

## INVESTIGATION OF DICTYONEMA OIL SHALE AND ITS NATURAL AND ARTIFICIAL TRANSFORMATION PRODUCTS BY A VANKREVELENOGRAM\*

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*The elemental composition of organic matter of Ordovician Dictyonema oil shale from Maardu, Toolse and other Estonian as well as from Russian and Swedish deposits (local name 'alum shale'), natural and artificial transformation (beneficiation, extraction, thermal and oxidative destruction) products of Dictyonema oil shale are visualized using a vankrevelenogram. It is a van Krevelen's H/C–O/C diagram used to compose a database of a certain fuel and its transformation products to characterize this object from different aspects. Graphostatistical investigations of the composition of Dictyonema oil shale organic matter indicate that the shale subjected to study by most researchers was unknowingly to them the weathered one. The methods to evaluate the composition of organic matter of Dictyonema oil shale used in coal and "common" oil shale chemistry had to be replaced by the ones used in dispersed organic matter study.*

### Abbreviations

DOS – Dictyonema oil shale; OM – organic matter; MM – mineral matter.

$S_t$ ,  $S_{SO_4}$ ,  $S_p$ , S – total, sulphatic, pyritic and organic sulphur, respectively.

HA – humic acids.

C – carbon; H – hydrogen; N – nitrogen; S – sulphur; O – oxygen of OM.

O is used in this paper in two different meanings:

(1)  $O = OM - C - H$ , then  $O = O^o + S + N$ ,

(2)  $O^o = OM - C - H - N - S$ .

Ratios of organic elements are given as atomic ones. If mass ratios used it is specially mentioned.

All indices about oil shale composition are presented on dry basis, percentage expressed as mass per cent, if not, then specially mentioned.

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## Introduction

DOS is a formation of the Tremadoc stage (Pakerord and Varangu regional stages) of the Early Ordovician. It is often called Dictyonema shale, 'Dictyonema argillite', 'alum shale', etc. The name '*dictyonema*' was given after the benthonic root-bearing *Dictyonema flabelliforme*, which turns afterward to a planktonic nema-bearing *Rhabdinopora flabelliformis* [1]. DOS is not a metamorphosed formation like a common argillite, so the fragments of name '*dictyonema*' or '*argillite*' do not carry the true scientific meaning. In our works we stressed the quality of Dictyonema shale to be a low-grade oil shale, but DOS was mostly known as a source rock for uranium and some other heavy metals [2].

Promising geological reserves of DOS in Estonia were estimated approximately to 70 billion tonnes [3]. The OM content of DOS is on an average 15 % with oil yield about 20 % on OM basis. So, the potential reserves of oil in Estonian DOS are 2.1 billion tonnes. The potential reserves of uranium and molybdenum of DOS in the Baltic basin are approximately 5 and 10 million tonnes, respectively [2].

The oil reserve of DOS is almost unused until now. The amount of the shale mined for uranium production at Sillamäe, Estonia, between 1948 and 1952 was 271,000 tonnes, from which 22.4 tonnes of uranium in 40-% chemical concentrate was separated [4]. Between 1964 and 1991 approximately 73 million tonnes of DOS were mined as a covering layer of phosphorite ore at Maardu near Tallinn. DOS was mixed up with other covering deposits such as limestone, sandstone, glauconite sandstone, pyrite and Quaternary sediments or buried under the quarry waste heaps.

So, beginning from 1964 DOS including its geochemically active OM, pyrite and easily leaching heavy metals turned from a technological subject to an ecological problem mostly [5–11]. Investigations of the chemical composition of the weathered DOS left on the surface and in the dumps of the open-pit quarry at Maardu bring us [7, 12–14] to the question about the actual chemical composition of OM of DOS in natural series protected from external influences and also about DOS OM uniformity.

The aim of the study was to organize and visualize all published data concerning DOS OM elemental composition and its changes during natural and artificial processes by employing vankrevelenogram to select the most probable data of elemental composition.

## General Characteristics of DOS

DOS is an OM-rich (10–20 %) brown lithified clay belonging to the formation of black shales of sapropelic origin, OM being rich in N, S and O [15, 16]. In black shale classification DOS from Estonia and Leningrad region of Russia, as well as alum shale from Sweden, Denmark and Poland

belong to the first type of non-metamorphosed horizontally lying black shales of a uniform distribution of U in bed [2].

Moisture content of freshly-mined DOS was from 11.9 to 12.5 % [4], elemental composition of the combustible part (%): C – 67.6, H – 7.6, O – 18.5, N – 3.6 and S – 2.6, calorific value – on the average 1200 kcal/kg. Fischer assay yields (% OM basis): oil 19.8, gas 16.5 and pyrogenetic water 18.9 [3]. These figures are given as often referred ones.

