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ESTONIAN GRAPTOLITE ARGILLITES REVISITED: A FUTURE RESOURCE?

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Abstract. *The occurrence of Cambrian to Ordovician organic-rich black shale deposits has been known in Baltoscandia, including Estonia, for a long time. The Estonian graptolite argillite (GA) shows high to very high concentrations of U (800 ppm), Mo (1000 ppm), V (1600 ppm), Ni and other heavy metals, and are rich in N, S and O, unlike normal shale. The present study provides a new estimate of the total GA tonnage in Estonia, including estimates for U, Zn and Mo. The total preserved volume of GA is about 31.92 billion m^3, while about 9.02 billion m^3 has been eroded between the Estonian mainland and western islands. The total mass of GA is about 67 billion tonnes at a specific gravity of 2.1 g/cm^3. About 18.93 billion tonnes of GA has been eroded and re-deposited, including 1.8 million tonnes of U, 22.7 million tonnes of Zn, 6.6 million tonnes of Pb, 4.4 million tonnes of Mo and 13.3 million tonnes of V. In Estonian GA the total U_3O_8 reaches 6.7 million tonnes, ZnO 20.6 million tonnes and MoO_3 19.1 million tonnes as calculated using a cell size of 400 m.*

Keywords: *graptolite argillite, black shale, metals, resource, Estonia.*

1. Introduction

The occurrence of Middle Cambrian to Late Ordovician organic-rich black shale deposits in an extensive area of Sweden (alum shale [1]), the Oslo region [2], Bornholm [3], Estonia (known as graptolite argillite, "Dictyonema shale" [4], and kukersite as proper oil shale), Poland [5] and North-West Russia [6] has been known for a long time.

Alum shale, as well as graptolite argillite, contains remarkably high concentrations of trace metals such as U, Mo, V and Ni, but may also be locally enriched with rare earth elements (REE), Cd, Au, Sb, As, Pt [7]. The beds have historically been exploited for uranium production in Sweden and Estonia. Also, a high content of potassium, sulphur and organic matter is

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characteristic of those beds. Kerogen in black shale is of algal origin and the content of total organic carbon is mostly between 10 and 25 wt% [1]. The mineral matter of black shale is dominated by clay minerals – illite-smectite and illite [8, 9]. Distinctive of black shale is its high concentration of pyrite, which, together with kerogen, is thought to be the main carrier of some rare elements. Alum shale and graptolite argillite form patches over extensive areas in the outskirts of the Baltica palaeocontinent [1]. Possible spatial continuities of those complexes are graphitic phyllites, which are found in the tectonically disrupted allochthonous and autochthonous Caledonian complexes in central and northern Sweden and Norway. The metal-enriched phyllites exhibit similar geochemical signatures to the unmetamorphozed black shale of Baltoscandia [10]. These geochemical similarities suggest that the organic-rich muds might have accumulated over a wide geographic area and under fairly different depositional conditions – from pericratonic shallow marine settings to continental slope environments. The Fennoscandian black shale and Estonian graptolite argillite (GA) can thus be treated as metal ore and a twofold source of energy (including U and shale oil), the rocks have a high scientific and significant economic value.

Despite the long history of exploration and exploitation of Baltoscandian black shale and graptolite argillite [1, 11–14], the origin of high metal concentrations of the beds has remained controversial. Also, the volume of shale and argillite and the distribution pattern of metals are not well known.

Previous estimates of the graptolite argillite tonnage in Estonia range from 60 billion [15] to 70 billion tonnes [16]. GA occurs throughout Northern Estonia in an area covering about 11,000 km^2 (Fig. 1). However, large quantities of GA have been eroded away in the northern and north-western parts of Estonia. The extent of GA towards the north is unknown, but the amount of the eroded material can be interpolated and calculated between the Estonian mainland and Hiiumaa Island.

The present study provides a new estimate, based on calculations using ESRI ArcInfo software, of the total GA resource in Estonia, and of the GA that has been eroded away between the Estonian mainland and Hiiumaa. Also, based on the new estimates, some total metal amounts have been calculated, and the GA thickness and metal concentration dynamics shown.

