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THE DICTYONEMA SHALE OF ESTONIA

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ABSTRACT

In the northeastern Baltic, Tremadocian Dictyonema Shale is found in northern Estonia and in the St.Petersburg (former Leningrad) Region in Russia. The formation can be seen in the Baltic-Ladoga Cliff forming the southern edge of the Finnish Bay. The Estonian Dictyonema Shale is characterized by low carbonate (Ca, Mg, Mn), Na and high potassium feldspar (K) content. Its trace element composition resembles also to the Scandinavian Alum (Dictyonema) Shale having high concentrations of U, V and Mo. Up to now, only a few investigations related to the geochemistry and lithology of the Estonian Dictyonema Shale have been presented in English. This work was done to give a short review of studies in Russian and Estonian literature. New data about trace element and organic geochemistry were added into this paper. Titles of the references were given in English, the language of the articles and summaries has been mentioned also.

THE DISTRIBUTION OF THE TREMADOCIAN DICTYONEMA SHALE[1] OF ESTONIA AND THE BIOSTRATIGRAPHICAL CORRELATION TO OTHER SECTIONS IN THE EAST EUROPEAN PLATFORM

The Tremadocian organic-rich mudstone of the Türisalu Formation, traditionally named Dictyonema Shale, is distributed in northern Estonia from Hiiumaa Island in the west to the town of Narva in the east (Fig. 1). In the St.Petersburg (Leningrad) Region it belongs to the Koporye Formation and extends as far as the Syas river at the southeastern part of Lake Ladoga.

The Türisalu Formation crops out in the Baltic-Ladoga Cliff at the southern shore of the Gulf of Finland. The cliff forms the northern boundary of the formation, which from here dips slowly southward. The northwestern corner of the Estonian mainland is characterized by the largest thickness of the Türisalu Formation (7 m). Here, it is found at a depth of 30 meters. Further south, the formation thins out and finally disappears. Near the southern boundary of the subcrop, the Türisalu Formation is covered by Ordovician and Silurian limestone with a thickness up to 300 meters.

More than 40 good outcrops of the Tremadocian and Upper Cambrian rocks are found in the Baltic-Ladoga Cliff and in the river valleys crossing it (see Fig. 2, after KALJO et al. 1985). The outcrops have been thoroughly studied by sedimentologists and palaeontologists from Estonia (KALJO et al. 1988, HEINSALU et al. 1987, MENS et al. 1989, VIIRA et al. 1987, HEINSALU et al. 1991a, HEINSALU et al. 1991b) and St.Petersburg (POPOV et al. 1989, BOROVKO et al. 1983 a.o.). In these studies, main attention was given to bio- and lithostratigraphic investigation of the phosphoritic sandstone layer of the Kallavere Formation that here includes the Cambrian-Ordovician boundary.

Correlation of the Lower Palaeozoic rocks on the East European Platform is summarized in Figure 3 and Figure 4. Cambrian sections were compiled after MENS et al. (1987 and 1989), while the Tremadocian sections were based on the following authors: North Estonia and St.Petersburg Region (see above), Moscow Syneclise after Heinsalu (1986) and DMITROVSKAYA (1988 and 1989), South Estonia, Latvia, Lithuania after MÄNNIL (1966), LASHKOV (1968), ULST et al. (1983) and HEINSALU (1986), Poland and Byelorussia after SZYMANSKI (1974 and 1984), HEINSALU (1986), and BEDNARCZYK (1989). The location of the sections is given in Figure 4.

As shown in Figure 3, the Türisalu Formation and its lateral equivalent (Dictyonema Shale) is found in Scandinavia, northern Poland, northern Estonia and in the St.Petersburg Region near the Baltic-Ladoga Cliff. In South Estonia, Latvia and Lithuania, the Tremadocian is represented by

[1] The Tremadocian organic-rich mudstone of the Baltoscandian region is traditionally named as Dictyonema Shale by the graptolite specimen *Dictyonema flabelliforme*. In fact, the graptolite species of the group *Dictyonema flabelliforme* belong to the group of *Rhabdinopora flabelliforme* (Erdtmann 1982).

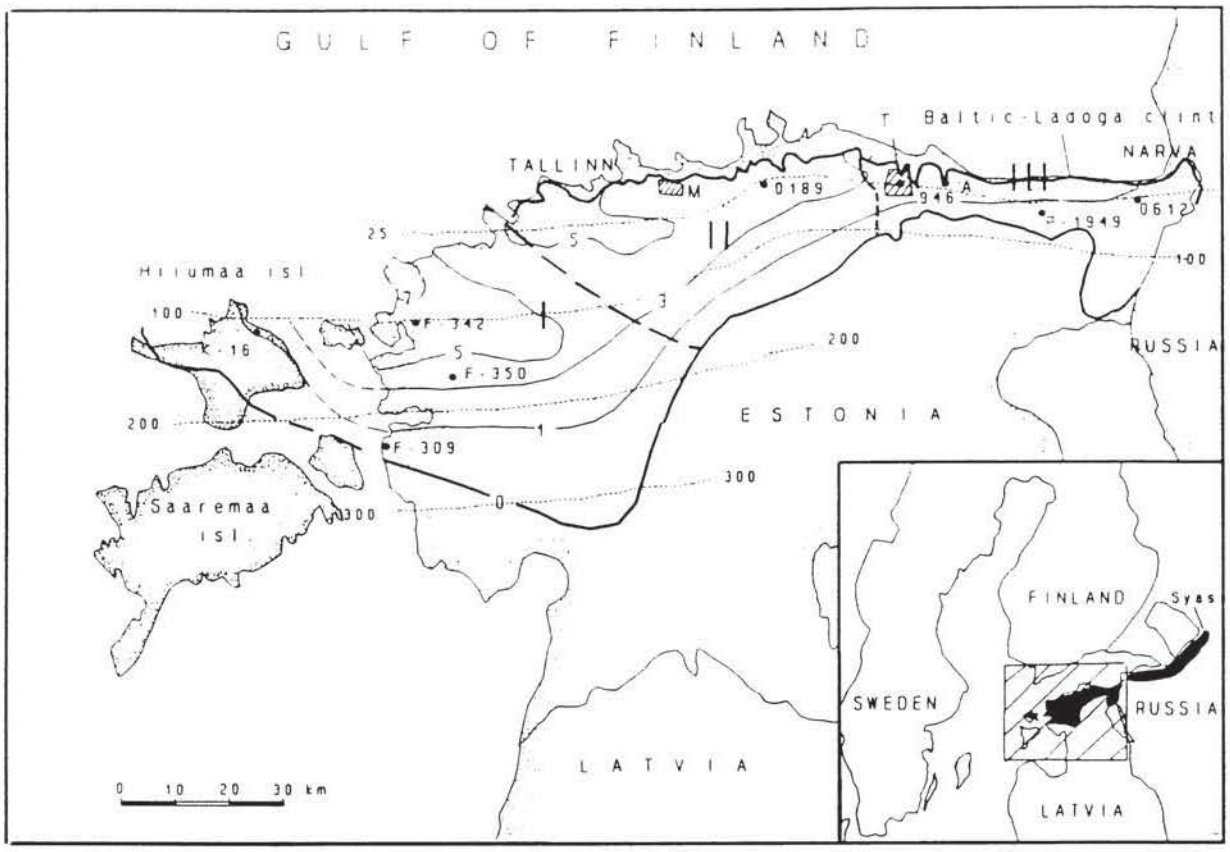

Figure 1. Distribution of the Estonian Dictyonema Shale (subcrop map). Outcrops of the Tremadocian rocks are found also in the Baltic-Ladoga clint. Legend: bold dashed lines - boundaries between the different geochemical provinces: I - western, II - central, III - eastern; phosphorite deposits: M - Maardu, T - Toolse, A - Aseri; continuous lines with numbers - isopachytes (in m) dotted lines - isopachs of the Tremadocian rocks (in m); bold dot with number - location and number of drill core.

sandstone with a thickness varying from 0.1 to 20 meters (mainly less than 1 m), sometimes containing thin mudstone interlayers. Eastward the Tremadocian sequence becomes more clayey and in the central part of the Moscow Syneclise it is characterized by claystone with a thickness up to 25 meters underlied by sandstone. The total thickness of the Tremadocian strata in Moscow Syneclise reaches 40 m (DMITROVSKAYA 1989).

PUKKONEN (1989) divided the Türisalu Formation) into three geochemical provinces: western (I), central (II) and eastern (III) province. This division has been maintained in the present work (Figure 1). Based on graptolite biostratigraphy, the formation has been divided into a Lower Tremadocian (Pakerort) and an Upper Tremadocian (Varangu or Ceratopyge) part (KALJO & KIVIMÄGI 1976, KALJO & KIVIMÄGI 1970). The sections of the Lower Tremadocian, which are characterized by the graptolite species group of *Rhabdinopora flabelliforme* (*R.f.desmograptoides, R.f.rossica, R.f.socialis, R.f.norvegica, R.f.flabelliforme, R.f.anglica, R.f.multithecata*) and

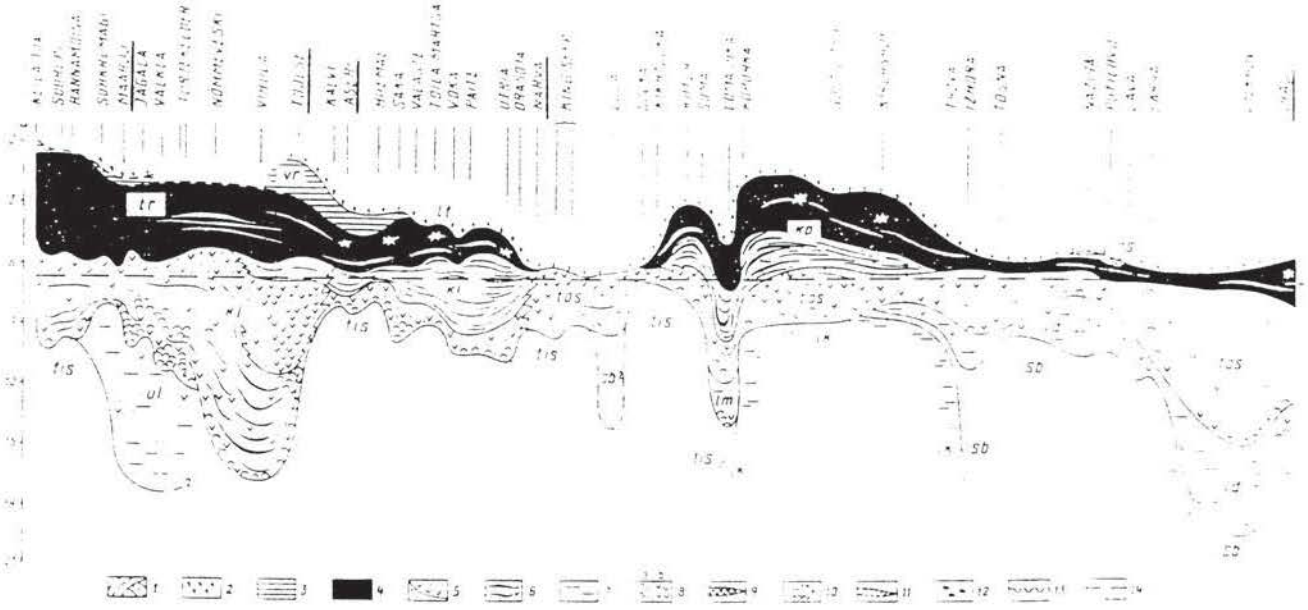

Figure 2. Sequence of the Cambrian-Ordovician Boundary deposits in the outcrops of the Baltic-Ladoga clint area (after KALJO et al. 1986).

Legend: **1** - Quaternary deposits; **2** - glauconitic sandstone; **3** - silty clay; **4** - mudstone (Dictyonema Shale); **5** - cross-bedded detritic sandstone; **6** - sandstone or siltstone with mudstone interbeds; **7** - clay interbeds; **8** - complete valves (a) and detritus (b) of brachiopods; **9** - pyrite concretions and lensis; **10** - anthraconite concretions; **11** - lenses of (amorphous) chert; **12** - phosphatic pebble; **13** - discontinuity surfaces; **14** - base of the *Cordylodus angulatus-C.rotundatus* Zone. Index of the units: **tis** - Tiskre Form.; **lk** - Lükati Form.; **sb** - Sablino Form.; **ül** - Ülgase Form.; **ld** - Ladoga Form.; **kl** - Kallavere Form.; **tos** - Tosna Form.; **lm** - Lomashka Form.; **tr** - Türisalu Form.; **kp** - Koporye Form.; **vr** - Varangu Form.; **ns** - Naziya Form.; **lt** - Leetse Form.

by the conodont zone *Cordylodus rotundatus* - *C.angulatus*, are found in the western geochemical province (HEINSALU 1990) and in the lower part of Türisalu Formation in the central province (KALJO & VIIRA, 1989). The Türisalu Formation in the eastern geochemical province is of Late Tremadocian age and contains very rare graptolite specimens of *Didymograptus, Clonograptus, Anisograptus* and (or) *Bryograptus* and conodont specimens of the *Drepanoistodus deltifer pristinus* subspecies (KALJO & VIIRA 1989).