### Vankrevelenogram

From the very time the elemental composition of fuels' OM was determined and data became available, scientists and engineers started to visualize them to help making scientific or practical conclusions. Already in 1826 an attempt was made to use the mass ratios of H/C in coal classification, but the first fairly accurate elemental analysis data of coals was published in 1837 (after Rose [17]). The first elemental analysis data of DOS were also published in the 19th century [18]. The mass percentage of O + N and mass ratio O/H were decided to be good indicators of coal's nature. In 1865–1870 an attempt was made to use so-called available H (the excess of the amount required to combine with all the O in the coal) to classify coals, in 1874 Gruner (after Rose [17]) used mass ratio (O + N)/H (as the degree of natural oxidation by Aronov and Nesterenko [19]) to type coals. Seyler's classifications based on the C and H mass percentage became more widely known. He and some other scientists made extensive use of H/C mass ratio in coal classification, Bode also of C/H mass ratio, but C/O mass ratio was also in use [17].

The first C, H, O diagrams by Grout, 1907; Ralston, 1915; Himus and Basak, 1949, and others were triangular ones where atomic values were standardized to 100 either mass or atom % [20, 21].

The next step was van Krevelen's rectangular diagram of H/C and O/C. The diagram is a practical tool for processing and interpreting elemental analysis data of organic formations of the Earth's crust including dispersed OM as well as oil shales. Simple reactions such as a loss of CH<sub>4</sub>, CO<sub>2</sub> or H<sub>2</sub>O and the other simple molecules are represented in the diagram by straight lines [21]. This explains why oil researchers have used the diagram to elucidate oil and gas potential of organic formations and coal researchers to solve various problems of classification (for example, [22]).

In the case the van Krevelen's H/C–O/C diagram is used to compose a database of a certain fuel and its natural and artificial transformation products to characterize this object in detail, it is proposed by us to name this diagram vankrevelenogram (further also H/C–O/C diagram or simply diagram). It underwent the first test in the case of kukersite oil shale [23].

## State of Oxidation

Oxygen is a substantial OM component of most solid fuels, in the first place of low-maturity ones, such as oil shales. If the structural formula of a chemical compound is known, one may calculate the average degree of oxidation of C:  $\omega = (\Sigma\text{CH} - \Sigma\text{CX}) / \Sigma\text{C}$ , where  $\Sigma\text{CH}$  is a sum of all C–H bonds,  $\Sigma\text{CX}$  is a sum of all bonds with electronegative heteroatoms, and  $\Sigma\text{C}$  is a number of C atoms in the molecule [24].

State of oxidation  $c\text{O} = (2 \cdot \text{O} - \text{H}) / 4\text{C}$  for solid fuels does not specify the nature of chemical bonds between carbon and the other atoms [19, 25]. Content of O was calculated as the difference  $100 - \text{C} - \text{H}$ , %. Almost the same formula ( $\omega = (2 \cdot \text{O}^\circ - \text{H}) / \text{C}$ ) instead of the ratio  $\text{O}^\circ/\text{C}$  – as a new method in humus (more specifically soil humic and fulvic acids) studies – was proposed by Orlov [26].

Leifman and Vassoevich [27] proposed H/C –  $F_1$  diagram where coefficient  $F_1 = (\text{H} - 2 \cdot \text{O}) / \text{C}$  and the sum of all heteroatoms were also reduced to O. Actually the states of oxidation are in a simple dependence as follows:  $\omega$  [24]  $\approx -4c\text{O}$  [19, 25]  $\approx -\omega$  [26]  $\approx F_1$  [27], at the same time authors of these states do not cite the others' works.

In this study the modified Orlov's formula  $\omega = (2 \cdot \text{O} - \text{H}) / \text{C}$  was used. The sum of all electronegative heteroatoms is calculated as  $\text{O} = 100 - \text{C} - \text{H}$ , %. On the hydration line starting from the zero point of the diagram  $\omega$  is equal to 0. The atomic ratios of OM situated on this line are described by the formula  $\text{C} + n\text{H}_2\text{O}$ , on parallel lines upward and downward by  $\text{CH}_x + n\text{H}_2\text{O}$  ( $\omega < 0$ ) and  $\text{CO}_y + n\text{H}_2\text{O}$  ( $\omega > 0$ ), respectively, where the values of  $x$  and  $y$  are equal to those in the points of intersection with the H/C or O/C axis. In some studies (HA and regenerated sapropelic acids) instead of H/C–O/C diagram H/C– $\omega$  diagram is used [28, 29].

