DISTRIBUTION OF MOLYBDENUM AND URANIUM IN THE TREMADOC GRAPTOLITIC ARGILLITE (DICTYONEMA SHALE) OF NORTH-WESTERN ESTONIA

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Pukkonen, E. and Rammo, M. 1992. Distribution of Molybdenum and Uranium in the Tremadoc Graptolitic Argillite (Dictyonema Shale) of North-Western Estonia. Bull. of the Geol. Survey of Estonia, 2/1, 3-15.

The distribution of uranium, molybdenum and calorific value in the Dictyonema Shale is presented basing data obtained through the study of about 130 drill cores. The north-western part of Estonia is divided into two geochemical zones. The boundary between these zones is the most distinct near the Paldiski-Rapla line (Fig. 1), which is also rather clear limit for the distribution of graptolites. In the western zone (zone I) sedimentation took place mainly in the stable anoxic conditions, where the toxic sulphide-rich bottom water was covered by a well-defined denitrified water layer serving as an abundant source of food for graptolites. In the younger, eastern zone (zone II) the bottom layer was hydrodynamically more active. Fine lamination was not formed in that zone, and due to the higher oxygen content in the bottom water the concentrations of uranium, molybdenum, vanadium etc. had decreased in the sediment.

Key words: Tremadoc, Dictyonema Shale, genesis, lithology, biostratigraphy, conodonts, graptolites, geochemistry, uranium, molybdenum, vanadium, north-western Estonia.

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INTRODUCTION

Estonian Tremadoc organic-rich argillite, traditionally known as Dictyonema Shale, is distributed in northern Estonia, including the mainland, Vormsi and Hiiumaa islands (Fig. 1). Like other Baltoscandian black shales of Lower Palaeozoic age (Andersson et al., 1935; Wilde et al., 1989; Gee, 1981), the Estonian Dictyonema Shale (EDS) has relatively high concentrations of molybdenum (up to 1990 ppm), uranium (up to 1038 ppm) and vanadium (up to 1910 ppm) (Pukkonen, 1989).

North-western Estonia is characterized by a thick (up to 7.4 m) homogeneous Dictyonema Shale layer (Fig. 1), which is gently dipping southwards. In the north-eastern corner of the study area it is lying at a depth of 7 m, near the southern boundary at a depth of 220 m. Up to now the distribution of minor elements in the Dictyonema Shale of this area has been discussed only in one work (Petersell et al., 1981) from the point of view of the productivity of the layer (concentration of the metals in relation to the thickness of the layer). In present article main attention has been paid to the detailed description of the uranium and molybdenum distribution - to the elements highly sensitive to oxydation-reduction conditions in the water basin. The first attempt was made at the geochemical stratigraphy of the EDS, taking into account also the biostratigraphical studies.

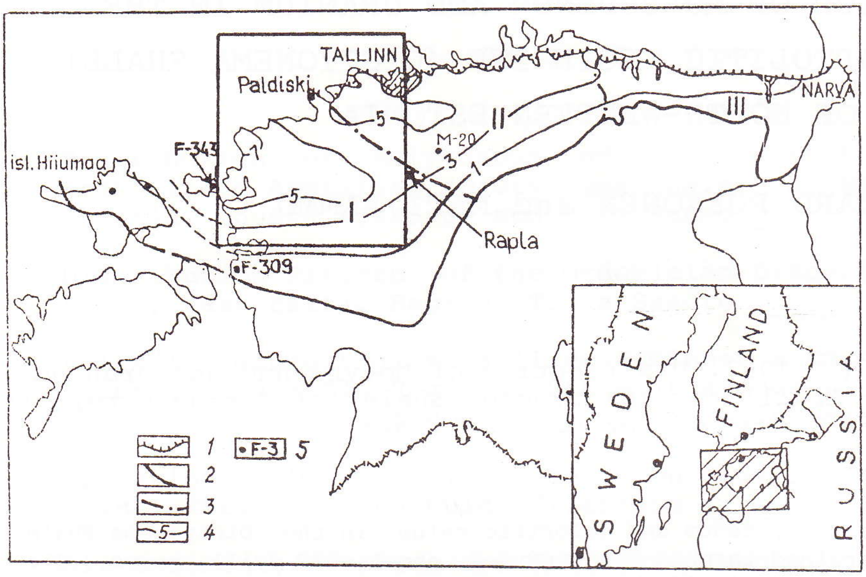


Fig. 1. Scheme of the study area; geochemical zones: I - western, II - central, III - eastern (Pukkonen, 1989); 1 - clint, 2 - 0-isopachyte, 3 - boundary between the geochemical zones, 4 - isopachytes (in m), 5 - drillholes.

SAMPLING AND ANALYTICAL METHODS

The data generalized here have been presented by the authors in unpublished reports 4-5 years ago and are stored at the archives of the Geological Survey of Estonia. More than 130 drill cores have been documented and sampled. The core samples with an average sampling interval of 30-40 cm were powdered and analysed by the emission spectroscopy (Kivisilla et al., 1975) and X-ray fluorescence (U, Mo, Pb etc.) methods in the laboratory of the Geological Survey of Estonia. Additionally, the calorific value and the total sulphur content were measured. Vanadium was determined in 52 samples (from 6 cores) by atom-adsorption method at "Sevukrgeologija" in Kiev, Ukraine. Determination of the major elements (oxides) was carried out by the classical wet chemical analysis at the Geological Survey of Estonia. Two sections were analysed by the neutron activation method at the Geological Survey of Latvia in Riga.

Besides Estonian sections, the Bårstad core 85001 (Östergötland, Sweden) was sampled and analysed.

LITHOLOGY AND BIOSTRATIGRAPHY

The Dictyonema Shale belongs to the Türisalu Formation (O_1tr) and is represented in the study area by horizontally laminated dark organic-rich argillite containing lighter, about 0.2-2 mm thick silty-pelitic or coarse-pelitic laminae of variable frequency (Heinsalu, 1990). It is mainly overlain by Upper Tremadoc sandstones and clays of the Varangu Formation (O_1vr). Only at the north-western margin of the mainland and on Vormsi and Hiiumaa islands the Dictyonema Shale is covered by Arenig sandy limestones of the Volkhov or Kunda stages (O_1vl, O_1kn). The underlying Kallavere Formation (O_1kl) of early Tremadoc age is represented by a phosphatic quartzose sandstone layer with a thickness from 0-0.5 m in the NW corner to 8.9 m near the eastern boundary of the study area. Very often, at the base of the sandstones an organic-rich argillite bed with a thickness of up to 20 cm (usually 5-10 cm) occurs. Thin (1-2 cm) intercalations of argillite are also typical of the phosphatic sandstone section.

The Türisalu Formation (Dictyonema Shale) contains also up to 25 cm thick interlayers of anthraconite or limestone, especially in the western sections of the study area. As a rule, these carbonate layers are missing in the central zone. Near the thinning-out line (in core F-309, Fig. 1) the silt- or sandstone and anthraconite interbeds make up about 50 % of the 40 cm thick Türisalu Formation. Usually, the distribution of siltstone and anthraconite interlayers is irregular. An exception is the district in the western side (subzone 1, Fig. 4d), where the middle part of the Dictyonema Shale section with a thickness of up to 50 cm is represented by more sandy (silty) argillite or by intercalation of thin (1-2 cm) argillite and sand- or siltstone layers. This distribution pattern occurs also on Vormsi Island (core F-343, Fig. 1).