LITHOLOGY AND MINERALOGY

Lithology and lithostratigraphy. The lithostratigraphic subdivision of the Estonian Tremadocian deposits has been discussed by MÜÜRISEPP (1960), VIIRA et al. (1970), LOOG & KIVIMÄGI (1968), STUMBUR (1962), and HEINSALU (1987). The Türisalu Formation of the western province of North Estonia is represented by horizontally laminated, dark-brown, organic-rich

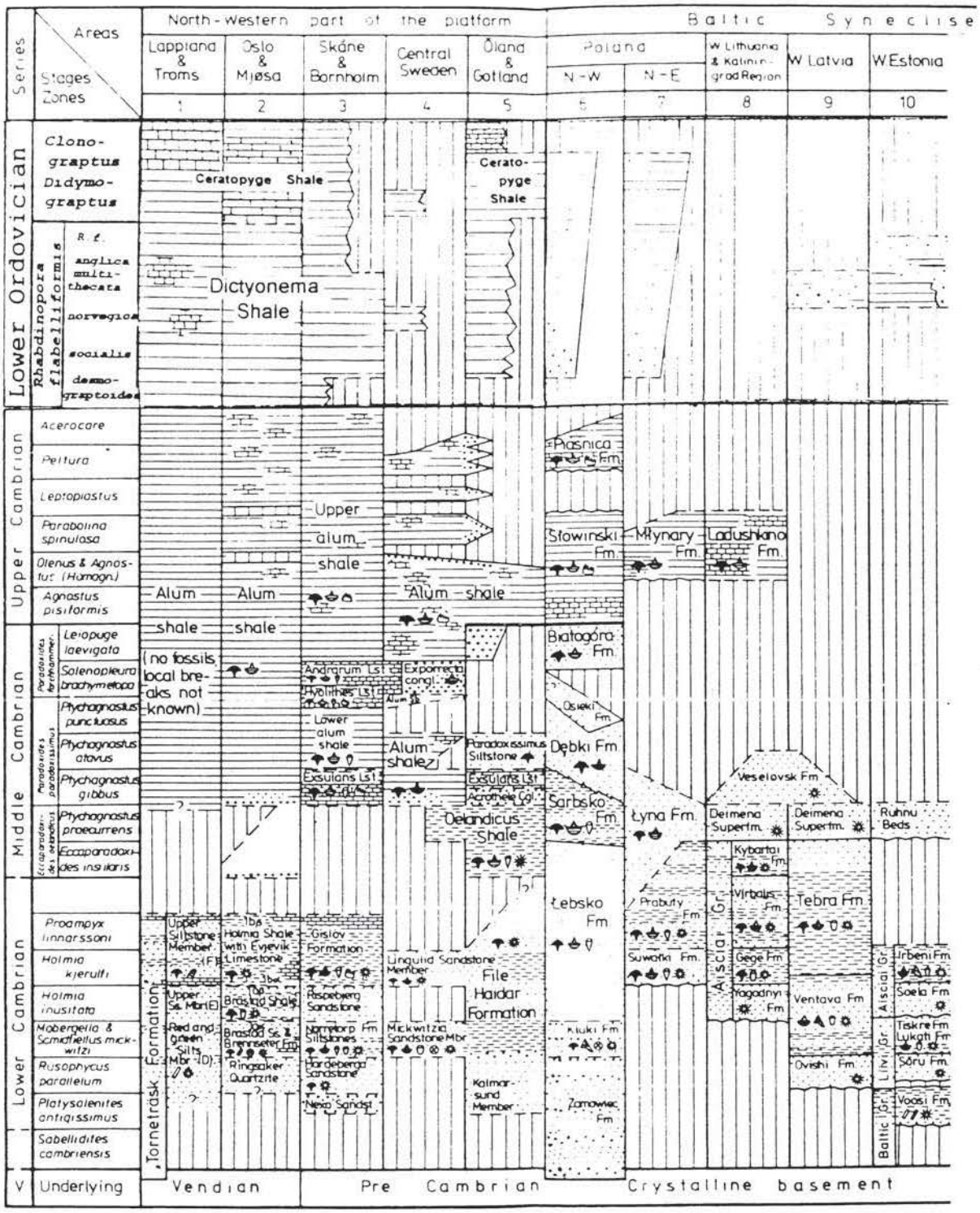

Figure 3. Correlation chart of the Lower Palaeozoic rocks in the East-European Platform (the Cambrian part after MENS et al. 1987)

- stromatolites
- acritarchs
- algae
- gastropods
- trilobites
- brachiopods
- hyoliths
- phosphatic scalerites
- conodonts
- Volborthrella
- sabelliditids
- platysolenitids
- Mobergella
- Conglomerate/arkose
- Sandstone/siltstone
- Claystone/mudstone
- Limestone/dolomite
- Black shale/siltstone/ kerogen-bearing mudstone

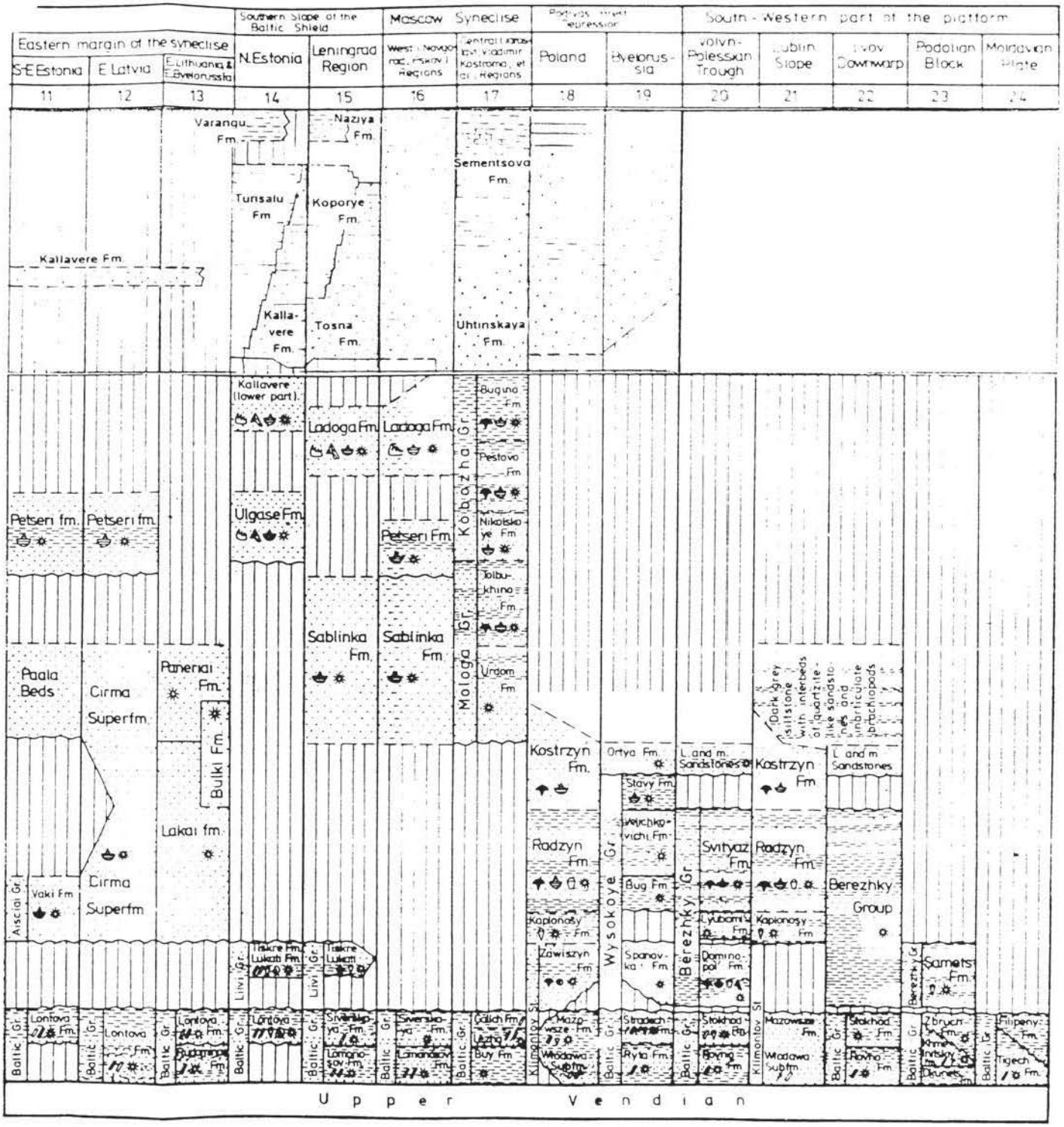

Figure 3. Continued

(kerogenous) mudstone containing pale-brown, 0.2-2 mm thick silty laminae of variable frequency (HEINSALU 1990). These laminae are often pyritized, containing up to 50% pyrite, and show enrichment in Ni and Co (up to 4000 ppm and 170 ppm respectively, KALLASTE & PUKKONEN 1992). Anthraconite concretions (locally named "roses" after their radial structure)

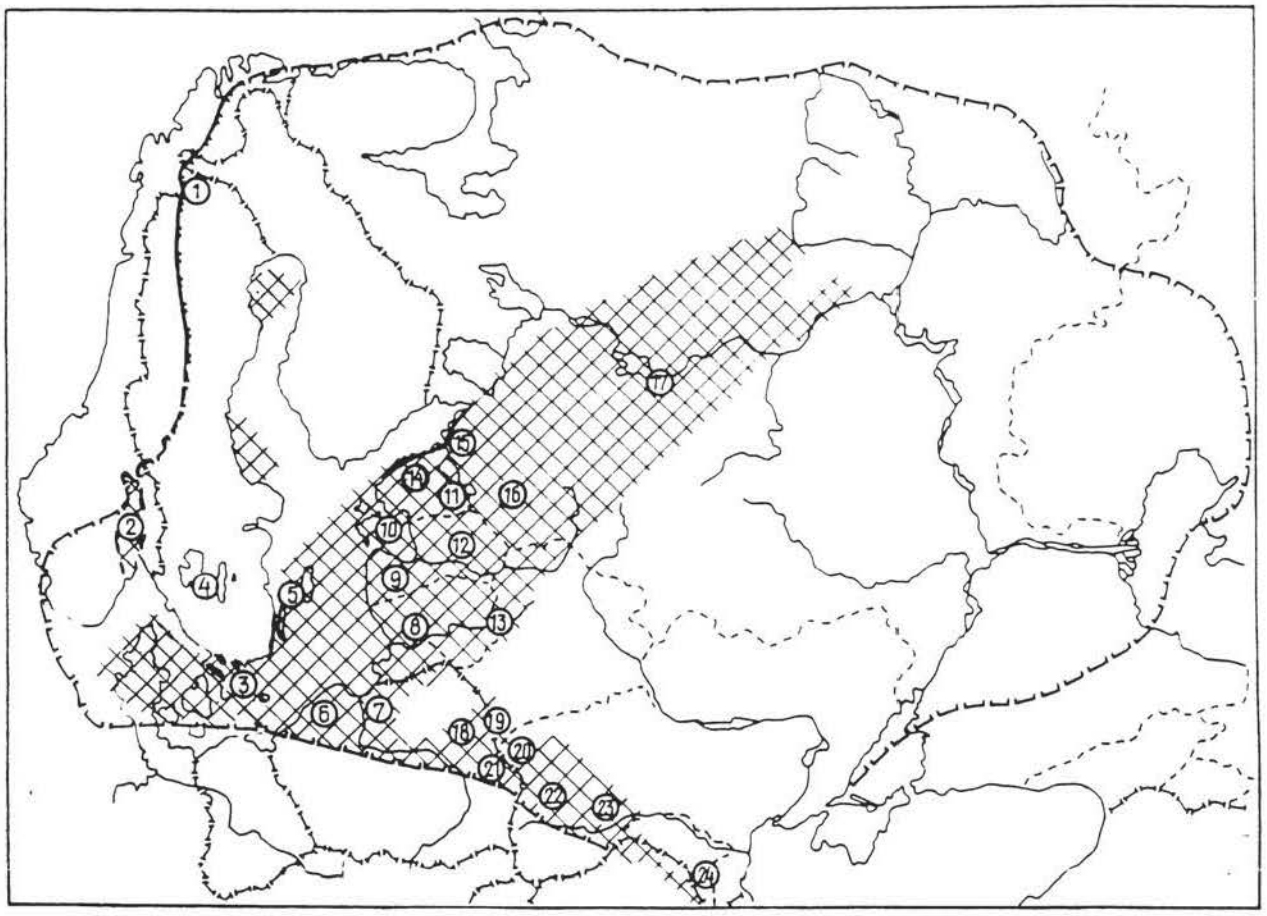

Figure 4. Map of the present-day distribution of Cambrian deposits on the platform with location of stratigraphical column. In black - outcrop area; cross-hatching - subsurface area.

are predominantly found in the lower part, but also occur in the upper part of the formation.

The Türisalu Formation is overlain by Upper Tremadocian sandstone and clay/claystone of the Varangu Formation (Fig. 5). In the southern part, it is covered by the Leetse glauconitic sandstone (Latorp) and in the northwestern corner (incl. Hiiumaa and Vormsi islands) by the Kunda (or Volkhov) sandy limestone (PUKKONEN & RAMMO 1992). Phosphatic sandstone of the Kallavere Formation with a thickness from 1 to 20 m (predominantly 3-4 m) underlies the Türisalu Formation and contains organic-rich mudstone interlayers. In some places, e.g. on the Hiiumaa Island, a layer of dark mudstone occurs at the base of the Kallavere Formation. This layer contains less organic matter than the Türisalu Formation (6-9% and 14-16% TOC respectively, PUKKONEN 1993). Southwards, the thickness of the Türisalu Formation decreases and the number of sand- or siltstone interlayers increases. For example, in the core F-309 located near the thinning-out line (see Fig. 1), the Türisalu Formation (0.4 m) is characterized by the intercalation of mudstone (0.17 m), sandstone (0.06 m) and anthraconite concretions (0.17 m).