## Initial Data

The values of H/C, O/C and  $\omega$  were calculated on the basis of literature data (Table 1). 227 data on elemental composition of OM of DOS from Maardu, Toolse and other Estonian as well as Russian and Swedish deposits, of their natural and artificial transformation (beneficiation, extraction, thermal and oxidative destruction) products and of four sapropelites from the brown coal stage to the gas coal stage (Table 1, pos. 25; Fig. 1, *F*) were used in this study, the data of 136 DOS among them (Table 1, pos. 1–14, Fig. 1, *A–E, G–J*):

- 56 samples from Maardu (7 of them concentrates);
- 10 samples from Toolse (5 of them concentrates);
- 15 samples from other locations of Estonia (Aseri, Ellamaa, Keila, Kunda, Paldiski, Saka, Tallinn and Viitna);

- 10 obviously weathered samples from Estonia (Maardu, Mäeküla, Ontika, Paldiski and Tallinn);
- 11 samples from Russia (*Krasnoe* collective farm at Shungarovo, Gorodistshe, Izhora, Kotly-Koporye Gostilitsy, Nazia-Volhov-Syas, Popovka, Pulkovo, Ranolovo, Sablinka), mostly weathered;
- 34 alum shale samples (Bårstad, Gotland, Hallenberg-Hunneberg, Hynneberg, Kvarntorp, Närke, Ranstad, Västergötland, Öland, Östergötland, etc.), some of them highly metamorphosed.

**Table 1. Range of H/C, O/C, and Oxidation State  $\omega$  Values of OM in DOS Samples and Their Transformation Products**

No.	Location/products	Spots	H/C	O/C	$\omega$	Calculated using:
1	Maardu, OM concentrates	4	1.11–1.37	0.22–0.26	–0.85...–0.65	[30–33]
2	Maardu, OM concentrates	2	1.15; 1.16	0.15; 0.16	–0.84	[34]
3	Maardu, OM concentrate	1	1.24	0.16	–0.91	[35]
4	Maardu, OM concentrates (18.1–75.9 %)*	15	1.11–1.20	0.12–0.19	–0.88...–0.79	[30]
5	Maardu*	9	1.07–1.28	0.16–0.21	–0.93...–0.78	[30]
6	Maardu, the other samples	25	1.11–1.45	0.16–0.33	–1.09...–0.60	[30–34, 35–45]
7	Toolse	5	0.98–1.35	0.21–0.25	–0.94...–0.49	[38, 41, 46]
9	Toolse, OM concentrates	5	0.98–1.17	0.18–0.34	–0.81...–0.29	[47]
10	Estonia, the other locations	15	0.95–1.48	0.17–0.36	–1.12...–0.48	[18, 31, 32, 34, 48, 49]
11	Estonia, weathered	10	1.09–1.46	0.26–0.48	–0.80...–0.15	[18, 31, 32, 34, 36, 39, 48, 50]
12	Russia	10	0.70–1.48	0.24–0.36	–0.99...–0.15	[49–52]
13	Russia (Ranolovo)	1	0.89	0.46	0.03	[49]
14	Sweden	34	0.21–1.31	0.03–0.26	–1.01...–0.006	[46, 54–56]
15	Russia, HA	2	0.86; 0.93	0.38; 0.42	–0.09; –0.10	[52]
16	Russia (Polist), HA, artificially made at 100 °C	1	0.48	0.58	0.39	[52]
17	Maardu, oxidation products (KMnO <sub>4</sub> )	7	0.99–1.52	0.32–0.71	–0.69...–0.10	[57]
18	Estonia, bitumen A	4	1.19–1.56	0.14–0.18	–1.28...–0.80	[40, 43, 52, 58]
19	Estonia, bitumen C	1	1.54	0.16	–1.21	[52]
20	Maardu, semicoking oil	7	1.22–1.45	0.04–0.07	–1.36...–1.09	[9, 41, 60–62]
21	Maardu, various other oils	37	1.21–1.46	0.04–0.11	–1.34...–1.08	[41, 60, 61, 63–65]
22	Toolse, semicoking oil	2	1.23; 1.29	0.06; 0.12	–1.16; –0.99	[64, 66]
23	Toolse, various other oils	15	1.14–1.28	0.1–0.14	–1.18...–0.87	[64, 66–68]
24	Maardu, semicoke**	5	0.57–1.00	0.26–0.36	–0.32...–0.00	[69]
25	Sapropelites from the brown to the gas coal stage	4	1.11–1.22	0.09–0.23	–0.92...–0.76	[70]

\* Calculation made by authors [30] using a diagram.

\*\* Our recalculation.

After plotting all O/C and H/C values in the diagram (Fig. 1,A–J) it became evident that H/C values of Estonian DOS (A) lie between 1.0–1.5 with very rare exceptions, as well as those of sapropelites from the brown to the gas coal stage (F) and of Sweden alum shales (H) except two very metamorphosed samples. A great part of Russian DOS samples remain below H/C 1.0 (G).

