CORRELATION STUDIES ON KEROGENEOUS ROCKS AND NATURAL BITUMENS OF ESTONIA AND CRUDE OILS OF THE BALTIC SYNECLISE

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By the results of capillary GC and computerized GC-MS investigation of seven natural bitumens and three kerogeneous rocks of Estonia, and four crude oils of the Baltic syneclise (from Lithuania, Latvia, Sweden and Russia) the similarity of stereoisomeric composition of polycyclic biomarkers and relative distribution of the latter and n-alkanes in oils and bitumens was elucidated in addition to the similarity of their carbon isotope composition established earlier. No correlation by the named geochemical parameters between oils and bitumens, and of any studied kerogeneous rock was observed.

The Baltic region is of interest to organic geochemists because of the occurence of crude oil accumulations, natural bitumen shows and oil shale deposits . The occurence of oil in this region is related to the Baltic syneclise. Several tens of oil accumulations have been discovered in its continental and shelf parts. Oil fields are exploited in Russia (Kaliningrad district), Lithuania and Sweden. Oil accumulations in Latvia are non-commercial. Main oil-bearing strata in the Baltic region are timed to the Middle Cambrian Deimena suite. There are oil-bearing strata in the Ordovician and Silurian.

Natural bitumen shows in Estonia have been discovered in its North-Eastern part, on the coast, and on the islands Hiiumaa and Saaremaa (Kattai et al., 1994, Kattai and Lokk, 1994). Stratigraphically, natural bitumens occur from the Lower Ordovician to the Lower Silurian. In Northeastern Estonia, mainly within Kukersite layers, a rather unique variety of the natural bitumens occurs - flat lenses of pure (92-99 %) asphaltite. They are allotigeneous and genetically not related to organic matter (OM) of Kukersite (Kattai and Lokk, 1994, Bondar et al., 1993, Kattai et al., 1995). In Western Estonia (except of islands) the natural bitumens occur mainly in viscid and solid states and have been recorded as impregnation spots and cavern fillings. On Hiiumaa Island viscid bitumen shows prevail over solid and liquid ones. The most common varieties are cavern fillings and impregnations. On Saaremaa Island dispersed bitumens prevail over cavern fillings.

EXPERIMENTAL

Crushed and powdered rocks and solid bitumens were extracted using chloroform. Asphaltenes were precipitated from crude oils and bitumen extracts with n-pentane (1:50). From the extracts of kerogeneous rocks neutral compounds were separated. The latter and malthenes of oils and bitumens were divided into four fractions of different polarity by thin layer silica-gel chromatography (TLC). Saturated hydrocarbon fractions were analysed using capillary gas chromatography (GC) (a Chrom 5 apparatus, Czechia) and computerized gas chromatography-mass spectrometry (GC-MS) (a Hitachi M 80 B system, Japan).

RESULTS AND DISCUSSION

A suite of seven natural bitumens and three kerogeneous rocks from Estonia and four crude oils from the Baltic syneclise was examined (Figs. 1, 2, Table 1).

The similarity of carbon isotope composition in oils and bitumens was established earlier (Bondar et al., 1996). Their $\delta^{13}C$ values fluctuate within 1‰ averaging -30.0‰. OM of Lower Ordovician Dictyonema shale, Middle Ordovician Kukersite oil shale and Early Silurian Mustjala reef limestone with dispersed kerogene do not correlate with oils and bitumens by $\delta^{13}C$ values (Fig. 2). $\delta^{13}C$ value -30.0‰ is characteristic of Cambrian OM.