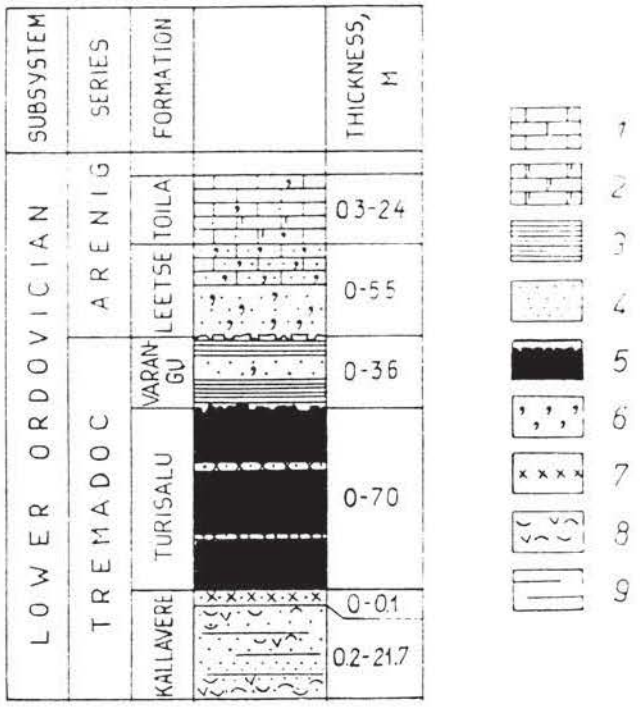

Figure 5. Stratigraphical scheme of the Tremadocian and Arenigian rocks in North Estonia. Legend: **1** - limestone; **2** - dolomitic limestone; **3** - clay (mudstone); **4** - quartzose sandstone and siltstone; **5** - organic-rich mudstone (Dictyonema Shale) with disconformity; **6** - glauconite; **7** - pyrite; **8** - complete shells and debris of inarticulate brachiopods; **9** - interlayers of organic-rich mudstone. Note: Part of the Kallavere Formation belongs to the Upper Cambrian

The thickness of the Türisalu Formation decreases eastwards towards the central province. Simultaneously, the upper part of the formation becomes more homogenous (massive) with fewer visible silty interlayers. The content of organic matter is slightly lower than in the western province, and the concentration of precious metals (U, Mo, V) drops 2-3 times. Graptolites are very rare or lacking in the upper part the Türisalu Formation. No anthraconite concretions are found. Eastwards from the Maardu phosphorite deposit, a sandstone interlayer appears in the middle part of the Türisalu Formation dividing it into a metal-lean, upper part and a metal-rich, lower part. This sandstone layer reaches its maximum thickness of 0.6 m in the eastern part of the central province, for example in the Nõmmeveski outcrop (see Fig. 2). The underlying sandstone of the Kallavere Formation contains numerous intercalations or films of kerogenous mudstone. The thickness of these intercalations varies from some millimeters to some centimeters and constitute less than 10% of the total thickness (MENS et al. 1989). The lower boundary of the Kallavere Formation (Fig. 2) is in some places marked by a thin layer of kerogenous mudstone. More frequently, the boundary is developed as a 0.2 m thick brachiopod coquina, containing densely packed valves of *Ungula ingrica*. The uppermost 4-10 cm of the sandstone formation, which forms the boundary to the overlying Türisalu Formation, is usually cemented with pyrite, forming the so-called pyrite layer (LOOG & KIVIMÄGI 1968). The boundary

between the Türisalu Formation and the overlying Varangu Formation is also distinct, marked by a disconformity with borings (VIIRA et al. 1970, MÄGI et al. 1989).

The lithological composition of the Türisalu Formation of the eastern province differs considerably from the western sections. Detailed prospecting for phosphorite was carried out in the Toolse phosphorite deposit in the period from 1968 to 1975 by the Geological Survey of Estonia (Fig. 1). Here, the Türisalu Formation with an average thickness of 1.4 m was divided into four units (upwards): A), B), C), D) (KIVIMÄGI & TEEDUMÄE 1971). Unit A (0.3 m) is characterized by homogenous, thinly laminated dark-brown mudstone, unit B (0.9 m) by intercalations of siltstone and mudstone interlayers containing pyrite, anthraconite and white lenses of chert (KIVIMÄGI & LOOG 1972). The quartzose sandstone of unit C (0.05 m) contains pyrite crystals, calcite, dolomite and debris of inarticulate brachiopods. Unit D (up to 0.15 m) consists of very homogenous dark-brown mudstone, sometimes intercalated by thin (up to 4-5 mm) siltstone layers. The Türisalu Formation is overlain by clays (or claystones) of the Varangu Formation with thicknesses reaching 3 m. In the eastern part of the subcrop area, the Türisalu Formation (less than 1 m) is very heterogenous showing intercalations of mud-, silt- and sandstone, anthraconite concretions and white lenses of chert. The formation is here overlain by glauconitic sandstone of the Hunneberg Stage. The chert lenses were described by K.Müürisepp as originating from spicules of silicious sponges (LOOG 1982).

Mineralogy. The mineralogical composition of the Türisalu Formation is dominated by clay minerals (30%), potassium-feldspar (20%) and quartz (15%). The average content of organic matter and pyrite is 15% and 4-5% respectively. According to UTSAL et al. (1982) and PALVADRE et al. (1984), about 15% of the shale consists of amorphous substances considered to be oxides of iron, alumina and silica. The clay minerals were divided into the following groups:

1) Genuine hydromica (illite) with a lattice spacing d = 10.00 to 10.10Å and hydrated hydromicas with d = 10.11 to 10.20Å (this group makes up 16% of the whole rock composition).
2) Expansive hydromica with d = 10.21 to 10.30Å and montmorillonite-hydromicas with disordered mixed-layer structure, d > 10.31 Å (10%).
3) Micas with d = 9.93 to 9.99 Å (muscovite).
4) Chlorite (0.5%).

The micas were mainly found in the fraction from 2 to 5 μ or more, the expansive and hydrated hydromicas in the fraction of 0.2 μ and the montmorillonite-hydromicas in the fraction less than 0.2 μ. The following processes have been proposed for the formation of the latter: Vulcanic activity → fine volcanic ash → authigenic montmorillonite → diagenesis → disordered mixed layer hydromicas.

The influence of volcanic activity on the genesis of the Türisalu Formation has been mentioned also in other studies (ZHUKOV et al. 1987, PETERSELL et al. 1987, JUDOVITSCH &

KETRIS 1988). The main argument for volcanic influence is the occurrence of euhedral (authigenic?) K-feldspar crystals in the mudstone, also described as sanidin-like crystals (KLEESMENT & KURVITS 1987). Besides the authigenic K-feldspar, the problematical amorphous substances have also been considered as of volcanic origin.

Among the heavy mineral fractions, authigenic minerals are prevailing, first of all pyrite and marcasite. The different types of pyrite in the Estonian Türisalu Formation were studied by PYLINA (1966), LOOG (1982) and KALLASTE & PUKKONEN (1992). Allogenic translucent heavy minerals include mainly zircon, tourmaline and garnet (KLEESMENT & KURVITS 1987), but also corundum, sillimanite, brookite and Ti-minerals (ilmenite, leicoxene, rutile, anatase) have been reported. The Ti-minerals and the seldom occurring pyroxenes and amphiboles have well-rounded grain shapes. Also baryte has been reported in the Estonian Türisalu Formation. The sphalerite and galenite crystal modifications were described by (PUKKONEN 1991).

CHEMICAL COMPOSITION OF THE TÜRISALU FORMATION

The first detailed study of the major element and kerogen composition of the Türisalu Formation was carried out by KUPPFER (1870), who analysed material from three localities in western, central and eastern Estonia. N.Rägo studied the kerogen elemental composition of the Türisalu Formation from the Mäekalda outcrop (9 km from Tallinn) and gave data of kerogen, bensol-, xylol-, aceton-soluble bitumen extractions and of the major element composition (RÄGO 1928). Simultaneously, the Türisalu Formation of the St.Petersburg Region was studied by Russian geologists (POTULOVA 1927, ORLOV & KURBATOV 1934-1936, DOBRIYANSKIY 1947, USPENSKIY & GORSKAYA 1940). After the II World War and the annexation of Estonia by the Soviet Union, intensive uranium prospecting in the Estonian Türisalu Formation was started by Russian geologists (see ALTHAUSEN 1992 and MAREMÄE 1989). Also, detailed work on the thermal decomposition of the organic matter in the Türisalu Formation was carried out by O.Kirret, N.Gerassimov and A.Tikk in the Institute of Chemistry at the Estonian Academy of Science in 1947 (KIRRET et al. 1957).

When the mining of phosphorite in the Maardu quarry began in the late fifties, interest into the Türisalu Formation as a potential resource overlying the phosphoritic sandstone increased. Several thoroughful studies were carried out in the Institute of Chemistry during this time (KIRRET et al. 1957, KIRRET et al. 1959, POLIKARPOV 1957).

Detailed studies of the trace element geochemistry of the Türisalu Formation started at the Geological Survey of Estonia in the second half of the sixties and lasted about 25 years. Data were presented in more than 10 unpublished reports and are stored in the archive of the Geological Survey of Estonia. The chemical constituents of the Türisalu Formation can be roughly divided into three groups: (1) Major elements, (2) kerogen, and (3) trace elements.

1) Major elements. The major element composition of the Estonian Türisalu Formation was determined by wet chemical analyses, and in some later studies also by neutron activation (PELEKIS et al. 1985, PUKKONEN unpublished data). A comparison of old and new analyses was given by PUKKONEN (1989). This short review of the major element composition of the Türisalu Formation is based on the chemical analyses carried out in the laboratory at the Geological Survey of Estonia. As shown in the Table 2 and Figure 6, the composition of the major element oxides in the Türisalu Formation and in the Scandinavian Alum Shale is quite similar. The Alum Shale data given in the table were obtained from the Bårstad core (Östergötland, Sweden), where the sample B-1 represents the average Türisalu Formation and the sample B-2 Alum Shale of the *Leptoplastus* zone (Upper Cambrian). The Baltoscandian Alum Shales can be characterized as non-calcareous mudstones (or shales) with low CaO, MgO and MnO concentrations (TUREKIAN & WEDEPOHL 1961). The elevated P_2O_5 and Fe_2O_3 content in the Cambrian sample (Fig. 6) is related to the higher organic matter and pyrite content. Both the Türisalu Formation and the Swedish Alum Shales are enriched in K_2O and depleated in Na_2O.

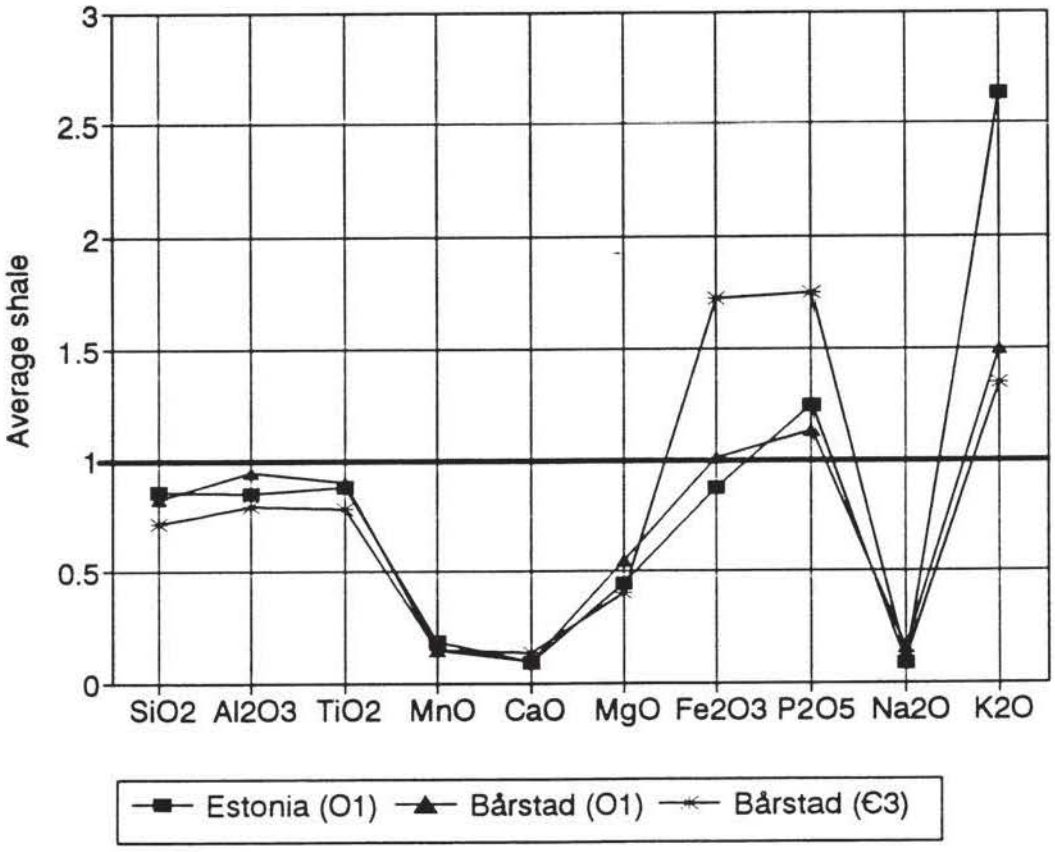

Figure 6. Plot showing ratios of major element oxides in the Estonian Dictyonema Shale to average shale by TUREKIAN & WEDEPOHL (1961).

The Türisalu Formation of Estonia contains 2.3 times more K_2O than the average shale by Turekian and Wedepohl (1961). This potassium is mainly found in K-feldspar (65%) and clay minerals (35%).

The changes in the major element composition in the different geochemical provinces are not remarkable. The heterogenous Türisalu Formation from the eastern province is characterized by higher and more uneven concentrations of pyrite and P_2O_5. The organic-lean shale from the central province has lower P_2O_5 content (see Table 3).

2) Kerogen composition and maturation. The Türisalu Formation contains up to 20% of organic matter (kerogen). Elemental composition of this kerogen has been studied in many earlier works (some data are given in Table 4). The kerogen is characterized by a high nitrogen content reaching 4 wt.%. Related to this fact, some researchers have considered the source material of the organic matter to be derived from graptolites (MANSKAYA & DROZDOVA 1962, YUSSUPOVA 1981), while others preferred primitive green and blue-green algae (PARPAROVA et al. 1984, KLESMENT 1985) and acritarchs (LAPO & MIKHAILOVA 1988) as the main source. ZHMUR (1988) described several microorganisms from the Türisalu Formation, such as the cyanobacteria *Microcoleus chthonoplastes, Colothrix,* the purple bacteria *Thiopsa* and *Thiocystes* and reached to the conclusion that the organic matter of the Türisalu Formation was generated by benthic microorganisms under brackish-water conditions.