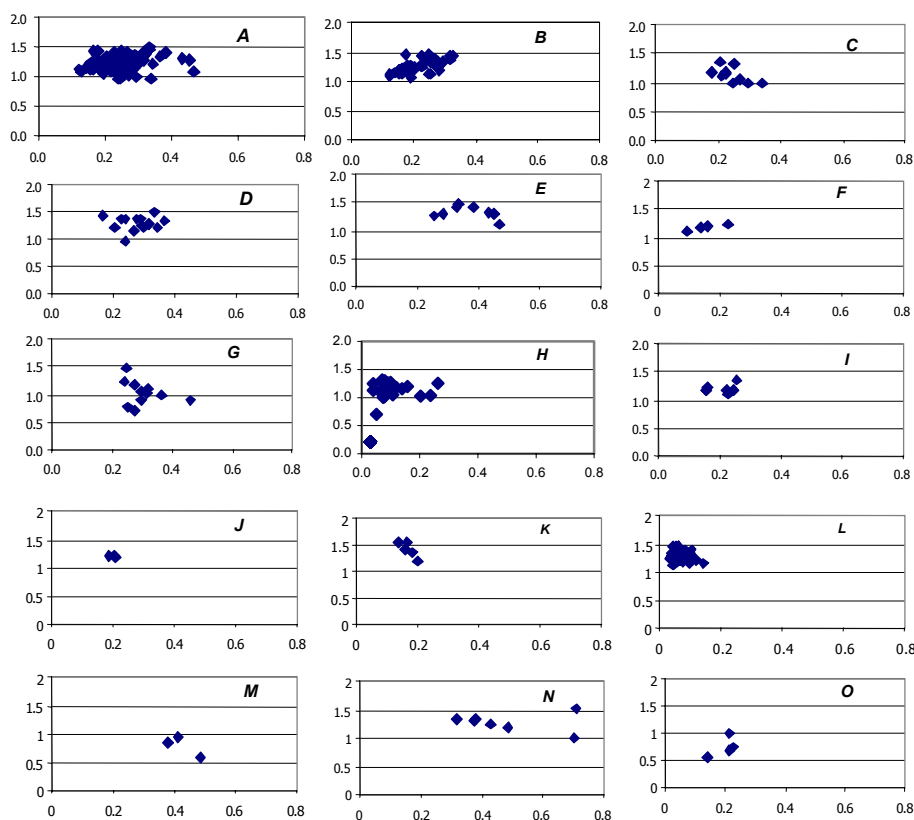


Fig. 1. H/C–O/C diagrams ( $y = \text{H/C}$ ,  $x = \text{O/C}$ ) of Estonian DOS (A–E: A – Estonian, among them B – Maardu, C – Toolse and D – other locations, E – weathered samples); OM concentrates (I and J: I – all samples, J – average values); Russian DOS (G); spropelites from the brown to the gas coal stage (F); Sweden alum shale (H); bitumen (K), oil (L), HA (M), oxidation products (N) and semicoke (O); all samples from A to N (in Fig. 3)

Variations in O/C values of Estonian DOS are very large, partly due to weathered samples. Eliminating weathered DOS (Fig. 2, E), the highest O/C value belongs to a core sample from Viitna (0.36); four samples from Ellamaa and Aseri have also rather high O/C values (over 0.3).

O/C values of Maardu DOS OM concentrates obtained by using different beneficiation methods (Table 1, pos. 1–3,) vary within narrower range (Fig. 1, I, J; Fig. 2, I, J) than non-weathered samples from Maardu. Most of alum shale samples, DOS analogues in Sweden, have lower O/C values because of mostly higher maturation degree, even higher than that of the gas coal stage of spropelites (0.09) (Table 1; Fig. 1, H, F). O/C values of Russian DOS (with anomalous low H/C values) almost suit with those of weathered samples of Estonian DOS (see Table 1).

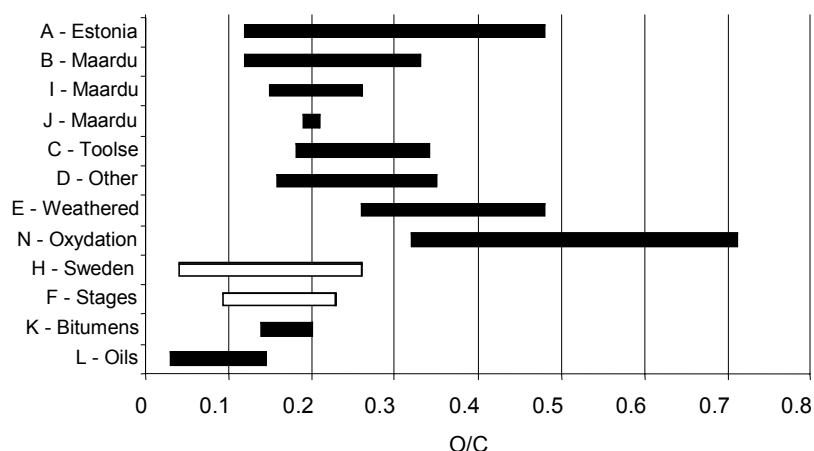


Fig. 2. O/C values of Estonian DOS (*A–E*: *A* – Estonian, among them *B* – Maardu, *C* – Toolse, and *D* – other locations, *E* – weathered samples); Maardu OM concentrates (*I* and *J*: *I* – all samples, *J* – average values); alum shale from Sweden (*H*); products of artificial oxidative destruction (*N*); sapropelites from the brown to the gas coal stage (*F*); bitumen (*K*) and oils (*L*)