2. Geological overview of Estonian graptolite argillite

The Lower Ordovician organic-rich marine metalliferous black shale – graptolite argillite (GA) lies beneath most of Northern Estonia (Fig. 1). Earlier it was called „Dictyonema shale“, „Dictyonema argillite“ or „alum shale“. The name *dictyonema* came from the benthonic root-bearing *Dictyonema flabelliforme*, which afterward turned to planktonic nema-bearing *Rhabdinopora flabelliformis* [17]. In this study, the term *graptolite argillite* is used. Graptolite argillite is fine-grained, unmetamorphosed,

(sub)horizontally lying organic-rich (8–20%) lithified clay and argillite (Türisalu Formation) belonging to the group of black shales of sapropelic origin [15]. GA is characterized by high to very high concentrations of U (up to 1200 ppm; unpublished data by A. Soesoo; database of the Institute of Geology, Tallinn University of Technology (TUT)), Mo (1000 ppm), V (1600 ppm), Ni and other heavy metals, and is rich in N, S and O [18, 19, 20], unlike normal sedimentary shales. High concentrations of certain elements may be potentially useful or hazardous. During the Soviet era, GA was mined for uranium production at Sillamäe, in North-East Estonia, between 1948 and 1952 [16]. A total of 22.5 tonnes of elemental uranium was produced from 271,575 tonnes of GA from an underground mine near Sillamäe. Between 1964 and 1991 approximately 73 million tonnes of GA was mined from the covering layer of phosphorite ore at Maardu, near Tallinn. GA was mixed up with other overlying deposits, such as carbonate rocks, sandstone, glauconite sandstone, and Quaternary sediments, and piled in waste heaps.

Although the tonnage of GA surpasses that of kukersite, its quality is poor for energy production purposes. The calorific value of GA ranges from 4.2 to 6.7 MJ/kg [18], and the Fischer Assay oil yield is 3–5% (for Estonian kukersite it is about 30–47%, for example [16]). The laboratory moisture content of fresh GA ranges from 11.9 to 12.5 %, while the average composition of the combustible part is as follows: C 67.6%, H 7.6%,

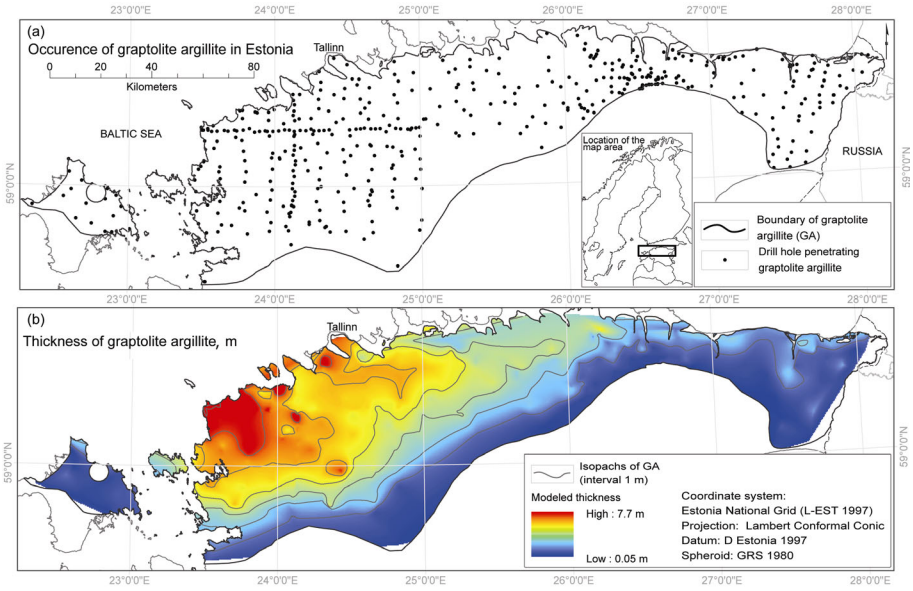

Fig. 1. (a) Location map of Estonian GA and location of the drill holes penetrating the graptolite argillite layers. (b) Modeled thickness of GA based on the studied drill holes (thickness grid created by the Natural Neighbour interpolation method, grid cell size 400 m).