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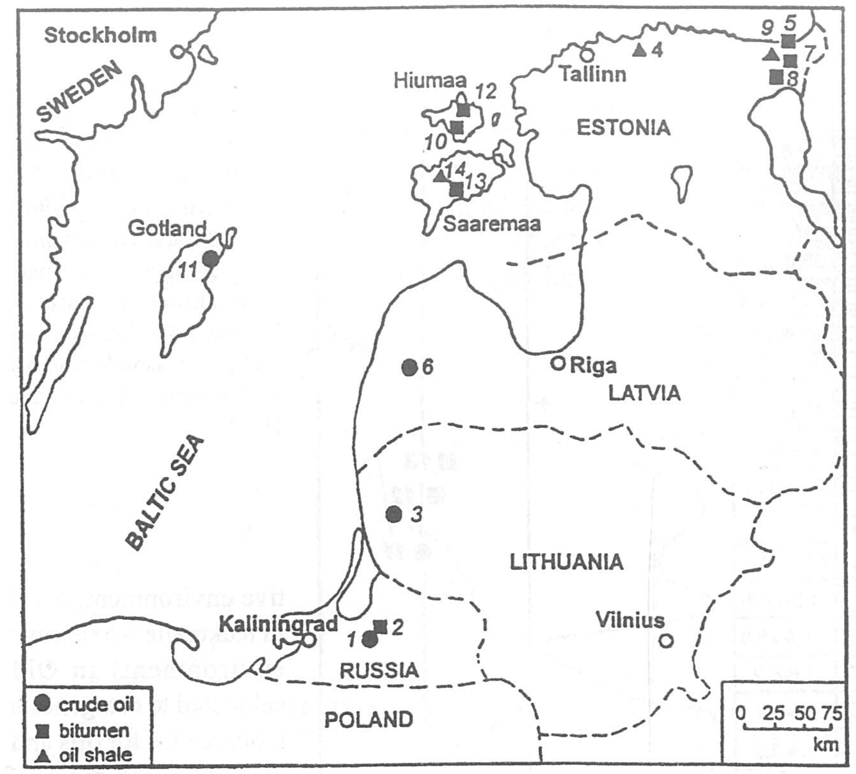


Fig. 1. A map of location of the studied samples of crude oils, natural bitumens and kerogeneous rocks. For show location see Table 1.

The yields of chloroform extract, and malthene and asphaltene contents are shown in (Bondar et al., 1996) as well as the data of TLC separation of malthenes of oils and bitumen extracts and neutral compounds of chloroform extracts from kerogeneous rocks. By the data of capillary GC of saturated hydrocarbon TLC fractions in all bitumens and Krasnyi Bor and Gotland oils even homologues predominate in n-alkane distribution (Fig. 3). In Šiūpariai oil even n-alkanes prevail after C_{21} and among low-molecular n-alkanes odd homologues predominate. Distribution of n-alkanes in Kuldiga oil is more complicated: n-alkanes C_{11}, C_{13}, C_{16}, C_{19}, C_{21}, C_{26} are predominant. In Dictyonema shale, Kukersite oil shale and Mustjala limestone strong odd/even predominance among n-alkanes is distinct being characteristic of immature OM with well preserved distribution of biogenic n-alkanes. Carbon predominance indices (CPI) (Table 2) cal-

Table 1. Information about sample location

Sample No.	Stage	Sample species	Country	Location	Depth, m
1	C_2dm	Sandstone impregnated with oil	Russia	Krasnyi Bor (borehole)	1961
2	C_2dm	Sandstone impregnated with maltha	Russia	Krasnyi Bor (borehole)	1950
3	C_2dm	Oil	Lithuania	Šiūpariai (borehole No. 1)	1972.1
4	O_1pk	Dictyonema shale	Estonia	Maardu (quarry)	4
5	O_1lt	Asphaltite lense in glauconitic sandstone	Estonia	Toila (cliff)	4
6	O_1vl	Oil	Latvia	Kuldiga (borehole No. 15)	972.5
7	O_2kk	Asphaltite lense in kukersite	Estonia	Tammiku (mine)	30
8	O_2kk	The same	Estonia	Estonia (mine)	55
9	O_2kk	Kukersite oil shale	Estonia	Sompa (mine)	25
10	O_2id	Sandstone impregnated with asphalt	Estonia	Hiiumaa (borehole No. 351F-2)	64.9
11	O_3pk	Oil	Sweden	Gotland (borehole)	~400
12	S_1jr	Reef limestone impregnated with asphalt	Estonia	Hiiumaa (borehole No. K-39-1)	22.4
13	S_1rk	Limestone with caverns filled with maltha	Estonia	Saaremaa (borehole No. K-3-3)	226.9
14	S_1jq	Reef limestone with dispersed kerogene	Estonia	Saaremaa, Mustjala (borehole No. 875-1)	46

