reach 0.5–1.1. There is no obvious relation between the aromaticity or carbon number distribution of the pyrolysate and Hydrogen Index. Prist-1-ene is present in many, but not all samples, and no identified peak between C_{11} and C_{12} (possibly naphthalene benzothiophene or cresol isomer) was determined in the samples from Akmenė-71, Baubliai-1, 4, Lauksargiai-4 and Nida-1 wells. Minor variations in the relative abundance of the unresolved complex mixture (the "hump" in the pyrolysis-gas chromatograms) and in the relative abundance of low- and high molecular weight compounds are possible due to maturity variations. This applies at least to the south-western part of Lithuania; there in Ramučiai-1, -3 samples were determined to be of light and aromatic-dominated pyrolysate composition. The unusually high aromaticity of an Ordovician sample from Akmenė-71 well (1610.2 m) was obtained, however, contrasts with the rather high Hydrogen Index of 511 mg/g TOC remain unexplained yet. The pyrolysis-gas chromatography results suggest (in agreement with the Rock-Eval results) that the organic matter in these rocks is of an aliphatic-rich Type II kerogen.

Oil generating rocks in the Silurian deposits comprise Llandovery, Wenlock

Table 2. **Data from pyrolysis-gas chromatograms**
2 lentelė. **Pirolizės-dujų chromatografijos duomenys**

Well No.	Depth, m	Age	Lithology	C_1	C_{2-5}	C_{6-14}	C15+	mpx/n-C_8*	S_2*	HI*	T_{max}*
Akmenė-71	1367.3	S_1	marl	4.7	21.9	41.8	31.6	0.84	37.4	717	432
Akmenė-71	1452.2	O_3	argillite	4.2	17.3	39.5	39.0	0.89	34.1	479	432
Akmenė-71	1471.5	O_2	argillite	3.9	17.0	36.7	42.4	0.88	26.7	476	434
Akmenė-71	1610.2	O_1	argillite	4.8	19.9	32.8	42.4	1.46	59.3	511	435
Baubliai-1	1813.0	S_1	marl	5.5	19.3	37.2	38.0	0.87	103.8	540	442
Baubliai-2	1868.7	O_3	argillite	4.6	19.4	38.6	37.4	0.69	52.1	521	448
Baubliai-4	1988.7	O_1	argillite	3.5	20.4	35.7	40.3	1.06	41.3	333	436
Klaipėda-1	2080.2	O_3	argillite	9.2	27.7	44.0	19.2	0.53	3.5	159	451
Lauksargiai-4	1715.6	O_3	argillite	5.4	20.4	37.1	37.1	0.90	1.9	148	444
Laužai-1	2085.4	Cm_2	argillite	4.7	18.5	47.3	29.5	0.71	71.2	478	442
Mamiai-1	1748.0	O_3	argillite	3.6	18.1	38.1	40.2	0.53	3.5	320	441
Nida-1	2044.2	S_1	argillite	5.7	20.3	38.0	36.1	0.79	23.5	473	438
Ramučiai-1	2009.1	S_1	argillite	16.8	40.4	37.3	5.5	2.0	42.5	383	443
Ramučiai-3	2047.7	O_3	argillite	7.9	34.4	48.6	9.2	0.67	6.0	134	446
Rukai-1	1919.6	O_3	argillite	5.7	21.5	38.7	34.0	0.85	4.2	93	455
Rukai-2	1901.9	O_2	argillite	5.2	24.0	43.3	27.6	0.63	24.3	301	448

*mpx/n-C_8 – (m+p)-xylene/n-octene ratio; S_2 – generated hydrocarbons, mg/g rock; HI – Hydrogen Index, mg/g TOC; T_{max} – maximum pyrolysis temperature, °C.

and Ludlow stages, while their thickness can reach 360 m. This is a dark grey, black argillite and clayey marl complex in which organic matter content ranges from 0.7 to 9–11%, but can also reach 16%. The oil and gas generation potential ranges from 7–10 kg to 57 kg HC/t_{rock}. Hydrogen Index varies within the range of 0.4–0.8% (Zdanavičiūtė, 1996). Silurian pyrolysis-gas chromatograms show a similar content of pyrolysates as the Ordovician ones, including well developed n-alkene/n-alkane doublets extending to about C_{25} and a low to moderate aromaticity (typical (m+p)-xylene/n-octene = 0.8–1.3). Most of the pyrolysis-gas chromatograms show a somewhat elevated baseline at higher carbon numbers, which indicates the presence of chromatographically unresolved material (UCM) in the pyrolysate. This is not unusual in pyrolysates from low mature samples. The pyrolysate from Ramučiai-1 well (2009.1 m) is more gas-rich and slightly more aromatic ((m+p)-xylene/n-octene = 2.0), which is consistent with the high thermal maturity of this sample.

