

COMPOSITION OF LOWER PALAEOZOIC NATURAL BITUMENS OF ESTONIA

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More than 160 natural bitumen occurrences have been recorded in the Lower Palaeozoic rocks of Estonia. The composition of natural bitumens of Estonia has been studied and compared with the composition of the petroleum of the Baltic Syncline. Two types of bitumen occurrences have been distinguished: flat lenses of solid bitumen (mainly in North-Eastern Estonia) and the occurrences of solid, viscid or liquid bitumens in Western Estonia and on Hiiumaa Island.

In the bitumens of North-Eastern Estonia the content of asphaltenes is remarkably higher and the content of oils smaller than of Western Estonia. The varieties of North-Eastern Estonia are represented by solid asphaltites containing both Ni- and V- porphyrines. In Western Estonia, highly resinous natural bitumens yielding V-metalloporphyrines occur. These differences in composition may indicate different origin and different conditions of formation for the two varieties. The composition of natural bitumens of Western Estonia resembles to that of the petroleum of the Baltic Syncline, suggesting their common origin. Their geochemical differences are related to the depth of occurrence and can be explained by hypergenous alterations.

Key words: natural bitumens, petroleum, Lower Paleozoic, Estonia, Baltic Syncline.

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INTRODUCTION

More than 160 natural bitumen occurrences have been recorded from the Lower Palaeozoic rocks in Estonia. The chemical composition of 33 bitumen samples, were analyzed from different stratigraphical levels in selected boreholes. The elemental and group composition analyses of natural bitumens, as well as hydrocarbon composition analyses, were made in 1989–1992 at the St. Petersburg Petroleum Investigation Institute (Tables 1 and 2).

By the distribution area, morphological features and bedding conditions, two types of bitumen occurrences have been distinguished (Kattai and Lokk, 1994; Kattai et al., 1994). The first type includes flat lenses of solid bitumen that occur in North-Eastern and Northern Estonia in the sequence ranging from the Lower Cambrian Lontova Regional Stage to the Middle Ordovician Kukruse Regional Stage (Llandeilo). The second type comprises the occurrences of liquid, viscid and solid natural bitumens in Western Estonia, mainly in the sequence of carbonaceous rocks from the Idavere (Caradoc) to the Raikküla regional stages (Llandovery) (see Kaljo and Nestor, 1990 and Raukas and Teedumäe, 1997 for Estonian regional stages and their tentative correlation with British Series).

ASPHALTITES IN NORTH-EASTERN ESTONIA

The first type of natural bitumen occurrences is represented by solid, shining coal-like matter, easily crushing at a strike. A natural bitumen sample from the kukersite

productive seam in Estonian Deposit has a density of 1.1–1.26 g/cm³ and hardness by Mohs scale 2–3. The content of mineral component is 5–6 %, the rest consists of organic matter. The bitumen sample is almost completely soluble in chloroform (Kattai and Kundel, 1987). Elemental composition of the bitumen: C 81.6–88.9 %, H 8.1–9.5 %, N 1.0–2.2 %, O+S 3–8 %. In group composition asphaltenes prevail, their content ranges from 46.4–85.7 %, the share of resins is 11.6–46.8 % and that of oils 2.6–17.2 %. These data coincide with those of the natural bitumens from the Volkhov Regional Stage in the Leningrad Region (Ljutkevič and Kurbackaja, 1964). The composition of the oil fraction of natural bitumens has been studied only in two samples from the Kukruse Regional Stage. In one sample saturated hydrocarbons (79 %) prevailed, in the other sample the content of aromatic hydrocarbons reached 67 % (Klubov and Urov, 1988).

The $\delta^{13}\text{C}$ values of the natural bitumens in the kukersite of the Kukruse Regional Stage and the glauconitic sandstone of the Hunneberg Regional Stage largely coincide, ranging from –29.3 to –29.7 ‰ (Bondar et al., 1993). In natural bitumen lenses, the content of SiO₂ is considerably higher and the concentration of CaO lower than in the surrounding rock. The bitumen yields both Ni- and V-metalloporphyrines (Kattai et al., 1995). Considering the reaction of bitumens with organic solvents, as well as their elemental and group composition, the above-described solid natural bitumens can be assigned to the class of asphaltites (Fig. 1), to the subclass of grahamites (Radčenko and Uspenskij, 1979; Klubov, 1983).