Conodont studies have shown that in the study area the whole argillite band belongs to the uppermost *Cordylodus rotundatus- C.angulatus-* Zone of the Pakerort Stage (Fig. 2) (Kaljo, Viira, 1989). But to the east of the Paldiski-Rapla line (Fig. 1), the upper part of the section is represented

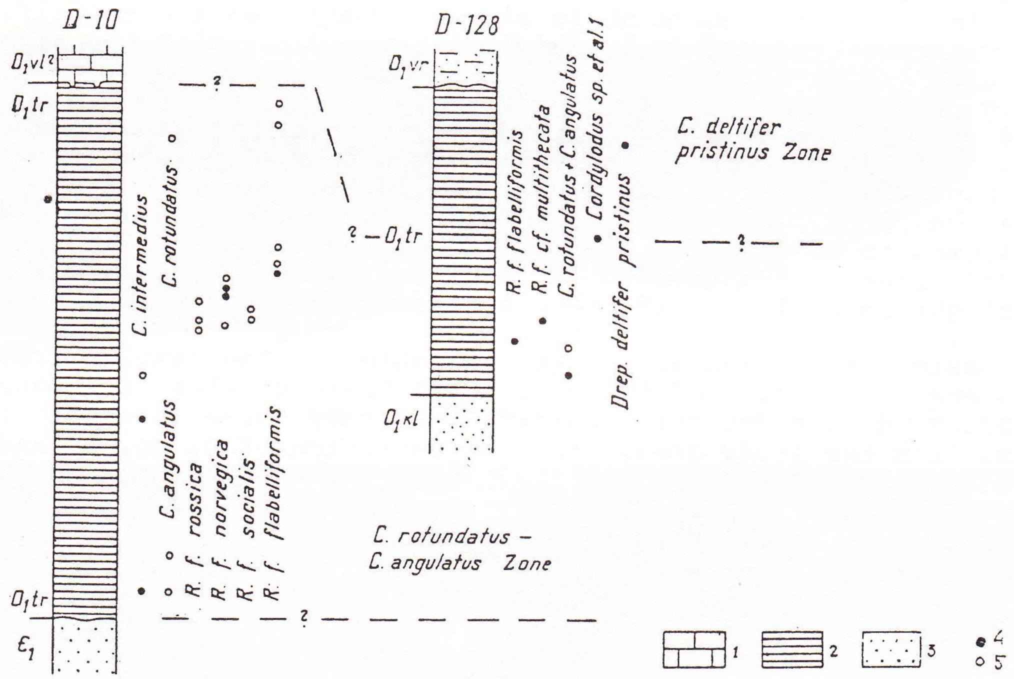


Fig. 2. Correlation of the sections showing the ranges of graptolites and conodonts (after Kaljo, Viira, 1989): 1 - limestone, 2 - Dictyonema Shale, 3 - sandstone, 4 - exact identification, 5 - identification on cf. level.

by the *Drepanoistodus deltifer pristinus* Zone of the Varangu (Ceratopyge) Stage. The biostratigraphical subdivision based on the *Rhabdinopora* (earlier named as *Dictyonema;* Erdtmann, 1982a) *flabelliformis multhithecata-R.f. anglica* Subzone has revealed the similar correlation with the conodont stratigraphy (Kaljo, Viira, 1989). As shown in Fig. 3, graptolites are distributed in the upper part of western sections (see profiles I-I, IV-IV) and in the lower part of eastern sections (profiles III-III, IV-IV). Thickness of the intervals with graptolites decreases sharply eastwards from the Paldiski-Rapla line (Heinsalu, 1990). Usually, the graptolites occur in thin laminated argillite, but are very rare in homogeneous (non-laminated) Dictyonema Shale layer, for example, in the upper part of eastern sections.

DISTRIBUTION OF Mo, U AND OTHER ELEMENTS

According to the minimum enrichment values (m.e.v.) of minor elements given by Vine and Tourtelot (1970) for black shales, the EDS is enriched with uranium (m.e.v. 30 ppm), molybdenum (200 ppm), vanadium (1000 ppm) and lead (100 ppm). As compared to the US black shale standard SDO-1 (Huyck, 1991), the EDS is also enriched with silver. The m.e.v. proposed by Huyck would be 0.18-0.34 ppm, but the concentration of Ag in the EDS reaches 1-2 ppm (mean 0.5-0.7 ppm).

Molybdenum and uranium. The Dictyonema Shale sections with the highest contents of these elements occur in the southern part of the study area, near the thinning-out line (Fig. 4a, b). Decrease in the concentrations is most considerable in the north-eastern direction. The Dictyonema Shale from core F-309 (see Fig. 1) has the average uranium content of 354 ppm, but the concentration of molybdenum is only 128 ppm. The calorific value of this shale reaches 1080 kcal/kg (4.5 MJ/kg). Because of even pyrite distribution in the Dictyonema Shale of the study area the calorific value reflects a rather high yield of organic matter. Shale with the highest calorific value (organic matter content) occurs in thick monotonous NW sections (Fig. 4c). In core F-343 (Vormsi Island) the Dictyonema Shale contains 118 ppm of uranium and 200 ppm of molybdenum, on Hiiumaa Island (cores K-16, 399) the concentrations are 100 ppm and 270 ppm, respectively. As shown in Fig. 4a, b, c, the rapid decrease in the calorific value and the concentrations of U, Mo (also V, Ni, Pb, Ag etc.) near the Paldiski-Rapla line, allowed to divide the Türisalu Formation into the western (1) and central (II) zones. This geochemical division is in very good correspondence with slight lateral age differences revealed by biostratigraphic studies (see above).

The basic statistics are given in Table 1. The samples from the islands and analytical data of the Dictyonema Shale samples from zone II (except vanadium determinations) outside the study area are not included. Eastwards, from the study area, the concentration of U, Mo, S and organic matter decreases (Pukkonen, 1989). The correlation between Mo and U is strong at low values (up to 250 ppm, $r \geq 0.75$, Table 2), and weakens at high concentrations (Fig. 5a, b). As shown in Fig. 5, the slope of the regression lines of samples with low concentrations of these elements is similar for both zones, but gives a clear intercept of the Mo axis at high (above 500 ppm) Mo values in zone II. The comparison of graptolite occurrence (Fig. 3, profile IV-IV) and Mo, U distribution (Fig. 6) in the west-east cross-section shows a good correlation between them. The lower part of

