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CARBON ISOTOPE COMPOSITION IN THE EARLY PALAEOZOIC CRUDE OILS, NATURAL BITUMENS AND KEROGENEOUS ROCKS OF THE BALTIC REGION

E. BONDAR
M. BITYUKOV
V. PALU

Institute of Chemistry,
Tallinn, Estonia

V. KATTAI

Geological Survey of Estonia
Tallinn, Estonia

The Baltic region is of interest to organic geochemists because of the occurrence of crude oil accumulations, natural bitumen shows and oil shale deposits. For elucidating possible correlation between them, a suite of four crude oils, eight natural bitumens and three kerogeneous rocks was examined for organic carbon isotope composition. $\delta^{13}\text{C}$ values for the studied crude oils and natural bitumens are similar and on an average -30.0‰ inherent in the Cambrian organic matter. In the series: oil \longrightarrow maltha \longrightarrow asphalt \longrightarrow asphaltite the value of $\delta^{13}\text{C}$ increases gradually showing the genetical relationship between the members of the series. No correlation by the carbon isotope composition between crude oils and natural bitumens, and organic matter of any studied kerogeneous rock is observed.

Carbon occurs in the Earth's sedimentary shell in two different forms, namely (1) as oxidized or carbonate carbon and (2) as reduced or organic carbon, the latter consisting of the fossil residue of primary biogenic substances. Sedimentary carbonates commonly preserve the isotopic composition of their parent carbonate muds within $\pm 1\text{‰}$ of the original value. In contrast, isotopic changes during burial and subsequent reconstitution of sedimentary organic matter (OM) are more pronounced, spanning the range from a few to several per mill over the maturation pathway of these substances in the sediment. This maturation ultimately leads to the formation of kerogen (insoluble OM), end product of the diagenetic alteration of primary biogenic substances.

Isotopic differentiation of sedimentary OM during maturation is specifically due to: (1) separation of isotopically light lipids and hydrocarbon derivatives from the bulk kerogen; (2) preferential cleavage and subsequent loss of isotopically distinctive functional groups (e.g. "heavy" COOH groups) during biological and/or thermal degradation; and (3) selective scission of ^{12}C - ^{12}C bonds in response to increasing thermocatalytic stress. It should be noted, however, that these secondary effects do not efface the isotopic signature of the primary biological material [1, 2]. The processes listed above are capable of bringing about an enrichment of ^{13}C in the residual kerogen of the order of +3 ‰. Only metamorphic alteration of kerogen is capable of entailed shifts of $\delta^{13}\text{C}$ from original means around -26 ‰ to -10 ‰ (in metamorphic terrains).

$\delta^{13}\text{C}$ values of kerogens from Phanerozoic sedimentary rocks show a distinct dichotomy. One group is referred to as *h*-kerogens which have the values ranging from -20 to -24 ‰. The other group is referred to as *l*-kerogens which have the values ranging from -26 to -35 ‰. The sources of CO_2 utilized by phytoplankton as the biological precursor of kerogen are considered the most plausible explanation of the dichotomy. Phytoplankton residing in environments where isotopically heavy atmospheric-derived CO_2 dominates results in *h*-kerogens, while those in environments that are dominated by isotopically light CO_2 of organic origin result in *l*-kerogens [3]. According to the available carbon isotope composition data, Early Palaeozoic sedimentary OM of the Baltic syncline has to be attributed to *l*-kerogens.

Systematic assays for organic carbon carried out on Phanerozoic sedimentary rocks of the East European platform indicate the uniformity of $\delta^{13}\text{C}$ values of extractable and insoluble OM in the Early Palaeozoic. The differentiation (up to 3.5 ‰) of their carbon isotope composition is observed only beginning from the Carboniferous, when the carbon of insoluble OM becomes isotopically heavier than that of extractable OM [4].

Carbon isotope composition is recognized an efficient parameter for the estimation of OM type and degree of maturity, and of the "oil - oil source rock" correlation [5]. $\delta^{13}\text{C}$ value of OM increases in response to increasing of geothermal stress. In the series from crude oil to solid bitumen, where all members are genetically related to each other, $\delta^{13}\text{C}$ increases gradually [6]. In the process of migration, carbon isotope composition of oil becomes a little lighter.