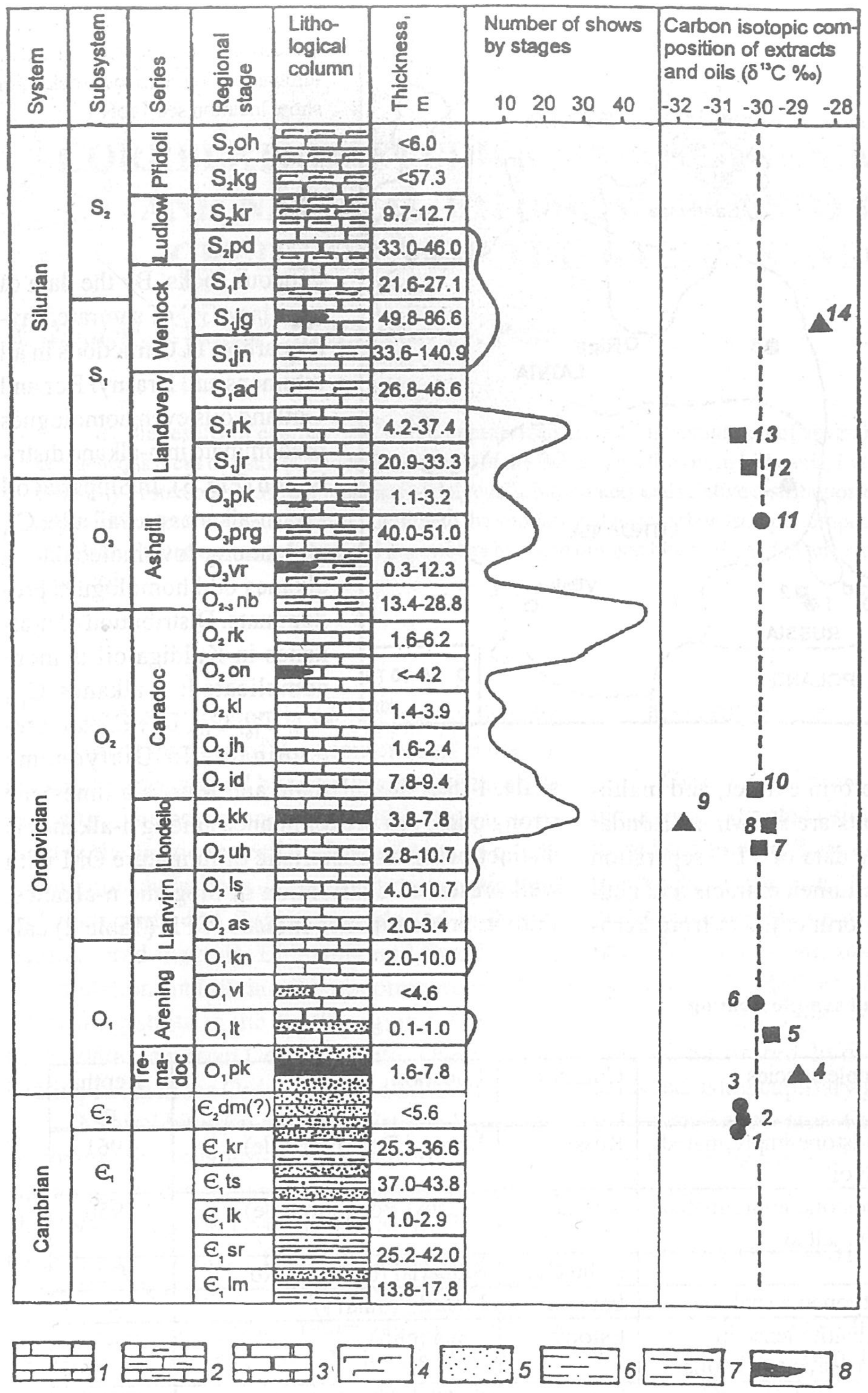


Fig. 2. Stratigraphical distribution and variations in organic carbon isotope composition of the studied samples of natural bitumens and kerogeneous rocks of Estonia and of Baltic crude oils. 1 – limestone, 2 – argillaceous limestone, 3 – dolomite, 4 – marl, 5 – sandstone, 6 – siltstone, 7 – clay, 8 – kerogeneous rocks. For sample number and location see Table 1 and Fig. 2.

culated on the basis of GC data illustrate the abovesaid observations. Its values are about 0.9 in Krasnyi Bor and Kuldiga oils, and about 1.2 in Šiūpariai and Kuldiga ones. CPI values in bitumens are similar and fluctuate within 0.8–0.9.