Table 1

COMPOSITION OF NATURAL BITUMENS IN DIFFERENT STRATIGRAPHICAL LEVELS

	Elemental composition, %				H/C _{at}	δ ¹³ C, ‰	Group composition, %			Composition of oil fraction, %	
	C	H	N	O			S	oils	resins	asphaltenes	SHC*
NORTH-EASTERN ESTONIA											
Llandeilo	84.9-88.9	8.7-9.1	1.0-2.2	1.5-4.3	0.4-0.8	-29.3- -29.6	2.6-6.8	6.8-17.5	46.4-85.7	33-79	21-67
Llanvirm	84.8-85.7	8.7-8.8		5.4-6.5							
Arenig	84.6-87.5	9.0-9.5	2.4-3.5		2.4		-29.7	17.2	15.8	55.5	
€ ₁ ln	81.6	9.4	1.2		7.8						
WESTERN-ESTONIA											
Ludlow							37	50.4	12.6		
Wenlock							27.4	62.3	10.4	49.3	50.7
Llandoverly	76.8-86.9	8.9-11.6	0.9-10.0		0.5-4.2	-30.2	34.7-70.7	24.8-55.2	2.0-10.1	54.4-76.5	23.5-45.6
Ashgill	82.5-85.8	8.6-11.6	1.9-6.9		0.4-2.0		38.0-62.6	35.4-49.4	3.0-12.6	36.6-77.9	22.1-63.4
Caradoc	81.6-87.5	9.6-11.9	0.6-7.0		0.6-1.9	-29.8	40.3-74.6	27.1-58.3	3.7-17.5	46.5-88.5	11.5-53.5
Llandeilo	85.8-86.7	11.4-11.9	0.2	0.8-1.6	0.6-0.8		60.8	34.9	4.3	69.0	31
Llanvirm	85.4-86.4	11.0-11.2	0.2-0.7	0.8-2.6	0.8-0.9		50.3-57.5	39.4-44.3	3.1-5.4	60.1-68.7	31.3-39.9

* saturated hydrocarbons

** aromatic hydrocarbons

Table 2

COMPOSITION OF NATURAL BITUMENS

	NE Estonian asphaltine	Western Estonia		
		asphalt	maltha	petroleum
Sampling depth, m	3-56	2-66	2-226	30-75
Bitumen content of the rock, %	92-99	0.03-10.4	0.05-1.3	0.4-1.9
Elemental composition, %:				
C	81.6-88.9	76.8-83.3	81.6-87.5	85.6-86.4
H	8.7-9.5	9.1-10.3	9.6-11.9	10.6-11.9
O+N+S	2.9-9.0	7.4-14.2	1.1-8.8	1.7-3.8
C/H	8.7-10.0	8.3-9.5	7.2-8.6	7.3-8.1
H/C _{at}	1.2-1.38	1.25-1.45	1.32-1.66	1.50-1.65
δ ¹³ C, ‰	-29.3- -29.7	-29.8- -30.2	-30.5	
Group composition, %:				
oils	2.6-17.2	34.7-40.0	42.2-62.6	69.2-74.6
resins	11.6-46.8	42.0-55.0	34.0-50.0	24.8-27.1
asphaltenes	46.4-85.7	10.1-17.5	1.8-14.4	3.7-6.1
Composition of hydrocarbons, %:				
saturated hydrocarbons	33-79	36.6-69.2	46.5-91.5	76.5-88.5
aromatic hydrocarbons	21-67	30.8-63.4	8.5-53.5	11.5-23.5
Composition of saturated hydrocarbons:				
n-alkanes		0-20.2	2.1-8.7	1.2
isoprenoid alkanes		0-3.6	0.2-6.6	1.04
iso + cycloalkanes		76.1-100	90.5-97.5	97.8
Composition of n-alkanes:				
C _{<16}		0.2-7.4	1.0-2.7	2.7
C ₁₆ -C ₂₀		21.1-25.0	19.7-36.4	22.9
C ₂₁ -C ₂₅		33.8-47.8	37.5-52.7	56.4
C ₂₆ -C ₃₀		26.9-32.2	16.9-24.8	14.5
C _{>30}		1.6-4.1	1.5-3.4	3.6
ΣC _{2n-1} /ΣC _{2n}		0.94-1.13	0.93-1.04	1.0
pristane/phytane	0.78	0.97-1.48	0.21-1.31	0.84
Composition of aromatic hydrocarbons:				
monoaromatic	66.9	59.9-60.7	58.8-62.4	59.6
diaromatic	21.6	16.9-26.0	19.6-30.3	29.8
triaromatic	6.8	8.1-12.1	6.7-10.6	7.2
tetraaromatic	4.7	5.8-12.0	3.6-9.8	3.4

NATURAL BITUMENS IN WESTERN ESTONIA

The natural bitumens of the second type do not occur as high-concentration bodies. They occur as impregnation blotches and stripes, faunal and plant remnants, pore, cavern and fissure fillings, or small nest-like inclusions. In most studied samples the bitumen content does not exceed 1 %, reaching 1.2-3.2 % only in five samples. Ex-

ceptionally, in about 20 cm thick layer of limy siltstone in the lower part of the Idavere Regional Stage the bitumen content reaches 10 %.