The Baltic region is of interest to organic geochemists because of the occurrence of crude oil accumulations, natural bitumen shows and oil shale deposits. The occurrence of oil in this region is related to the Baltic syncline. 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 west coast, and on the islands of Hiiumaa and Saaremaa [7, 8]. Stratigraphically, natural bitumens occur from the Low Ordovician to the Low 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 allotigenous and genetically not related to OM of kukersite [7, 9, 10]. In Western Estonia (except for the 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.

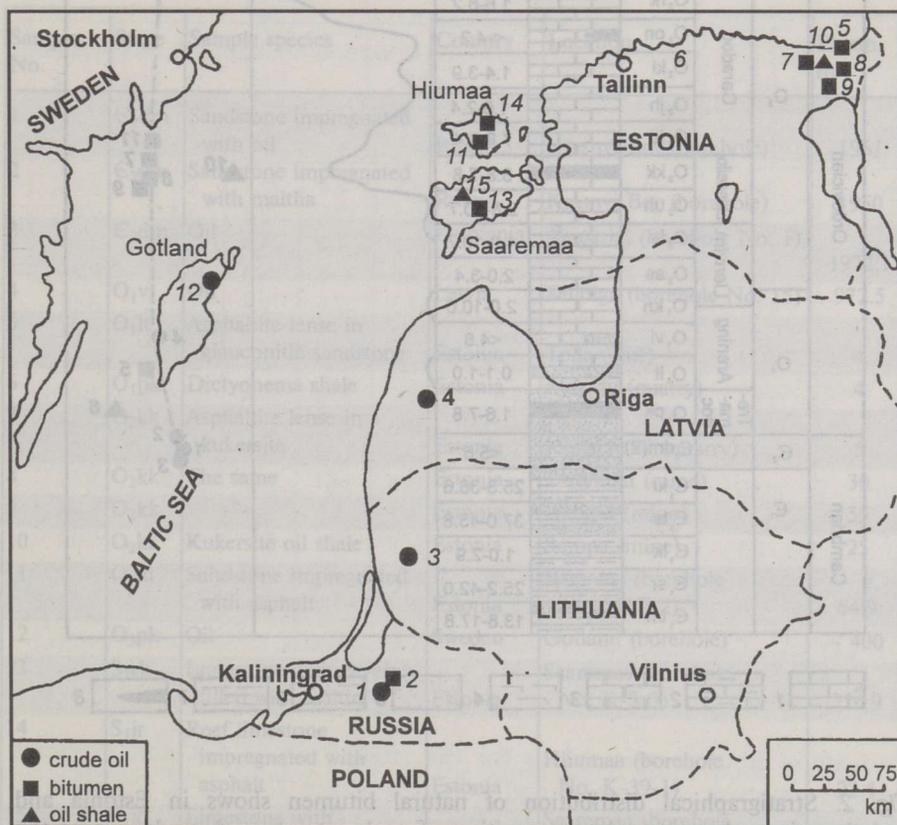


Fig. 1. A map of location of natural bitumens, crude oils, and kerogenaceous rocks in the Baltic region. For show location see Table 1