As shown in Table 5, the total organic carbon (TOC) content of the Türisalu Formation varies between 6 and 13%. The very low vitrinite reflectance (R_o = 0.53%) and T_{max} (404-408°C) prove that the Türisalu Formation is thermally immature. The formation is characterized by little extractable bitumen, by methano-naphtene type of bitumoids (YUSSUPOVA 1978) and, as in the Swedish Alum Shale, by high H/C-ratios (Table 4). In comparison with the kukersite (Estonian oil shale of Middle Ordovician age), which formed under oxidizing conditions, the organic matter of the Türisalu Formation is enriched in NSO compounds (oxygen, sulphur and nitrogen), 12-14% and 17-25% respectively (KLESMENT 1985). Rock Eval hydrogen index values are considerably lower (HI from 300 to 430 mg HC/g TOC) than those found in contemporaneous shales of similar maturity from Öland and Västergötland (HI up to 630), probably reflecting the higher content of non-hydrocarbons in the kerogen. In the van Krevelen diagram (WILKEN & BUCHARDT 1994), the Türisalu kerogen can be classified as a mixed type II and III. Klesment supposed that the high content of rare elements in the Türisalu Formation results not only from the reducing depositional environment, but also from the high concentration of NSO compounds in the organic matter, which formed chelate complexes with the multivalent metals (Table 5).

The amount of nitrogen released upon pyrolysis of the Türisalu Formation varies from 4 to 17 % and increases in the eastern province (NAPPA et al. 1978). It is worth to notice that the NSO content in the Swedish Alum Shale kerogen is remarkably lower than in the Türisalu Formation (WILKEN et al. 1994).

The lateral and vertical distribution of the organic matter in the Türisalu Formation coincides with the calorific values, which have been determined from more than 2500 samples in 400 drill cores. Only part of these data have been published (PUKKONEN & RAMMO 1989). Pure kerogen of the Türisalu Formation has a calorific value of 35.1 MJ/kg (8350 kcal/kg, KIRRET et al. 1959). The highest calorific values of the Türisalu Formation were found in the northwestern corner of the mainland, where the thickness of the Türisalu Formation is also the biggest (up to 7 m). The calorific values decrease eastwards and southwards, but is usually higher than 4.2 MJ/kg (1000 kcal/kg). The oil yield of the Türisalu Formation by the Fisher Assay correlates well with the organic matter content and shows the highest value in the western zone (3-4%). In the Toolse phosphorite deposit of the eastern province, where the average calorific value of the Türisalu Formation is 4.8 MJ/kg, the oil yield of the mudstone is 2.1-2.2% (KIVIMÄGI & TEEDUMÄE 1971). Probably, this low oil yield is caused by the long-time exposure of the organic matter to radiation from decay of uranium (LEWAN & BUCHARDT 1989). The comparison of the uranium-poor and uranium-rich Türisalu Formation in thermo-oxidation curves led to the same conclusion (VESKI et al., 1993).

3) Trace elements. The trace element composition of the Türisalu Formation is mainly known from the Maardu and Toolse phosphorite deposits (IVANOV et al. 1984, PELEKIS et al. 1985, KIRRET et al. 1986, KIRRET et al. 1987, PIHLAK & ISAND 1989). Outside these areas, the distribution of U, Mo, and V has been described by the geologists from the Geological Survey of Estonia (PETERSELL et al. 1981, PUKKONEN & RAMMO 1992, PUKKONEN 1993). The average trace element composition of the Türisalu Formation is given in Table 6. As shown there, the eastern (III) geochemical province is characterized by elevated concentrations of U, Mo, (V), RE, Ag, and elements of sulphide association - Ni, Pb, As. The same distribution pattern can be seen in the western province near the thinning-out line, where the thin Türisalu Formation contains also many sand- or siltstone intercalations.

Usually, the lower part of the Türisalu Formation is characterized by elevated concentrations of U, Mo and V (PUKKONEN & RAMMO 1992, KIVIMÄGI & TEEDUMÄE 1971, see Table 7). The thickest and most organic-rich parts of the Türisalu Formation in the northwestern corner of the mainland contain vanadium in high concentration (1200-1300 ppm). Vanadium is mainly associated with the organic matter, and vanadyl porhyrin complexes has been described from the benzene extraction fraction (800 ppm in bitumen extract, DROZDOVA & CHINENOV 1974). Part of the vanadium occurs in clay minerals (PALVADRE et al. 1984). Molybdenum has a positive correlation with the organic matter (PALVADRE et al. 1984, PETERSELL et al. 1981, PELEKIS et al. 1988), but is also incorporated into the pyrite phase (PETERSELL et al. 1981, KALLASTE & PUKKONEN 1992, PALMRE 1969). No molybdenium minerals have been found in the Türisalu Formation, although some authors (MALDRE 1976) considered the molybdenum to be bound as molybdenite.

Uranium concentrations are higher in the more sandy (or silty) sections of the Türisalu Formation. Therefore, it is assumed that the uranium was enriched preferably in the near-shore or more

shallow part of the depositional basin, where good organic matter preservation conditions occurred locally. For example, the mudstone interlayers inside the Kallavere Formation sandstone in the eastern part of North Estonia contain uranium up to 1200 ppm (core 0612, see Fig. 1). ALTHAUSEN (1992) considered 5-10% of the uranium to be in mineral form as the uraninite mineral nasturane.

The lead concentration, which averages 100 ppm in the Türisalu Formation, is about 2 times higher than normally in the Alum Shales of Scandinavia. This enrichment can probably be explained by the high content of authigenic K-feldspar in the Türisalu Formation. The zinc content in the Türisalu Formation (average 100 ppm) is several times lower than in the Swedish Alum Shales. The distribution patterns of Pb and Zn are different in the Türisalu Formation basin. Nevertheless, three areas in the basin show co-enrichment of Pb and Zn above the values mentioned above: on Hiiumaa Island, near the Maardu deposit and in the northeastern part of Estonia (Viivikonna). These enrichments have been explained by submarine polymetal-rich hydrothermal activity during the deposition of the Türisalu Formation (PUKKONEN 1991).

STABLE ISOTOPES

Sulphur isotope analyses of 19 samples of disseminated and discrete pyrite were performed by PETERSELL et al. (1987). The $\delta^{34}S$ varied from -16.1 o/oo to +2.9 o/oo. The main part of these samples (58%) had $\delta^{34}S$ values similar to the meteoritic standard (from -3.8 o/oo to +2.9 o/oo) and the authors could not exclude the possibility of significant flux of magmatic sulphur by postvolcanic solutions. Carbon isotope composition of organic carbon determined from seven samples in the Türisalu Formation range from -29.31 o/oo to -27.58 o/oo versus PDB. These numbers are 1 to 2 o/oo more positive than the corresponding values from the Djupvik-1 and Gislövshammar-2 cores. No geographical or stratigraphical trends can be identified in the data.

DEPOSITIONAL ENVIRONMENT

Estonia is located on the southeastern slope of the Baltic Shield, where the southwards tilted crystalline basement forms the socalled Estonian Monocline. The basement is covered by Upper Vendian and Lower Palaeozoic (incl. Devonian) sedimentary rocks with a total thickness of up to 1 km in the southern part of Estonia. Development of the main basinal structure in the Baltic - the Baltic Syneclise - started in Late Cambrian time (SUVEIDIS et al. 1987).

The Lower Palaeozoic sedimentary cycle (the Caledonian structural complex of Russian authors) was preceded by deposits of Upper Vendian to Lower Cambrian age (Baikalian Platform structural complex), which mainly consist of conglomerates, arcosic sandstones, and - in the younger part - siltstones. Deposition of the Vendian sediments took place in the present Estonian area and in the eastern part of Latvia and Lithuania under subcontinental and near-shore, marine conditions

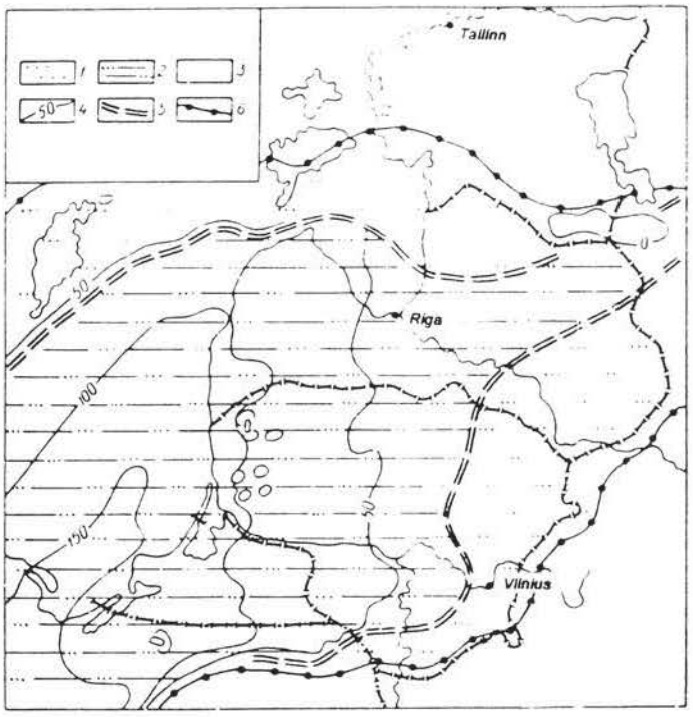

Figure 7. Scheme of the isopachytes and types of the Middle Cambrian terrigenous-sandy marin formations (after BRANGULIS et al. 1987). Legend: **1** - sandy deposits; **2** - silty-clayey deposits; **3** - area without deposits; **4** - isopachytes; **5** - boundary between deposits of the different types; **6** - subcrop area of the formations.

(BRANGULIS et al. 1987). Probably, the Vendian and Lower Cambrian deposits also covered the eastern part of the Baltic Shield (the present Finland and Karelian areas, PUURA et al. 1987, p.74). At the beginning of the Caledonian structural complex (Middle Cambrian), sedimentation took place in the western, northern and central parts of the East Baltic[2] where mainly silty-clayey deposits were formed. The Middle Cambrian deposits in the western and central part of the East Baltic (see Fig. 7) are characterized by sandy quartzose siltstones containing kaolinite. The Upper Cambrian is represented by siliciclastic rocks, mainly quartzose sand- and siltstone containing thin interlayers of greenish-gray clays in the lower and dark kerogenous shales and mudstones in the upper part of the section. These rocks are developed predominantly in the northern part of the East Baltic (Fig. 8 and MENS et al. 1993). The Cambrian deposits of the East Baltic are mainly marine, but may sometimes have formed under brackish-water conditions (PIRRUS 1981).

At the beginning of the Ordovician, the Baltic (NE Poland, SW Baltic) and Moscow Syneclises

[2] The term East Baltic is here used as a synonym to the area today defined by the three Baltic republics Estonia, Latvia and Lithuania and the St. Petersburg Region.

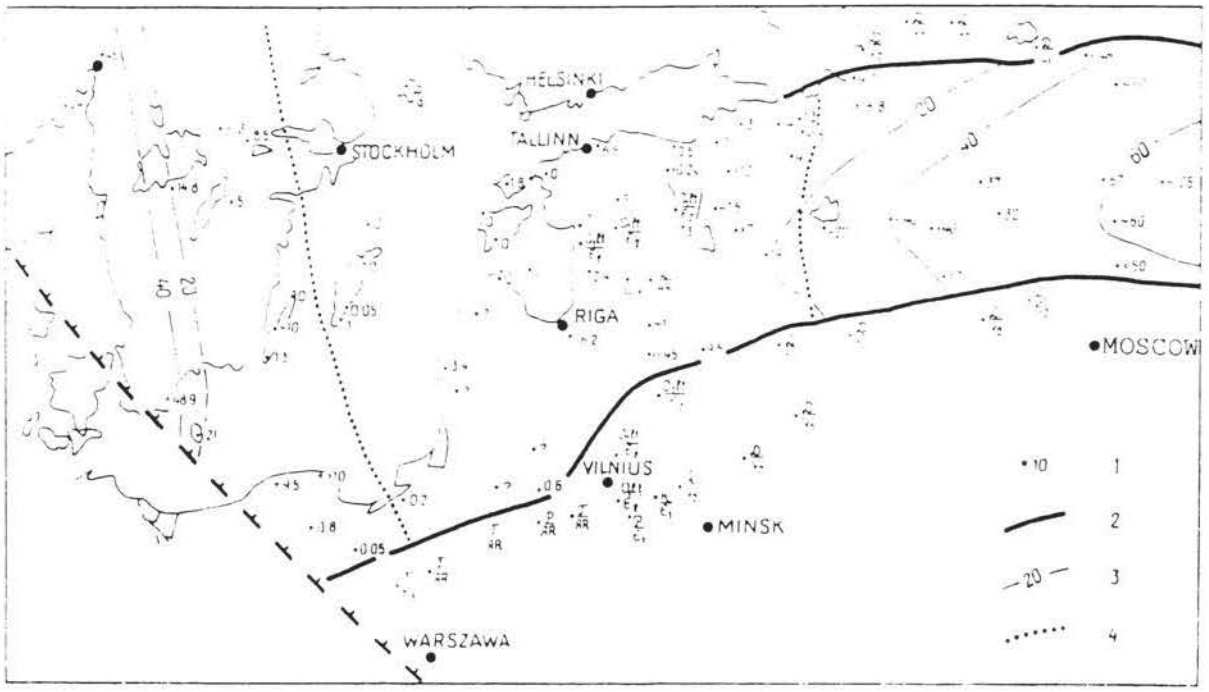

Figure 8. The distribution, thickness and facies of the Upper Cambrian in the northwestern part of the East European Platform (after MENS et al. 1993).
Legend: **1** - thickness of the corresponding deposits, m (up to the base of the Cordylodus succession); question mark shows the undetermined Cambrian or Ordovician age of deposits; **2** - recent erosional boundary of the Upper Cambrian; **3** - isopachytes, m ; **4** - boundary of a facies belt.

came into existence. At that time, the central part of the East Baltic formed an east-west trending swell (the Latvian Saddle). North of this high, the basement was tilted to the north and formed a basin, where phosphatic sandstones and organic-rich mudstones were deposited during the Tremadocian transgression (Fig. 9). The Tremadocian sea in the East Baltic probably was very shallow and with an even bottom topography. The distribution of bioclastic phosphoritic sandstone and kerogenous mudstone was controlled by bottom topography and currents, but also by movements of minor basement blocks (HEINSALU 1979). The organic-rich muds in North Estonia were deposited in the deepest part of the basin, which probably extended into the present-day Finnish Gulf. Further to the east, the basin had connection to the Moscow Syneclise through the area of the present-day Lake Ladoga (DAVYDOVA & GOL'DSHTEIN 1960). During periods of sea level highstands, the East Baltic basin acted as a strait linking the major Scandinavian and Russian basins, and water movement from the west to the east took place affecting the formation of the phoshorite deposits and organic-rich mudstones, and also the Middle Ordovician kukersites (PUURA et al. 1987).