We intuitively placed a part of Estonian DOS samples (mostly taken from outcrops) to the group of “weathered” ones (Table 1, pos 11; Fig. 1,*E*). Very high value of O/C usually shows that the solid fuel under study may be weathered. However, a part of samples with high O/C values, as appeared after our calculations on the basis of literature data, were not taken from outcrops.

The content of total, sulphatic and pyritic sulphur also may give strong signals that the sample of DOS is weathered (Table 2).

Table 2. Characterization of Weathered DOS Samples (bold figures indicate weathered samples)

Location/Author	Sulphur forms, %			Elemental composition, %				O/C	H/C	$\omega$
	S <sub>t</sub>	S <sub>SO<sub>4</sub></sub>	S <sub>p</sub>	C	H	O	N			
Ontika [18]	4.20	–	–	58.3	5.3	<b>36.4</b>	2.57	<b>0.47</b>	1.10	–0.16
Ontika [50]	2.57	<b>2.25</b>	<b>0.2</b>	58.3	6.3	<b>35.4</b>	2.00	<b>0.46</b>	1.30	–0.39
Paldiski [50]	3.07	<b>1.94</b>	<b>0.6</b>	59.2	6.5	<b>34.3</b>	2.81	0.43	1.32	–0.45
Popovka [52]	<b>1.98</b>	<b>1.48</b>	<b>0.4</b>	66.5	5.6	27.9	2.77	0.31	1.00	–0.37
Pulkovo [52]	2.57	<b>2.25</b>	<b>0.2</b>	68.2	6.6	25.2	2.26	0.28	1.16	–0.60
Sablinka [52]	<b>0.74</b>	0.13	<b>0.6</b>	67.4	5.8	26.8	3.41	0.30	1.04	–0.45

Low pyrite content (Table 2) is the best parameter to indicate if the DOS sample analyzed is weathered, as well as the very high O and S<sub>SO<sub>4</sub></sub> content or high value of O/C. At the same time low S<sub>SO<sub>4</sub></sub> content may indicate that sulphates formed have been washed out.