The most common is the viscid variety, which according to the classification belongs to the class of malthas (Fig. 1) (Radčenko and Uspenskij, 1979). Their elemental composition is the following: C mainly 85-86 %,

H 9.6–11.9 % and O+N+S 1.1–8.8 %. The content of oil fraction is 42–63 %, from which the saturated hydrocarbons form 46–91 % and aromatic hydrocarbons 8–53 %. The content of resins is 34–50 %, and that of asphaltenes up to 15 %.

The composition of liquid oil-like bitumens greatly resembles that of malthas, with somewhat higher content of oils (70–74%), and lower contents of resins (25–27 %) and asphaltenes (4–6 %). In the oil fraction the share of saturated hydrocarbons (77–89 %) exceeds that of aromatic ones (11–23 %). Considering the great share of resins and asphaltenes, this liquid natural bitumen is considered to belong to high-resinous petroleums (Fig. 1).

In the elemental composition of solid bitumens the contents of C and H are lower (76.8–83.3 % and 9.1–10.3 %, respectively), and the content of O+N+S is higher – 7.4–14.2 %. The solid bitumens contain 35–40 % of oils, which consist of approximately equal portions of saturated and aromatic hydrocarbons, 42–55 % of resins and 10–18 % of asphaltenes. According to the classification (Fig.1) (Radčenko and Uspenskij, 1979), the solid bitumens belong to the class of asphalts.

The composition of the saturated hydrocarbons of different classes of natural bitumens (petroleums, malthas, asphalts) is rather similar (Table 2): the content of nor-

mal (n-) and isoprenoid alkanes is low (0–8.7 and 0–6.6 % correspondingly), while the content of iso- and cycloalkanes is high (76.1–100 %). Exceptionally, only in one asphalt sample the content of n- and isoprenoid alkanes reaches 23.8 %. In general, petroleums contain all n-alkanes, from C₁ to C₄₀ (Tissot and Welte, 1981). In Estonia, the variety of n-alkanes mainly ranges from C₁₃ to C₃₂, of which the content of C₂₁–C₂₅ n-alkanes forms 33.8–56.4 %. The ratio of the n-alkanes with odd and even numbers of C-atoms is rather stable, ranging from 0.93–1.13. Among the isoprenoid alkanes the hydrocarbons with C₁–C₂₀ prevail with the highest content of pristane (C₁₉) and phytane (C₂₀). The pristane/phytane ratio varies from 0.65 to 1.50 (Table 3). Pristane and phytane are chemofossils formed from phytol (related with chlorophyll in modern organisms); pristane in the oxygen-rich and phytane in the oxygen-poor environment. The decomposition of phytol takes place during a couple of months (Tissot and Welte, 1981). Thus, the above-described ratio reflects the diagenetic environment of the source matter. The great variation of the pristane/phytane ratio is probably due to the occurrence of different sources of hydrocarbons and is not reflecting the Eh of the corresponding diagenetic environments.