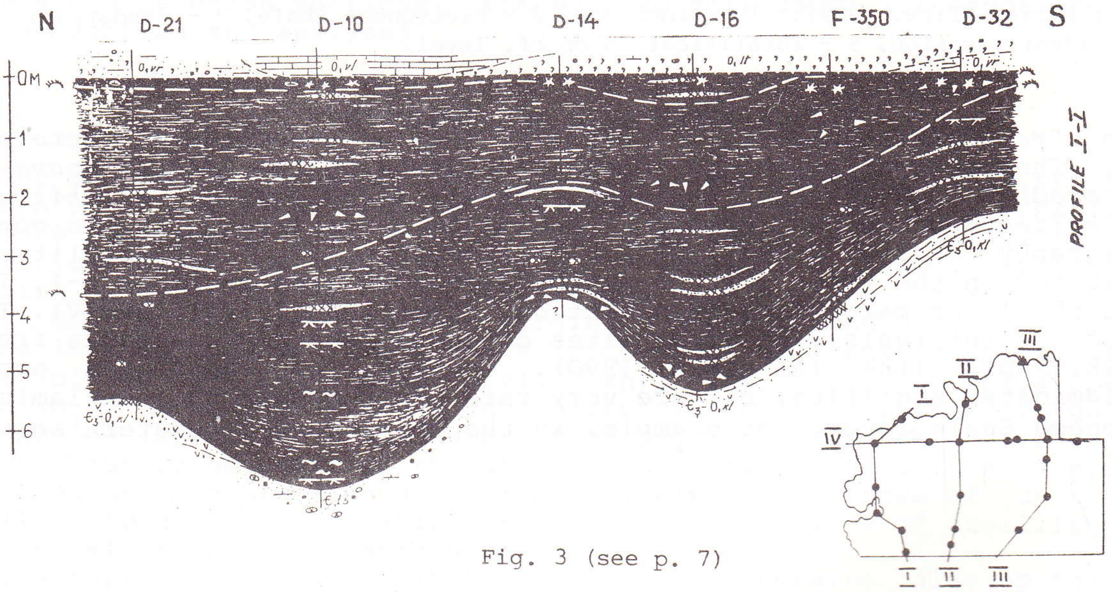


Fig. 3 (see p. 7)

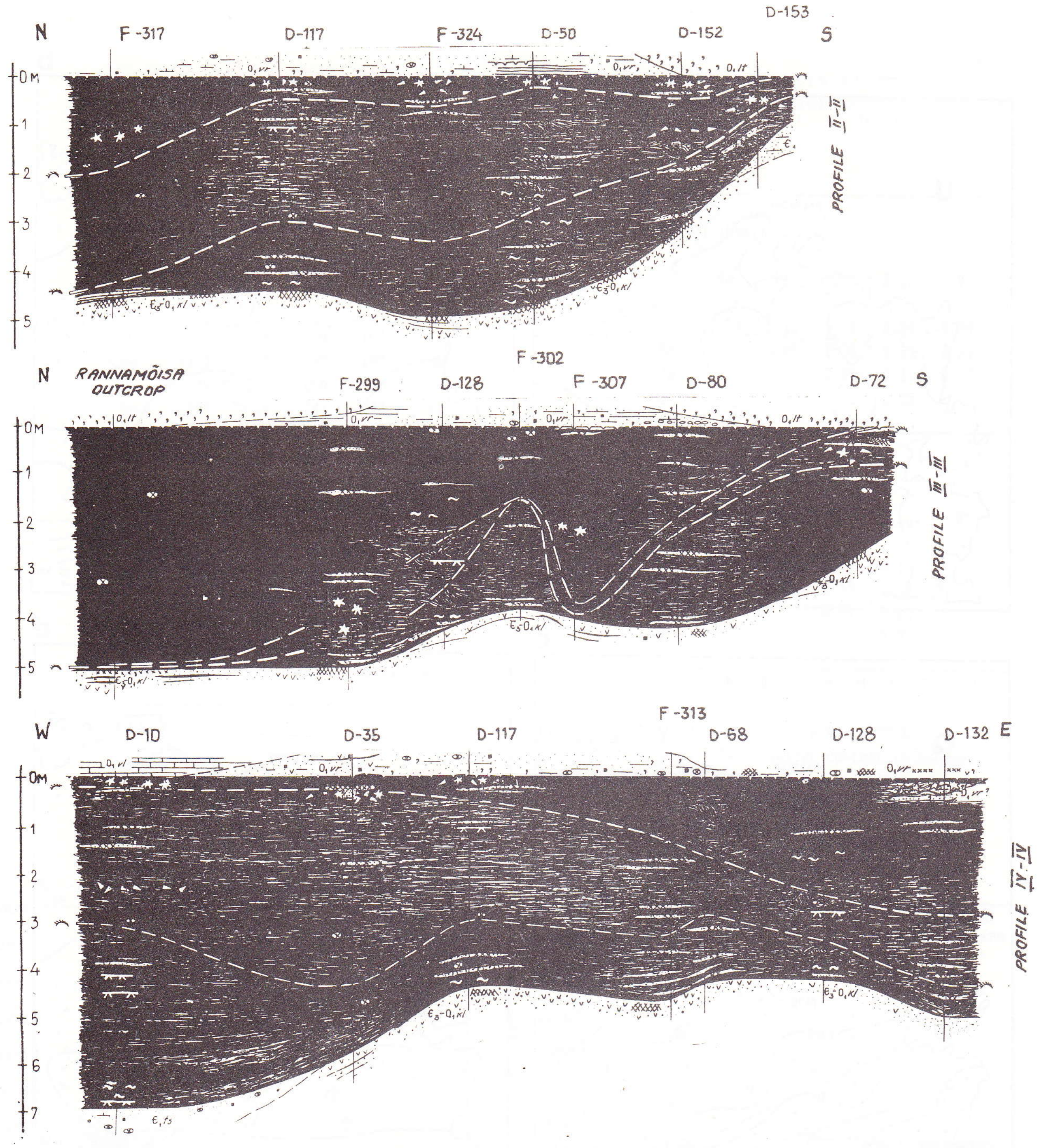


Fig. 3. Lithological cross-sections (after Heinsalu, 1990).
The distribution of graptolites is marked by two light dash lines.

the sections with a thickness of 1-2 m is barren of graptolites. This layer is roughly bounded with Mo isocon 200 ppm and with uranium isocon 125 ppm. The thick homogeneous (non-laminated) Dictyonema Shale layer in the upper part of the eastern sections, where the graptolites are lacking, is characterized by low contents of U (up to 50 ppm), Mo (up to 100 ppm) and organic matter. The same distribution patterns can be seen in the submeridional profile (Fig. 3, profile II-II; Fig. 7). In general, the Mo content increases also near the upper boundary of the Dictyonema Shale Formation. The southern sections of the study area are characterized by higher concentrations of Mo and U not only in their lower, but also in the upper parts (Fig. 4d, subzone 2). This subzone coincides with the area, where the Türisalu Formation is directly covered by the glauconitic sandstones of the La-