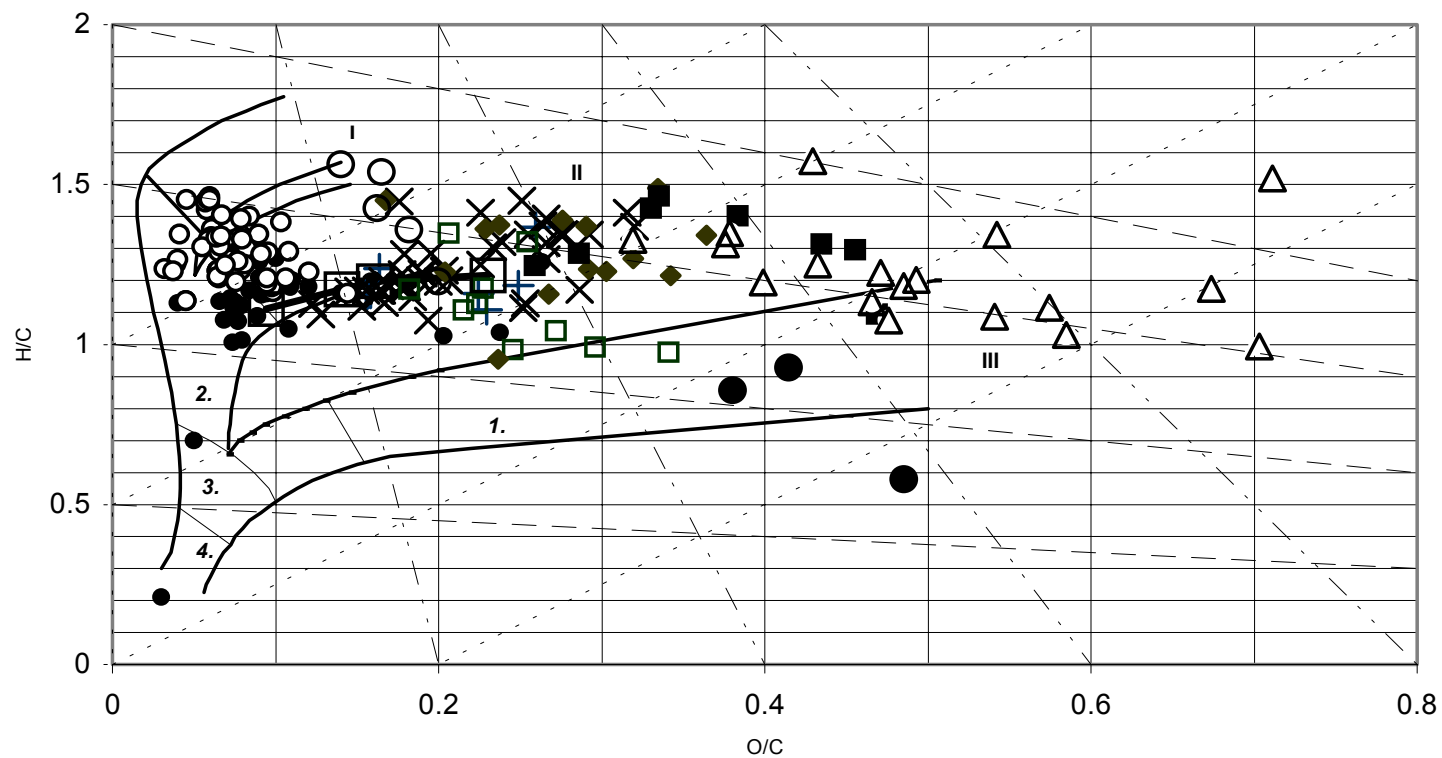


Fig. 3. H/C–O/C diagram of Estonian DOS: Maardu (×), Toolse (□), other locations (◆), weathered samples (■), Maardu concentrates (+) and HA (●); alum shale from Sweden (•), oils (◊), bitumen (○); DOS oxidation products –  $\text{KMnO}_4$  (△); sapropelites from the brown to the gas coal stage with trendline (□). I – main evolution path of the 1st type; II – main evolution path of the 2nd type; III – main evolution path of the 3rd type; 1. – immature zone, 2. – principal zone of oil formation, 3. – maximum of oil formation, 4. – structural reorganization of the carbon skeleton (after [21])



## Vankrevelenogram of DOS

Maardu DOS situates on the 2nd evolution path of kerogens and partly between the 2nd and 3rd paths (Fig. 3) in the immature zone, what means that its OM has not reached the principal zone of natural oil formation. It is interesting to point out that also a half of oils obtained at thermal decomposition of DOS formally remains in the immature zone, too. The gas coal stage (Figs 2 and 3) is already out of the DOS area that corresponds to the opinion about oil shales as a formation of mainly in the brown coal stage. H/C and O/C values of all kinds of organic formations decreased in the course of natural maturation almost to zero (graphite). According to vankrevelenogram, the Sweden alum shale is present in all mentioned stages up to the gas coal stage and further to the graphitic stage, characteristic of super-maturity [63].

For comparison, 39 kukersite samples have narrower ranges of H/C and O/C values than DOS ones: 1.38–1.57 and 0.12–0.17, respectively, and even the weathered ones (10 samples): 1.22–1.45 and 0.15–0.24 [23]. So, kukersite OM situates almost between the 1st and 2nd evolution paths of kerogens.

DOS concentrates have H/C values of 1.11–1.37 and O/C of 0.16–0.26, the average ones obtained by flotation 1.19 and 0.21, and by HF and HCl treatment 1.20 and 0.19, respectively (Table 3). These values are conditionally comparable with Ginzburg's [35] results: H/C 1.24 and O/C 0.16, the elemental composition: C 75.7, H 7.8, N 2.3, and O 14.2 % (Table 3). For comparison, the more common data characterizing kukersite are: C 77.4, H 9.7, N 0.4, and O 12.5 % [71].

**Table 3. OM Concentrates of Maardu DOS Obtained by Flotation (FC) and by HCl and HF Treatment (HF-Cl)**

Method/Author	OM, %	Elemental composition, %				O/C	H/C	$\omega$
		C	H	O	N			
FC <sup>*1</sup> [31]	30.0	71.5	6.6	21.9	2.07	0.23	1.11	-0.652
FC [32]	55.8	68.5	7.8	23.7	3.30	0.26	1.37	-0.852
FC <sup>*2</sup> [33]	50.9	69.9	6.9	23.2	2.10	0.25	1.18	-0.682
FC <sup>*3</sup> [34]	41.2	76.7	7.4	15.9	1.68	0.16	1.15	-0.843
FC <sup>*4</sup> [34]	47.6	76.5	7.4	16.1	1.56	0.16	1.16	-0.843
HF-C 1 [30]	75.8	71.7	6.9	21.4	1.53	0.22	1.16	-0.712
HF-C 1 [35]	88.3	75.7	7.8	16.5	2.27	0.16	1.24	-0.912
Average for FC	45.1	72.6	7.2	20.2	2.14	0.21	1.19	-0.774
Average for HF-Cl	82.1	73.7	7.4	19.0	1.90	0.19	1.20	-0.812
Average for both	55.7	72.9	7.3	19.8	2.07	0.21	1.20	-0.785

<sup>\*1</sup> S 1.4, <sup>\*2</sup> S 2.2, <sup>\*3</sup> S 1.9 and <sup>\*4</sup> S 2.2; average 1.9 %.