Summarising it can be said that the Py-GC results suggest the kerogen composition and maturity in most samples from the potential Silurian source rocks to be basically the same as in the organic-rich Ordovician shale.

CONCLUSIONS

1. Lower Palaeozoc rocks were found to contain prevailing syngenetic, sapropel organic matter of marine origin with vitrinite-like particles and large amounts of charred fauna remains. Fine detrital sapropel is spread among mineral components as very fine particles, or in a lens or nest shape. The major part of organic matter is represented by liptinite, with its content equal to or exceeding 20%. It is found together with dispersed liptodetrinite most often in sapropel matter, or rarer among mineral components. Fragments or well-preserved tasmanites are often observed, while sporinite, kutinite or matter originated from resins or wax are rarer.

2. The maturity of organic matter depends mainly on rock occurrence depth and increase in the direction from NE to SW. A large difference is determined (measurements were made in the same sample) between R_o for bituminite and for vitrinite-like particles, which are mainly composed of charred remains of graptolite. Bituminites, being at an early stage of diagenesis, are notable for lower reflectance than vitrinite; moreover, the reflectance of charred graptolite remains increased at a higher rate than that of vitrinite.

3. All the kerogen samples of source rocks are rich in paraffin pyrolysates with alkanes/alkenes in their chain having 25 or more carbon atoms. No obvious relationship was determined between aromatic hydrocarbon content or carbon atom number distribution and the Hydrogen Index. The south-western part of Lithuania (Ramučiai-1, -3 wells) was found to contain light hydrocarbons with aromatic pyrolysates prevailing, indicating a significant maturity of organic matter.

4. Both pyrolysis-gas chromatography data and Rock Eval analyses showed that organic matter was of Type II and rich in aliphatic hydrocarbons.

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Onytė Zdanavičiūtė, Elźbieta Swadowska

LIETUVOS APATINIO PALEOZOJAUS ORGANINĖS MEDŽIAGOS PETROGRAFINIAI BEI PIROLIZĖS-DUJŲ CHROMATOGRAFIJOS TYRIMAI

S a n t r a u k a

Dispersinės organinės medžiagos petrografiniai bei kerogeno pirolizės-dujų chromatografijos tyrimų duomenys leido nustatyti organinės medžiagos sudėtį, katagenezės laipsnį bei jos paplitimo kambro, ordoviko ir silūro naftos motininėse uolienose pobūdį. Organinės medžiagos kiekis apatinio paleozojaus uolienose yra labai kaitus, bet petrografiniu požiūriu ji mažai diferencijuota. Vyrauja singenetinė, sapropelinė, jūrinės kilmės organinė medžiaga, dalelės panašios į vitrinitą, nemažai apanglėjusių gyvūnijos liekanų. Smulkus detritinis sapropelis tarp mineralinių komponentų paplitęs labai smulkiai išsibarsčiusiais lęšiais arba lizdais. Dažnai panašios į vitrinitą dalelės turi morfologinių bruožų, rodančių, kad tai apanglėjusios gyvūnijos liekanos (graptolitai). Liptinitas sudaro didelę organinės medžiagos dalį, jo kiekis siekia 20% arba ir daugiau. Liptinito dalelių aptinkama kartu su dispersiniu liptodetrinitu dažniausiai sapropelinėje medžiagoje, rečiau tarp mineralinių komponentų. Dažnos nuolaužos arba gerai išsilaikę tasmanitai, kurie yra būdingi sapropelinių jūrinių nuosėdų komponentai. Rečiau randamas sporinitas, kutinitas arba medžiaga iš dervų ar vaško.

Organinės medžiagos subrendimo laipsnis yra nustatytas pagal singenetinių bituminitų ir į vitrinitą panašių dalelių šviesos atspindžio rodiklius. Katagenezės laipsnio kaita dažniausiai priklauso nuo uolienų slūgsojimo gylio, rodiklis R_o rodo jo padidėjimą iš ŠR į PV. Pastebimas didelis R_o skirtumas (matavimai atlikti tame pačiame pavyzdyje) tarp bituminito ir į vitrinitą panašių dalelių, kurios daugiausia sudarytos iš apanglėjusių graptolito liekanų. Ankstyvoje diagenezės stadijoje bituminitai mažiau reflektiški negu vitrinitas, tuo tarpu apanglėjusių graptolito liekanų reflektiškumas didėja greičiau nei vitrinito.