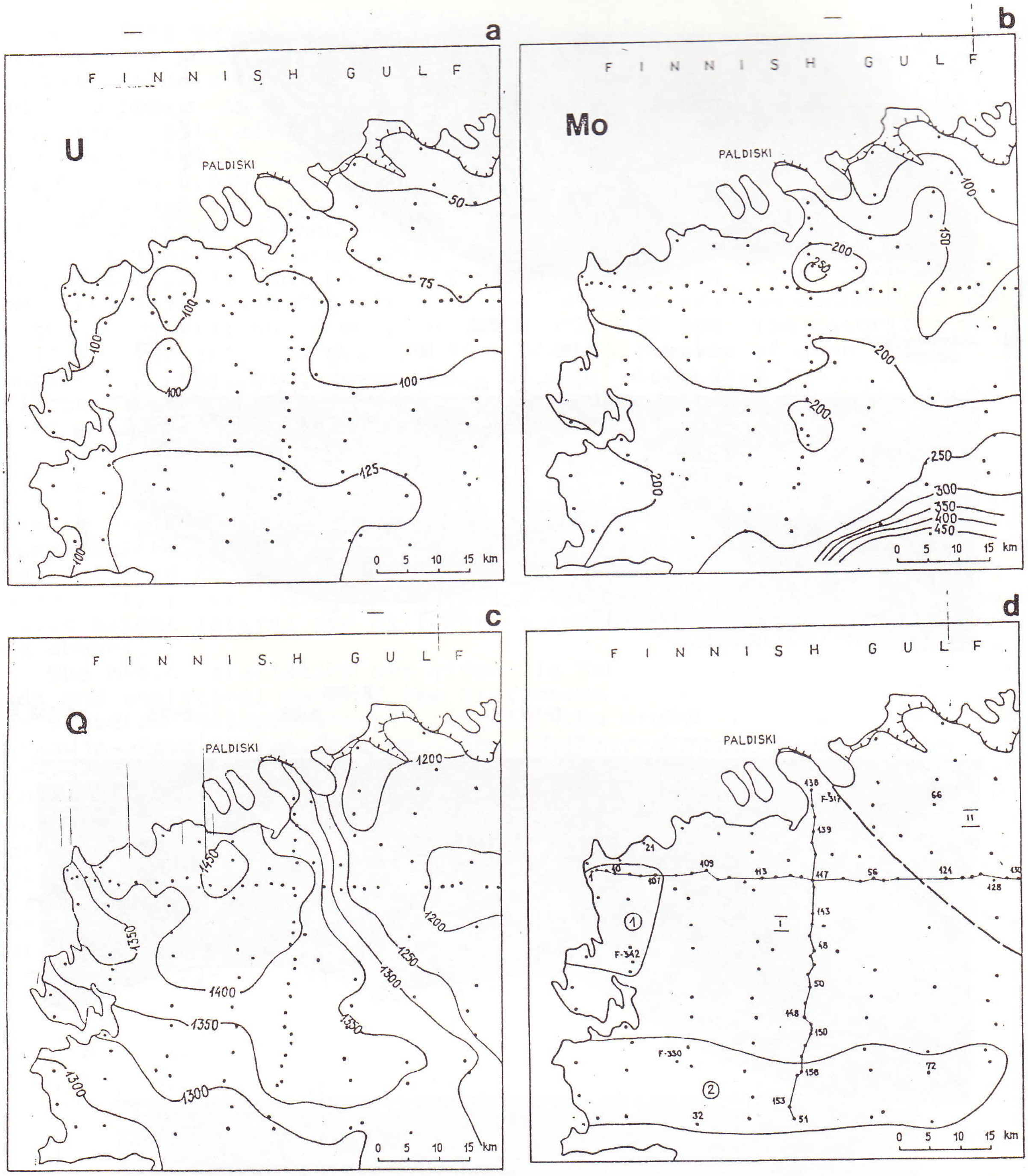


Fig. 4. Distribution of U, Mo and calorific value (calculated as average weight content of the Dictyonema Shale section). Legend, see Fig. 1; a - U (in ppm), b - Mo (in ppm), c - calorific value (in kcal/kg, 1000 kcal/kg = 4.2 MJ/kg), d - scheme of location of the profiles and drill cores analysed (names of the drill cores are given without the label prefix "D-"); 1 - subzone 1, 2 - subzone 2.

torp Stage. The clay- and siltstones of the intermediate Varangu Stage, distributed north of this area, are lacking here.

The more sandy (silty) interval in the middle part of the western sections (subzone 1, Fig. 4d) contains more Mo and U than surrounding pure argillite (e.g. see Table 3, F-342, sample nr. 849). The increased content of phosphorus (P_2O_5), but also of Sr, Mn, F and lantanoids, is probably related to the elevated amount of inarticulate brachiopod debris there. It is likely, that besides organic matter U is concentrated in phosphates and Mo in sulphides.

Table 1

The basic statistics of the minor elements, total sulphur content and calorific value in the Dictyonema Shale of NW Estonia

Element	n	Min	Max	Mean	Std.Dev.
		Zone I (West)			
U	1739	3	710	103	49
Mo	1712	19	1680	197	166
V	38	220	1850	1150	300
Pb	1739	30	741	127	41
S_{tot}	444	1.6	12.1	3.7	1.5
Q	1665	310	1870	1340	180
		Zone II (Central)			
U	269	10	410	84	62
Mo	269	21	1669	189	272
V	13	390	900	650	170
Pb	269	57	741	131	59
S_{tot}	62	2.1	9.0	4.0	1.7
Q	269	490	1650	1220	170

Table 2

Correlation analysis of the minor elements, total sulphur content and calorific value

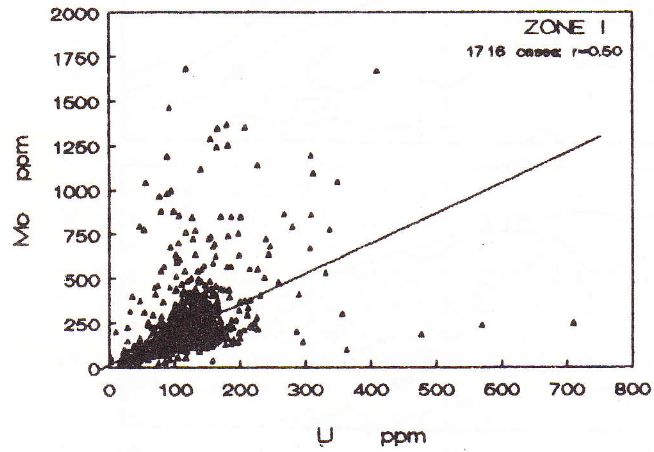
Zone I (West)

	Mo	Pb	Q	S_{tot}	V
U	0.50	0.12	0.34	0.04	0.30
Mo		-0.07	0.30	0.15	0.50
Pb			0.07	0.32	0.12
Q				-0.08	

Zone II (Central)

	Mo	Pb	Q	S_{tot}	V
U	0.75	0.05	0.44	0.11	
Mo		0.00	0.19	0.27	
Pb			0.19	0.62	
Q				0.27	

U, Mo, Pb, V - in ppm (10^{-4} %)
S_{tot} - total sulfur content in percents
Q - calorific value in kcal/kg
1000 kcal/kg= 4.2 MJ/kg
n - number of samples



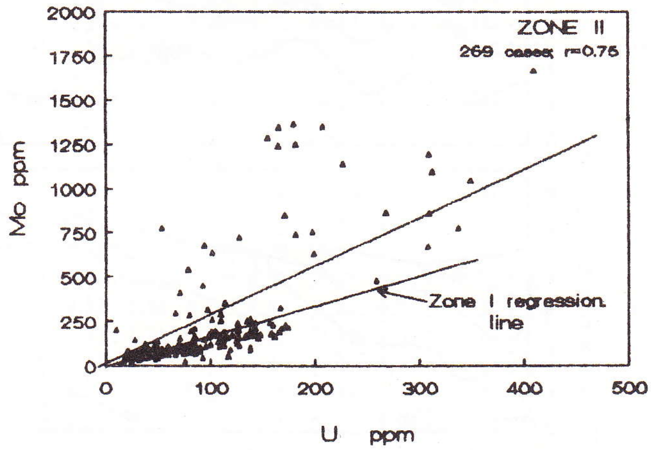


Fig. 5. Uranium versus molybdenum plots for Dictyonema Shale of the western zone (a) and central zone (b)

Other elements. The basic statistics for vanadium and lead- elements, which are also abundant in the Dictyonema Shale, are given in Table 1. Semiquantitative spectroscopic analyses have shown, that the highest vanadium concentrations occur in the NW and central parts of the study area, where the Dictyonema Shale layer has the maximum thickness and calorific value (organic matter content). Atom-adsorption analyses of 13 samples from zone II outside the study area showed the arithmetical mean value for vanadium 650 ppm.