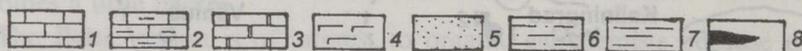
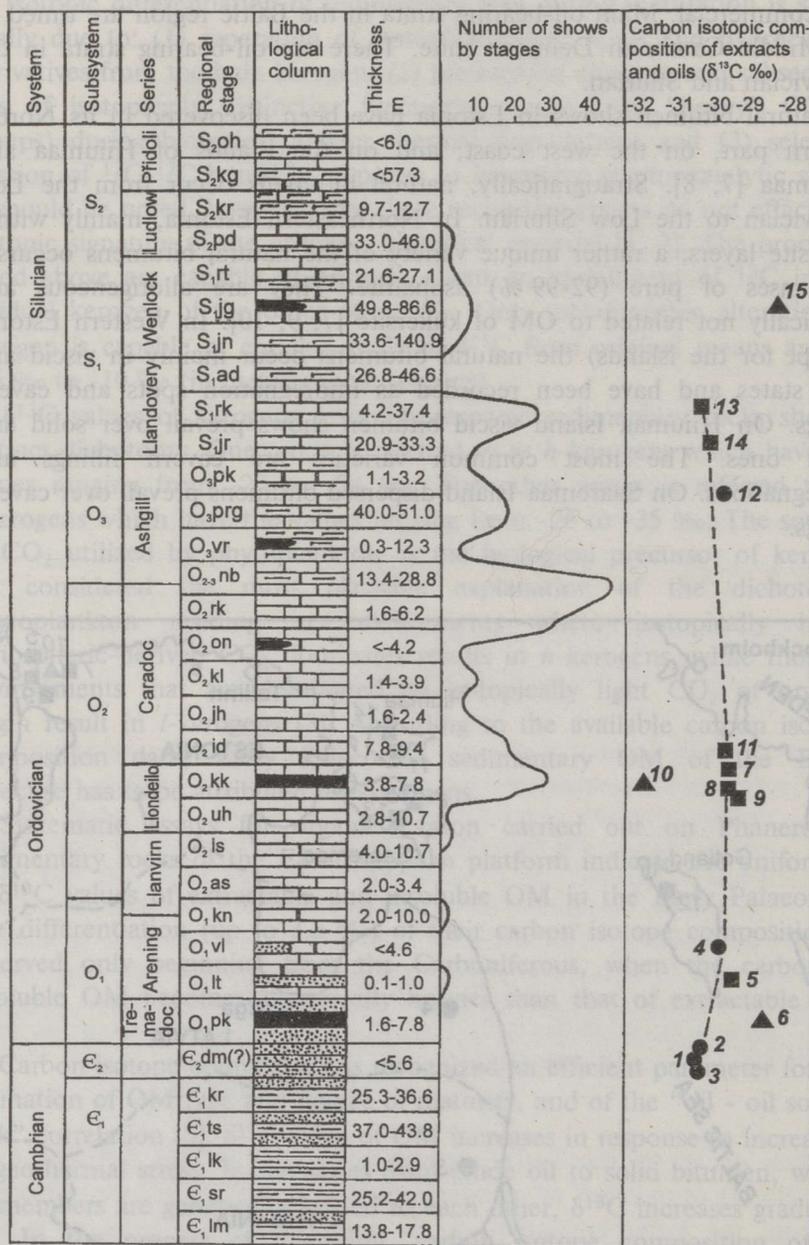


Fig. 2. Stratigraphical distribution of natural bitumen shows in Estonia and variations in carbon isotopic composition of rock extracts and crude oils of the Baltic syncline. 1 - limestone, 2 - argillaceous limestone, 3 - dolomite, 4 - marl, 5 - sandstone, 6 - siltstone, 7 - clay, 8 - kerogeneous rocks. For numbers and location of samples see Table 1 and Fig. 1

Experimental

Crushed and powdered rocks and solid bitumens were extracted using chloroform. Asphaltenes were precipitated from crude oils and extracts obtained with *n*-pentane (1 : 50). From the extracts of kukersite, Dictyonema shale and Mustjala limestone neutral compounds were separated. The latter and malthenes of oils and bitumens were divided into four fractions of different polarity using thin layer silica-gel chromatography (TLC). Oils and extracts, and their constituents converted to carbon dioxide were analysed by stable isotope ratio mass spectrometry (a Finnigan MAT Delta E apparatus). All $\delta^{13}\text{C}$ values are reported relative to the PDB standard:

$$\delta^{13}\text{C}(\text{‰}) = \frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{PDB}}}{(^{13}\text{C}/^{12}\text{C})_{\text{PDB}}} \times 1000$$