Pristane-to-phytane ratio in all oils is over 1.0 being the highest in Šiūpariai oil and the lowest in Krasnyi Bor one (Table 2). The same ratios in bitumens are not similar fluctuating within 0.5 – 1.0. While in immature OM the ratio pristane/phytane reflects the conditions of OM deposition (< 1.0 in Dictyonema shale and Mustjala limestone – reductive environment, > 1.0 in Kukersite – oxidative environment) in OM subjected to catagenesis (source OM for oils and bitumens) high-molecular isoprenoid alkanes are degraded up to lower homologues and the ratio pristane/phytane is no more original.

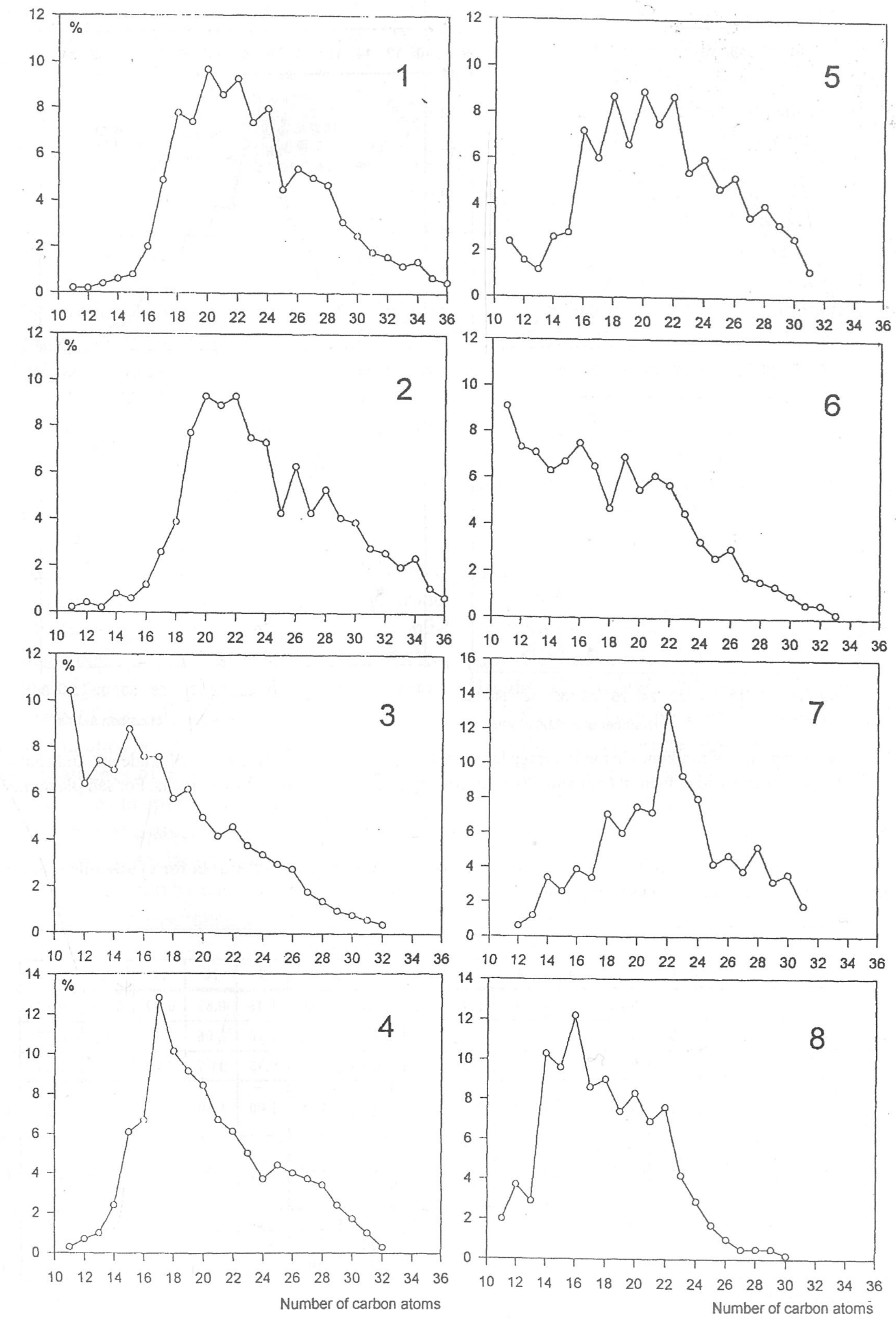
The ratio pristane+phytane/n-C_{17}+n-C_{18} used as the index of biodegradation of OM is the highest in Gotland oil and the lowest in Šiūpariai one (Table 2). Saaremaa bitumens are degraded in more degree than Hiiumaa ones.

