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THE DISTRIBUTION OF MICROELEMENTS IN TREMADOC GRAPTOLITIC ARGILLITE OF ESTONIA

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Tremadoc graptolitic argillite of Estonia (Dictyonema shale) forms the upper part of the rocks of the Cambrian-Ordovician "black shale" formation distributed in northwestern Europe. In Sweden they are known under the name of Alum shale (Andersen et al., 1985) and are everywhere characterized by increased contents of several microelements, first of all U, Mo and V, but also of S and organic carbon (Safronov, 1971). The content of microelements in Tremadoc graptolitic argillite of Estonia has been treated by several researchers (Loog, 1962; Loog, Petersell, 1981; Pukkonen, 1989; Pukkonen, Rammo, 1992). In these studies the main stress has been laid on the analysis of the mean content of microelements in the sections of outcrops and drill cores with an attempt to find out general regularities in their distribution.

Particularly significant is the study of the occurrence of elements in concrete vertical sections as this permits to get an idea about their distribution in space and time, possible direct and indirect sources of their intrusion and relations with other elements, with rock and its components, etc., i.e. to draw conclusions about the geochemical evolution of the basin.

Basing on the more detailed analysis of the published data, as well as on the materials of archives and those additionally collected by the authors, in the present paper the distribution of the organic matter (OM), mineral CO_2 $(CO_2)m$, uranium (U), molybdenum (Mo), vanadium (V), lead (Pb) and zinc (Zn) is considered on the example of concrete core sections (Fig. 1).

For this purpose three north-southerly profiles (Figs. 2, 3, 4) have been compiled in different parts of the distribution area of graptolitic argillite, i.e. they are directed from the areas of greater thicknesses to the southern margin where argillite thins out. Fig. 5 presents the contents of the corresponding elements on the west-easterly profile.

In all sections the boundary between argillite and overlying beds is lithologic, without a break in sedimentation. The upper boundary of graptolitic argillite is, however, erosional. Sampling of all sections was performed by means of the trenching. Determination of the conventional OM and (CO_2) m were carried out at the former specialized oil shale laboratory of the Kohtla-Järve Geology Department, microelements were established at the laboratory of the Geological Survey of Estonia (U, Mo and Pb by the X-ray fluorescence and V, Zn by the emission spectroscopy methods. High Zn contents were checked on AAS).

As is seen in the figures, the OM, as the concentrator and carrier of generally known microelements, first of all U, Mo and V in the formations of black shales, is of quite even distribution within the strata of graptolitic argillite (Table 1), also in the vertical section, the carbon content of OM exceeding the clark of black shales (Vine, Tourtelot, 1970) 3–4 times.

Only in some core sections the content of OM is notably higher in the lower or middle part of the section boreholes (b.h.-s D-78, D-155, etc.). Also certain increase in the mean content of OM from east to west has been recorded (Fig. 5), whereas in north-south profiles its values are similar ewerywhere. Still, some increase in the mean OM content with the growth of the thickness of the graptolitic argillite strata has been recorded. Contrasting minimums of OM in graptolitic argillite are due to occurrence of silt interbeds in Toolse region and of carbonate-rich interlayers (?) in western Estonia (Figs. 2–4).

Against the background of such relatively even distribution of OM, we can observe extremely uneven distribution of microelements in the vertical section and its alteration, compared to their mean content in concrete sections. Considering the uneven distribution of microelements, contents of separate elements in the vertical section of the strata are changing according to very different regularities.

The U content is differing in separate parts of the distribution area of graptolitic argillite, but exceeds the clark of black shales in all core sections 5 to 14 and more times. The mean U content decreases from west to east up to Maardu, being again high in the east, in Toolse and particularly Sillamäe regions. In the west and middle parts of the area the mean U content of the strata increases also southwards.