Aromatic hydrocarbons are characterized by rather

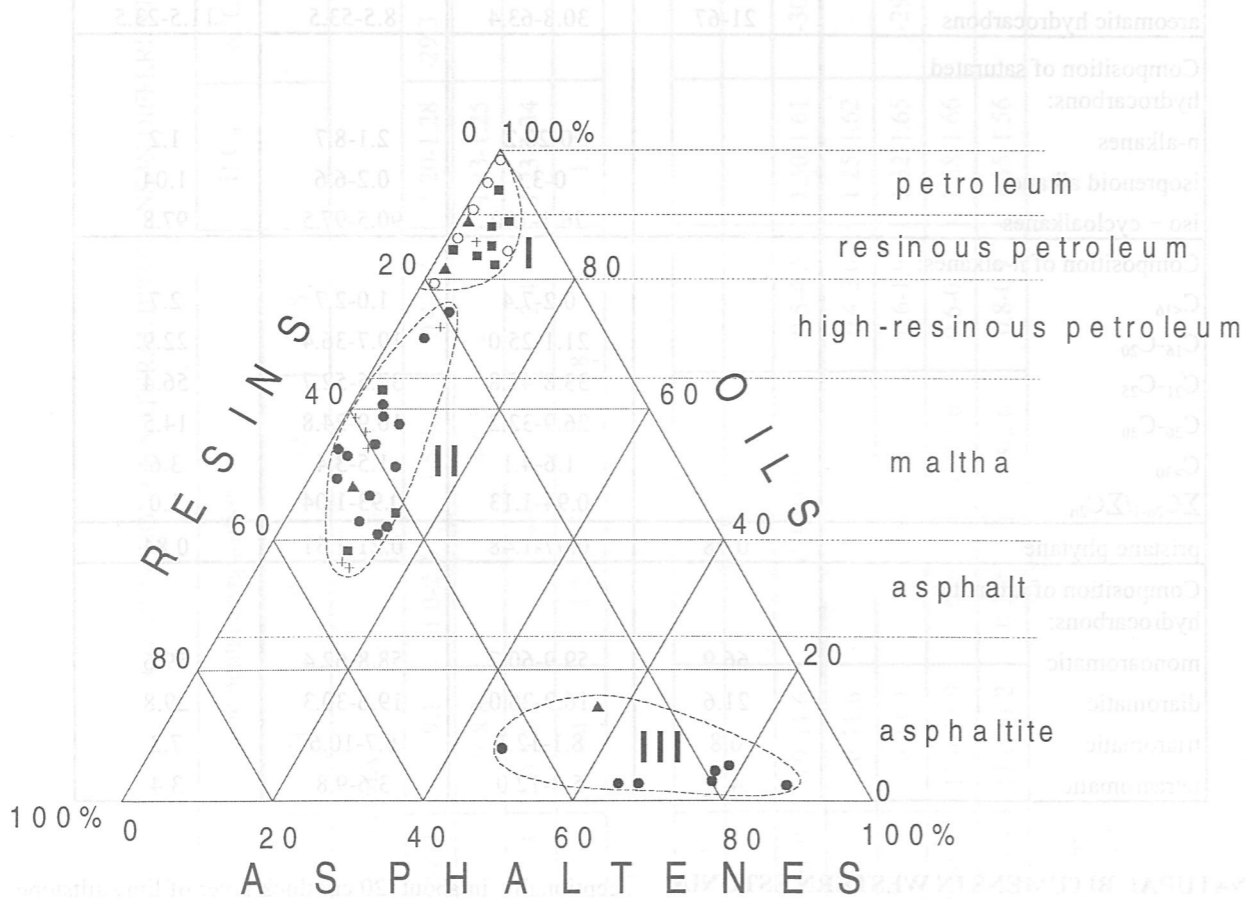


Figure 1. Group composition (oils-resins-asphaltenes) of the petroleum in the Baltic Syneclise (I) and natural bitumens in Estonia (II – Western Estonia, III – North-Eastern Estonia).

Age of the surrounding rocks: ○ - E₂; ▲ - O₁; ● - O₂; ■ - O₃; + - S_{1,2}.

The classification of bitumen types is given after (Radčenko and Uspenskij 1979)

THE PRISTANE/PHTYANE RATIO OF SATURATED HYDROCARBONS IN PETROLEUM AND NATURAL BITUMENS

Petroleum-bearing layer	Central and southern parts of Baltic Syneclise, petroleum	Gotland Island, petroleum	Western Estonia, natural bitumens and petroleum
S	2.0		0.84–1.50
O ₃	2.87	1.15	0.65–1.31
O ₂			1.10–1.48
E ₂	2.4		

stable high content of monoaromatic hydrocarbons 58.8–62.4 %. The content of diaromatic hydrocarbons (16.9–30.3 %) exceeds that of tri- (6.7–12.1 %) and tetraaromatic hydrocarbons (3.4–12.0 %). A common characteristic feature for all samples is the usual distribution of aromatic hydrocarbons: monoaromatic hydrocarbons → diaromatic hydrocarbons → polyaromatic hydrocarbons. The δ¹³C isotope composition is stable, ranging from -29.8– -30.5 ‰ (Bondar et al., 1993). The biomarkers in bitumens are represented by vanadyle porphyrines (Kattai et al., 1995).