Table 1. Information About Sample Location

Sample No.	Stage	Sample species	Country	Location	Depth, m
1	E ₂ dm	Sandstone impregnated with oil	Russia	Krasnyi Bor (borehole)	1961
2	E ₂ dm	Sandstone impregnated with maltha	Russia	Krasnyi Bor (borehole)	1950
3	E ₂ dm	Oil	Lithuania	Šiupariai (borehole No. 1)	1972.1
4	O ₁ vl	Oil	Latvia	Kuldiga (borehole No. 15)	972.5
5	O ₁ lt	Asphaltite lense in glauconitic sandstone	Estonia	Toila (cliff)	4
6	O ₁ pk	Dictyonema shale	Estonia	Maardu (quarry)	4
7	O ₂ kk	Asphaltite lense in kukersite	Estonia	Kütte Jõud (quarry)	5
8	O ₂ kk	The same	Estonia	Tammiku (mine)	30
9	O ₂ kk	"-	Estonia	Estonia (mine)	55
10	O ₂ kk	Kukersite oil shale	Estonia	Sompa (mine)	25
11	O ₂ id	Sandstone impregnated with asphalt	Estonia	Hiiumaa (borehole No. 351F-2)	64.9
12	O ₃ pk	Oil	Sweden	Gotland (borehole)	~ 400
13	S ₁ rk	Limestone with caverns filled with maltha	Estonia	Saaremaa (borehole No. K-3-3)	226.9
14	S ₁ jr	Reef limestone impregnated with asphalt	Estonia	Hiiumaa (borehole No. K-39-1)	22.4
15	S ₁ jq	Limestone with dispersed kerogene	Estonia	Saaremaa (borehole No. 875-1)	46

Results and Discussion

A suite of four oils, eight bitumens and three kerogeneous rocks from the Baltic region was examined. Figures 1 and 2 give the view of the location and stratigraphical distribution of the samples studied. In Table 1 the samples are disposed in the order of decreasing geological age. According to the increasing content of asphaltenes (Table 2), oils and bitumens form the series: oil \rightarrow maltha \rightarrow asphalt \rightarrow asphaltite. Malthene content and atomic H/C ratio decrease in the same order. As shown by TLC data (Table 2), contents of polar and neutral heteroatomic compounds increase from oil to asphaltite. At the same time aliphatic-to-aromatic ratio decreases with the exception of samples 1 and 2 in which atomic H/C ratio does not correlate with high aromatic fraction content. In all probability, in samples 1 and 2 naphthenic and hybrid aromatic-naphthenic compounds prevail being co-eluted together with aromatic hydrocarbons.

Table 2. Some Geochemical Data for Samples Studied

Sample No.	Yield of extract, %	Malthenes, %	Asphaltenes, %	TLC fractions of malthenes*, rel.%				Aliph./arom. ratio
				1	2	3	4	
1	0.4	97.4	2.6	9.8	8.4	77.8	4.0	0.05
2	0.7	91.7	8.3	12.5	13.8	70.3	3.4	0.05
3	-	99.5	0.5	3.2	4.2	24.6	68.0	2.76
4	-	95.7	4.3	9.5	17.3	58.3	14.9	0.26
5	93.5	15.0	85.0	43.3	37.6	12.8	6.3	0.49
6	0.3	54.4	45.6	58.1	13.2	10.8	17.9	1.65
7	96.5	n.d.**	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8	97.5	11.1	88.9	48.7	27.4	10.8	13.1	1.21
9	86.8	13.2	86.8	42.4	23.5	18.2	15.9	0.88
10	0.4	55.2	44.8	27.0	21.4	15.8	35.8	2.26
11	8.0	79.5	20.5	53.0	14.7	19.4	12.9	0.66
12	-	98.9	1.1	5.2	5.5	54.6	34.7	0.64
13	1.3	91.3	8.7	30.9	8.1	28.3	32.7	1.16
14	5.3	82.4	17.6	44.6	23.2	18.9	13.3	0.70
15	0.06	63.1	36.9	68.5	7.5	8.9	15.1	1.70

* 1 - polar heteroatomic compounds, 2 - neutral heteroatomic compounds, 3 - aromatic hydrocarbons, 4 - aliphatic hydrocarbons

** n.d. - not determined.

Carbon isotope ratio values for the studied crude oils and extracted natural bitumens are similar and fluctuate within 1 ‰ (Fig. 2; Table 3) averaging -30.0 ‰. Chloroform extracts of Low Ordovician Dictyonema shale, Middle Ordovician kukersite and Early Silurian Mustjala limestone do not correlate with oils and bitumens by $\delta^{13}\text{C}$ values (Table 3). Organic

carbon of Dictyonema shale and Mustjala limestone is isotopically heavier and that of kukersite is lighter than the carbon of oils and bitumens. It is interesting that oils and bitumens from the strata of different geological ages (from the Cambrian to the Silurian) have $\delta^{13}\text{C}$ characteristic of the Cambrian OM (-30.0 ‰, [11]).