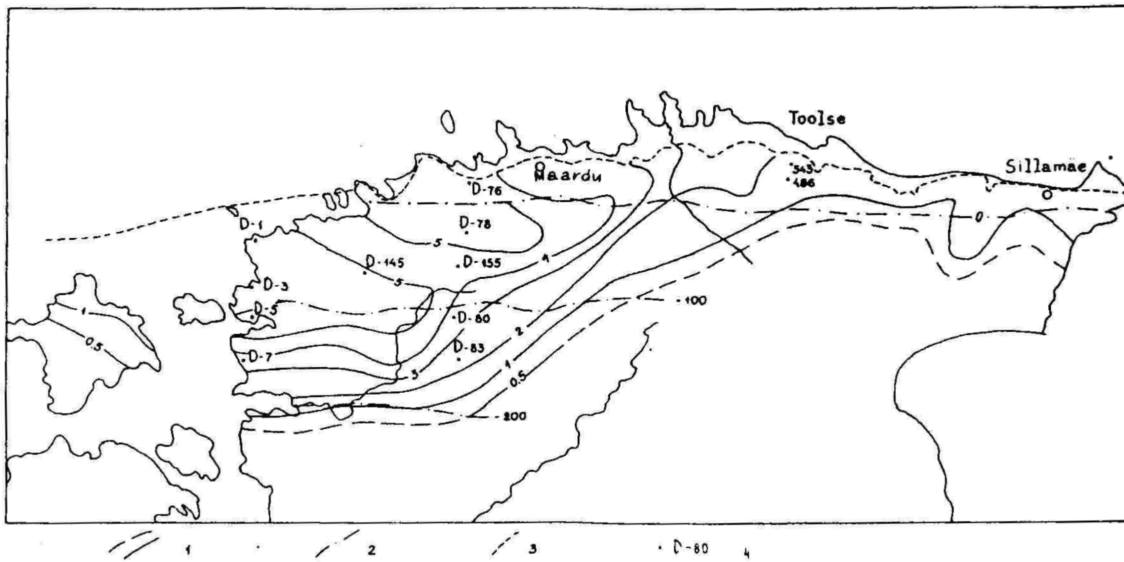
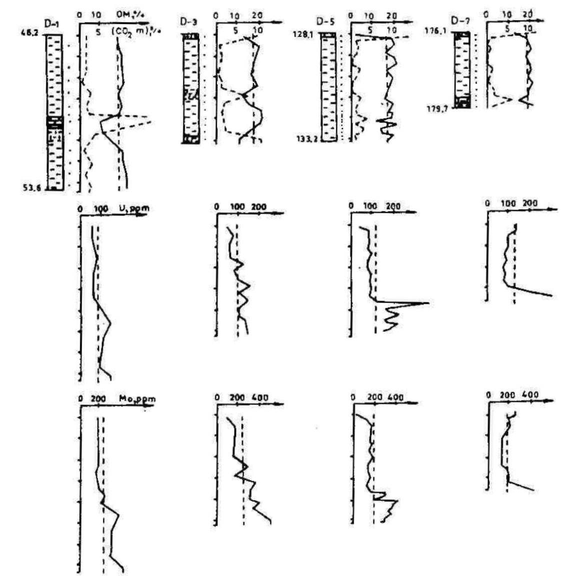


Fig. 1. Occurrence of graptolitic argillie strata in northern Estonia:
1 – isopachyte of the strata, m; 2 – isobath of the upper surface of the strata, m; 3 – erosional northern boundary of the strata; 4 - borehole



D-1
46,2
53,6
OM,%
(CO2 m),%
D-3
D-5
128,1
133,2
D-7
176,1
179,7
U,ppm
Mo,ppm

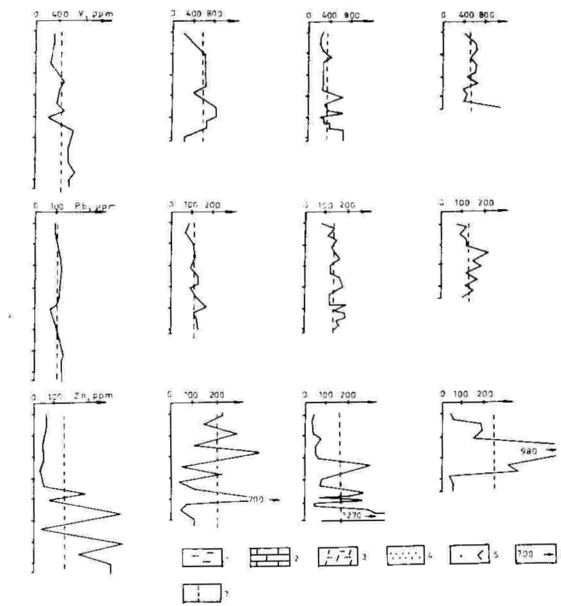
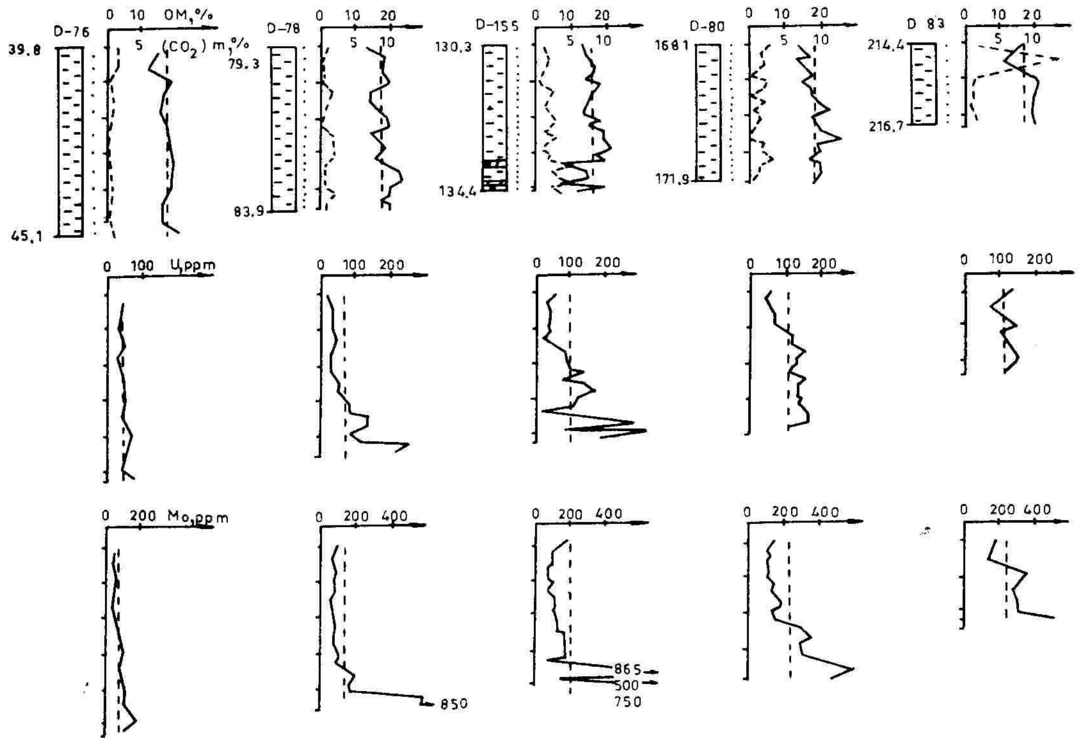