By the opinion of several authors, the elevated content of OM in the Türisalu Formation was caused by high productivity linked to upwelling from the pericontinental part of the basin in the west (PUURA et al. 1987, POPOV et al. 1989). However, the low sedimentation rates seen in the Baltoscandian Alum Shales seem to contradict this interpretation (THICKPENNY 1984).

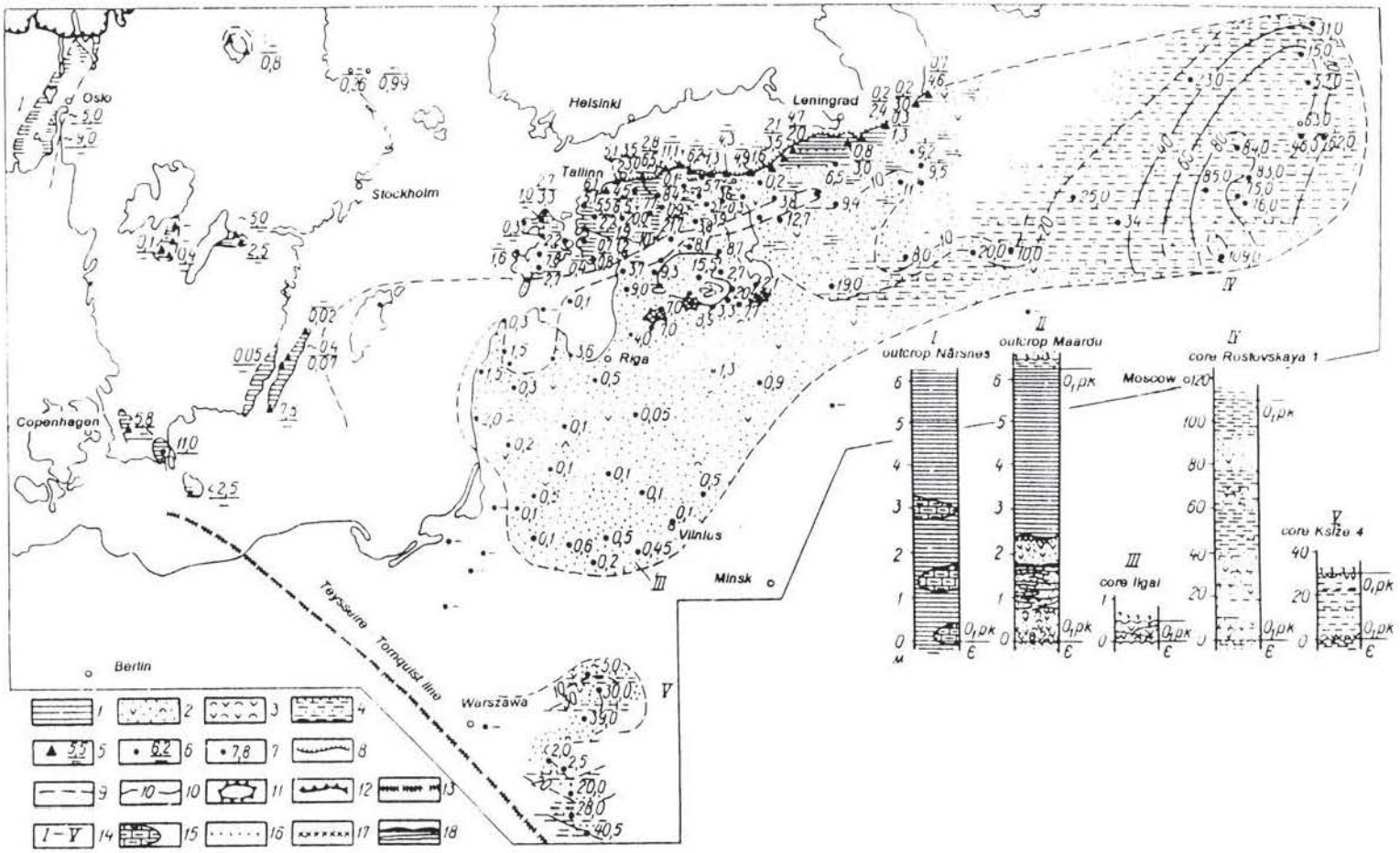

Fig.9 Lithological-facial scheme of the Pakerort time in the East-European Platform with the type sections (after Heinsalu, 1985).
Legend: 1 - Dictyonema Shale; 2 - quartzose sandstone or siltstone with brachiopod detritus; 3 - brachiopod coquina (*Obolus* phosphorite); 4 - intercalation of sandy and clayey rocks; 5 - outcrops, thickness of the Dictyonema Shale, m (in the denominator), and *Obolus* sandstone (in the numerator); 6 - drill cores, numbers - thickness of the deposits, m; 7 - drill cores, thickness of the *Obolus* sandstone (or sandy-clayey rocks), m; 8 - Baltic-Ladoga clint; 9 - presentday distribution area of the sedimentary rocks of the Pakerort Stage; 10 - isopachytes, m; 11 - Valmiera-Môniste-Lokno nose of the crystalline basement; 12 - overlap to the platform; 13 - Teysseire-Tornquist line; 14 - **type sections**: I - Närsnes (South Scandinavian); II - Maardu (North Baltic); III - Ilgai (South Baltic); IV - Rostovskaya (Moscow Syneclise); V - Kšiže (Polish type); additional conventional signs: 15 - stinkstone; 16 - glauconite; 17 - pyrite; 18 - interlayers of kerogenous mudstone

Note: By the new data (Dmitrovskaya, 1989) the thickness of the sedimentary rocks of the (Lower Tremadocian) Pakerort Stage in the Moscow Syneclise is about two times smaller than given in the figure.

ECONOMICAL INTERESTS, TECHNOLOGICAL STUDIES AND THE RESOURCES OF THE ESTONIAN TÜRISALU FORMATION

At the end of the Second World War, the demand for uranium for nuclear power and weapons aroused. Because the Estonian Türisalu Formation was a potential resource for uranium, several uranium prospecting studies were carried out by St.Petersburg geologists. Also, technological investigations into the methods of uranium enrichment were initiated. The first uranium concentrate from the Türisalu Formation was presented at a high-level meeting in the Kremlin, Moscow, attended by L.Beria, K.Voroshilov, G.Malenkov and other members of the Soviet Government (ALTHAUSEN 1992). Later, several technologies for uranium extraction were developed, the most effective were as follows (MAREMÄE 1989, ALTHAUSEN 1992):

1) The method of heap bacterial leaching of metals from lump material of the Türisalu Formation developed in the All-Union Institute of Raw Materials in Leningrad (ALTHAUSEN et al. 1965, ZVEREV et al. 1965). This method gave a yield of 70-80% of uranium, 40-60% of molybdenum and 13-20% vanadium.

2) The method of oxidizing autoclave leaching of the Türisalu Formation from the acid pulp with an anion-exchange resin, which enabled to extract into solution 73-76% U (SMIRNOV et al. 1973).

3) The sulphuric acid method of complex extraction of metals performed by the Institute of Chemistry, Academy of Sciences of the Estonian SSR (MAREMÄE & KIRRET 1989 and 1990). This method enabled to extract from the Türisalu Formation 80-90% U and V, 65-75% Mo and other elements, but was uneconomical due to the huge consumption of sulphuric acid.

The Türisalu Formation was also investigated for heating purposes (KÔLL et al. 1959, LÖÖNE & UUESOO 1966 a.o.), for oil and gas generation (STEPANOV & RIKKEN 1957), and as a raw material for concrete production and for many other purposes (see MAREMÄE 1988). Since 1942, more than 40 institutes in the former Soviet Union have studied the potential of the Türisalu Formation as fertilizer (VESKI 1986). According to ZHZEZHZEL' (1955, see VESKI 1986) the growth of different agricultural plants after applying powdered rocks from the Türisalu Formation increased from 5 to 95 %. Using combined processes of hydrocycling and flotation, AHELIK & PALVADRE (1992) obtained a concentrate with an organic matter content of 62% from the Türisalu Formation. No economically effective technologies for use of the Türisalu Formation have been worked out yet.

RESOURCES

The total reserves of the Türisalu Formation in Estonia are close to 64 billion tons. Considering the average concentrations of uranium (106 ppm), vanadium (910 ppm) and molybdenum (180 ppm) given in Table 5, the total reserves of these elements in the Türisalu Formation can be calculated: Uranium 6.8 million tons, vanadium 58.2 million tons, and molybdenum 11.5 million tons.

Economically important are the resources of the Türisalu Formation in the Toolse phosphorite deposit (see Fig. 1), where the formation overlies the phosphoritic sandstone. Here, future phosphorite mining may make it economically attractive to exploit also the Türisalu Formation. The resources of the Türisalu Formation in the Toolse phosphorite deposit were calculated using data from more that 150 drill cores (KIVIMÄGI 1975): Total resources are more than 141.4 million tons, uranium 21 100 tons, vanadium 147 000 tons, and molybdenum 57 400 tons.

The resources of the Türisalu Formation have been calculated also in the northwestern part of Estonian, where the thickness and organic matter content of the formation is at the highest. Based on the data from 250 drill cores and about 2000 analyses, the resources of the Türisalu Formation with a thickness above 3.5 m (in the area of 1607 km^2) were as follows (RAMMO et al. 1989): Total resources 10 651 million tons, uranium 1.176 million tons, vanadium 7.260 million tons, and molybdenum 2.444 million tons.

ENVIRONMENTAL STUDIES

Over the last 15 years, a great deal of attention has been given to the environmental problems arisen from the mining of the phosphorite deposit in the Maardu open pit. Here, the overlying Türisalu Formation with a thickness up to 4 m was removed and dumped in the quarry. As a result of self-ignition processes and burning of the shale dumps, sulphur and heavy elements (e.g. uranium) were released from the rock and polluted air, surface and ground water.

The environmental aspect of the Türisalu Formation studies includes investigations of the groundwater pollution (JOHANNES et al. 1979, PIHLAK et al. 1984, NAUMOV 1991 a.o.) and leaching processes of the metals (ALTHAUSEN et al. 1980, PALVADRE & KLEEMEIER 1982, MAREMÄE et al. 1979). Different aspects of the self-ignition processes have been studied by EPSTEIN et al. (1964), UROV & VYSSOTSKAYA (1981), VESKI & SIDOROVA (1981), PEVZNER et al. (1982), KOCH & KIIS (1984), and PIHLAK (1984a and 1984b). Most of the studies related to the environmental hazard of the Türisalu Formation have been published in the journal "Goryuchie Slantsy" ("Oil Shales") founded in Tallinn, 1984.

REFERENCES

Althausen M. 1992. Lower Paleozoic (Riphean) metalliferous black shales (in Russian with long English summary). Goryuchie Slantsy (Oil Shales), 9, 3, 194-207.

Althausen M., Maremäe E., Johannes E., Lippmaa E. 1980. Weathering of metalliferous alum shales (in Russian with short English summary).- Proc. Acad. Sci. of Estonian SSR[3]. Chemistry, 29, 3, 165-169.

Althausen M.N., Kuznetsova J.G., Kuligina I.P. 1965. On the bacterial method of leaching of the Dictyonema Shale of Estonia (in Russian). Materialy po geologiy i metodam ishucheniya mineral'nogo syriya. Moskva, v.48, 27-52.

Bednarczyk W. 1989. Cambrian-Lower Ordovician boundary beds in Northern Poland. Proc. Acad. Sci. of Estonian SSR. Geology, 38, 2, 60-67.

Borovko N., Popov L., Sergeyeva S. 1983. Upper Tremadoc of the eastern part of the Baltic-Ladoga clint (in Russian). Doklady AN SSSR, vol.273, 2, 404-407.

Brangulis A., Korkutis V., Mens K., Pirrus E. 1987. Vendium and Cambrian terrigenous formations in Baltic (in Russian). In: Tektonika, fatsiy i formatsiy zapada vostochno-evropeiskoi platformy. Minsk, 65-73.

Davydova T.N., Gol'dshtein T.L. 1960. Genesis of sediments and the palaeogeography of the Early Ordovic in the nortern part of the Soviet Baltic (in Russian). Dok. sov.geol. Probl.12. Mezhd. geol. kongress, XXI sessiya, 15-24.

Dmitrovskaya J. 1988. New data on Lower Paleozoic stratigraphy in Moscow Syneclise. Article I. Cambrian (in Russian). Bull. Moskovskogo o-va ispytatelei prirody, odt. Geol., 63, 2, 47-54.

Dmitrovskaya J. 1989. New data on Lower Paleozoic stratigraphy in Moscow Syneclise. Article 2. Ordovician and Silurian (in Russian with very short English summary). Bull. Moskovskogo o-va ispytatelei prirody, odt. Geol., 64, 2, 82-94.

Dobrjanskiy A. 1947. Oil shales in the SSSR (in Russian). Gostoptehizdat, Mosk.-Len., 17-19.

Drozdova T.V., Chinenov V.A. 1974. Metalloporphyrins in the bituminous shales of the Baltic Region and Eastern Ciscaucasia (in Russian). Geokhimiya, 1, 56-64.

[3]Proc. Acad. Sci. of Estonia (or Estonian SSR) - Izvestiya Akademiy Nauk Estonii (Estonskoi SSR) Chemistry - Khimiya, Geology - Geologiya

Epstein S., Paalme T., Anso J. 1965. On the self-ignition of the Dictyonema Shale (in Russian). Slantsevaiya i khimitsheskaiya promyshlennost', 6, 2-3.

Erdtmann B.-D. 1982. Palaeobiography and environments of planctic dictyonemid graptolites during the earliest Ordovician. In: M.G.Basset and W.T.Dean (Editors), The Cambrian-Ordovician boundary: Sections, Fossils Distributions, and Correlations. Nat. Mus. Wales Geol. Ser., 3, 9-27.

Heinsalu H. 1979. On the tectonic influence to the formation of the shelly phosphorite in the Estonian Early Tremadocian basin (in Russian with English summary). Proc. Acad. Sci. of Estonia. Geology, 28, 3, 89-93.