Thus, a wide range of natural bitumens – from highly resinous petroleums to asphalts is documented in Western Estonia. Classifying them on the basis of their oil content is rather conventional. In fact, they represent a constant series of associated bitumens: resinous petroleum–maltha–asphalt, probably formed from a uniform source of hydrocarbon fluids. The variations in their composition can be explained by differential influence of hypergenesis. At a regressive bitumenogenesis, the hypergenetic changes in the composition of petroleums–malthas–asphalts are expressed by the decreasing contents of C (86.4→76.8 %), H (11.9→9.1 %) and the H/C_{at} atomic ratio (1.66→1.25), and increasing content of hetero-elements O+N+S (1.7→14.2 %) and the C/H ratio (7.3→9.5). In the group composition the following changes are observed: the content of oil fraction decreases (74.6→34.7 %), as does the content of saturated hydrocarbons in the oil fraction (91.5→36.6 %); the contents of resins (21.6→65.3 %), asphaltenes (1.8→17.5 %) and aromatic hydrocarbons in the oil fraction (8.5→63.4 %) increase. The content of aromatic hydrocarbons in bitumens varies from 5 to 25 %, while the content of saturated hydrocarbons is 9–61 %, and that of asphaltenes and resins 30–74 %. Thus, the decrease in the content of saturated hydrocarbons is compensated mainly by the increase of the content of resins, and to a lesser extent also by aromatic hydrocarbons and asphaltenes. However, the considerable decrease in the content of saturated hydrocarbons in the oil fraction of asphalts (36–69 %) as compared with petroleum (76–88 %) is the evidence of biogenic oxidation (biodegradation) instead of pure chemical oxidation (Gol'dberg, 1981; Tissot and Welte, 1981).

The occurrence of considerable biodegradation is also supported by missing n- and isoprenoid alkanes in several asphalt samples.

There is no evident connection between the chemical composition and the depth of occurrence of natural bitumens (most of the samples have been taken from the depths less than 100 m). For example, in borehole K-39 (in south-western part of Hiiumaa Island) in the biohermal limestone of the Juuru Regional Stage at a depth of 22.4 m asphalt and at 30.6 m resinous petroleum was observed. On the other hand, in borehole F-353 (central part of Hiiumaa Island) petroleum was recorded at 75.2 m and maltha at 102.8 m. It is possible that the occurrence of different bitumen varieties at different depths gives the evidence of migration of fluids, which have taken place in different times.

NATURAL BITUMENS IN ESTONIA AND PETROLEUM IN THE BALTIC SYNECLISE

The investigations of petroleum in the Baltic Syneclise and natural bitumens have been carried out using the same methods, which makes the results comparable. The data about petroleum composition are based on the published data by different authors (Gol'dberg and Gurko, 1972; Gurko and Bogomolov, 1978; Kaduniene et al., 1985; Kalinko, 1987) etc.

In Figure 3 the comparison of natural bitumens and the petroleums of different-aged layers along the line Kaliningrad Region–Lithuania–Latvia–Gotland Island–Western Estonia – North-Eastern Estonia is presented. The depth of the Lower Palaeozoic sedimentary cover and the depth of the petroleum-bearing layers increases towards the south. On Gotland Island the petroleum-bearing rocks are observed at 300–600 m, in Latvia at 800–1200 m, while in the Kaliningrad Region they lie at 2000 metres deeper (Fig. 3). In Estonia natural bitumens and high resinous petroleum are observed mostly at the depths up to 100 m. Below that depth, the content of oil fraction in petroleum reaches 85–90 %, while at smaller depths it decreases to 70–75 %. Natural bitumens contain 35–60 % of oil. The content of resins in petroleum increases from 1–6 % in the south to 15–25 % in the north;

in Estonian natural bitumens it ranges 35–55 % (Figs. 1 and 3). In the majority of samples (more than 80 %) the share of benzene resins is more than that of alcohol-benzene resins (ratio 1:1.1–1:1.8). The content of asphaltenes in all petroleum samples is up to 10 %, while in natural bitumens it reaches 17 %. In petroleum samples the ratio oils (resins+asphaltenes) is 6–8 % in the south, decreasing to 2–4 % in the north, in natural bitumens it is less than 1 % (Fig. 3). The increase of the share of resins and asphaltenes, making the petroleum heavier, is accompanied by the increase of sulfur content.

The petroleum from/all petroleum-bearing layers of the Baltic Syncline is characterized by an elevated resin content, with the share of resins+asphaltenes 10–20 % and is considered resinous (Kalinko, 1987), while the samples collected in Hiiumaa Island can be classified as highly resinous (20–30 %) (Figs. 1 and 3).

In the region of Baltic Syncline the petroleum has obvious paraffinic character. The content of alkanes is 50–70 %, the content of cycloalkanes 15–25 %, i.e. the total content of saturated hydrocarbons is 65–85 % and that of aromatic hydrocarbons only 5–15 %. Northward, the share of saturated hydrocarbons decreases, while the content of aromatic hydrocarbons increases. Thus, the content of aromatic hydrocarbons is the highest in the Gotland petroleum (25 %); as compared to 15–25 % in Estonian natural bitumens. In general, in both petroleum and natural bitumens, the content of saturated hydrocarbons exceeds that of aromatic ones. The ratio of saturated

and aromatic hydrocarbons is 6–11 in the south, decreasing to 1.5–2.5 in the north (Figs. 2 and 3).