Fig. 2. Distribution of OM, (CO2)m, U, Mo, V, Pb and Zn in the north-south directed western profile of the graptolitic argillite strata:
1 – graptolitic argillite; 2 – carbonate-rock interbed; 3 – carbonate-rich interbed; 4 – silt interbed; 5 – centre of trenching; 6 – high concentration of the element, ppm; 7 – mean concentration.



D-76
39.8
45.1
0 10 OM,%
5 (CO2) m,%
D-78
79.3
83.9
D-155
130.3
134.4
D-80
168.1
171.9
D 83
214.4
216.7
0 100 U,ppm
0 100 200
0 200 Mo,ppm
0 200 400
850
865
500
750

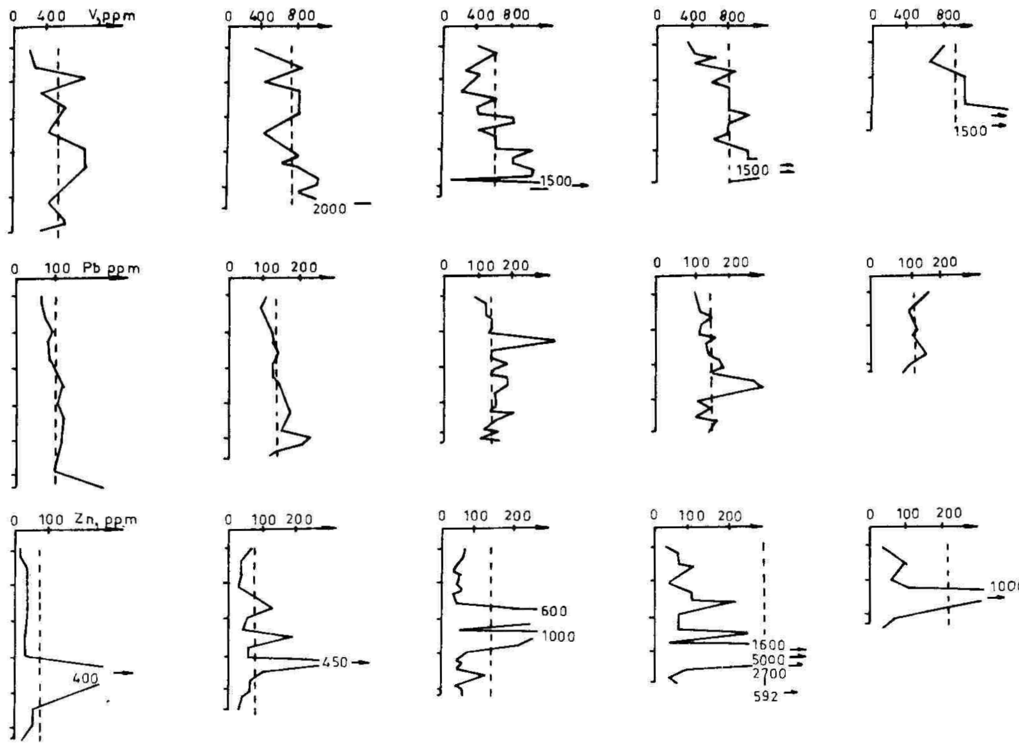


Fig. 3. Distribution of OM, (CO2)m, U, Mo, V, Pb and Zn in the north-south directed middle profile of the graptolitic argillite strata. Symbols as in Fig. 2.