Only a little part of DOS samples analyzed were classified by us, according to additional information available, as weathered ones (see Table 2).

Most of them were derived from shale's exposure, some of them contained HA up to 10–40 % [52]. According to Uspenski, HA, more common to Russian DOS, are not a result of weathering processes, even in rare cases (see pos. Sablinka in Table 2) when the HA content reaches from 50 to 80–90 % [52].

Obviously the high HA content is one of the reasons why Russian DOS stretch in the diagram to the direction characteristic to HA (see Fig. 3). High O/C values of most samples studied are caused by difficulties in determination of the influence of certain components of MM to the results of elemental analysis. Common non-weathered Estonian DOS samples have low HA content – only a few percent. HA differed from DOS by lower H/C and higher O/C values regardless of their yields or artificial origin (keeping DOS in thermostat at 100 °C during two months).

In the diagram DOS oxidation products are located in the region of higher O/C values compared to the DOS, to the direction of carboxylation. Figure 3 does not include oxidation products with O/C higher than 0.8.

DOS semicoke (artificially matured DOS) formed at temperature 400–520 °C with very high O/C values – 0.26–0.36, even after making correction on pyrite lowered up to 0.14–0.23 (shown only in Fig. 1,*O*) remains out of the area of naturally changed OM (kerogens).

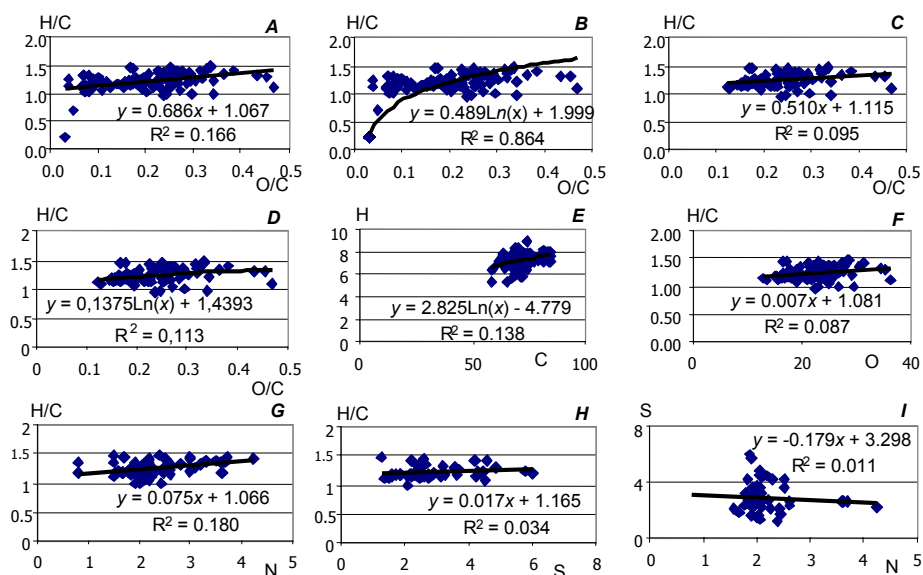


Fig. 4. Selected correlations between OM parameters of Estonian DOS (A–B) and Swedish alum shale (C–I)

There are weak correlations between parameters of OM of Estonian DOS and Sweden alum shale (Table 4; some of them in Fig. 4). Weak correlation between H/C and O/C of Estonian and Swedish shale samples or Estonian DOS is particularly pointed out (Fig. 4,*A–D*). In Figure 4,*B*, the trendline

was forced to pass the point H/C 0.21 and O/C 0.03 (increasing by 100 folds its share), as thermal evolution of all kinds of sedimentary OM ends with the graphite stage with H/C and O/C both equal to zero.

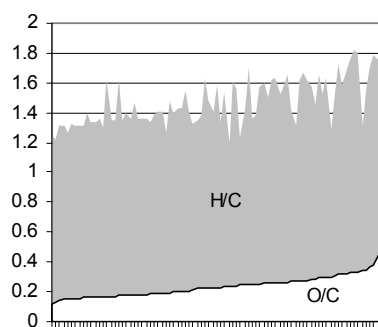
**Table 4. Correlation between the Parameters of OM of Estonian DOS and Sweden Alum Shale**