The changes in group composition of petroleum, as well as the composition of hydrocarbons are more considerable in north-east direction (along the Ušakovo–Krasnyi Bor–Gussev–Kybartai line), than in the longitudinal direction. According to Gubnicki and Sakalauskas (1973), it can be considered as an evidence of the prevailing lateral eastward migration of hydrocarbons. Similar conclusions have been suggested about the distribution regularities of natural bitumens on Hiiumaa Island (Kattai and Klubov, 1992).

According to the data presented by Gurko and Bogomolov (1978), the increase of the depth of petroleum-bearing layers is accompanied by the increase of n-alkanes in the saturated hydrocarbons of petroleum, as well as the concentration of light hydrocarbons. Thus, in the central region of the syncline the share of n-alkanes in petroleum forms 10–20 %, in Estonian natural bitumens and petroleum up to 3–4 %, while in some samples they are completely missing. Also, the content of n-alkanes is low in the Gotland petroleum (0.9 %).

In the petroleum of the central and southern parts of the Baltic Syncline, in the composition of n-alkanes light hydrocarbons C_7 – C_{11} prevail, while among the higher molecular alkanes C_{15} – C_{19} dominate. In the Gotland petroleum the content of C_{18} – C_{21} is the highest, while in the petroleum and natural bitumens of Hiiumaa Island C_{21} – C_{25} prevail. Consequently, within the borders of the Baltic

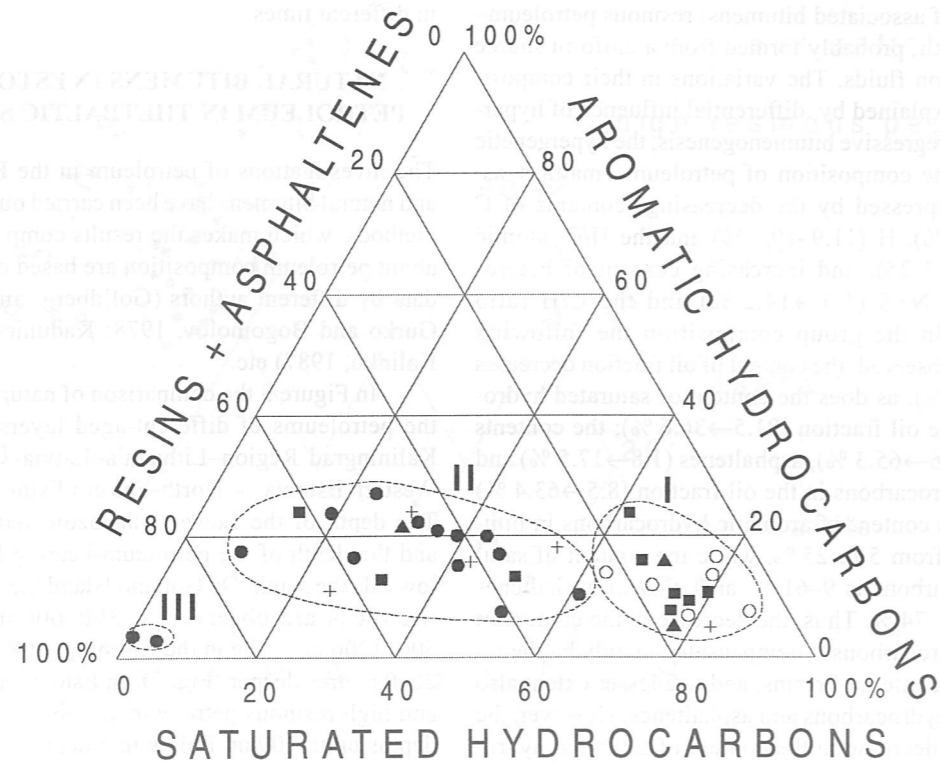


Figure 2. Composition (resins+asphaltenes-saturated hydrocarbons-aromatic hydrocarbons) of the petroleum in the Baltic Syncline (I) and natural bitumens in Estonia (II - Western Estonia, III - North-Eastern Estonia).

For the legend see Figure 1.