Visi tirti kambro motininių uolienų kerogeno mėginiai turtingi parafininių pirolizitų, savo grandinėje jungiančių alkanus/alkenus, turinčius 25 arba daugiau anglies atomų. Pirolizės-dujų chromatografijos duomenys, gauti tiriant Laužų-1 gręžinio argilito kerogeną (2085,4 m gylis), leidžia daryti išvadą, kad organinės medžiagos katagenezės laipsnis atitinka ankstyvosios naftos generacijos fazę. Šioje chromatogramoje vyrauja alifatiniai junginiai, (m+p)-ksileno ir n-okteno santykis yra 0,71. Be to, n-alkano ir n-alkeno smailių išsidėstymas rodo ženklų skystų angliavandenilių generacijos potencialą.

Ordoviko naftos motininių uolienų kerogeno tyrimo duomenimis, vyrauja n-alkenų/n-alkanų dubletai. Aromatinių junginių kiekis nedidelis, (m+p)-ksileno ir n-okteno santykis kinta 0,5–1,1 ribose. Nenustatyta akivaizdžios priklausomybės tarp aromatinių angliavandenilių kiekio arba anglies atomų kiekio pasiskirstymo pirolizituose ir vandenilio indekso. Prist-1-enas rastas daugelyje pavyzdžių (bet ne visuose), taip pat Akmenės-71, Baublių-1, 4 Lauksargių-4 ir Nidos-1 gręžiniuose nustatyta neidentifikuota smailė, esanti tarp C_{11} ir C_{12} (tai galbūt naftaleno, benztiofeno ar krezolio izomeras). Mažesnės variacijos – santykiniuose dydžiuose neišskaidytoje angliavandenilių dalyje (vadinamoje „kuproje") ir mažo bei didelio molekulinio svorio angliavandenilių pasiskirstyme. Tai, matyt, susiję su nedideliu organinės medžiagos brandumu. Pietvakarinėje Lietuvos dalyje, Ramučių-1, 3 gręžinyje, yra nustatyti lengvi angliavandeniliai, vyrauja aromatiniai pirolizitai. Kol kas negalima paaiškinti neįprastai didelio aromatinių pirolizitų kiekio ordoviko mėginyje iš Akmenės-71 gręžinio (1610,2 m gylis) ir labai aukšto vandenilio indekso (511 mg/g TOC), tam reikia papildomų tyrimų.

Silūro pirolizės-dujų chromatogramos rodo panašią organinės medžiagos sudėtį kaip ir ordoviko, įskaitant gerai išvystytus n-alkeno/n-alkano dubletus, esančius iki C_{25}, ir mažą arba vidutinį aromatinių pirolizitų kiekį (paprastai (m+p)-ksileno ir n-okteno santykis lygus 0,8–1,3). Ramučių-1 gręžinio pirolizitas (2009,1 m) yra turtingesnis dujų, šiek tiek daugiau turi aromatinių angliavandenilių ((m+p)-ksileno ir n-okteno santykis lygus 2,0), ir tai ati-

tinka aukštą šio pavyzdžio organinės medžiagos brandumą.

Pirolizės-dujų chromatografijos duomenys leidžia daryti analogišką Rock Eval duomenims išvadą, kad kerogenas gali būti priskirtas II tipui, turtingam alifatinių angliavandenilių.

Оните Зданавичюте, Элжбета Свадовска

ИССЛЕДОВАНИЯ ОРГАНИЧЕСКОГО ВЕЩЕСТВА НИЖНЕГО ПАЛЕОЗОЯ ЛИТВЫ ПЕТРОГРАФИЧЕСКИМ И ПИРОЛИТИЧЕСКИМ ГАЗО-ХРОМАТОГРАФИЧЕСКИМ МЕТОДАМИ