GC-MS analysis of stereoisomeric composition of tetra- and pentacyclic hydrocarbons (biomarkers) showed that rearranged 10αH, 13βH, 17αH-steranes (diasteranes) are abundant in all samples of oils and bitumens being indicative of: (1) deposition of source OM in the presence of clay minerals and (2) biodegradation of oils and bitumens by which diasteranes being the most resistant become predominant over regular 5αH, 14αH, 17αH-steranes. Thus, in Kukersite with the carbonate mineral matrix and in Mustjala limestone diasteranes were not found. In Dictyonema shale and Šiūpariai oil the composition of their biomarkers was not studied due to low content of the latter. As to Dictyonema shale, possibly high

content of uranium in it and, consequently its high radioactivity are responsible for disappearance of original biomarkers from OM (Lewan and Buchardt, 1989).

By the relative abundances of regular 5αH, 14αH, 17αH, 20R-steranes C_{27}, C_{28}, C_{29} all oils and bitumens studied fall into the limited area in the triangular diagram while Kukersite and Mustjala limestone are apart of the cluster formed by oils and bitumens (Fig. 4).

Migration indices calculated as the ratio of 20S- and 20R-epimers of 5αH, 14αH, 17αH-sterane C_{29} are the highest for the asphaltite lenses in Kukersite and decrease gradually in Saaremaa and Hiiumaa bitumens, Kuldiga and Gotland oils being the lowest in Krasnyi Bor oil and maltha (Table 2).