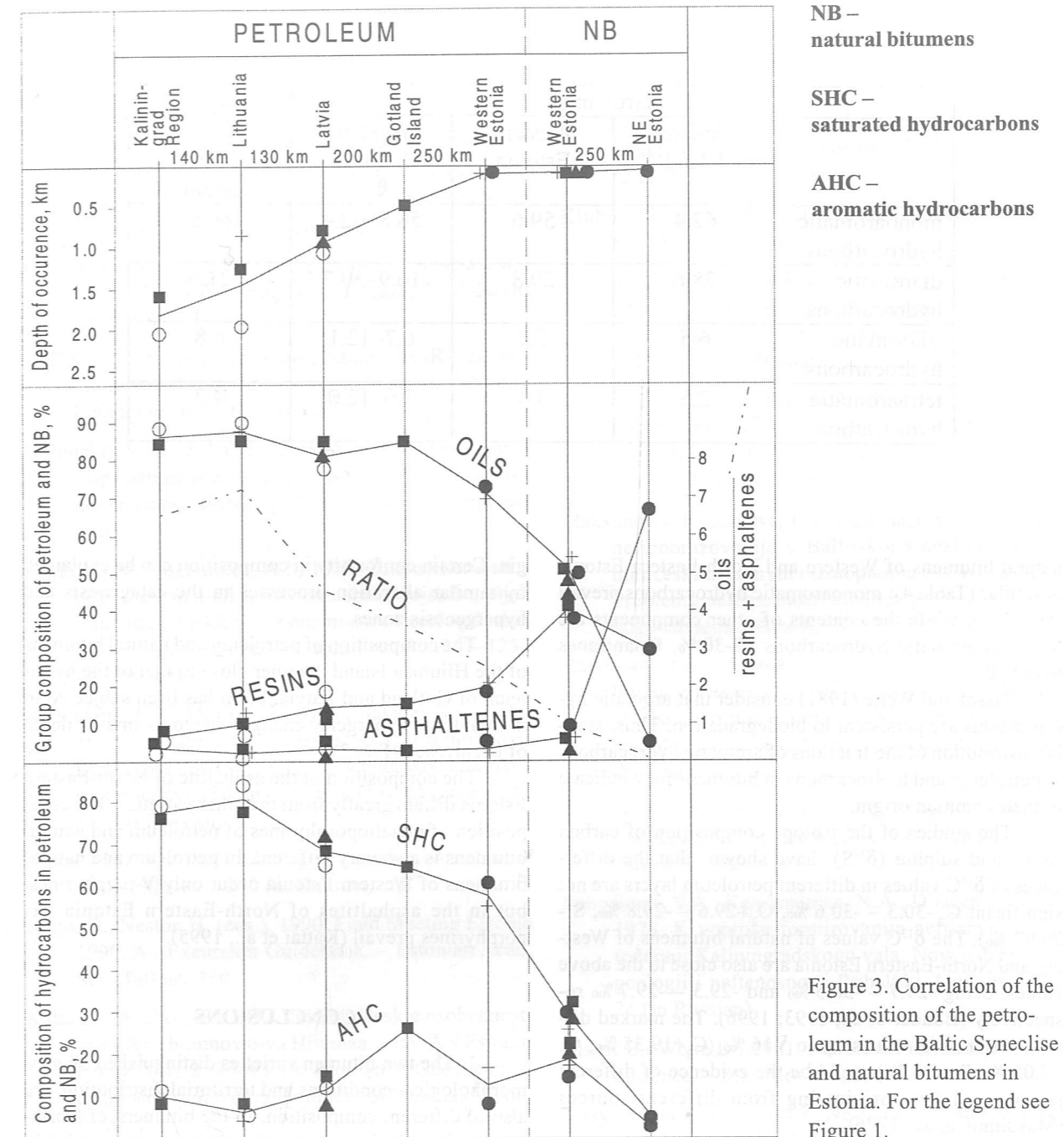


Figure 3. Correlation of the composition of the petroleum in the Baltic Syncline and natural bitumens in Estonia. For the legend see Figure 1.

Syncline from the south to the north and from the west to the east, the following changes in the composition of petroleum and natural bitumens can be observed:

(1) the share of resins, asphaltenes, S and aromatic hydrocarbons increases;

(2) the content of saturated hydrocarbons decreases, while the share of n-alkanes and light low-molecular hydrocarbons increase.

The above-described geochemical differences are related to the depth of occurrence of petroleum and may be caused by the hypergenic changes resulting in chemical (oxidation, polymerization), biological (biodegradation) and physical (outwashing the compounds soluble in water) processes (Tissot and Welte, 1981).