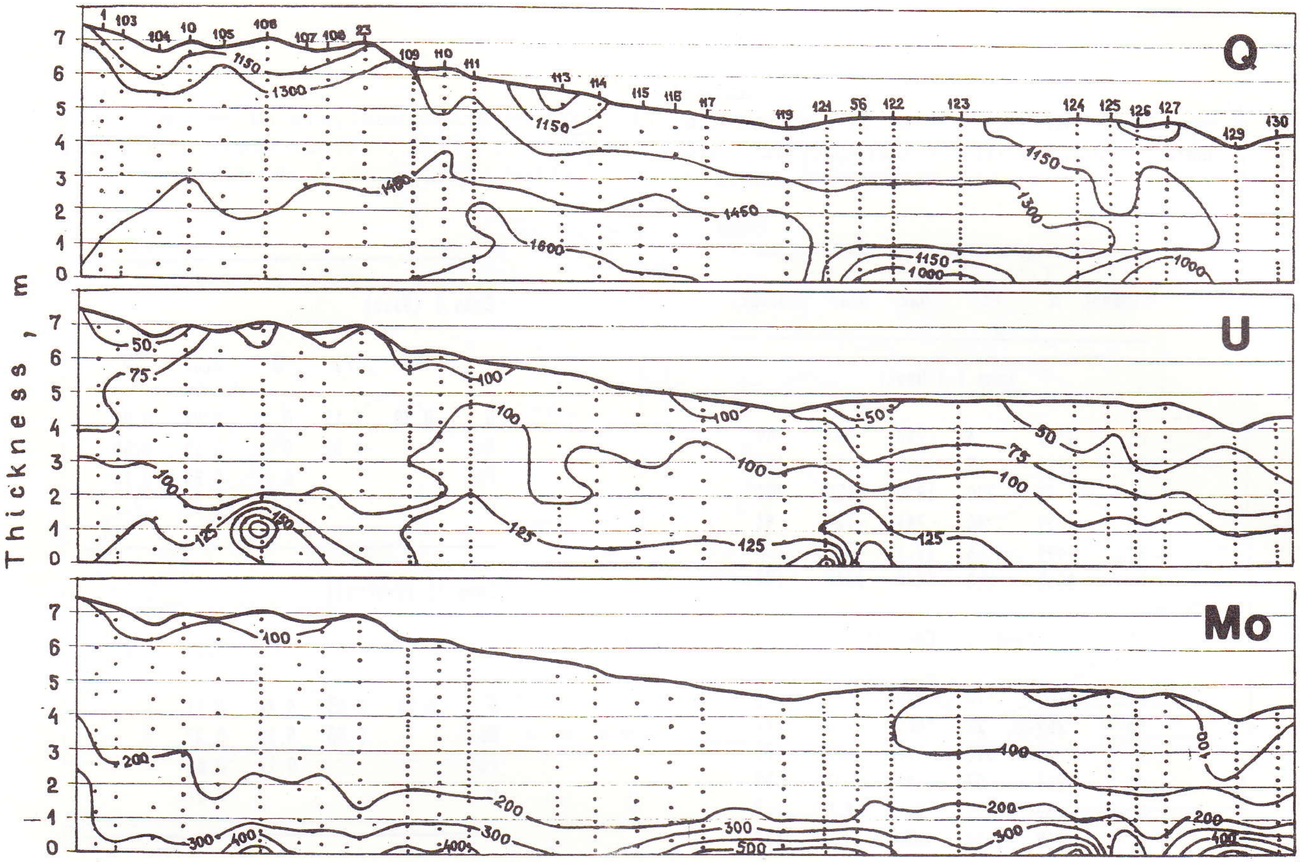


Fig. 6. Distribution of calorific value (in kcal/kg), U and Mo (in ppm) in the west-east profile. Numbers of drill cores in the upper figure are given without the label prefix "D-". Dots are showing average depths of the sampling intervals.

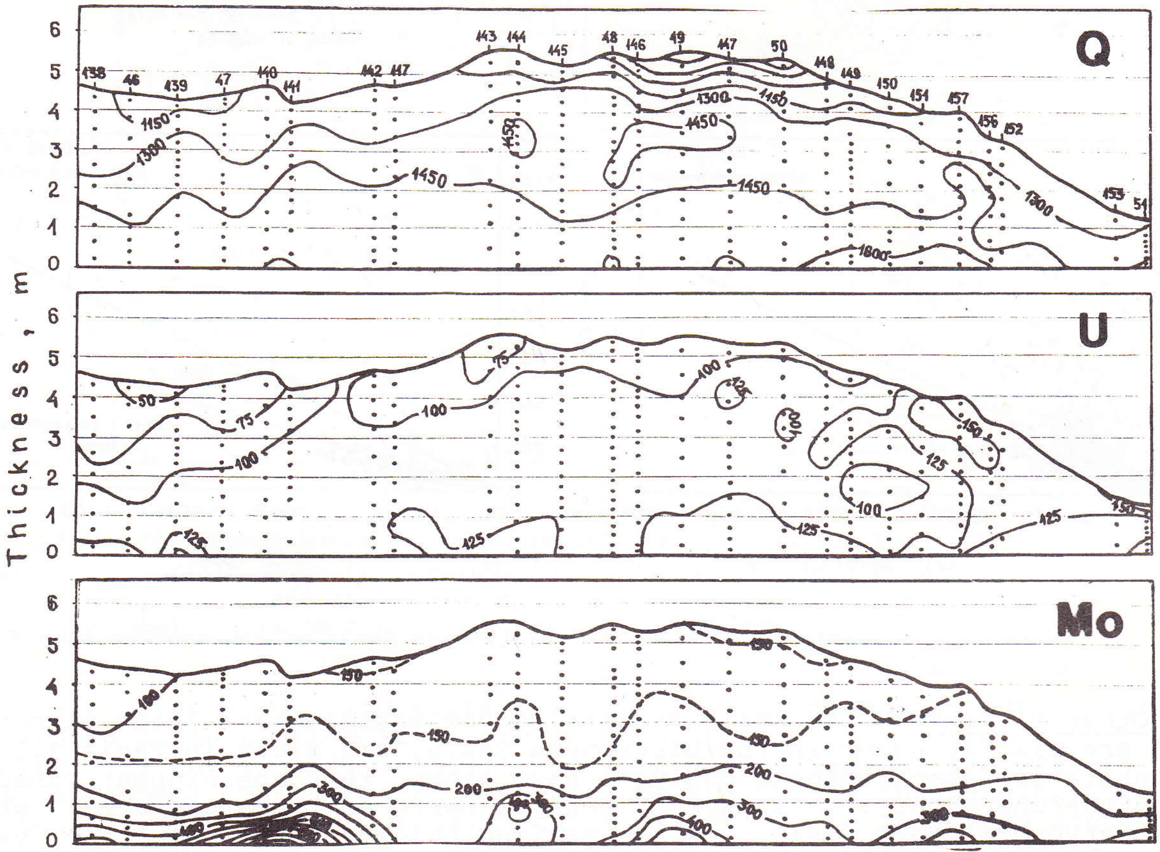


Fig. 7. Distribution of calorific value (in kcal/kg), U and Mo (in ppm) in the north-south profile.