O 18.5%, N 3.6% and S 2.6% [21]. However, considering it is a low-grade oil source, its potential oil yields are about 2.1 billion tonnes [16]. Scandinavian black shale together with Estonian GA is considered to be a potential energy reserve for the future.

The specific gravity of GA mostly varies between 1.8 and 2.5 g/cm^3 [15] (see also Fig. 2). The pyrite content of GA is also highly variable, from 1.5 to 9.0%, but mainly from 2.4 to 6%. Pyrite forms fine-crystalline disseminations, thin interlayers and concretions with different forms and sizes. The diameter of concretions is usually 2–3 cm. Some concretions are complex in structure and contain crystals of galenite, sphalerite and calcite. Sometimes pyrite comprises marcasite. Under atmospheric conditions, this part of pyrite is rapidly replaced by jarosite and anhydrite.

The mineral composition of GA is dominated by K-feldspars, quartz and clay minerals. In the lateral as well as vertical dimension the contents of major rock-forming minerals show slight, but pronounced variation patterns [20]. GA also contains light-brown phosphatic ooids. The rock contains accessory amounts of zircon, tourmaline, garnet, rutile, calcopyrite and glauconite, whereas corundum, amphiboles and disthen have been preserved in Western Estonia [22]. In general, the higher degree of sulphide mineralization within GA is associated with the occurrence of silt interbeds. Those interbeds might also contain a higher amount of other minor authigenic compounds typical of GA – phosphates (mainly apatite as biogenic detritus and nodules), carbonates (calcite and dolomite as cement and concretions), barite and glauconite. Carbonate minerals occur sporadically. They cement the terrigenous material in patches or form concretions: calcite occurs in the western sections and dolomite in the eastern ones. The occurrence of phosphatic cement, or even lumps of the earlier formed chemogeneous phosphatic layer, is characteristic of some silt interlayers [23]. Besides the highly resistant accessory terrigenic phases, a considerable abundance of micas in the GA beds has been documented [23, 20, 24]. Rare apatite, titanite, alkali amphibole (aegirine), baryte and diopside have also been found in GA [25].

Some sections of GA, especially in Eastern Estonia, contain small lense- or nest-shaped silica interlayers. The interlayers contain white or grey porous silica and terrigeneous quartz with the grain size of fine sand [23]. The average quartz content of GA gradually rises eastward with the corresponding decrease in clay minerals. In North-East Estonia, the argillite complex is intercalated with numerous quartzose silt beds [23].

Organic matter (OM), constituting about 15–20% of GA, is sapropelic in origin [8] and rich in N, S and O. The ratio of C to H in OM is about 9. OM is fine-dispersed and spread rather evenly. The OM concentration is the lowest in those parts of the sections where the interlayers of carbonate minerals or silt are high. The concentration of S ranges between 2 and 6%, of which 0.6–0.8% is comprised of OM, ca. 0.3% is sulphatic, and the remaining part is sulphitic S [13].

Recently, an XRD analysis of selected GA samples from the Pakri outcrop was performed [20]. The study confirmed the presence of K-feldspar (sanidine), illite (illite-smectite, micas), quartz, pyrite, marcasite, apatite, calcite, dolomite, galena and chlorite. The SEM analysis revealed high micrometer-scale morphological heterogeneity in the examined samples.

The chemical composition of GA is definitely of great interest and its specificities have been known for nearly a century. Besides the high concentration of a number of metals, its potassium and sulphur contents are much higher and the content of sodium and calcium lower than in average clays and shale. The concentration of K_2O in GA is higher than could be expected, based on the composition of known shale-forming minerals [15]. With the increase in the volume of silt interlayers from the west to the east, the concentration of SiO_2, CaO and P_2O_5 increases, while that of Al_2O_3, K_2O and MgO decreases. Based on previous geochemical exploration [18, 20], three geochemical zones have been distinguished in the Estonian GA – Western, Central and Eastern zones. These zones differ mainly in the concentration of metals that are characteristic of GA – Mo, V, U. However, based on a recent study [20] it was shown that the distribution of metals in GA has a more complex pattern. The study dealt with two vertical sections of graptolite argillite (Pakri in North-Western and Saka in North-Eastern Estonia) and indicated the existence of pronounced fine-scale trace metal variability and the remarkably different behaviour of trace elements. The content of enriched elements was shown to change greatly over the examined sections [20]. For example, an elevated abundance of a number of other trace metals, e.g. Pb, Zn, Cd, Cu, As and La, was detected in samples with an enhanced content of sulphur or phosphorus. The high variability of the trace metal composition of GA, including heterogeneous REE patterns, may point to the polygenetic nature of metal compositions, apparently formed as the cumulative product of multistage evolution. Currently, our knowledge about metal distribution, and especially its origin, is rather fragmentary and a multidisciplinary exploration is needed for adequately predicting potential metal resources of GA in the future.