Heinsalu H. 1986. The lithofacial zonality of Early Tremadoc deposits in the East-European Platform (in Russian with English summary). Proc. Acad. Sci.of Estonian SSR. Geology, 35, 3, 115-121.

Heinsalu H. 1987. Lithostratigraphical subdivision of Tremadoc deposits of North Estonia (in Russian with English summary). Proc. Acad. Sci. Estonian SSR. Geology, 36, 2, 66-78.

Heinsalu H. 1990. On the lithology and stratigraphy of the Late Tremadoc graptolitic argillites of North-West Estonia (in Russian with English summary). Proc. Acad. Sci. of Estonia. Geology, 39, 4, 142-151.

Heinsalu H., Viira V., Mens K., Oja T., Puura I. 1987. The section of the Cambrian-Ordovician boundary beds in Ülgase, Northern Estonia (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Geology, 36, 4, 154-165.

Heinsalu H., Kurvits T., Oja T. 1991a. Lithological-mineralogical characteristics of the stratotypical section of the Rannu Member (∈3-O1*kl*R) at Saka II, North-East Estonia (in Russian with English summary). Proc. Acad. Sci. of Estonia. Geology, 40, 1, 1-7.

Heinsalu H., Viira V., Paalits I. 1991b. Cambrian-Ordovician boundary beds in the Saka II section, North-East Estonia (in Russian with English summary). Proc. Acad. Sci. of Estonia. Geology, 40, 1, 8-15.

Ivanov V.V., Poplavko E.M., Timofeyeva O.S. 1984. Pecularities of the trace element distribution in the carbonarifous shales of Estonia (in Russian with English summary). Geokhimiya, 6, 903-912.

Johannes J., Karise V., Punning J., Hütt G. 1979. Hydrogeological-geochemical investigation of the natural environment conditions in the Maardu phosphorite deposit (in Russian). In: Sostojaniye zagriyazneniya okruzhayushchey sredy Severnoi Estonii. AN ESSR, Tallinn, 88-102.

Judovitsch J.E., Ketris M.P. 1988. Geohimiya chernykh slantsev (Black shale geochemistry) (in Russian). Leningrad, Nauka, 272pp.

Kaljo D., Borovko N., Heinsalu H., Khazanovich K., Mens K., Popov L., Sergeyeva S., Sobolevskaya R., Viira V. 1985. The Cambrian-Ordovician boundary in the Baltic-Ladoga clint area (North Estonia and Leningrad Region, USSR). Proc. Acad. Sci. of Estonian SSR. Geology, 35, 3, 97-108.

Kaljo D., Heinsalu H., Mens K., Puura I., Viira V. 1988. Cambrian-Ordo-vician beds at Tônismägi, Tallinn, North Estonia. Geol. Mag., 125(4), 457-463.

Kaljo D., Kivimägi E. 1976. Zonal stratigraphy of the Estonian Tremadocian (in Russian with English summary). In: Graptolity i stratigrafiya, Tallinn, 56-63.

Kaljo D., Kivimägi E. 1970. On the distribution of graptolites in the Dictyonema Shale of Estonia and on the uncontemporaneity of its different facies (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, Geology, 19, 4, 334-341.

Kaljo D., Viira V. 1989. Co-occurences of conodonts and graptolites in the Estonian Early Tremadoc. Proc. Acad. Sci. of Estonia. Geology, 38, 3, 97-100

Kallaste T., Pukkonen E. 1992. Pyrite varieties in Estonian Tremadocian argillite (Dictyonema Shale). Proc. Acad. Sci. of Estonia. Geology, 41, 1, 11-22.

Kirret O., Koch R., Ründal L. 1959. About the chemical composition of the Dictyonema Shale and its kerogen in Maardu deposit (in Estonian with German summary). Proc. Acad. Sci. of Estonian SSR. Ser. Phys.-Math. and Technical Sciences, 8, 1, 243-255.

Kirret O., Koch R., Ründal L., Johannes J., Talkop R. 1986. Chemical properties and composition of Alum Shale from Valkla-Tsitre and Toolse deposits (in Estonian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 35, 4, 237-244.

Kirret O., Koch R., Ründal L. 1987. The properties and the chemical composition of the Dictyonema Shale from the Villandi-Laheküla deposits (in Estonian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 36, 2, 89-92.

Kirret O., Polikarpov N., Lutskovskaja N., Valdek R., Eisen J. 1957. Compund, properties and thermal decomposition of Dictyonema Shale of the Maardu deposit (Estonian SSR) (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Ser. Phys.-Math. and Technical Sciences, 6, 2, 170-183.

Kivimägi E. 1975. Report: Complex usage of Toolse deposit (in Russian, unpublished). Keila. Stored in the archive at the Geol. Survey of Estonia.

Kivimägi E., Loog A. 1972. The main structural types of graptolitic argillites of the Toolse deposit (in Russian with short English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, Geology, 21, 2, 144-147.

Kivimägi E., Teedumäe A. 1971. Results of a complex estimation of the rocks in the phosphorite deposit of Toolse (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, Geology, 20, 3, 243-250.

Kleesment A.L., Kurvits T. 1987. Mineralogy of Tremadoc graptolitic argillites of North Estonia (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 4, 2, 130-138.

Klesment I. 1985. On the genesis of the Baltic Oil Shales. Goryuchie Slantsy (Oil Shales), 2, 1, 12-22.

Koch R., Kiis K. 1984. Peculiarities of thermolysis of organic matter in Maardu argillites (alum shale). 3. Compositional elements of organic matter and thermolysis (in Russian with short English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 33, 2, 110-116.

Kordikov A. 1962. The mineralogical characterization of the Dictyonema Shale from Maardu deposit (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Ser. Phys.-Math. and Technical Sciences, 1, 67-72.

Kuppfer A. 1870. Über Dictyonemaschiefer, Archiv für Naturkunde des Livlands, Estlands und Kurlands, Bd.I, Serie 1-5, Dorpat, 69-194.

Kôll A.T., Laus T.N., Elenurm A.A. 1959. Thermal treatment of the Dictyonema Shale with the using of solid thermocollector (in Russian). Goryuchie Slantsy, 3.

Lapo A.V., Mikhailova N.S. 1988. On the initial material of organic of the Baltic Dictyonema Shales. Goryuchie Slantsy (Oil Shales), 5, 4, 348-355.

Lashkov J. 1968. The Lower Ordovician lithostratigraphical complexes in the southern Baltic (in Russian). In: Stratigrafiya nizhnego paleozoiya Pribaltiki i korreliyatsiya s drugimi regionami. Vilnius, 139-154.

Loog A. 1982. About the geochemistry of the postsedimental mineral forma-tions in the Tremadocian argillite of North Estonia (in Russian with English summary). Acta et Comm. Univ. Tartuensis, v.527, 116-137.

Loog A., Kivimägi E. 1968. On the lithostratigraphy of the Pakerort Formation in Estonia (in Russian with English summary). Proc. Acad. Sci. Estonian SSR. Chemistry, Geology, 17, 4, 374-385.

Lööne R., Uuesoo R. 1966. Experimental investigation of the burning process of the Dictyonema Shale in the boiling layer (in Russian). Slantsevaya i khimicheskaya promyshlennost', 5.

Maldre J. 1976. Molybdenum in the Dictyonema Shale of North Estonia (in Russian). Litologiya i polesnyye iskopayemyye, 5, 94-98.

Manskaya S.M., Drozdova T.V. 1962. Transformation of the organic matter in the sedimentary rocks and the organic matter of the graptolites in the dictyonema shale (in Russian with English summary). Geochimiya, 11, 953-962.

Maremäe E. 1988. Utilization of Estonian Alum Shale in the national economy (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 5, 4, 407-418.

Maremäe E. 1989. A problem of complex processing of Estonian Alum Shale as a raw material for metallurgy (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 6, 1, 28-36.

Maremäe E., Kirret O. 1989. Effect of sulphuric acid on Alum Shale ashes by a high liquid phase content (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 6, 4, 354-361.

Maremäe E., Kirret O. 1990. Decomposition of Alum Shale ashes with sulphuric acid at low liquid phase content (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 7, 1, 59-65.

Maremäe E., Pihlak A., Lippmaa E. 1979. About the self-ignition of the Dictyonema Shale and the leaching of the heavy metals from the solid products of it. In: Sostojaniye zagrjaznenija okruzhayushchei sredy Severnoi Estonii. AN ESSR, Tallinn, 74-87.

Mens K., Bergström J., Lendzion K. 1987. The Cambrian System on the East European Platform (Correlation Chart and Explanatory Notes) (in Russian). Tallinn, "Valgus", 122p.

Mens K., Bergström J., Lendzion K. 1990. The Cambrian System on the East European Platform. International Union of Geological Sciences, publication N25, Canada, 75p.

Mens K., Viira V., Paalits I., Puura I. 1989. Cambrian-Ordovician boundary beds at Mäekalda, Tallinn, North Estonia. Proc. Acad. Sci. of Estonian SSR. Geology, 38, 3, 101-111.

Mens K., Viira V., Paalits I., Puura I. 1993. Upper Cambrian biostratigraphy of Estonia. Proc. Acad. Sci. of Estonia. Geology (in press).

Mägi S., Viira V., Aru H. 1989. On the correlation of the Tremadocian and Arenigian boundary beds in the East Baltic. Proc. Acad. Sci. of Estonian SSR. Geology, 38, 2, 63-67.

Männil R. 1966. Historiya razvitiya Baltiyskogo basseina v ordovike (Evolution of the Baltic basin during the Ordovician, in Russian with English summary). Tallinn, 200p.

Müürisepp . 1960. Lithostratigraphy of the Pakerort Formation in Estonia based on the outcrop data (in Russian). Trudy Instituta geologii Akad. Nauk Estonskoi SSR, 5, 37-44.

Nappa L., Fomina A., Kivimägi E., Kuusik M. 1978. About the nitrogen of kerogen of North-Estonian graptolitic argillites (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 27, 1, 21-25.

Naumov B. 1991. Pollution of hydrosphere by leaching of Dictyonema Shale in waste dumps of the Maardu deposits (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 8, 3, 266-274.

Orlo ,N., Kurbatov L. 1934-1936. To the radioactivity of the oil shales (in Russian). Khimiya tverdogo topliva, N5 (1934), 525-527; N6 (1936), 278-291; N7 (1936) 94-98.

Palmre H. 1969. On trace elements in pyrite and marcasite crystals and concretions in Paleozoic sediments of the Estonian SSR (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, Geology, 3, 247-254.

Palvadre R., Ahelik V. 1992. Possibilities of enhancing of efficiency of using organic-poor oil shales.1. (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 9, 2, 145-149.

Palvadr ,R., Loog A., Haldnu ,Ü., Ahelik V., Talkop R. 1984. Correlations between components in Estonian graptolitic argillites (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 1, 3, 292-300.

Palvadre R., Kleemeier T. 1982. Leaching of several heavy metals from argillites (in Russian with short English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 31, 4, 243-248.

Palvadre R., Utsal K., Ahelik V., Haldna Ü. 1984. On methodology and mineralogy of the graptolitic argillite of Estonia (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 1, 2, 162-170.

Parparova G.M., Neruchev S.G., Ginzburg A.I., Zhukova A.V., Trushkov P.A., Rudavskaya V.A., Stanitchnikova M.S., Stahheyeva A.V., Fedorova V.A., Faizulina Y.,M. 1984. The source material and the facial-geochemical conditions to the formation of organic matter in the different-aged domanicoids deposits (in Russian). Geochimija, 12, 1882-1885.

Pelekis L., Kirret O., Taure,J., Pelekis Z., Eglit E., Rajavee R., Ahelik V. 1988. Instrumental neutron activation analysis of Estonian Alum Shale and some other oil shales. Proc. Acad. Sci. of Estonian SSR. Chemistry, 37, 1, 1-5.

Pelekis L., Pelekis Z., Taure I., Kirret O., Rajavee E. 1985. Instrumental neutron activation analysis of Alum Shale from the Maardu deposit (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 34, 3, 161-164.

Petersell V., Mineyev D., Loog A. 1981. On the mineralogy and geochemistry of the North-Estonian *Obolus*-sandstones and *Dictyonema*-Shales (in Russian with English summary). Acta et Comm. Univ. Tartuensis, v.561, 30-49.

Petersell V., Zhukov F., Loog A., Fomin Yu. 1987. Origin of Tremadoc kerogen-bearing siltstones and argillites of North Estonia (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 4, 1, 8-13.

Pevzner M., Naumov B., Puura V., Belenkij P. 1982. Distribution of Dictyonema Shales and thermal regime and auto-heating in the tailings of the Maardu phosphate quarry (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Geology, 31, 4, 131-139.

Pihlak A. 1984a. A comparative study of spontaneous ignition tendency of minerals (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 1, 4, 379-387.

Pihlak A. 1984b. Spontaneous ignition tendency of the Dictyonema Shale of the Estonian phosphorite deposits (in Russian with English summary). Goryuchiye Slantsy (Oil Shales), 1, 3, 251-264.

Pihlak A., Isand D. 1989. Composition of the Maardu Dictyonema Shale and its tendency to self-ignition (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 6, 3, 247-258.

Pihlak A., Maremäe E., Lippmaa E. 1984. The influence of the Maardu tailings to the water pollution (in Estonian with English summary).- Proc. Acad. Sci. of Estonian SSR. Biology, 33, 2, 166-170.

Pirrus E. 1981. The main processes of the authigenic mineral formation in the terrigenous deposits of Vendian and Cambrian in the North Baltic (in Russian with English summary). In: Autigennye mineraly terrigennyh otlozheniy Pribaltiki. Tallinn, 5-21.

Polikarpov N. 1957. The Dictyonema Shale (in Russian). Priroda, 6, 83-85.

Popov L., Khazanovitch K., Borovko N., Sergeyeva S., Sobolevaskaya R. 1989. The key sections and stratigraphy of the phosphate-bearing *Obulus* beds on the Russian Platform (in

Russian). Leningrad, "Nauka", 248p.

Potulova N. 1927. Obolus sandstones and dictyonema shale from the Leningrad Region (in Russian). Izdatel'stvo Geologitcheskogo komiteta, Leningrad.