Table 3

Whole chemical analysis of major and minor oxides (in wt percent), minor elements (in ppm) and calorific value (in kcal/kg) of Dictyonema Shale

	Drill core	nr.	SiO_2	Al_2O_3	Fe_2O_3 tot	TiO_2	MnO	CaO	MgO	Stot	P_2O_5	FeO	Na_2O	K_2O	L.O.I.	CO_2	U	Mo ppm	V	Q kcal/kg
1	F-342	844	50.95	12.82	5.90	0.67	0.018	0.16	1.19	3.19	0.12	1.72	0.07	8.50	21.64	0.07	92	128	1010	1380
2	F-342	845	50.08	12.82	6.34	0.72	0.018	0.16	1.14	3.41	0.12	1.58	0.05	8.40	21.59	0.07	85	122	900	1383
3	F-342	846	49.90	12.82	5.47	0.65	0.018	0.21	1.14	2.88	0.13	1.72	0.07	8.40	22.47	0.07	82	142	1120	1458
4	F-342	847	52.00	12.94	5.47	0.69	0.023	0.18	1.13	2.88	0.12	2.44	0.07	8.70	20.42	0.07	107	180	1010	1255
5	F-342	848	50.64	12.84	6.55	0.68	0.021	0.25	1.13	3.94	0.19	2.01	0.07	8.22	20.75	0.07	158	258	1290	1247
6	F-342	849	55.56	11.81	5.72	0.62	0.018	0.94	0.94	3.32	0.68	1.87	0.07	8.32	16.77	0.07	204	360	1230	998
7	F-342	850	50.64	13.07	5.47	0.69	0.021	0.21	1.17	2.88	0.16	2.01	0.06	8.52	21.66	0.04	148	260	1570	1316
8	F-342	851	48.16	13.07	5.38	0.67	0.021	0.21	1.12	3.16	0.13	2.30	0.06	8.42	23.41	0.04	136	260	1400	1526
9	F-342	852	47.80	12.31	5.73	0.64	0.020	0.24	1.04	3.39	0.15	2.16	0.06	8.30	24.00	0.07	128	248	1400	1589
10	F-342	853	48.96	12.94	6.16	0.69	0.021	0.21	1.09	3.62	0.15	1.87	0.05	8.30	22.94	0.11	136	263	1230	1375
11	F-342	854	48.30	12.56	5.64	0.65	0.023	0.21	1.08	3.13	0.16	1.87	0.07	8.40	23.90	0.07	155	335	1180	1564
12	F-342	856	45.78	13.57	6.60	0.72	0.022	0.44	1.16	3.82	0.27	1.87	0.06	8.80	24.60	0.07	194	518	1510	1565
13	D-21	1	58.82	13.20	6.94	0.76	0.012	0.38	1.14	3.80	0.24	1.22	0.07	8.86	9.52	0.09	75	121		1183
14	D-21	2	49.60	12.94	6.25	0.72	0.012	0.33	1.14	3.71	0.17	2.08	0.07	8.42	20.46	0.07	63	81		1189
15	D-21	3	49.50	13.07	5.73	0.71	0.012	0.46	1.16	3.29	0.29	2.16	0.07	8.46	20.50	0.11	72	97		1306
16	D-21	4	47.70	12.31	6.08	0.68	0.011	0.25	1.10	3.78	0.17	2.44	0.07	8.16	23.48	0.08	103	145		1417
17	D-21	5	48.50	12.56	5.82	0.71	0.012	0.31	1.11	3.36	0.20	2.30	0.06	8.00	22.76	0.04	91	143		1339
18	D-21	6	48.68	12.69	5.29	0.71	0.013	0.25	1.07	3.00	0.13	2.16	0.06	8.16	22.48	0.04	123	160		1414
19	D-21	7	47.46	12.44	6.60	0.70	0.011	0.28	1.06	3.69	0.15	2.08	0.06	7.84	23.91	0.02	128	138		1345
20	D-21	8	48.04	12.31	6.42	0.67	0.011	0.38	1.10	4.07	0.15	2.08	0.08	7.28	22.73	0.18	125	117		1275
21	D-21	9	49.38	12.94	6.86	0.67	0.015	0.25	1.08	4.18	0.15	2.16	0.06	7.84	20.97	0.13	88	127		1256
22	D-21	10	49.12	12.82	6.08	0.68	0.013	0.23	1.13	3.64	0.15	2.01	0.06	8.14	21.22	0.09	79	124		1308
23	D-21	11	47.74	12.31	6.94	0.68	0.013	0.28	1.10	4.38	0.17	2.01	0.07	7.84	22.66	0.07	111	155		1431
24	D-21	12	47.38	12.31	6.25	0.66	0.015	0.45	1.16	3.65	0.25	2.16	0.07	7.84	23.60	0.04	144	179		1532
25	D-21	13	45.60	12.56	5.47	0.64	0.015	0.31	1.11	3.24	0.15	1.72	0.07	7.72	25.17	0.02	100	147		1444
26	D-21	14	48.36	12.82	6.08	0.70	0.017	0.31	1.14	3.68	0.19	1.94	0.07	7.86	22.33	0.02	68	171		1416
27	D-21	15	47.48	12.82	5.90	0.70	0.017	0.27	1.10	3.53	0.17	1.94	0.06	8.30	22.92	0.02	102	178		1472
28	D-21	16	48.22	12.69	5.90	0.70	0.016	0.31	1.07	3.54	0.16	1.72	0.06	7.76	21.67	0.02	142	253		1424
29	D-21	17	48.05	12.69	5.21	0.67	0.016	0.30	1.11	3.23	0.21	1.94	0.06	8.00	23.19	0.02	145	355		1563
30	D-21	18	45.70	12.31	5.29	0.68	0.017	0.35	1.10	3.32	0.21	2.01	0.07	7.86	26.39	0.02	136	296		1536
31	D-21	19	45.74	12.31	5.64	0.61	0.017	0.32	1.15	3.44	0.19	2.16	0.10	9.64	25.77	0.09	207	374		1637
32	D-66	1	52.36	13.07	5.55	0.66	0.019	0.33	1.14	3.04	0.18	1.15	0.08	8.58	18.38	0.17	31	75		1179
33	D-66	2	53.30	12.69	4.69	0.71	0.019	0.35	1.16	2.35	0.13	1.15	0.10	9.04	17.23	0.09	37	70		1148
34	D-66	3	53.02	12.43	5.55	0.68	0.020	0.39	1.12	3.01	0.16	1.29	0.10	8.42	17.95	0.13	33	67		1058
35	D-66	4	51.34	12.06	7.55	0.66	0.020	0.39	1.14	4.62	0.18	1.29	0.08	8.28	18.14	0.17	39	71		1116
36	D-66	5	52.68	12.94	6.34	0.72	0.020	0.33	1.16	3.30	0.16	1.72	0.10	8.56	17.39	0.09	36	60		1155
37	D-66	6	51.84	12.56	6.34	0.70	0.020	0.33	1.12	3.62	0.18	1.58	0.08	8.22	17.88	0.13	36	64		1199
38	D-66	7	51.68	12.06	6.42	0.80	0.016	0.62	1.11	3.86	0.23	2.51	0.16	8.28	18.41	0.20	60	79		1124
39	D-66	8	50.30	11.43	7.46	0.65	0.018	0.81	1.03	2.15	0.29	1.08	0.12	7.74	19.75	0.30	55	80		1128
40	D-66	9	52.00	12.06	5.39	0.74	0.016	0.49	1.13	3.27	0.25	1.72	0.14	8.30	17.96	0.24	85	100		1351
41	D-66	10	50.88	11.56	7.74	0.68	0.017	0.57	1.04	4.99	0.28	1.52	0.14	7.76	18.77	0.20	110	148		1389
42	D-66	11	49.10	12.19	5.55	0.67	0.017	0.57	1.16	3.26	0.19	1.52	0.14	8.06	22.14	0.28	129	773		1480