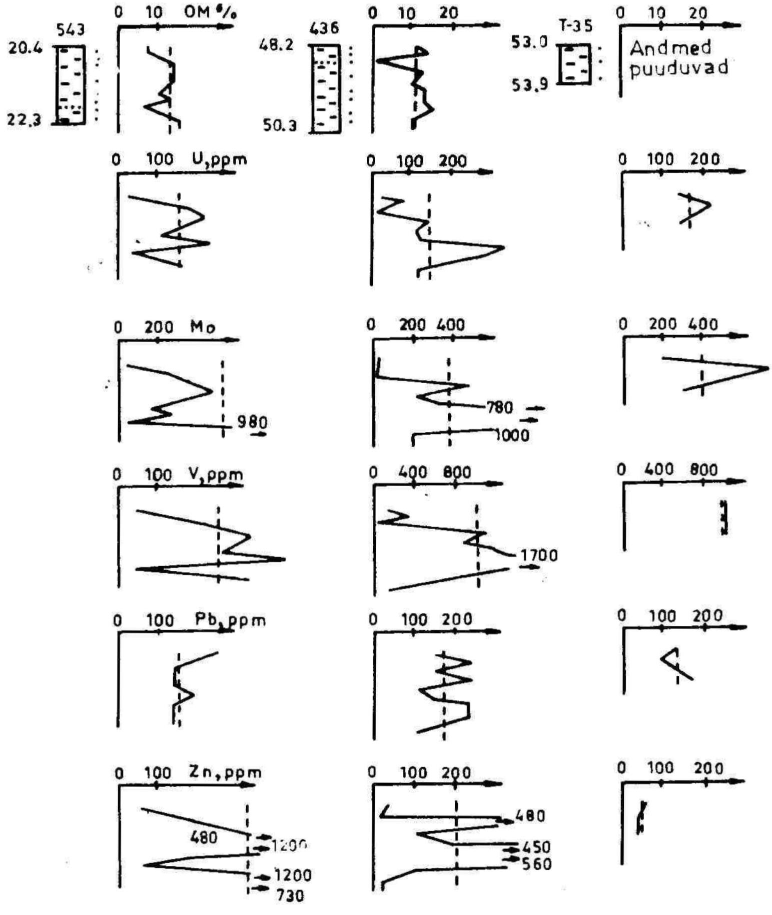


Fig. 4. Distribution of OM, U, Mo, V, Pb and Zn in the north-south directed eastern profile of the graptolitic argillite strata. Symbols as in Fig. 2.

Characteristically in most of the sections the U content increases in the lower part of the strata. In 0.3–0.6 m thick layers of several cores from the belt, lying close to the southern boundary of the distribution area, the U content is up to 200–300 ppm (Figs. 2–5), in the region of Sillamäe exceeding these values.

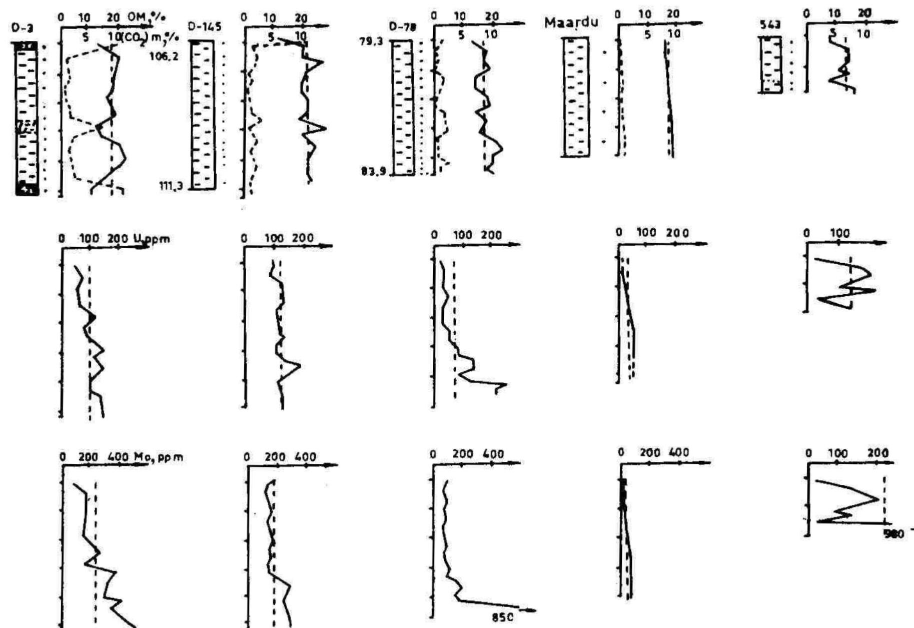
The content of Mo in graptolitic argillite is high and exceeds the clark of black shales 25 and more times. Its vertical and areal distribution is extremely uneven. In the vertical section the maximum contents have been registered in the basal part of the graptolitic argillite strata where in layers of some tens of a centimetre in thickness the Mo content may rise very high, up to 1000–1500 ppm. Higher Mo contents in the strata are observed in the eastern and western parts of the distribution area of graptolitic argillite. In the middle part of the area, in the region of Maardu the Mo content is low and distribution even.

The distribution pattern of V in the vertical core sections, also its mean content changes in the graptolitic argillite strata from north to south and from west to east are generally analogous to those of U and Mo, although somewhat more even in nature. Its concentration coefficient is also considerably lower than that of the above- discussed elements, exceeding the clark value of black shales only 2 to 6, very rarely more times. In concrete core sections the vertical distribution of V is rather uneven.

Profile II displays clearly the decrease in the V content from base to top, particulary in more southern core sections. At the same time in core sections of profile I such a change is either missing or hardly observable. Distinct increase in the V content is registered from west to east, from profile I towards profile II, followed by its lowering down to the minimum again in the region of Maardu (Fig. 5).

The contents are considerably higher in the eastern part of the distribution area of graptolitic argillite at Toolse and Sillamäe. Maximum V contents of up to 2000 ppm were recorded in the lowermost part of the strata.