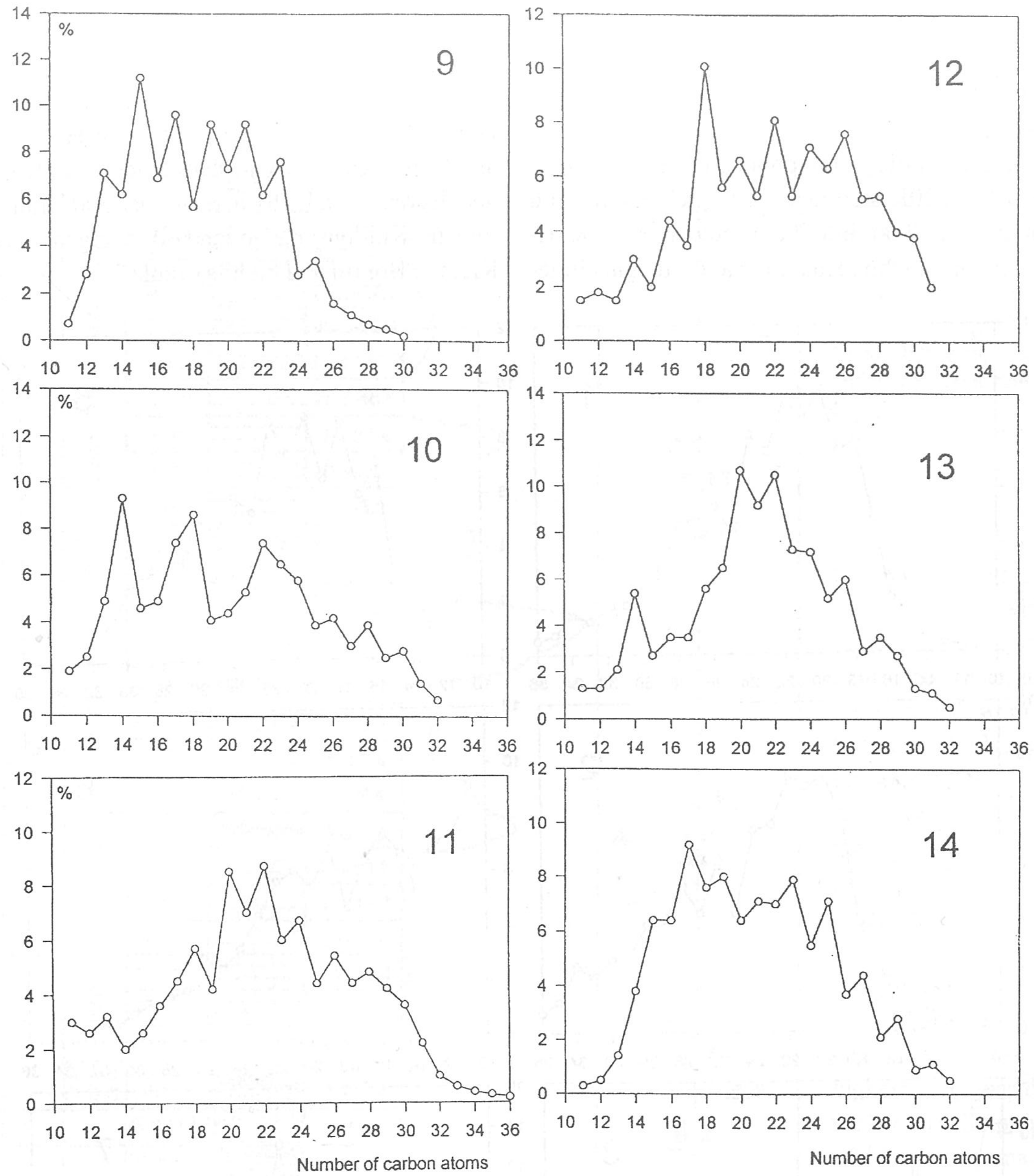


Fig. 3. Relative distribution of n-alkanes in the saturated hydrocarbon TLC fractions of malthenes of crude oils and chloroform extracts of natural bitumens and of neutral compounds of chloroform extracts from kerogeneous rocks. For sample number see Table 1 and Figs. 1, 2.