L.O.I.- total weight lost on ignition at 1000°C

Fe_2O_3 - total iron calculated as ferrous (III) oxide

The elevated lead content in the EDS is probably attributed to the ability of K-feldspar (authigenic orthoclase) to concentrate it; the average potassium concentration in the EDS is 6.2 %, exceeding the average black shale content (2 %; Vine, Tourtelot, 1970) about 3 times. Pb and Ni (Co) are concentrated in the pyritizised sand- and siltstone interlayers. The very thin (<2 mm) light coarse pelitic laminae in the argillite, containing pyrite up to 50 %, are in some cases highly enriched with Ni (up to

4000 ppm) and Co (up to 170 ppm) (Kallaste, Pukkonen, 1992). Concentration of V and Pb tends to increase towards the lower part of the Dictyonema Shale sequence, where organic matter and sulphur contents are usually higher.

DISCUSSION

The origin of the graptolite biofacies and its related black shale lithofacies has been under discussion in many earlier works (Bulman, 1970; Erdtmann, 1982b). There has been stated that as a result of the complete lack of bottom circulation and wave action the environmental conditions under which the "graptolite facies" accumulated were removed from oxygenated bottom waters. This view is supported by common occurence of fine-scale laminations, absence of bioturbation, and local abundance of pyrite in most black graptolite-bearing shales (Pettijohn, 1975, p. 282). Berry et al. (1987) discussed the potential effect on the evolution of graptolites with changes in thickness and depth of the denitrification zone lying between the underlying toxic sulphide-rich (anoxic) waters and overlying oxic waters. By analogy with indigenous faunas of the modern Eastern Tropical Pacific, graptolite facies organisms potentially could migrate downward into denitrified waters for food, then upward into more oxic waters to respire (Berry et al., 1989).

Although the Dictyonema Shale layer in NW Estonia is macroscopically quite uniform, the distribution of graptolites there is uneven. They occur mainly in the thin-laminated argillite and usually can be found on the surface of the very thin (2 mm) light coarse pelitic or aleuritic laminae. They are rare or absent in the more homogeneous (less laminated) Dictyonema Shale, for example, in the lower part of the western sections and in the upper part of the eastern sections (Fig. 3). But geochemical characteristics of these two sections differ considerably. The lower part is enriched with trace metals and organic matter and reflects, possibly, more reduced conditions during the time of its formation. It is noteworthy, that the argillite interlayers in the upper part of the underlying phosphatic sandstone contain more organic matter than the main body of the Dictyonema Shale. The increase in the organic matter content in these interlayers and, also, in the lower part of the Türisalu Formation, is accompanied by the increasing of Al_2O_3/SiO_2 ratio showing roughly the illite/quartz ratio. This relation is mainly related to the depletion of the quartz content, and, hence, to the occurrence of finer sediment (Utsal et al., 1982). Therefore, the argillite beds lying inside or close to the coarse grained quartzose sandstone are more fine-grained and contain less quartz, compared to the thick argillite intervals inside the Türisalu Formation. This contradiction leads to the conclusion that the lower part of the Dictyonema Shale formed quite quickly from very fine-grained material brought into the sedimentary basin from far distances and did not make up well-expressed lamination. This layer, as mentioned above, does not contain graptolites or their fragments, and is characterized with molybdenum concentration above 250 ppm and uranium content above 150 ppm. After the formation of this bottom layer, the sedimentary basin became more calm (with lower water energy) and distinct thin lamination was developed. Intercalation of pelitic organic-rich argillite and light-grey very thin aleuritic of coarse-pelitic lamellae could be caused by seasonal or other events changing water activity in superficial layers. In these stable conditions the water column became clearly stratified. The denitrified water layer reached the maximum thickness being an abundant food supply for graptolites, who, after death, sank to the anoxic waters and preserved delicately in the organic-rich sediment. At the came time the slow regression of the sea led to decrease in the thickness of the anoxic bottom water layer compared with the upper oxic layer, what, in turn, brought about the increased organic matter decay by oxygen.

The non-laminated upper part of the eastern sections is younger than that of the western sections (Fig. 2) and contains less organic matter. Taking into account also its more coarse-grained texture (Al_2O_3/Si_2 ratio is lower) (Fig. 8), it can been said, that this part of the Türisalu Formation formed in shallow conditions, where uneven water movement did not allow development of thin horizontal lamination. Due to the increased ventilation in the surface layers, both denitrified and anoxic layers existed deeper and were thinner. Using models of the early Paleozoic shelly and black shale lithofacies related to chemical oceanography (Berry et al., 1989), it can be said, that the accumulation of these sediments took place at a depth of about 130-180 m. The organic-rich sediment formed in these conditions contains less U, Mo, V and other elements than that deposited in a more reduced environment. The decrease in element concentrations toward younger sediments cannot explain as diminution of these elements in the vater basin, because argillites in the NE part of Estonia (in the so-called eastern zone) being also of younger Varangu (Ceratopyge) age, are ábundant in minor elements (Pukkonen, 1989).