3. Resource estimate of Estonian graptolite argillite

Most of the geological information on GA is obtained from basement mapping and exploration projects conducted by the Geological Survey of Estonia, which started in the 1950s. The vast amount of detailed information on the GA lithology and geochemistry was collected during the prospecting of Estonia's phosphorite resources [15]. The previous estimates of the graptolite argillite resource in Estonia range from 60 billion [15] to 70 billion tonnes [16] and little is known about the calculation methods and initial data (number of drill cores, etc.) used. Although there has practically been no new data during the last two decades, the GIS-based methods now

allow us to obtain more precise estimates of the total resource and metal distribution.

In this work, a new estimate of the GA resource in Estonia is presented. The Natural Neighbour interpolation method in the ArcGIS Spatial Analyst (Environmental Systems Research Institute, Inc. (ESRI), versions 9.3.1 and 10.1) software was used in the present assessment for generating resource maps and computing resource volumes. The algorithm used by the Natural Neighbour interpolation tool finds the closest subset of input samples to a query point and applies weights to them based on proportionate areas to interpolate a value [26]. The value in an unsampled location is computed as a weighted average of the nearest neighbour values with weights dependent on areas or volumes rather than distances. It does not infer trends and will not produce peaks, pits, ridges, or valleys that are not already represented by the input samples. However, the surface grid and volume estimation results obtained by the Natural Neighbour interpolation method have been compared with other geo-statistical methods, such as Kriging (in ArcGIS Spatial Analyst, ESRI, and Geochemistry for ArcGIS, Geosoft Inc., version 2.1). Kriging is based on statistical models that include the statistical relationships among the measured points. The Kriging method [27, 28] assumes that the distance or direction between sample points reflects a spatial correlation that can be used to explain variation in the surface. Generally, Kriging is most appropriate when you know that there is a spatially correlated distance or directional bias in the data. Kriging seems to be appropriate for phenomena with a very strong random component or for the estimation of statistical characteristics (uncertainty). However, most of the surfaces or volumes in the sedimentary environment are neither stochastic nor elastic media, but are the result of natural (e.g. sediment fluxes, deposition speed, hydromechanics, etc.) processes. Therefore, the Natural Neighbour interpolation method is thought to be more appropriate in case of the GA resource spatial/volume calculations in the present geological situation. In this case, the gridded GA thickness surface created by the Kriging method is slightly wider and calculated volumes are slightly higher (less than 1%).

On the other hand, average metal concentrations in sedimentary sections may be more stochastic, and there may not be a clear special relationship between the element concentrations as well as between the elements. In the given case, the metal concentrations in the initial data represent the average of the entire drill core. As seen from the calculated thickness map (Fig. 1), there is quite a large variation in the thickness of GA, ranging mostly from 0.5 m to 6 m. The large variability in the thickness of GA thus excludes making a direct comparison of elemental averages between the drill cores. This is the reason why metal concentration grids are calculated using the Kriging method.

As initial data, the combined database of 468 drill cores (Geological Survey of Estonia and Estonian Land Board database, see at www.maaamet.ee) has been used. A vast amount of GA has been eroded and

carried away between the West-Estonian islands (Figs. 1 and 3). An attempt has been made to calculate the volume and tonnage of this eroded material by an extrapolation of GA thickness data. In this extrapolation, the northern boundary has been fixed at the current erosional line of the Türisalu strata, as no knowledge exists about the northern extension of the Estonian-(Russian) graptolite argillite basin.