The content of Pb in graptolitic argillite is everywhere high and unaltered, almost always exceeding the clark of black shales 5–8 times. Anomalously high concentrations are either lacking or occur very rarely. Neither has there been observed strict regularity in the distribution of Pb in vertical sections. Thus, in the western part of the distribution area the contents are somewhat higher in the lower beds of the section, in the east of the area


D-3
0 10 20 OM, %
5 10 $(CO_2)_m$, %
D-145
106,2
111,3
D-78
79,3
83,9
Maardu
543
0 100 200 U, ppm
0 200 400 Mo, ppm
850
980

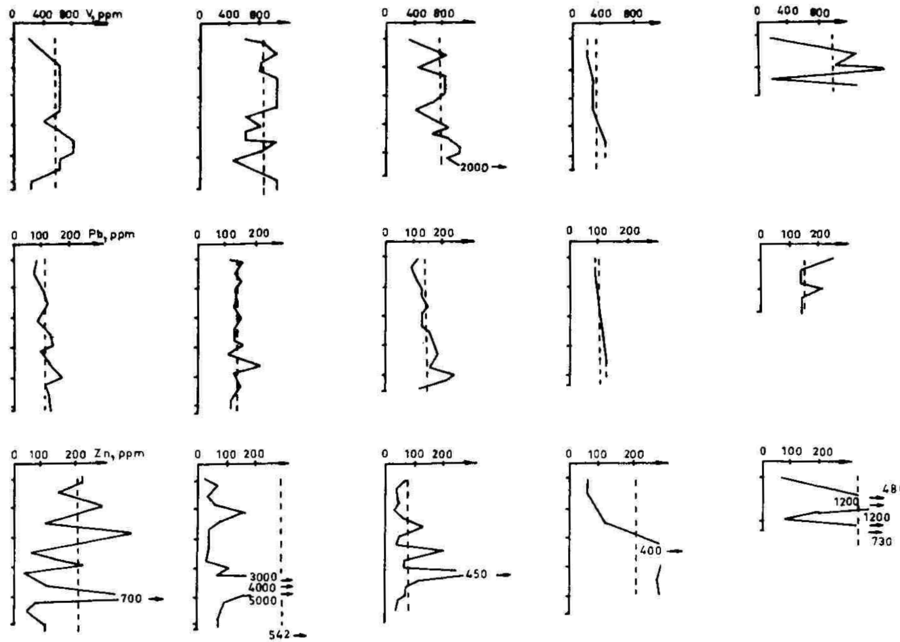


Fig. 5. Distribution of OM, (CO2)m, U, Mo, V, Pb and Zn in the west-eastern profile of the graptolitic argillite strata Symbols as in Fig. 2.

(Toolse), however, in its upper part. At the same time, on several levels some samples have yielded increased Pb contents, which is directly related to the occurrence of ore minerals. In the north-south direction there occur no changes in the mean lead content within the graptolitic argillite strata (Fig. 2), but in the eastern part of the area the Pb content is somewhat higher (Fig. 5) than in its middle and western parts.

Among the elements considered, Zn is the only one, the content of which in graptolitic argillite is often lower than the clark of not only black shales, but also below that of the earth crust, in places, however, being very high. Its mean content in the core sections of the western part of the distribution area increases from north to south. Differently from Mo and Pb, the maximum Zn contents occur in the western part of the distribution area of graptolitic argillite, in the region of the greatest thicknesses (Figs. 1 and 2), in the whole distribution area of graptolitic argillite almost all core sections show the presence of intervals with a high and very high Zn content. In the vertical section they may be observed mainly in the lower part of the strata, more rarely also in the middle part. In the limits of these intervals the Zn content rises to 0.5–1% and they related to the occurence of sphalerite in a few mm to 2–3 cm thick silty interlayers of graptolitic argillite.

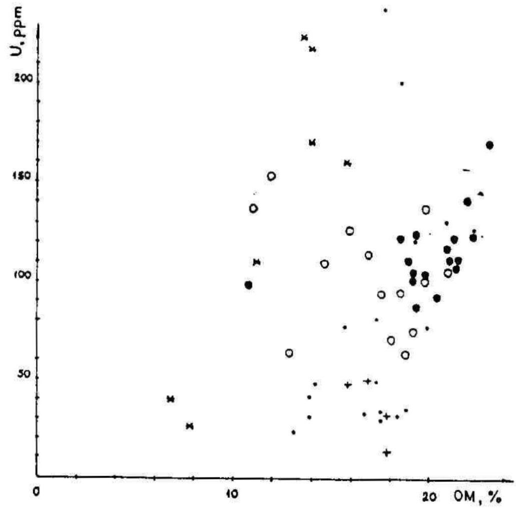
Sphalerite and pyrite constitute the main ore minerals in these interlayers, the amount of sphalerite reaching up to 8–10% of the whole rock mass.

In publications very often the distinct correlation between OM and the content of microelements in graptolitic argillite has bees pointed out (Loog, 1962; Petersell et al., 1981; Pukkonen, 1992). Data of paired correlation have also revealed positive relation between OM and U, Mo, V and Pb contents in the core sections of the western part of the area.