Table 3. Carbon Isotope Ratios (‰, relative to the PDB standard) of Oil and Extract Constituents

Sample No.	Extract or crude oil	Malthenes	Asphaltenes	Malthene TLC fractions			
				1	2	3	4
1	-30.5	-30.7	-30.2	-29.5	-29.5	-30.6	-30.7
2	-30.6	-30.4	-29.7	-29.7	-29.6	-30.7	-30.5
3	-30.6	-30.5	-30.6	-29.3	-29.6	-29.5	-30.6
4	-30.0	-30.0	-30.3	-30.3	-29.6	-29.7	-30.7
5	-29.7	-29.6	-29.8	-29.5	-28.5	-29.9	-30.7
6	-28.5	-28.9	-28.0	-28.8	-28.2	-28.0	-29.3
7	-29.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8	-29.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
9	-29.5	-30.0	-29.5	-29.9	-29.8	-29.9	-30.5
10	-31.2	-31.5	-30.7	-29.7	-30.4	-30.1	-31.2
11	-29.8	-29.8	-30.0	-29.8	-28.9	-29.6	-29.9
12	-29.8	-29.8	-30.5	-29.7	-28.8	-29.3	-30.2
13	-30.5	-30.6	-30.0	-29.2	-29.3	-29.4	-29.8
14	-30.2	-30.4	-29.8	-29.9	-29.3	-29.6	-30.2
15	-28.4	-28.2	-28.8	-28.8	-29.6	-28.2	-29.0

Among the Early Palaeozoic sedimentary rocks of the Baltic region the alum shale of Scandinavia is studied as a possible source rock for Gotland's oil. It contains Lower Ordovician to Middle Cambrian black shales with organic carbon content 5-20 %. Thermal stress experienced by the alum shale ranges from thermal immaturity in outliers of Central Sweden to low-grade metamorphism in the Oslo Graben. OM of thermally immature alum shale is attributed to type II kerogen. Its $\delta^{13}\text{C}$ values range from -30.1 to -27.5 ‰ being -30.0 ‰ for the Upper Cambrian samples [12]. By $\delta^{13}\text{C}$ data, organic carbon of the Ordovician strata isotopically is somewhat heavier (from -30.2 to -27.9 ‰) than that of the Cambrian ones (from -32.9 to -28.9 ‰) [13]. No correlation between $\delta^{13}\text{C}$ value and degree of OM maturity is observed.

While the insoluble OM of the alum shale from both Eastern and Central Sweden is immature with respect to oil generation, extractable OM in some areas of Central Sweden is marginally mature or mature. It is suggested that extractable OM from mature alum shales, being in close

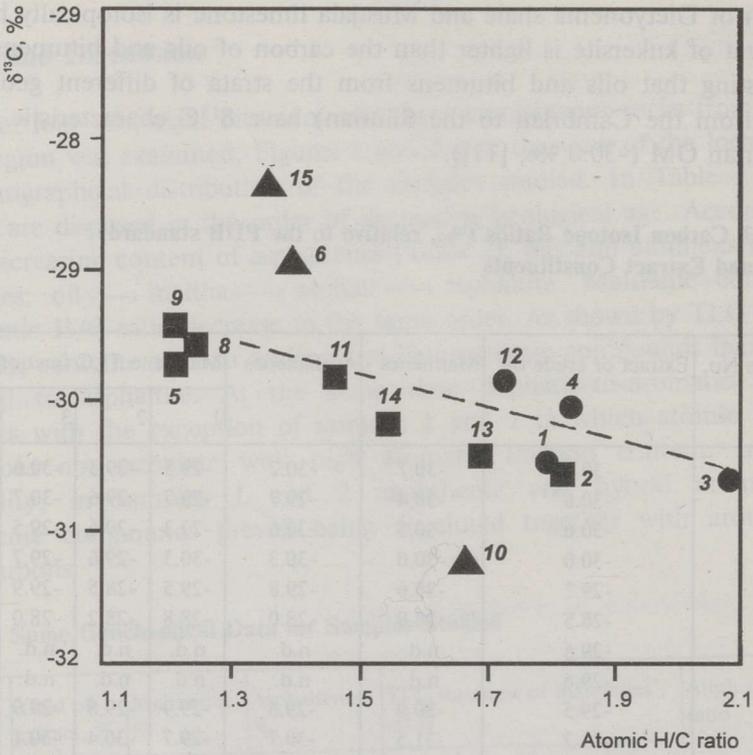


Fig. 3. Relationship between atomic H/C ratio and carbon isotope composition of oils (circles), and bitumen (squares) and kerogenaceous rock (triangles) extracts. For sample numbers see Table 1