Pukkonen E. 1989. Major and minor elements in the Estonian graptolite argillite (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 6, 1, 11-18.

Pukkonen E. 1991. Lead and zinc in the Estonian Dictyonema Shale. In: Black shale basins and related mineral deposits (abstracts of the international symposium), Novosibirsk, 242-243.

Pukkonen E. 1993. Uranium in the Estonian Dictyonema Shale (in Estonian with English abstract). Master theses. Tartu, 87p.

Pukkonen E., 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.

Puura V., Mens K., Männil R., Pirrus E., Heinsalu H. 1987. Paleotectonics and facies of the Baltic basin in Cambrian and during the phosphorite and kukersite deposition in the Ordovician (in Russian). In: Tektonika, fatsiy i formatsiy zapada vostochno-evropeiskoi platformy. Minsk, 74-86.

Pylina A. 1966. Pyrite concretions in the Dictyonema Shale (in Russian). Uchiyonyye zapiski Leningr. Ped. Instituta, 290, 284-330.

Rammo M., Morozov O. et al., 1989. Unpublished report: Prospecting of phosphorite in the south-west of Maardu deposit (in Russian). Kohtla-Järve. Stored in the archive at the Geol. Survey of Estonia.

Rägo N. 1928. Beiträge zur Kenntnis des Estländischen Dictyonemaschiefers. Acta et commentationes Universitis Tartuensis (Dorpatensis). Mathemathica, physica, medica. A-XIII, 9, 3-14.

Smirnov I.P., Ivanov G.F., Trusova V.N. 1973. Investigation of the technology to the complex usage of the Baltic Dictyonema Shale (in Russian). Spetsialnyye voprosy atomnoi nauki i tekhniki, 2, 5, 142-148.

Stepanov I., Rikken V. 1957. High-calorific gas from the Dictyonema Shale (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Ser. Phys.-Math. and Technical Sciences, 6, 2.

Stumbur H. 1962. On the stratigraphy of the Varangu Member (in Russian).- Trudy Instituta geologii Akad. Nauk Estonskoi SSR, 10, 61-65.

Suveidis P., Brangulis A., Puura V. 1987. Types of structures, structural and formational division of the sedimentary cover in Baltic (in Russian). In: Tektonika, fatsiy i formatsiy zapada vostochno-evropeiskoi platformy. Minsk, 64-65.

Szymanski B. 1974. Tremadocian in the Peribaltic Depression (in Polish with English summary). Kwartalnik Geologiczny, 18, 2, 223-245.

Szymanski B. 1984. Tremadocian and Arenigian deposits in North-Eastern Poland. Prace Instytutu Geologicznego CXVIII, Warszava, 25p.

Thickpenny A. 1984. The sedimentology of the Swedish Alum Shales. In: D.Stow, D.Piper (Editors), Deep-water processes and facies. Oxford, 511-525.

Turekian K., Wedepohl,K.H. 1961. Distributions of the elements in some major units of the Earth's crust. Bull. Geol. Soc. Amer., 72, 2, 175-192.

Ulst R., Gailite L., Jakovleva V. 1982. Ordovik Latvii (Ordovician in Latvia, in Russian). Riga, "Zinatne", 294p.

Urov K., Vôssotskaya V. 1981. About oil secretion of buried burning Dictyonema Oil Shale. 2. The chemical composition of the oil (in Russian with very short English summary). Proc. Acad. Sci. of Estonian SSR. Chemistry, 30, 2, 101-105.

Uspenskiy V., Gorskaya A. 1940. About the dictyonema shale (in Russian). Khimiya Tverdogo Topliva, IX, 1, 7-17.

Utsal K., Kivimägi E., Utsal V. 1982. About the method of investigating Estonian graptolitic argillite and its mineralogy (in Russian with English summary). Acta et Comm. Univ. Tartuensis, v.527, 117-139.

Veski R. 1986. Use of oil shales as fertilizers and ameliorants (in Russian with English summary). Goryuchie Slantsy (Oil Shales), 3, 4, 337-351).

Veski R., Palu V., Taal H., Pukkonen E., Pobul L., Sidorova S., Rajavee E. 1993. Thermooxydative and oxydative destruction of the weathered and uranium-rich Estonian Dictyonema Oil Shale. Goryuchie Slantsy (Oil Shales), 10, 2-3, 123-134.

Veski R., Sidorova S. 1981. About the tar in the self-ignition of the Dictyonema Oil Shale. 1. Sulphur in the tar (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR.

Chemistry, 30, 2, 195-199.

Viira V., Kivimägi E., Loog A. 1970. On the lithology and age of the Varangu Member (Tremadocian, North-Estonia) (in Russian with short English summary). Proc. Acad. Sci. of Estonia. Chemistry, Geology, 19, 2, 147-155.

Viira V., Sergeyeva S., Popov L. 1987. Earliest representatives of the genus *Cordylodus* (Conodonta) from Cambro-Ordovician boundary beds of North Estonia and Leningrad Region. Proc. Acad. Sci. of Estonian SSR. Geology, 36, 4, 145-153.

Yussupova I.F. 1978. The geochemical investigation of the Dictyonema Shale (in Russian). In: Geochimiya goryuchikh slantsev (abstracts of the presentations), Tallinn, 97-98.

Yussupova I.F. 1981. The organic matter of the Baltic graptolitic argil-lites (in Russian). In: Problemy ossadochnoi geologiy dokembriya. M., Nauka, book 2., 141-146.

Zhmur S.I. 1988. The origin of the Ordovician oil shales of the Baltic Syneclise. Part 1, Dictyonema Shales (in Russian). Litologija i poleznyye iskopaemyye, 6, 78-86.

Zhukov F., Petersell V., Fomin Yu. 1987. The signs of Palaeozoic volcanity in Estonia (in Russian with English summary). Proc. Acad. Sci. of Estonian SSR. Geology, 36, 1, 5-12.

Zverev L.V., Smirnova N.N., Shegolkova N.F. 1965. Uranium leaching kinetics by the sulphate solutions of the iron oxide (in Russian). Materialy po geologiy i metodam ishutsheniya mineral'nogo syriya. Moskva, v.48, 53-68.

Table 1

The average mineral composition of the crystalline phase of the mudstone in the different particle size fractions (after UTSAL et al. 1982)

Fraction, (in um)	Mineral composition (in %)						
	M-Hm	Exp.Hm +Hm	Mica	Chlo-rite	Quartz	Ortho-clase	Pyrite
>0.2	100	-	-	-	-	-	-
0.2 - 0.35	-	93.57	-	1.43	2.14	2.86	-
0.35 - 0.5	-	92.14	-	-	5.00	2.86	-
0.5 - 0.75	-	93.57	-	-	2.14	4.29	-
0.75 - 1.0	-	84.29	-	-	7.17	8.57	-
1.0 - 2.0	-	76.43	-	1.43	8.00	14.14	-
2.0 - 5.0	-	40.71	-	0.71	24.29	34.29	-
5.0 - 10.0	-	-	19.29	-	35.43	43.71	1.57
10.0 - 100.0	-	-	10.29	0.57	37.86	50.14	1.00

M-Hm - mixed-layer montmorillonite-hydromica (illite)
Exp. Hm. - expansive hydromica (illite)

Table 2

The major element composition of the Estonian Dictyonema Shale (F-342), Swedish Dictyonema Shale (Bårstad, B-1) and Swedish Cambrian Alum Shale (Bårstad, B-2), and comparison with the average shale by (Turekian and Wedepohl, 1961)

Location	Sample	SiO2	Al2O3	TiO2	MnO	CaO	MgO	Fe2O3 tot	P2O5	Na2O	K2O	L.O.I.	S tot	CO2
BÅRSTAD	O1 (B-1)	48.00	14.19	0.69	0.016	0.30	1.36	6.80	0.18	0.20	4.80	22.64	3.97	0.09
BÅRSTAD	Є3 (B-2)	41.70	11.93	0.60	0.016	0.42	1.01	11.61	0.28	0.14	4.31	28.50	8.47	0.17
F-342	O1	49.90	12.80	0.67	0.020	0.29	1.11	5.87	0.20	0.11	8.44	22.01	3.30	0.07
Average black shale: (Turekian and Wedepohl, 1961)		58.50	15.10	0.77	0.110	3.09	2.51	6.74	0.16	1.29	3.21		0.24	

Ratios to the average shale

Location	Sample	SiO2	Al2O3	TiO2	MnO	CaO	MgO	Fe2O3 tot	P2O5	Na2O	K2O	L.O.I.	S tot	CO2
BÅRSTAD	O1 (B-1)	0.82	0.94	0.90	0.15	0.10	0.54	1.01	1.13	0.16	1.50		16.54	
BÅRSTAD	Є3 (B-2)	0.71	0.79	0.78	0.15	0.14	0.40	1.72	1.75	0.11	1.34		35.29	
F-342	O1	0.85	0.85	0.88	0.18	0.09	0.44	0.87	1.24	0.09	2.63		13.75	

L.O.I. - Total weight lost on ignition at 1000°C
O1 : Tremadocian
Є3 : Upper Cambrian

Table 3

Whole chemical analysis of the major and minor oxides in the Estonian Dictyonema Shale (in weight %) from the selected cores

Core	Zone	Depth	Nr.	SiO2	Al2O3	Fe2O3 tot	TiO2	MnO	CaO	MgO	S tot	P2O5	FeO	Na2O	K2O	LOI	Moist.	SO3	CO2
F-342	I	111.00	844	50.95	12.82	5.90	0.67	0.018	0.16	1.19	3.19	0.12	1.72	0.09	8.50	21.64	1.64	1.49	0.07
F-342	I	111.55	845	50.08	12.82	6.34	0.72	0.018	0.16	1.14	3.41	0.12	1.58	0.07	8.40	21.59	1.65	1.63	0.07
F-342	I	112.20	846	49.90	12.82	5.47	0.65	0.018	0.21	1.14	2.88	0.13	1.72	0.09	8.40	22.47	1.72	1.47	0.07
F-342	I	112.80	847	52.00	12.94	5.47	0.69	0.023	0.18	1.13	2.88	0.12	2.44	0.09	8.70	20.42	1.75	1.68	0.07
F-342	I	113.35	848	50.64	12.84	6.55	0.68	0.021	0.25	1.13	3.94	0.19	2.01	0.09	8.22	20.75	1.91	1.94	0.07
F-342	I	113.70	849	55.56	11.81	5.72	0.62	0.018	0.94	0.94	3.32	0.68	1.87	0.09	8.32	16.77	1.40	1.23	0.07
F-342	I	114.10	850	50.64	13.07	5.47	0.69	0.021	0.21	1.17	2.88	0.16	2.01	0.08	8.52	21.66	1.90	1.72	0.04
F-342	I	114.70	851	48.16	13.07	5.38	0.67	0.021	0.21	1.12	3.16	0.13	2.30	0.08	8.42	23.41	1.95	1.73	0.04
F-342	I	115.30	852	47.80	12.31	5.73	0.64	0.020	0.24	1.04	3.39	0.15	2.16	0.08	8.30	24.00	1.91	1.70	0.07
F-342	I	115.90	853	48.96	12.94	6.16	0.69	0.021	0.21	1.09	3.62	0.15	1.87	0.07	8.30	22.94	1.98	1.86	0.11
F-342	I	116.35	854	48.30	12.56	5.64	0.65	0.023	0.21	1.08	3.13	0.16	1.87	0.09	8.40	23.90	1.96	1.67	0.07
F-342	I	116.60	856	45.78	13.57	6.60	0.72	0.022	0.44	1.16	3.82	0.27	1.87	0.07	8.80	24.60	2.24	1.79	0.07
0189 (V)	II	58.71	672	52.94	14.16	4.17	0.77	0.017	0.18	1.23	1.92	0.08	1.15	0.10	9.94	16.73	1.42	0.91	0.15
0189 (V)	II	58.83	675	55.90	14.36	5.73	0.77	0.018	0.58	1.23	3.06	0.22	1.44	0.10	9.92	11.94	1.55	1.30	0.20
0189 (V)	II	58.98	678	58.92	14.36	4.63	0.77	0.018	0.70	1.08	2.05	0.41	1.31	0.11	9.76	10.06	1.31	0.99	0.20
0189 (C)	II	59.20	680	61.70	16.65	4.34	0.88	0.026	0.27	1.53	1.35	0.08	1.29	0.12	10.96	4.48	1.10	0.34	0.09
0189	II	59.65	682	52.80	14.10	6.68	0.77	0.023	0.21	1.32	3.68	0.10	2.16	0.11	9.32	15.04	1.42	1.68	0.04
0189	II	59.95	683	52.00	14.10	6.42	0.75	0.019	0.21	1.28	3.68	0.10	1.72	0.10	8.84	16.84	1.40	1.68	0.04
0189	II	60.25	684	49.32	13.45	7.12	0.70	0.018	0.21	1.20	4.36	0.08	1.87	0.10	8.46	19.83	1.69	2.26	0.04
0189	II	60.55	685	51.58	14.10	5.55	0.72	0.019	0.25	1.30	3.18	0.08	1.94	0.10	8.86	18.01	1.71	2.21	0.04
0189	II	60.90	687	48.32	13.70	6.60	0.67	0.021	0.23	1.28	3.88	0.11	2.23	0.10	8.34	21.38	1.82	2.26	0.07
0189	II	61.20	688	50.00	14.36	4.86	0.70	0.021	0.21	1.34	2.31	0.09	2.01	0.10	9.08	20.11	1.58	1.58	0.04
0189	II	61.55	689	50.90	12.69	6.08	0.62	0.019	0.35	1.12	3.67	0.22	1.77	0.10	8.00	20.31	1.59	1.83	0.11
0189 (K)	II	62.03	695	52.50	14.99	5.90	0.80	0.020	0.33	1.46	2.75	0.17	2.01	0.11	9.08	14.81	1.75	2.00	0.07
0189 (K)	II	62.27	697	43.92	11.81	6.08	0.62	0.044	1.73	1.72	3.40	0.34	2.44	0.10	7.62	24.90	2.12	2.16	1.72
0189 (K)	II	62.72	699	46.96	14.10	5.47	0.70	0.018	0.35	1.37	2.85	0.23	2.73	0.11	8.34	22.70	2.54	2.43	0.11
0189 (K)	II	62.98	701	48.14	13.07	5.47	0.67	0.019	0.47	1.25	2.96	0.27	2.21	0.11	8.00	22.51	2.43	2.70	0.15
0189 (K)	II	67.62	718	45.76	14.36	6.86	0.77	0.018	0.25	1.24	4.18	0.13	1.94	0.09	8.92	22.42	1.66	2.27	0.17
946	III	33.20	62	48.20	12.44	5.73	0.72	0.021	0.19	0.94	3.13	0.12	2.59	0.06	8.40	23.33	3.19	4.90	0.07
946	III	33.50	64	48.20	11.68	5.03	0.59	0.022	0.52	0.98	2.79	0.30	2.87	0.06	7.90	25.48	3.48	4.71	0.15
946	III	33.80	65	47.24	12.31	4.69	0.63	0.014	0.35	0.99	3.43	0.20	2.73	0.12	7.80	26.05	3.68	4.72	0.11
946	III	34.10	66	49.60	11.56	4.86	0.65	0.015	0.64	0.98	2.76	0.40	2.73	0.12	8.24	23.65	3.80	4.75	0.07
946	III	34.25	67	51.20	9.76	6.94	0.55	0.011	1.05	0.81	4.64	0.72	2.44	0.12	6.52	22.39	3.59	5.13	0.07
946	III	34.60	68	43.08	11.43	8.85	0.59	0.014	0.35	1.05	5.64	0.26	3.31	0.11	7.10	27.45	4.59	6.19	0.09
P-1949	III	54.37	650	38.94	9.51	9.37	0.49	0.009	7.16	0.90	6.40	5.02	2.01	0.15	5.80	21.34	2.20	2.43	0.56
P-1949	III	54.48	651	42.20	12.56	8.25	0.67	0.014	1.93	1.29	4.81	1.34	1.72	0.11	7.54	24.61	2.43	2.41	0.17
P-1949	III	54.59	653	43.56	12.69	7.03	0.59	0.014	0.70	1.26	4.28	0.41	2.01	0.10	7.58	26.07	2.95	3.72	0.07
P-1949	III	54.62	654	45.60	9.13	14.41	0.47	0.015	1.75	0.83	10.27	1.10	1.94	0.11	5.36	22.44	2.82	4.59	0.11
P-1949	III	54.75	655	45.56	13.85	5.82	0.70	0.018	0.41	1.37	2.99	0.25	2.23	0.10	8.08	23.95	2.58	2.54	0.13