The estimated area of Estonian GA on the mainland and islands is about 12,210 km^2, with the corresponding volume of 31.92 billion m^3 (Fig. 2). The estimated eroded area between the West-Estonian islands (Fig. 3) is about 3,190.4 km^2 with the corresponding volume of 9.02 billion m^3. The calculated total volume of Estonian GA (on the mainland and in the eroded part in Western Estonia) extends up to 40,935 km^3 with an area of more than 15,400 km^2. For instance, Estonian oil shale – kukersite occupies an area of 2,884 km^2, and its reserves (active and passive) in 2012 were about 4.774 billion tonnes [29]. In order to calculate the tonnage of GA, the value of specific gravity is needed. It is known [15] that the specific gravity of graptolite argillite varies to a great degree, mostly between 1.8 and 2.5 g/cm^3. So, assuming an average specific gravity of 1.8 g/cm^3, the tonnage of GA is about 57.45 billion tonnes, while in case of 2.5 g/cm^3 the mass is 79.80 billion tonnes (Fig. 2). Assuming the average specific gravity to be 2.1 g/cm^3, the tonnage of GA is about 67 billion tonnes, which is in between the earlier estimates of 60 to 70 billion tonnes.

In a similar way we can calculate the tonnage of eroded material, in between the Estonian mainland and Hiiumaa Island. Assuming the average specific gravity of 1.8 g/cm^3, the tonnage of the eroded GA is about 16.23 billion tonnes, while 2.5 g/cm^3 gives 22.54 billion tonnes and 2.1 g/cm^3

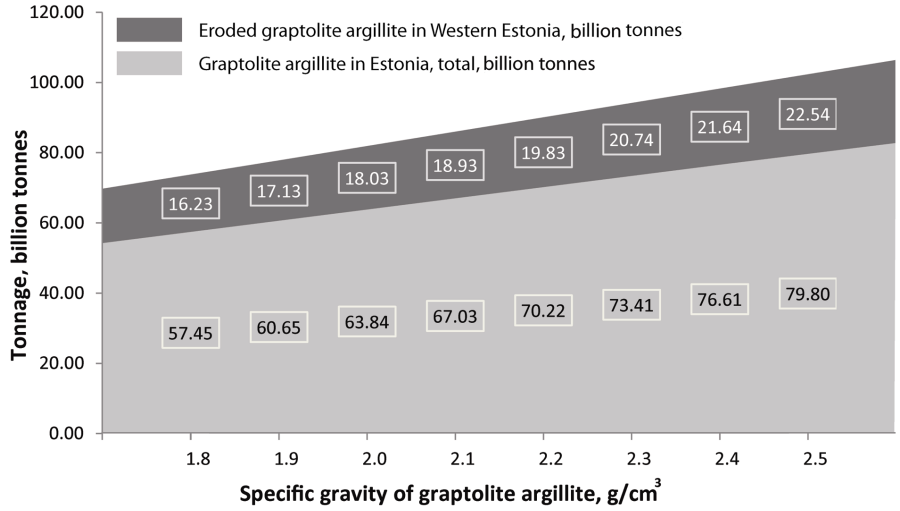

Fig. 2. Calculated volume and tonnage of Estonian GA (in situ and in an eroded area between the Estonian mainland and West-Esonian islands) as a function of specific gravity.