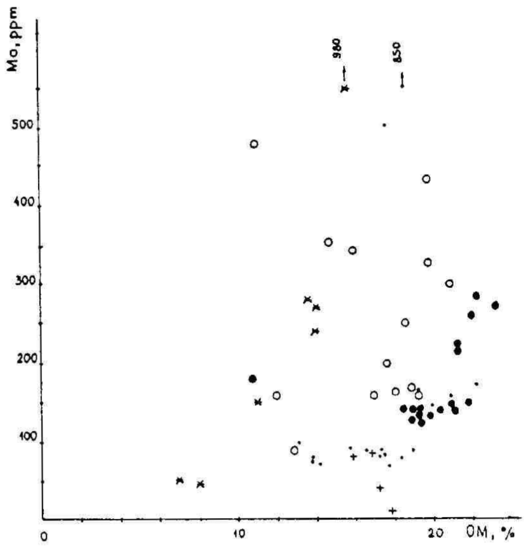
The possibility of such a relation between the elements and OM is, however, very different in the core sections studied (Table 1). There appears regularity — the more positive anomalies the element considered form in the graptolitic argillite strata, and the more contrastive they are, the smaller will be be the probability of positive correlation between the elements and OM. By the decreasing probability of positive paired correlation the microelements form an order Pb, V, U and Mo. There is no correlation between Zn and OM in the core sections considered, thus their relations are neutral.

Fig. 6. Relation between OM and U (a), Mo (b), V (c), Pb (d), Zn (e) in differnt sections of graptolitic argellite strata 1–4 – boreholes: 1 – D-3, 2 – D-145, 3 – D-78, 4 – 543; 5 – Maardu quarry; 6 – high concentration of the element, ppm.

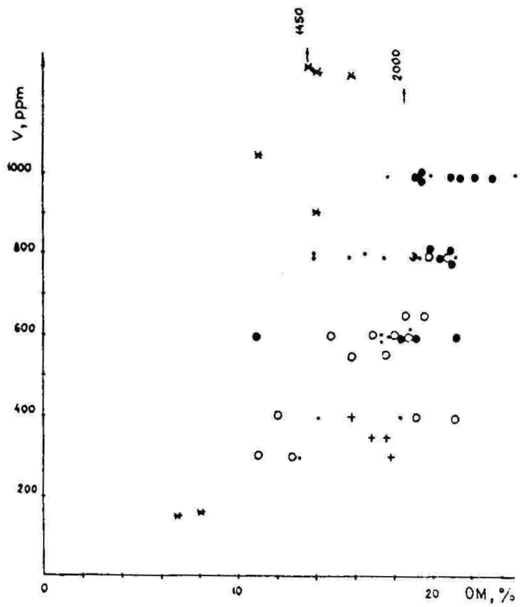
a



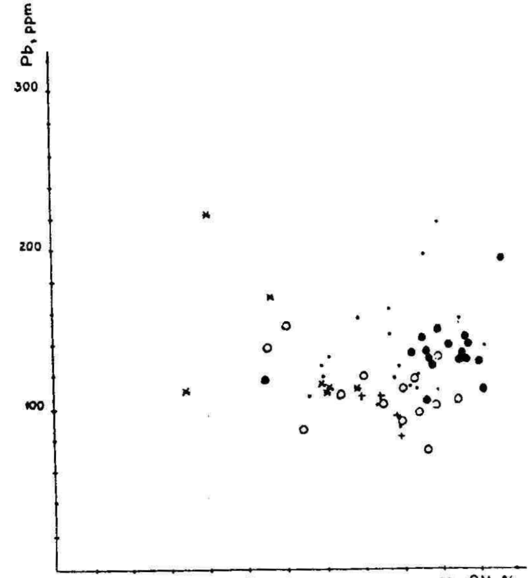
b



c


1450
2000
V, ppm
1000
800
600
400
200
0
10
20
OM, %

d


Pb, ppm
300
200
100
0
10
20
OM, %

e

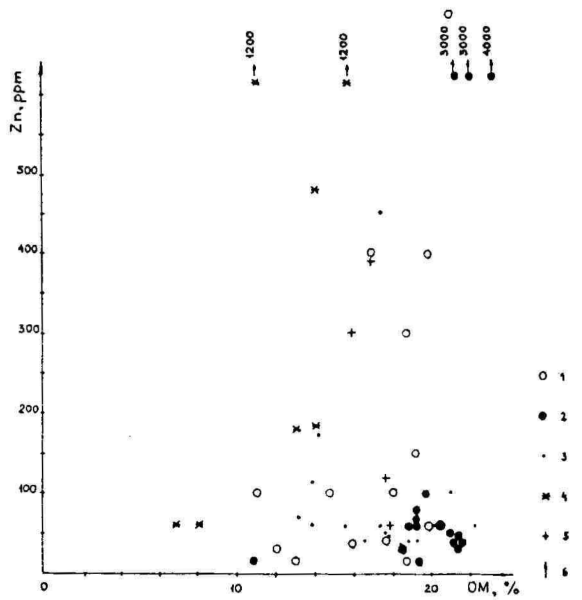


Table 1. Probability of positive correlation between OM and microelements

Borehole nr.	Number of samples	Probability of correlation					
		U	Mo	V	Pb	Zn	$(CO_2)m$
D-1	12	–	–	–	+++	–	—
D-3	14	+	–	++	+	–	–
D-5	22	–	+	+	++	–	—
D-7	13	–	+	+++	+++	–	–
D-76	12	+++	++	+++	+++	–	–
D-78	19	++	–	++	++	–	–
D-155	24	++	–	++	+	–	–
D-80	20	+++	++	+++	+++	–	–

correlation lacking (–), positive correlation with probabilities of 90–95% (+), 95–99% (++), more 99% (+++); negative correlation (—)

Table 2. Mo, V, Pb and Zn contents in monomineralic pyrite of graptolitic argillite and in graptolitic argillite (ppm)