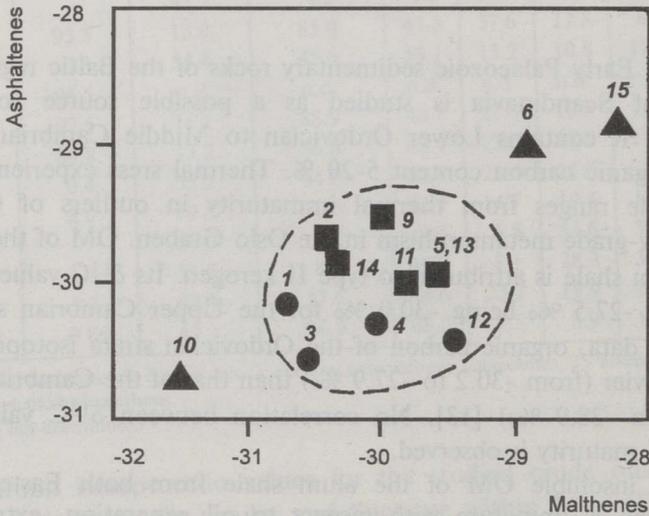


Fig. 4. Carbon isotope ratios ($\delta^{13}\text{C}$, ‰) of malthenes and asphaltenes. For sample numbers and signs see Table 1 and Fig. 3

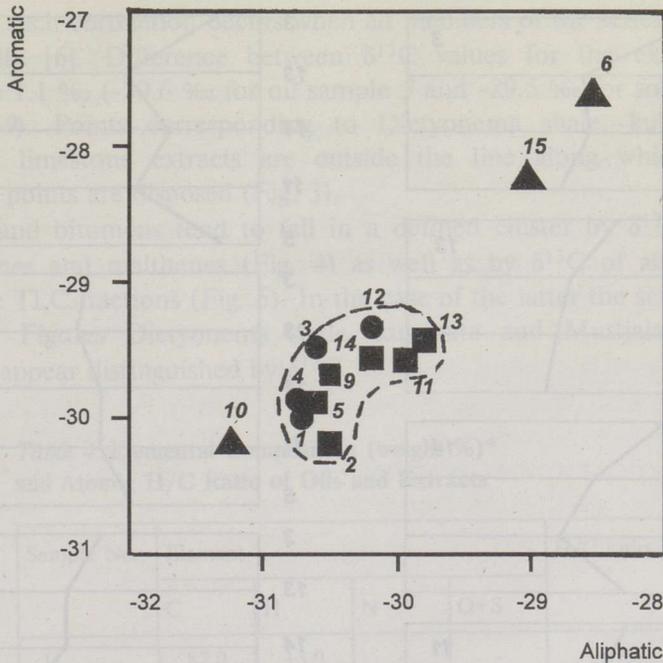


Fig. 5. Carbon isotope ratios ($\delta^{13}\text{C}$, ‰) of aliphatic and aromatic TLC fractions. For sample numbers and signs see Table 1 and Fig. 3

proximity to Permo-Carboniferous diabase intrusions, has migrated into the alum shales of Central Sweden. With regard to the correlation of crude oil and alum shale as source rock on the island of Gotland: alum shale extractable and insoluble OM are thermally immature with respect to oil generation and extractable OM shows no sign of a migrated component [14]. Thus, in spite of similarity of $\delta^{13}\text{C}$ values of Gotland oil and OM of many alum shale samples, genetical relationship between them seems to be questionable.

Recent investigations on alum shale oil potential using flash pyrolysis revealed that its OM does not produce liquid oil on simulated maturation. The primary maturation products include low molecular mass compounds, mainly aromatic ones with anomalously high gas : oil ratios. OM of the alum shale attributed to type II kerogen which is found to possess a substantial oil potential nevertheless partially converts into inert "dead" carbon, resulting in considerable reduction in the actual oil masses which are expellable. The alum shale OM is therefore more different and uncommon than most other type II kerogens [15].