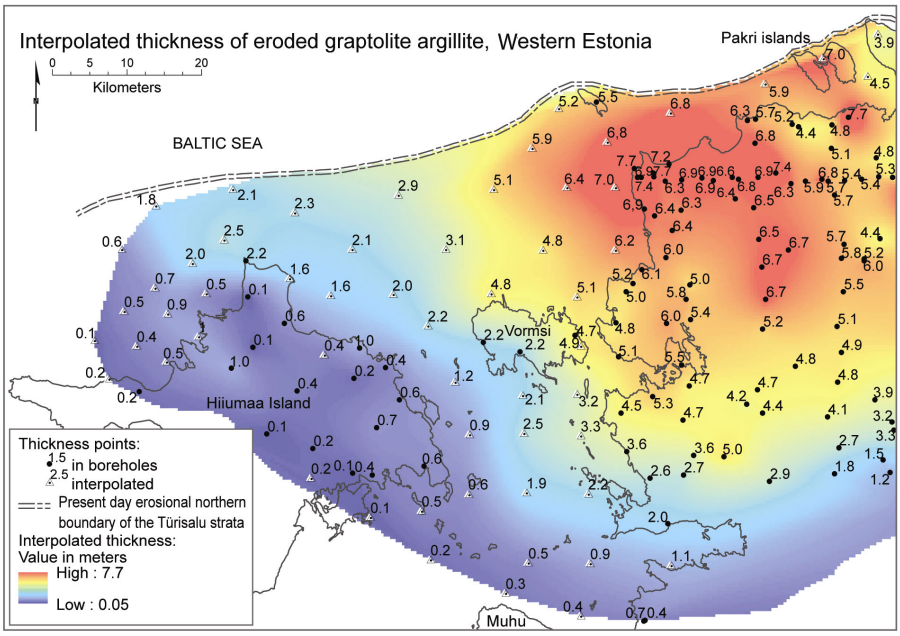

Fig. 3. Interpolated thickness grid of GA between Western Estonia and the islands.

gives about 18.93 billion tonnes (Figs. 2 and 3). This is an enormously large amount of material.

Very little is known about the timing and cause of erosion in Northern and Western Estonia. The most prominent feature of this erosion is the North Estonian Klint. One hypothesis which explains the klint formation is related to a large, old, possibly Late Cenozoic, river system [30, 31]. A vast amount of terrigenous sediments is known to exist in the North Sea with an area of 100,000 km^2 [32]. The Eridanos river system, which drained most of North and North-Western Europe, developed during the Late Cenozoic as a result of the simultaneous uplift of the Fennoscandian Shield and the accelerated subsidence in the North Sea Basin. The erosion of the area to the north of the present mainland of Estonia and Western Estonia is most likely attributable to the Pra-Neva River, the tributary of the Eridanos.

It is well known that the fluvial deposits of Miocene to Early Pleistocene Age in Germany and the Netherlands were transported to the delta of the Eridanos River System [33]. However, the exact provenance of this sedimentary material continues to be a subject of discussion. Some of the sand from the Fennoscandian crystalline rocks, Ordovician terrigenous material, erratics with well-defined Ordovician fossils, which are similar to those in Northern Estonia and the St. Petersburg region (Russia) [33], are known to exist within the sediments in the Eridanos fluvio-deltaic system in the North Sea area, the Netherlands and Germany. Most likely, the erosion of the Lower Paleozoic sections in Western Estonia, including graptolite argillite,

is related to those processes which generated the klint. The exact timing of those processes remains unknown, however, the original erosional processes were most likely active during the Late Miocene (some 20 to 5.332 million years ago) to Pliocene (5.332 to 2.588 million years ago). Some of the material may have been re-deposited during the Quaternary.

Knowing the volume and average chemical composition of the eroded graptolite argillite (Figs. 2 and 3), the amount of eroded, partly dissolved and redeposited metals can be calculated. Based on the extrapolated GA thickness and average metal contents in the drill cores from the most westerly part of Estonia, and from Vormsi and Hiiumaa islands, the total amount of uranium (elemental U) that has been eroded and re-deposited reaches 1.798 million tonnes (at an average content of 95 grams per tonne), zinc (Zn) 22.716 million tonnes (average 1200 g/t), lead (Pb) 6.625 million tonnes (average 350 g/t), molybdenum (Mo) 4.448 million tonnes (average 235 g/t) and vanadium (V) 13.251 million tonnes (average 700 g/t).

As for volume, the contribution of graptolite argillite from Western Estonia to the Eridanos sedimentary budget is not high, considering the overall 62,000 km^3 of sediments in the Southern North Sea Basin alone [32] versus 9,015 km^3 derived by erosion from Western Estonia. However, the metal contribution of GA to the overall Eridanos sedimentary budget is remarkable. The total amount of the elements that have now been re-deposited is extremely large. One can only imagine approximately 1.8 million tonnes of uranium and 13 million tonnes of vanadium incorporated into sediments somewhere below the Holocene sediments of the North Sea!