Monomineralic pyrite							Graptolitic argillite				
Bore-hole nr.	Sampling depth, m	Pyrite-bearing rock	V	Mo	Pb	Zn	Sampling depth, m	V	Mo	Pb	Zn
4 (Ellamaa	139.6	S.i.b.	24	130	1600	4200	139.6–140.5	780	110	140	100
	140.2	S.i.b	60	92	320	30					
	141.6	P.c.	300	66	680	24	141.3–142.2	830	220	230	150
	142.0	S.i.b.	100	66	610	2100					
	142.6	S.i.b.	69	210	460	10000	142.2–143.2	1010	200	220	1850
	143.1	P.c.	100	99	460	30					
	143.9	P.c.	24	66	76	35	143.8–144.5	1500	87	120	630
F-237	61.0	P.c.	12	450	27	40	61.0–61.5	420	110	90	80
	62.2	S.i.b.	27	530	30	240	61.5–62.5	410	285	105	90
	62.3	P.c.	35	320	37	60					
	62.6	P.l.	80	110	610	30	62.5–63.0	350	60	120	490
	63.6	S.i.b.	80	230	460	10000	63.5–64.0	490	60	110	320
	66.6	S.i.b.	10	280	30	24	66.3–67.0	690	490	170	30

S.i.b.– up to 3-cm-thick silt interbed
P.c.– pyrite concretion
P.l.– pyrite lens

More detailed observation of the relations between OM and microelements on the reverse diagrams (Fig. 6) shows, that the contents of elements in core sections fall into different parts of the diagrams, stressing in this way the different relations between OM and microelements in separate areas. These data, together with the ones presented in Figs. 2–5, allow to state that positive anomalous contents of different microelements occur frequently on different levels in graptolitic argillite, they are not correlating.

In several publications pyrite is mentioned as the main concentrator and bearer of microelements (Mo, Pb, Zn) in graptolitic argillite (Maldre, 1976, Kallaste, Pukkonen 1992). The significance of pyrite in this respect is considered basing on the data of spectral analysis of monomineralic pyrite collected from core sections 4 (Ellamaa) and F-257 (Table 2). The pyrite analysed has been separated from point samples under binocular microscope, but the analysis of graptolitic argillite has been performed on samples, taken using the trenching, due to which the results cannot be compared unambiguously. Still, they permit to get a general idea about the problem.

Characteristically the content of the elements studied is very heterogeneous in pyrite. Quite clearly there can be observed a low V content in pyrite. It is everywhere lower than that of the host rock, exceeding the clark of the lithosphere only in one case. Therefore pyrite is not the carrier and concentrator of V in graptolitic argillite. The content of Mo, Pb and Zn in pyrite is variable. In some samples their content is higher than in the surrounding graptolitic argillite, in several cases however, being lower. It should be noted that often pyrite is enriched with Mo, as well as with Pb, particularly with Zn, their amounts being larger in pyrite than in the host rock. There occur also samples in which pyrite is enriched with only one or two of the elements considered, or where the content of all three elements – Mo, Pb and Zn is lower than in graptolitic argillite. Therefore pyrite serves often as the concentrator and carrier of Mo, Pb and Zn. Such a characteristic distribution of microelements in pyrite can be explained by the variable content of elements in the sedimentary basin, on one hand, and by different possibilities of the appearance of mineral forms in natural conditions, on the other hand.

Main mineral forms of Mo, Pb nad Zn are sulphides. In pyrite they either replace Fe or occur as an independent sulphide phase depending on the degree of concentration in the sedimentary basin. V occurs predominantly in non-sulphide minerals, the formation or concentration of which in pyrite had no geochemical preconditions in the sedimentary basin.

Reasons of relatively high contents of OM, U, Mo, V, Pb, Zn and other elements in graptolitic argillite are not understood unambiguously. The associations, occurrence and distribution patterns of these elements, the isotopic composition of S, C and Pb (Petersell et al., 1987), chemical and mineralogical composition of graptolitic argillite permit to suggest the concentration of these elements to be related to deep geology.

At that, Caledonian folding and the accompanying magmatic activity caused activation of tectonic deep latitudinal dislocations in the Tremadoc, which resulted in the inflow of subaqueous hydrothermas into the Baltic paleobasin. There appeared in the geological sense short-term specific paleoecological conditions which caused stormy development of organisms and preservation of organic matter. The enviromental settings formed were favourable for mass occurrence of only some species. In the result of all this metal-rich organic material was accumulated in clay muds. By the burial into sediments and during the following diagenesis they turned into argillite containing OM (mostly 13–19%). Burial of abundant OM in clay facies was possible due to mass occurrence of bacterial mats and algae in the basin water. Therefore sea-water served as one of immediate sources of elements concentrated in the clay facies. This is also evidenced by a stable mineralogical composition of sediments, even distribution of numerous non-hydrothermal elements and their content nearing the clark of the lithosphere. Local anomalously high contents of U, Mo, Zn, Pb, and other elements in graptolitic argillite as well as in pyrite could be explained only by their local concentration changes in sea water. Occurrence of contrasting geochemical anomalies and polymetallic ore formation, often the predominance of mantle sulphur, show directly that the material, carried into the basin water, come not only from the denudation areas and from the ocean with possible deep currents, but included also considerable amounts of endogenic matter.