A characteristic feature of different petroleum layers of the Baltic Syncline is that rather constant carbon predominance index (CPI) of n-alkanes, ranging from 0.91–1.11 (Gurko and Bogomolov, 1978). The index increases with the increasing depth of the petroleum-bearing layers: Silurian – 0.75, Ordovician – 0.92, Cambrian – 1.0 (Vosylius, 1987). CPI of the petroleum of Gotland and Hiiumaa islands is 1.0, CPI of the natural bitumen of Hiiumaa Island ranges from 0.93 to 1.13.

The differences in the pristane/phytane ratio are more significant laterally than in vertical distribution (Table 3).

The composition of aromatic hydrocarbons of the petroleum of Gotland and Hiiumaa islands, as well as

COMPOSITION OF AROMATIC HYDROCARBONS, %

	Petroleum		Natural bitumens	
	Gotland Island	Western Estonia	Western Estonia	North-Eastern Estonia
monoaromatic hydrocarbons	62.4	59.6	58.8–62.4	66.9
diaromatic hydrocarbons	28.6	29.8	16.9–30.3	21.6
triaromatic hydrocarbons	6.5	7.2	6.7–12.1	6.8
tetraaromatic hydrocarbons	2.5	3.4	3.6–12.0	4.7

natural bitumens of Western and North-Eastern Estonia is similar (Table 4): monoaromatic hydrocarbons prevail (59–67%), while the contents of other components are lower (diaromatic hydrocarbons 17–30%, phenantrenes 6–11%).

Tissot and Welte (1981) consider that aromatic hydrocarbons are persistent to biodegradation. Thus, similar distribution of the fractions of aromatic hydrocarbons in petroleum and hydrocarbons in bitumens may indicate to their common origin.

The studies of the isotope composition of carbon ($\delta^{13}C$) and sulphur ($\delta^{34}S$) have shown that the differences of $\delta^{13}C$ values in different petroleum layers are not significant (C_2 -30.3 – -30.6‰, O_2 -29.6 – -29.8‰, S -29.97‰). The $\delta^{13}C$ values of natural bitumens of Western and North-Eastern Estonia are also close to the above values, being -29.7 – -30.5‰ and -29.3 – -29.7‰ respectively (Bondar et al., 1993; 1996). The marked differences in $\delta^{34}S$ values up to 16‰ (C_2 +19.35‰, O_2 +7.05‰, S +3.4‰) could be the evidence of different petroleum layers originating from different sources (Maksimov et al., 1976).

Analyzing the composition of petroleum of different levels showed, that most characteristics allow to suggest their common origin, while other features do not support this version.

Baltic petroleum researchers have suggested different versions about the origin of petroleum in the Baltic Syncline. Some of them (Gurko and Bogomolov, 1978; Šehodanov et al., 1975; Gol'dberg and Gurko, 1972) consider that the petroleum of different levels has common origin and has been formed from Cambrian alum shales. They explain the differences in the chemical composition of petroleum by uneven hypergenous transformation and migration processes.

Other researchers (Gubnickij, Sakalauskas, 1973; Maksimov et al., 1976; Kaduniene et al., 1985; Zdanavičiute et al., 1986) suggest that the petroleum in the Cambrian, Ordovician and Silurian rocks is of different ori-

gin. Certain conformity in composition can be explained by similar alteration processes in the catagenesis and hypergenesis zones.

The composition of petroleum and natural bitumens of the Hiiu-maa Island is rather close to that of the petroleum of Gotland and Latvia, but it has been subjected to more intense hypergenic changes due to its smaller depth of occurrence (Fig. 3).

The composition of the asphaltite of North-Eastern Estonia differs greatly from the other varieties. The composition of metalloporphyrines of petroleum and natural bitumens is also very different. In petroleum and natural bitumens of Western Estonia occur only V-porphyrines, but in the asphaltites of North-Eastern Estonia Ni-porphyrines prevail (Kattai et al., 1995).

CONCLUSIONS

1. The two bitumen varieties distinguished by geomorphological conditions and territorial distribution, are also of different composition. In the bitumens of North-Eastern Estonia the content of asphaltenes is remarkably higher and the content of oils smaller than in the bitumens of Western Estonia. The North-East Estonian varieties have also been subjected to greater hypergenic changes (up to solid asphaltites) than these of Western Estonia (highly resinous petroleum–maltha–asphalt). The first ones contain both Ni- and V- porphyrines, while in the second ones only V-metalloporphyrines have been recorded. The two varieties may be of different origin and formed under different conditions.

2. The natural bitumens of Western Estonia and the petroleum of the Baltic Syncline are rather similar in composition, which may indicate their common origin. Their geochemical differences are related to the depth of occurrence and can be explained by hypergenic alterations.

Table 4

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