Indices	Equation	R <sup>2</sup>	Source*
H/C – O/C	$y = 0.489\text{Ln}(x) + 1.999$	0.864**	E + S
H/C – O/C	$y = 0.686x + 1.0673$	0.166	E + S
H/C – O/C	$y = 0.1375\text{Ln}(x) + 1.4493$	0.113	E
H/C – O/C	$y = 0.510x + 1.115$	0.095	E
H/C – O	$y = 0.007x + 1.081$	0.087	E
H/C – N	$y = 0.0075x + 1.066$	0.180	E
H/C – S	$y = 0.017x + 1.1165$	0.034	E
H – C	$y = 0.0421x + 4.1828$	0.227	E + S
H – C	$y = 2.8251\text{Ln}(x) - 4.779$	0.138	E + S
H – C	$y = 0.0023x + 7.2155$	0.001	E
H – C	$y = 6.4179x + 0.0325$	0.001	E
N – C	$y = -0.0572x + 6.2875$	0.178	E + S
N – C	$y = 2285.1x - 1.6376$	0.149	E + S
N – C	$y = -0.054x + 6.0857$	0.149	E
N – C	$y = -3.6874\text{Ln}(x) + 17.959$	0.143	E
S – C	$y = -0.0234x + 4.6015$	0.009	E + S
S – C	$y = 7.6531x - 0.241$	0.002	E + S
S – C	$y = -0.0108x + 3.7147$	0.002	E
S – C	$y = -0.1771x + 3.325$	0.010	E
S – N	$y = -0.179x + 3.298$	0.011	E
O – C	$y = -1.0565x + 96.73$	0.974	E
O – S	$y = -0.4948\text{Ln}(x) + 20.483$	0.002	E
O – N	$y = 2.5723x + 15.848$	0.113	E
O – N	$y = 17.353x + 0.2534$	0.106	E

\* E – Estonia, S – Sweden.

\*\* Forced through the point H/C 0.21 and O/C 0.03.

H/C as a parameter to elucidate correlations was selected because it is calculable with minimum errors caused by MM content of DOS. Numerical values of DOS OM elemental composition calculated vary depending on how many corrections for the MM composition was taken into consideration by investigators. In the case of determining S and N content, errors caused by MM are in the same direction, but R<sup>2</sup> turned out to be one of the smallest (Fig. 4, D). It evidences that these characteristics of DOS heteroatoms have, at different independent mechanisms of their entering into



**Fig. 5.** Variations in H/C values of Estonian DOS samples arranged according to increasing O/C values

OM, great local variations.

Variations in H/C values of the collection of all Estonian DOS samples, which take place with increasing O/C values, are chaotic (Fig. 5).

## Discussion and Conclusions

Historically the first chemical investigations of DOS were done using mostly samples taken from exposure. So, using sound methods valid results about the weathered DOS were obtained. However, these results were used not for weathered DOS, but, unfortunately, for characterizing DOS as a native object. The first results obtained were cited very often. That shaped the wrong idea of DOS elemental composition. Sometimes the notions such as “unexpired shale” [36] and also descriptions how the samples were taken appeared later. On the other side, there was almost a total absence of constructive critical works on the matter of real composition of native DOS.

DOS is an oil shale with low OM content reaching that of dispersed OM. Its  $S_t$  and clay mineral crystal-hydrate water content is high compared to kukersite. So, the role of corrections to elemental composition is ought to be higher. As could be expected, the vankrevelenogram of DOS differs from that of kukersite. These differences are only partly due to chemical differences between DOS and kukersite. There is also a possibility that the differences in elemental composition data of DOS OM elucidated in the diagrams (see Figs 1, 3, 5) may be due to the natural variations of DOS and/or degrees of weathering processes, but we strongly insist that in most cases great variability in elemental composition is caused by insufficient amendments to consider the influence of MM (pyrite, crystal-hydrate water of shale clay minerals). It also means that HA are the secondary formations of DOS notwithstanding its locality, except a few percent which are characteristic to all non-weathered oil shales.

Some conclusions obtained in this study including organizing and visualizing experimental data about DOS are as follows:

1. Many investigators have unconsciously used weathered DOS samples supposing they were non-weathered ones.
2. The analysis of weathered and non-weathered DOS samples needs different approach based on dispersed OM analysis methods.
3. To obtain valid elemental analysis data of DOS, corrections for the MM composition, especially pyrite content, should be taken into consideration in calculations.
4. To obtain truthful elemental composition data, only fresh samples of DOS from strata not exposed to natural weathering processes and changes in laboratory conditions must be investigated.
5. Proper sampling and storing conditions of DOS have to be settled.

6. There is a need in DOS chemistry and chemical technology to recalculate the results of shale oil yields and other DOS indices obtained to elucidate its nature and chemical properties as a raw material.
7. Heteroatoms such as N and S have, at different independent mechanisms of their entering into OM of DOS, great local variations.
8. The probable elemental composition of native DOS OM elucidated from this study is (see Table 3): C 75.7, H 7.8, N 2.3, O 14.2 %, atomic ratios H/C 1.24 and O/C 0.16.

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