Table 2. Some geochemical parameters calculated on the basis of GC and GC-MS data for crude oils and chloroform extracts from natural bitumens and kerogeneous rocks

Parameter	Sample No.													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
CPI	0.86	0.87	1.21	1.11	0.90	1.26	0.83	0.80	1.48	0.83	0.92	0.76	0.87	1.23
Pristane/Phytane	1.07	0.92	2.82	0.89	0.50	2.02	1.00	0.78	1.10	0.66	1.33	0.68	0.83	0.96
Pr+Phy/n-C_{17}+n-C_{18}	0.47	0.89	0.36	0.78	0.17	0.98	0.56	0.77	0.40	0.77	2.10	0.53	1.04	0.77
$K_{migr} = \frac{52.20S}{52.20R} C_{29}$	0.85	0.89	n.d.*	n.d.	2.00	1.33	0.94	0.95	1.00	1.60	0.89	1.09	1.38	0.55
$K_{matur} = \frac{\alpha,\beta,22S}{\alpha,\beta,22S+\alpha,\beta,22R} C_{31}$	0.55	0.57	n.d.	n.d.	0.61	0.61	0.63	0.58	0.47	0.56	0.58	0.58	0.64	0.32
5α,20R C_{27}:C_{28}:C_{29}	33:22:45	32:19:49	n.d.	n.d.	27:18:55	35:27:38	33:23:44	27:23:50	29:35:36	37:19:44	35:19:46	32:22:46	35:27:38	21:17:62

* n.d. – not determined.

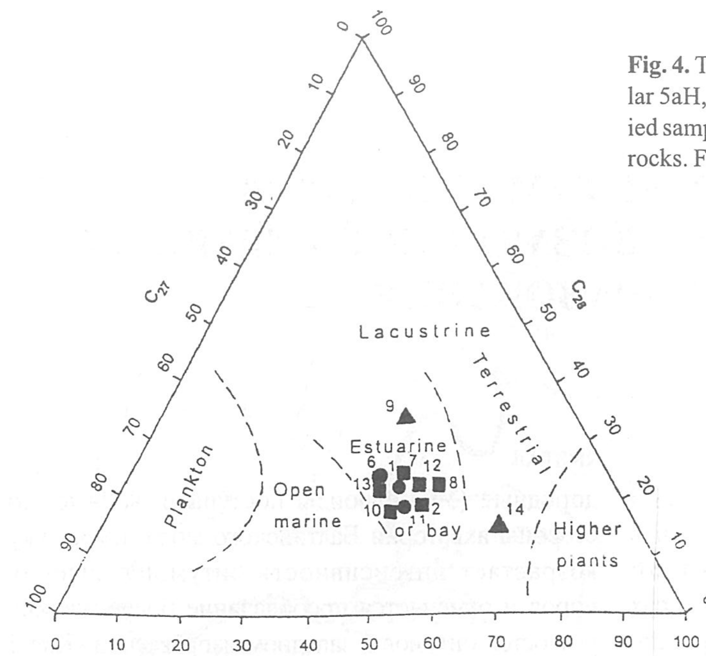


Fig. 4. Triangular diagram of the relative abundances of regular 5aH, 14aH, 17aH, 20R-steranes C_{27}, C_{28}, C_{29} in the studied samples of crude oils, natural bitumens and kerogeneous rocks. For sample number see Table 1.

Maturation indices calculated as the ratio of 22S-epimer and the sum of 22S- and 22R-epimers of 17αH, 21βH-hopane C_{31} are similar for all oils and bitumens. Naturally, their values for immature OM of Kukersite and Mustjala limestone are much lower (Table 2).

CONCLUSIONS

In addition to the similarity of carbon isotope composition in natural bitumens of Estonia and crude oils of the Baltic syneclise elucidated earlier the similarity in stereoisomeric composition and relative distribution of polycyclic hydrocarbons (biomarkers) was observed. Correlation by the relative distribution of n-alkanes is not so total. Possibly, low-molecular n-alkanes of oils were lost during preparation of samples to analysis and therefore even/odd predominance of n-alkanes was safed mainly in the range of high-molecular homologues.

No correlation by the relative distribution of n-alkanes and stereoisomeric composition and relative distribution of biomarkers as well as by organic carbon isotope composition between oils and bitumens, and OM of any studied kerogeneous rocks was observed.

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