4. Estonian graptolite argillite as a metal resource

The vertical and lateral geochemical heterogeneity in GA has not been well understood, especially the scale of the heterogeneity and specific distribution pattern of elements. Recently, a study on vertical geochemical heterogeneity based on two cross-sections has showed distinctive differences between the eastern and western parts of GA [20]. The previous geochemical explorations [20] revealed that the studied sequences demonstrate pronounced vertical variations in U, V, Mo and Zn concentrations. The common distinctive feature of the sections is the occurrence of highest concentrations of the elements in the lower half of the section.

The distribution of V, Mo and Pb in the Estonian GA has been modeled in an earlier study [20] and the U distributions have been shown in Figure 4. The initial data were selected from the database of the Geological Survey of Estonia. This elemental concentration data represents the average concentrations in GA in the drill core. The central and western parts of the Eastern Zone show the highest concentrations for V and Mo, whereas V is also high in the southern part of the Eastern and Central Zones. Uranium shows the highest concentrations in the most easterly part of Estonia, while in Western

Estonia the concentrations show medium values and the lowest values are characteristic of the Central Zone (Fig. 4). The U distribution has not been modeled in the Estonian islands due to a small number of analyses (only 3 cores). The high concentrations in the south-western corner may be an artifact of the model, since there are only a few drill cores available and those show locally high contents of U. Generally, it can be concluded that the concentration of most of the metals (except Zn) is relatively low in the Central Zone of the GA area.

However, it is important to emphasize that the available chemical data is relatively unevenly distributed across the area and the present geochemical generalization is informative, and must be taken with caution. There is very little data on the southern margin of the GA area, so the concentrations may vary, but due to its limited thickness (less than 0.5 m); the total elemental amounts have not affected the calculations very much.

With respect to the standard values, such as PAAS and NASC, the Estonian GA is extremely rich in U and V. For example, the average U concentration in the Saka section (267 ppm) is a hundred times higher than the corresponding values for NASC. In case of V, there is a nine-fold difference between the concentrations in NASC and the average concentrations detected, for example, in the Saka section, in Eastern Estonia (190 ppm; [20]). In general, the U content of GA shows quite a strong positive correlation with the organic matter content, which most likely indicates early fixation via metal-organic complexes. At the same time, the correlation of P_2O_5 with other enriched trace elements, such as U, was not detected.

In general, the dominance of common marine redox-sensitive elements among the enriched metals in GA may favor a syngenetic enrichment as the major process of trace metal sequestration. The recent data [20] indicate that besides the elements, which are well known in the partitioning in the marine systems, the Estonian GA sporadically presents elevated levels of certain trace elements such as PGE and W, which are generally characterized by a

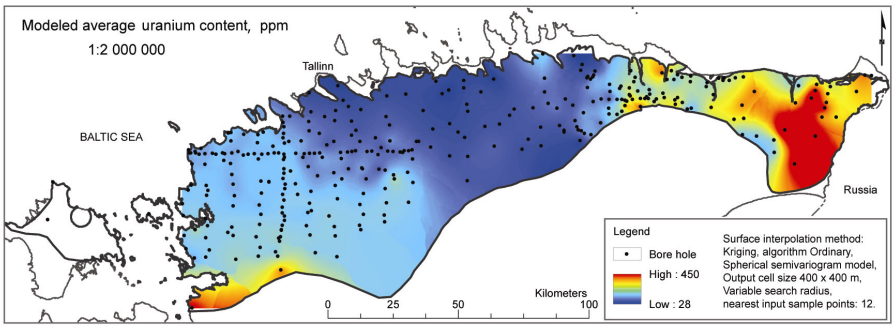

Fig. 4. Modeled uranium content in Estonian GA based on calculated average drill core analyses (data: Geological Survey of Estonia; www.maaamet.ee). Element concentration surface modeled by the Ordinary Kriging interpolation method.

very low abundance in the crust and modern marine sediments. The accumulation of such minor compounds in GA underlines the possible role of external input of metals into the sedimentary or diagenetic environment.