Fe2O3 tot - total iron was calculated into Fe2O3

LOI - total weight lost on ignition at 1000°C

(V) - argillite interlayers in the glauconitic sandstone of Varangu Formation

(C) - clay of the Varangu Formation

(K) - argillite interlayers in the phosphatic sandstone of the Kallavere Formation

Geochemical provinces: I- western, II- central, III- eastern

Table 4

Kerogen elemental composition of the Estonian Dictyonema Shale (in percents)

Author	Locality	C	H	N	O + Cl	S	H/C atom.
KUPPFER (1870)	Tallinn	69.00	7.17	2.57	21,26	...	1.24
RÄGO (1928)	Tallinn	61.43	7.18	4.24	24,93	2.22	1.40
KIRRET et al. (1957)	Maardu	68.88	7.72	3.69	17,59*	2.66	1.34
KIRRET et al. (1959)	Maardu	76.00	7.40	1.88	12,22	2.50	1.17
NAPPA et al. (1978)	Aseri	65.50	6.80	2.10	...	...	1.25
RAMMO et al. (unpublished report 1989)	NW Estonia	62.53	6.56	2.63	10,67	...	1.26

* - only oxygen content

Table 5

Total carbon (TC), total sulphur (TS), vitrinite reflectance (Ro), Rock Eval and IATROSCAN data of the Estonian Dictyonema Shale (Schovsbo, Wilken and Buchardt, 199)

Core	Nr. Est.	Nr. Denm.	Depth m	TC %	TS %	Ro %	S1	S2	S3	S2/S3	HI	OI	PP	PI	Tmax °C	EOM wt ppm	Satur. HC %	Arom. HC %	NSO compound %	Asphal-tenes %
F-342		ESTO-1	111.30	9.15	2.71		2.41	39.18	1.82	21.53	428	20	41.60	0.06	408	4203	10.4	5.63	28.92	0.99
F-342	845	ESTO-9	111.55	10.93	3.66															
F-342	849	ESTO-10	113.70	7.51	3.51															
F-342	852	ESTO-11	115.30	12.53	3.47															
F-342		ESTO-2	116.15	12.53	2.96		1.62	37.59	3.26	11.53	300	26	39.20	0.04	405	3382	1.32	2.45	22.35	0.65
F-342	856	ESTO-12	116.60	12.10	3.95															
K-14		ESTO-4	69.50	11.92	2.54	0.53	2.49	45.38	3.62	12.54	381	30	47.90	0.05	404	5274	1.13	7.23	33.86	1.72
K-16		ESTO-3	103.60	10.52	2.28		1.39	35.31	3.43	10.29	336	33	36.70	0.04	409	2464	0.82	4.02	18.09	0.58
O189	675	ESTO-5	58.83	4.21	2.99															
O189	682	ESTO-6	59.65	5.99	3.68															
O189	688	ESTO-7	61.20	10.24	2.36															
O189	701	ESTO-8	62.98	10.38	2.96															
P-1949	650	ESTO-13	54.37	6.86	6.10															
P-1949	651	ESTO-14	54.48	11.00	4.78															
P-1949	655	ESTO-15	54.59	11.26	2.93															

Note: Sample ESTO-4 (core K-14) was taken from the impact breccia in the Kardla impact structure (Hiiumaa isl.), 3 km southwest from the core K-16.

HI - Hydrogen Index (S2/TOC)*100, mg HC/g TOC
OI - Oxygen Index (S3/TOC)*100, mg CO2/g TOC
PP - Production Potential S1+S2, mg HC/g sample
PI - Production Index S1/(S1+S2)
S1 - mg HC/g sample
S2 - mg HC/g sample
S3 - mg CO2/g sample

Table 6

The supposed average trace element composition of the Estonian Dictyonema Shale (after Pukkonen, 1989, with some corrections), in ppm

Element	Method	Min	Max	Mean	Zones I	II	III
Li	ESA	10	27	17			
Be	ESA	1	6	2.8			
B	ESA	30	150	75			
Cl	NAA			280			
Sc	NAA	3	15	11			
V	AA	210	1910	910	+	-	+
Cr	ESA	27	89	50			
Co	NAA	4.1	49	12			
Ni	NAA	24	300	120		-	+
Cu	AA	15	290	110			
Zn	AA	<25	7100	100			
Ga	ESA	7	25	15		+	-
Ge	ESA	<1.5	2.4	1.5			
As	ESA	10	350	30		-	+
Se	XRF	1.5	8	2.6			
Br	NAA	1.1	7.3	3.4			
Rb	XRF	42	137	110			-
Sr	XRF	39	192	70		-	+
Y	XRF	11	119	37			+
Zr	XRF	123	373	170			+
Nb	XRF	5	44	24			-
Mo	XRF	3	1990	180			+
Ag	ESA	0.11	2.46	0.7		-	+
Cd	AA	1	6.2	2.9			
In	ESA			<1.6			
Sn	ESA	2.5	14	4.6			
Sb	NAA	<2	100	10			
Cs	NAA	1.7	6.9	5			
Ba	NAA	300	1050	500			
La	NAA	13	140	40			
Ce	NAA	53	170	85			
Nd	NAA	<0.5	18.3	8.4			
Sm	NAA	<0.06	20.8	6.8			
Eu	NAA	0.66	5.02	1.4			
Gd	ESA	<10	15	<10			
Tb	NAA	0.39	2.8	1.2			
Dy	ESA	<6	15	<6			
Ho	ESA	<6	10	<6			
Er	ESA	<4	10	<4			
Yb	NAA	0.9	10	2.7			
Lu	NAA	0.3	2.3	0.7			
Hf	NAA	2.3	6.1	3.3			
Ta	NAA	0.5	1.2	0.8			
W	NAA			0.9			
Re	AA	<0.02	1.33	0.1		-	+
Au	NAA	<0.02	0.25	0.03			
Hg	AA	0.72	1.06	0.84		-	+
Tl	ESA	2.8	27.5	15			
Pb	XRF	28	1050	140		-	+
Bi	ESA	<1	1.1	1?			
Th	XRF	7	17	12			
U	XRF	3	1200	106		-	+

Methods:

ESA - emission spectroscopy analysis
NAA - neutron-activation analysis
XRF - X-ray fluorescence spectroscopy
AA - atom-adsorbtsion analysis

+ , - - higher or lower concentration in the geochemical provinces: I- western, II- central, III- eastern zone

Table 7

Trace element composition of the Estonian Dictyonema Shale from the selected cores (in ppm)

Core	Zone	Depth	Nr.	X-ray fluorescence					Emission spectroscopy											
				U	Mo	Sr	Rb	Pb	Cr	Co	Ni	Cu	Zn	Ga	Sn	Ag	Y	Yb	Sc	B
F-342	I	111.00	844	92	128			143	60	12	100	110	<30	15	0.5	0.7	30	3.0	10	60
F-342	I	111.55	845	85	122			129	60	10	80	150	30	17	3.0	0.7	40	3.0	10	60
F-342	I	112.20	846	82	142			128	49	6	80	110	<30	12	2.7	0.8	30	3.0	10	80
F-342	I	112.80	847	107	180			89	42	10	90	90	30	15	3.0	0.8	25	3.0	10	80
F-342	I	113.35	848	158	258			139	42	10	90	90	30	12	3.0	0.9	30	3.0	8	80
F-342	I	113.70	849	204	360			150	42	10	80	80	<30	10	2.5	1.1	60	4.0	8	100
F-342	I	114.10	850	148	260			111	60	11	90	80	<30	17	2.7	0.8	25	2.5	6	80
F-342	I	114.70	851	136	260			113	49	10	90	80	1230	15	3.0	0.6	30	3.0	10	100
F-342	I	115.30	852	128	248			112	49	9	120	80	350	15	2.7	0.7	40	3.0	6	60
F-342	I	115.90	853	136	263			93	49	10	100	80	1230	15	3.0	0.7	30	3.0	8	80
F-342	I	116.35	854	155	335			88	40	8	70	60	<30	15	2.0	0.5	25	2.0	6	60
F-342	I	116.60	856	194	518			139	40	8	110	80	40	15	3.0	1.0	40	4.0	6	40
0189 (V)	II	58.71	672	30	12	67		36	49	27	60	80	40	17	3.5	0.2	40	4.0	10	100
0189 (V)	II	58.83	675	25	11	76		46	49	20	60	80	60	20	3.0	0.3	40	4.0	10	100
0189 (V)	II	58.98	678	51	10	95		38	49	12	40	90	60	17	3.5	0.2	40	3.0	6	150
0189 (C)	II	59.20	680	30	4	79		26	89	10	40	60	60	22	4.9	0.1	20	4.0	10	200
0189	II	59.65	682	16	13	67		75	49	9	40	100	40	22	2.7	0.3	30	3.0	10	100
0189	II	59.95	683	17	12	67		94	49	12	50	100	600	20	3.0	0.3	30	2.5	10	150
0189	II	60.25	684	14	14	63		106	37	14	60	90	90	16	3.0	0.3	40	4.0	15	100
0189	II	60.55	685	21	13	69		80	49	12	60	100	270	15	3.2	0.3	30	3.0	10	150
0189	II	60.90	687	47	83	65		131	49	15	90	90	1500	17	3.0	0.8	30	4.0	10	100
0189	II	61.20	688	53	89	69		93	49	15	80	90	200	15	2.7	0.6	20	4.0	10	150
0189	II	61.55	689	44	246	72		101	40	10	70	120	800	15	2.5	0.6	40	3.0	10	100
0189 (K)	II	62.03	695	77	37	85		95	57	12	80	90	60	15	3.5	0.7	25	4.0	8	150
0189 (K)	II	62.27	697	78	162	78		132	40	12	80	80	<30	12	0.5	0.7	30	3.0	6	60
0189 (K)	II	62.72	699	188	1540	80		113	57	17	120	80	40	15	2.5	1.4	60	8.0	10	40
0189 (K)	II	62.98	701	207	2050	78		121	49	17	100	110	30	15	2.5	1.4	40	6.0	10	40
0189 (K)	II	67.62	718	15	250			106	40	15	50	110	30	24	2.5	0.3	25	3.0	8	150
946	III	33.20	62	8	24	60	110	75	42	12	70	80	40	12	3.0	0.5	15	4.0	8	35
946	III	33.50	64	222	770	64	116	79	35	10	100	60	100	15	4.0	0.7	40	4.0	10	80
946	III	33.80	65	200	730	61	114	74	38	9	90	90	80	12	3.0	0.6	30	3.0	9	69
946	III	34.10	66	245	460	63	119	81	35	9	80	100	80	10	0.5	0.7	60	3.0	8	60
946	III	34.25	67	122	410	76	96	118	32	9	90	50	<30	10	1.5	0.7	100	6.0	10	60
946	III	34.60	68	103	715	53	114	155	40	10	140	100	30	12	3.0	0.7	25	4.0	8	80
P-1949	III	54.37	650	323	647	192	84	110	40	20	120	80	<30	15	2.0	0.8	60	6.0	8	80
P-1949	III	54.48	651	241	969	102	105	239	42	12	200	70	<30	15	3.0	0.7	30	6.0	10	60
P-1949	III	54.59	653	224	249	75	116	224	49	20	200	120	40	12	2.0	1.2	40	6.0	8	150
P-1949	III	54.62	654	221	211	101	86	134	44	19	280	200	30	14	0.5	1.4	89	8.0	8	80
P-1949	III	54.75	655	346	1132	80	127	96	69	12	100	100	30	15	3.0	1.2	40	4.0	8	100

(V) - argillite interlayers in the glauconitic sandstone of the Varangu Formation

(C) - clay of the Varangu Formation

(K) - argillite interlayers in the phosphatic sandstone of the Kallavere Formation

Geochemical provinces: I- western, II- central, III- eastern