In spite of small differences between $\delta^{13}\text{C}$ values for the studied Baltic oils and bitumen extracts, a correlation between their $\delta^{13}\text{C}$ and atomic H/C ratio is observed (Fig. 3). In the series: oil \rightarrow maltha \rightarrow asphalt \rightarrow asphaltite $\delta^{13}\text{C}$ value increases as H/C ratio decreases.

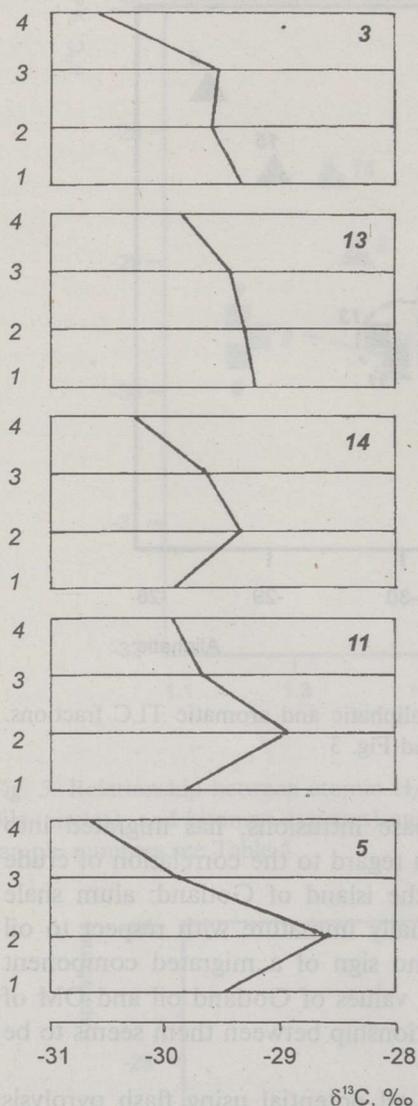


Fig. 6. Variations of carbon isotope ratios in TLC fractions (1-4) in the series: oil (3) \rightarrow maltha (13) \rightarrow asphalt (14, 11) \rightarrow asphaltite (5). For sample (on the right) and TLC fraction (on the left) numbers see Tables 1 and 3

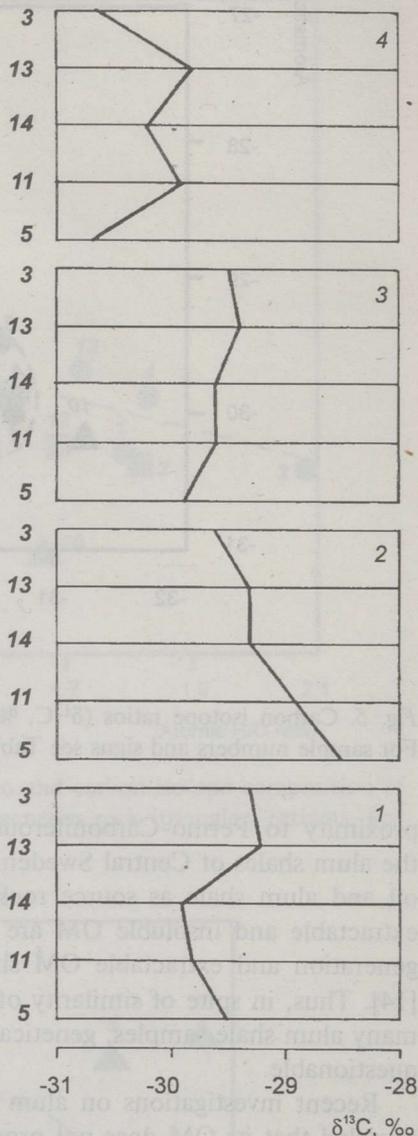


Fig. 7. Variations of carbon isotope ratios of different TLC fractions (1-4) in samples of the series: oil (3) \rightarrow maltha (13) \rightarrow asphalt (14, 11) \rightarrow asphaltite (5). For TLC fraction (on the right) and sample (on the left) numbers see Tables 1 and 3

Usually, such correlation occurs when all members of the series are related genetically [6]. Difference between $\delta^{13}\text{C}$ values for the extremes just accounts 1.1 ‰ (-30.6 ‰ for oil sample 3 and -29.5 ‰ for solid bitumen sample 9). Points corresponding to Dictyonema shale, kukersite and Mustjala limestone extracts are outside the line along which oil and bitumen points are disposed (Fig. 3).