Proceeding from the above standpoints, in the last years more and more attention has been paid to polymetallic ore formation in graptolitic argillites, also to contrasting anomalies of Au, Pt and other elements. Yet, additional detailed mineralogical, geochemical, etc. investigations are needed in order to prove the existence of the endogenic source of several elements.

References

Andersson, A., Dahlman, B., Gee, D. G., Sna"ll, S., 1985. The Scandinavian alum Shales. Sver. Geol. Unders., The Scandinavian alum Shales. Sver. Geol. Unders., Ca56, 50 p.

Kallaste T., Pukkonen E. 1992. Pyrite varieties in Estonian Tremadocian argillite (Dictyonema Shale). Proc. Estonian Acad. Sci. Geol, 41. No 1. p. 11–22.

Loog, 1962 – **Лоог А.,** 1962. К геохимии нижнего ордовика Эстонии. Тр. Ин-та геол. АН ЭССР, Т. X. с. 273–291.

Loog, Petersell, 1978 – Лоог А., Петерселль В., 1978. Геохимические особенности граптолитовых аргиллитов (диктионемовых сланцев) Эстонии. В кн.: Тез. докл. совещ. „Геохимия горючих сланцев". Таллин, с. 109–110.

Maldre, 1976 – **Малдре Я. Я.**, 1976. Молибден в диктионемовых сланцах Северной Эстонии. Литология и Полезные Ископаемые, 5, с. 94–98.
Petersell et al., **Петерсельль В., Минеев Д., Лоог А.**, 1981. О минералогии и геохимии оболовых песчаников и диктоинемовых сланцев Северной Эстонии. Уч. зап. Тарт. ун-та. Вып. 759: Труды по гелологии, м. Х. с. 27–55.
Petersell et al., 1987 – **Петерсельль В., Жуков Ф., Лоог А., Фомин Ю.**, 1987 – Происхождение термадоксеих керогенсодержащих алевро, литов Северной Эстонии. Горючие сланцы 4/1, с. 3–13.
Pukkonen, 1989 – **Пукконен Э.**, 1989. Макроэлементы и малые элементы в граптолитовом агриллите Эстонии. Горючие сланцы 6/1, с. 11–18.
Pukkonen, E., Rammo, H., 1992. Distribution of Molybdenum and Uranium in the Tremadoc Graptolitic Argillite (Dictyonema Shale) of North-Western Estonia. Bull. of the Geol. Sur. of Estonia, 2/1. p. 3–15.
Safronov, 1971 – **Сафронов Н. И.**, 1971. Основы геохимических методов поисков рудных месторождений. Изд. „Недра", 164 с.
Vine J. D., Tourtelot E. B., 1970. Geochemistry of black shales — A Summary Report. Econ. Geol., 65, p. 253–272.

MIKROELEMENTIDE JAOTUSSEADUSPÄRASUSTEST EESTI TREMADOCI GRAPTOLIITARGILLIIDIS

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Resümee

Vaadeldakse orgaanilise ainese, mineraalse CO_2, uraani, molübdeeni, vanaadiumi, plii ja tsingi jaotust graptoliitargilliidis puuraukude näidete varal (jn.1).

Graptoliitargilliidi levila piirkondades on koostatud 3 põhja-lõunasuunalist läbilõiget (jn. 2. 3. 4), s.o. suurema paksusega aladelt levila lõunapiirile, kus argilliit suidub. Joonisel 5 on esitatud elementide sisaldused lääne-idasuunalisel läbilõikel.

Proovimisel on kasutatud vaomeetodit. Orgaaniline aines (OM) ja mineraalne CO_2 on määrangud endises Kohtla-Järve Geoloogiatöökonna põlevkivi spetsialiseeritud laboratooriumis, mikroelemen-

did Eesti Geoloogiakeskuse laboratooriumis; U, Mo ja Pb RF-meetodil, V ja Zn spektraalanalüüsi meetodil.

Orgaanilise ainese suhteliselt ühtlase jaotuse taustal (jn. 2–5) on jälgitav, et mikroelementide jaotumine vertikaalses läbilõikes, võrrelduna läbilõigete keskmiste sisaldustega, on äärmiselt ebaühtlane ja elemendití erinev. Paariskorrelatsiooni andmetel on positiivne seos orgaanilise ainese ja U, Mo, V ning Pb sisalduste vahel jälgitav levila läänepiirkonna puuraukude läbilõigetes. Selgub seaduspärasus mida rohkem positiivseid anomaaliaid moodustab element ja mida kontrastsemad nad on, seda väiksemaks muutub elemendi positiivse korrelatsiooni tõenäosus orgaanilise ainesega (tabel 1 ja 2).

Graptoliitargilliidis on Mo, Pb ja Zn kontsentraatoriks ja ka kandjaks ka püriit (tabel 2).

Graptoliitargilliitides OM, U, Mo, V, Pb, Zn jt. elementide suhteliselt kõrge sisalduse lähteallikate kohta pole üheseid arusaamu. Vaadeldavate elementide assotsiatsioonid, leviku- ja jaotusseaduspära, väävli, süsiniku ja plii isotoopne koostis ning graptoliitargilliidi mineraalne koostis viivad järeldusele nende elementide kontsentratsioonide tekke seosest süvageoloogiaga.