Р е з ю м е

Исследования рассеянного органического вещества петрографическими методами и изучение керогена пиролитическим газо-хроматографическим методом позволяют установить состав органического вещества, степень катагенеза и характер распространения в нефтематеринских породах кембрия, ордовика и силура. Количество органического вещества в породах нижнего палеозоя неодинаково, но с петрографической точки зрения мало дифференцировано. Преобладают сингенетичноеии сапропелевое органическое вещество морского происхождения и частицы, похожие на витринит, а также присутствует большое количество обугленных остатков живых организмов. Мелко-детритовый сапропель среди минеральных компонентов мелко рассеян или представлен в форме капель и гнезд. Морфологические черты похожих на витринит частиц указывают на то, что это – обугленные органические остатки (граптолиты). Значительную часть (20% или больше) органического вещества составляет лейптинит. Чаще всего частицы лейптинита вместе с рассеянным лейптодетринитом встречаются в сапропелевом веществе, реже среди минеральных компонентов. Часто наблюдаются хорошо сохранившиеся тасманиты или их обломки, являющиеся компонентами морских сапропелевых отложений. Реже присутствуют споринит, кутинит или вещество, образованное из смолы и воска.

Степень катагенеза органического вещества установлена по показаниям отражения света сингенетичных битуминитов и частиц, похожих на витринит. Изменение степени катагенеза зависит, в основном, от глубины залегания пород, показатель Ro указывает на ее увеличение с СВ на ЮЗ. Была отмечена большая разница (измерения выполнены на том же самом образце) между измеренными значениями Ro битуминита и Ro частиц, сходных с витринитом, значительную часть которых составляют обугленные остатки граптолита. На ранней стадии диагенеза битуминиты имеют меньшую рефлективность, чем витринит, тогда как рефлективность обугленных остатков граптолита увеличивается значительно быстрее по сравнению с рефлективностью витринита.

Все исследованные пробы керогена из материнских пород кембрия богаты парафиновыми пиролизитами, соединяющими в своей цепочке алканы/алкены и имеющими 25 и больше атомов углерода. Данные пиролитической газовой хроматографии, полученные при изучении керогена из аргиллита скважины Лаужай-1 (глуб. 2085,4 м), позволяют сделать вывод о том, что степень катагенеза органического вещества соответствует ранней фазе генерации нефти. На этой хроматограмме преобладают алифатические соединения, соотношение (m+p)-ксилена и n-октена равно 0,71. Кроме того, расположение пиков n-алкана и n-алкена свидетельствует о существенном потенциале генерации жидких углеводородов.

Данные исследования керогена материнских пород ордовика также указывают на преобладание дуплетов n-алкана и n-алкена. Количество ароматических соединений незначительно, соотношение (m+p)-ксилена и n-октена колеблется в пределах 0,5–1,1. Видимой зависимости между количеством ароматических углеводородов или количеством атомов углерода, распределенных в пиролизитах, и водородным индексом не установлено. Прист-1-ен установлен в большинстве образцов (но не во всех), кроме того, в скважинах Акмяне-71, Баубляй-1, -4; Лауксаргяй-4 и Нида-1 между пиками C_{11} и C_{12} обнаружен неидентифицированный пик (возможно, это изомер нафталена, бензтиофена или крезоля). Вариации относительных величин в нерасчлененной части хроматограммы (в так называемом «горбу») и в распределении маленького и большого молекулярного веса углеводородов незначительны. Это, по-видимому, связано с небольшим созреванием органического вещества. В юго-западной части Литвы, в скважинах Рамучяй-1, -3, установлены легкие углеводороды и преобладают ароматические пиролизиты. Наличие необычно большого количества ароматических пиролизитов в образце ордовика из скважины Акмяне-71 (глуб. 1610,2 м) и установление очень высокого водородного индекса (511 мг/г TOC) пока не имеют объяснения и требуют дополнительных исследований.

Хроматограмма силурийского образца показывает сходный состав с образцом ордовика, включая хорошо развитые дуплеты n-алкана/n-алкена, существующие до C_{25}, и небольшое или среднее количество ароматических пиролизитов (обычно соотношение (m+p)-ксилена и n-октена от 0,8 до 1,3). Пиролизит из скважины Рамучяй-1 (глуб. 2009,1 м) насыщен газом. В нем присутствует немного больше ароматических соединений (соотношение (m+p)-ксилена и n-октена равно 2,0), что указывает на более высокую степень катагенеза органического вещества в исследуемом образце. Данные пиролитической газовой хроматографии, как и данные Rock Eval, позволяют сделать вывод о том, что кероген богат алифатическими углеводородами и может быть отнесен ко II типу.