Oils and bitumens tend to fall in a defined cluster by $\delta^{13}\text{C}$ ratios of asphaltenes and malthenes (Fig. 4) as well as by $\delta^{13}\text{C}$ of aliphatic and aromatic TLC fractions (Fig. 5). In the case of the latter the scatter is less. In both Figures Dictyonema shale, kukersite and Mustjala limestone extracts appear distinguished by $\delta^{13}\text{C}$.

Table 4. Elemental Composition (weight %)* and Atomic H/C Ratio of Oils and Extracts

Sample No.	Element				H/C ratio
	C	H	N	O+S	
1	87.0	13.0	-	-	1.79
2	86.2	13.0	-	0.8	1.81
3	83.7	14.5	-	1.8	2.08
4	85.5	13.1	-	1.4	1.84
5	84.3	8.6	1.9	5.2	1.22
6	76.1	8.8	1.6	13.5	1.39
8	85.1	9.0	1.7	3.4	1.26
9	86.2	8.7	1.7	3.4	1.21
10	83.3	11.6	-	5.1	1.67
11	83.8	10.2	0.5	5.5	1.46
12	86.4	12.5	-	1.1	1.74
13	87.3	12.3	0.4	-	1.69
14	80.9	10.3	0.4	8.4	1.53
15	74.9	8.5	0.7	15.9	1.36

* For measurements the "Hewlett-Packard 185 CNH" analyser was used.

In the series: oil \rightarrow maltha \rightarrow asphalt \rightarrow asphaltite distribution of $\delta^{13}\text{C}$ in TLC fractions changes gradually (Fig. 6) and mainly due to the tendency of neutral heteroatomic compound carbon to become isotopically heavier. More distinctly it is obvious in Fig. 7. The scatter of $\delta^{13}\text{C}$ values for TLC fractions 1, 3 and 4 does not exceed ± 0.45 ‰ while $\delta^{13}\text{C}$ of TLC fraction 2 increases invariably by 1.1 ‰ from oil to asphaltite. Studying the elemental composition of oils and bitumens considered in Figs. 6 and 7 and TLC fraction distribution (Table 2) one can note the increasing of nitrogen content in the series: oil \rightarrow maltha \rightarrow asphalt \rightarrow asphaltite from zero to 1.9 % (Table 4) with the simultaneous increasing of the content of TLC fraction 2 (Table 2).

Nitrogen in oils is concentrated mainly in neutral resins and asphaltenes [16] or, in other words, in the neutral heteroatomic compounds (TLC fraction 2). Up to 50 % of vanadium and nickel of oils are included into porphyrine complexes [16]. In the ash of asphaltite inclusions in kukersite, the content of vanadium and nickel is 600 and 1000 g per ton, respectively, being higher than their content (both 30 g per ton) in the ash of kukersite [17]. Up to 33 % of vanadium present in oils are included into volatile vanadium-containing compounds, mainly vanadyl-porphyrines in free monomolecular state. Non-volatile vanadium compounds are concentrated in asphaltenes being chemically combined with the latter as a result of condensation [16].

It is suggested that the increasing of $\delta^{13}\text{C}$ value of TLC fraction 2 with the simultaneous increasing of this fraction content in oil or bitumen extract, together with the increasing of nitrogen content in the latter, is related to the presence of porphyrines usually enriched by about 3 ‰ heavy carbon isotope in relation to the total carbon of crude oil [18].

Conclusions

$\delta^{13}\text{C}$ values for the studied crude oils and natural bitumens of the Baltic region show the similarity and an average -30.0 ‰ inherent in the Cambrian OM.

In the series: oil \longrightarrow maltha \longrightarrow asphalt \longrightarrow asphaltite $\delta^{13}\text{C}$ increases gradually showing the genetic relationship between the members of the series.

No correlation by organic carbon isotope composition between oils and bitumens, and OM of any studied kerogeneous rock is observed. With regard to alum shale of Scandinavia as a possible oil source rock and structural characteristics of its OM, a far greater multi-disciplinary approach is needed.

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