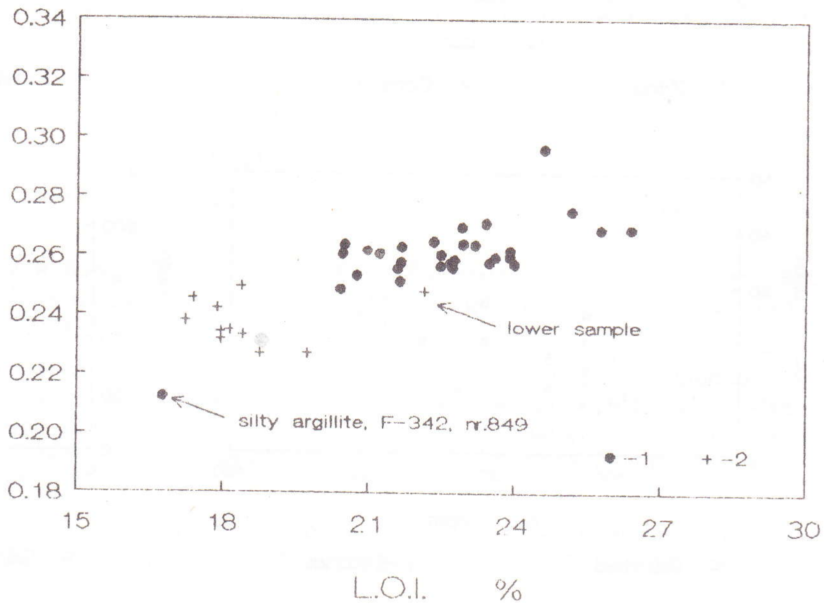


Fig. 8. Total loss on ignition (L.O.I., in weight %) versus Al_2O_3/SiO_2 ratio in the Dictyonema Shale of: 1 - western zone (cores F-342, D-21); 2 - central zone (core D-66).

The metals of the basaltic source (Cr, Ni, Cu, Co) have also a quite peculiar distribution pattern. The concentration of these elements decreases eastwards and comparison of the western sections with Swedish Dictyonema Shale in Bårstad (Östergötland) (Fig. 9) has shown a considerable decrease in the influence of a more basaltic that the influence of more basaltic (Swedish or Norwegian) source and the increase in the terrestrial input of (Finnish) granitic rocks during the formation of the Dictyonema Shale. The examination of the potassium distribution confirms the same conclusion - its concentration, on the contrary, increases in the eastern direction and towards the younger intervals. It is worth mentioning here, that this distribution pattern can be observed also between the Upper Cambrian Alum Shale and the Lower Ordovician Dictyonema Shale in Sweden (in Öland, in Östergötland).

CONCLUSION

The two biostratigraphically distinguishable levels of the Dictyonema Shale in the NW part of Estonia have slightly different geochemical characteristics. Graptolites occur mainly in fine-scale laminated argillite, but are rare of absent in the younger homogeneous sections. The diminishing number of graptolite specimens toward younger sediments can be explained with the regression of the Tremadoc sea in the Varangu (Ceratopyge) age, where water activity increased and thickness of the anoxic bottom layer and the overlying denitrified zone decreased compared to the upper oxic zone. This resulted in a poorer organic matter preservation and lower minor element concentration.

The distribution of the metals of the basaltic source (Cr, Ni, Cu, Co) has shown, that during the early Tremadoc the influence of the basaltic rock source diminished in the western Estonian, and also in the eastern

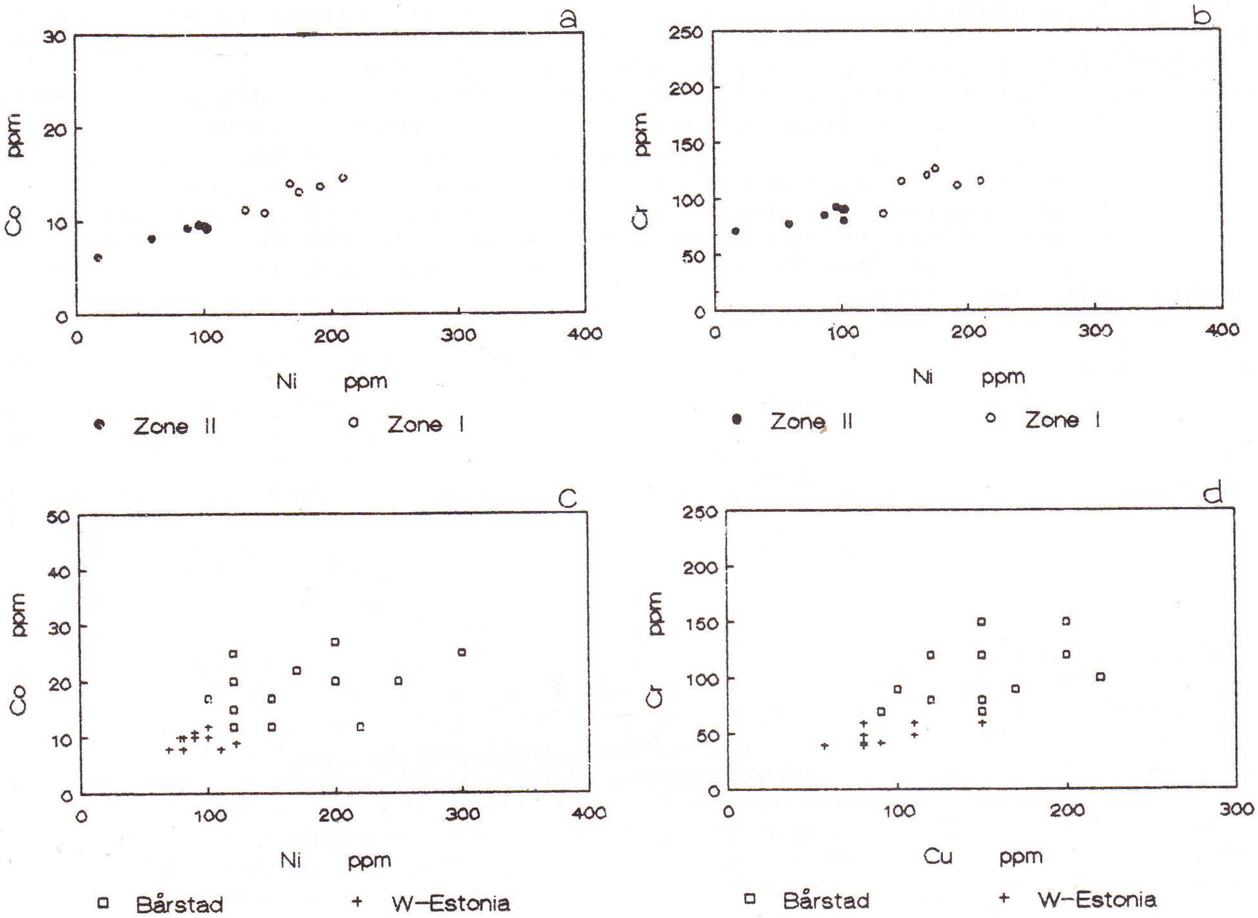


Fig. 9. Distribution of minor elements of basaltic source (Ni, Co, Cr, Cu): a, b - comparison of western and central zones of Estonian Dictyonema Shales (by neutron-activation analysis); c, d - comparison of Bårstad (Östergötland, Sweden) and W-Estonian Dictyonema Shales (by emission spectroscopical analysis).

Sweden sections. The input of the more terrigenous granitic rocks, however, increases in the black shale formation. In the future more detailed examination of this distribution pattern should be carried out, as it would add valuable information on early Paleozoic paleaogeography and enable to correlate geochemically different black shale sections in Baltoscandia.

ACKNOWLEDGEMENTS

We are very grateful to Prof. D. Kaljo and to colleague Ivar Puura for critical reviewing of this manuscript.

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