As average metal concentrations are very useful in indicating "poor" and "rich" deposits, the total content of a certain element depends on the thickness of the deposit layer. In order to calculate the total amount of the element/metal based on square meters, ESRI ArcGIS software was employed. The total amount of uranium, zinc and molybdenum in the Estonian GA is shown in Figure 5. This calculation is based: 1) on the element/metal grid which shows the element distribution in ppm (e.g. Fig. 4 for U); 2) on an interpolated grid of the GA thickness, in meters; 3) on an assumption that the average specific gravity of GA is 2.1 g/cm^3. As the element/metal and thickness grids were calculated using the cell size of 400 m × 400 m, the same cell size was used for the calculation of the total amount of element/metal.

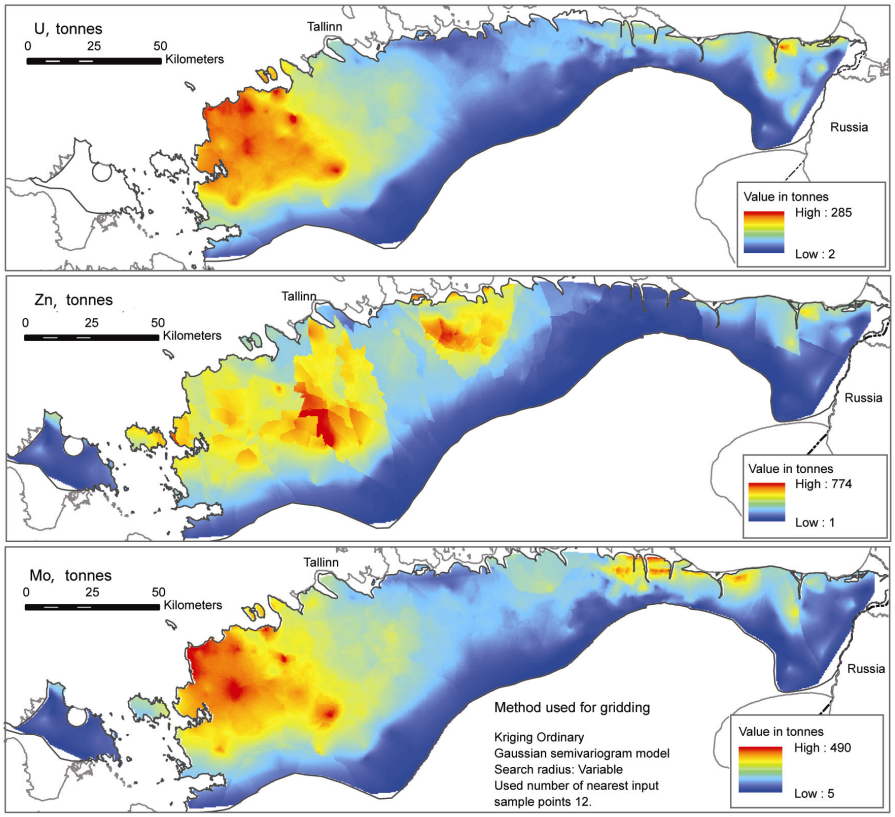

Fig. 5. U, Zn and V tonnage (in tonnes) model in the 400 m × 400 m cell at the modeled thickness of graptolite argillite.

The U, Zn and Mo tonnage in the 400 m × 400 m cell (at the corresponding thickness of GA) is shown in Figure 5. These calculations allow for the provision of a more realistic total amount of metals in the Estonian GA (not just based on an average concentration value). The calculated amount of U is about 5.67 million tonnes (6.68 million tonnes as U_3O_8), Zn is 16.53 million tonnes (20.58 million tonnes as ZnO) and Mo is 12.76 million tonnes (19.15 million tonnes as MoO_3). The highest studied element amounts (Fig. 5) show a somewhat similar pattern – Western Estonia has the highest potential, especially for U and Mo. However, there are also distinctions between those elements. For example, the Central Zone, where the enrichment is the lowest, still shows high amounts of Zn. As an economic baseline, the pure metal market value can be calculated. The market value of these metals is high: about € 460 billion for uranium, € 30 billion for zinc and about € 350 billion for molybdenum, considering the average market prices in April 2013. It must be mentioned that this value does not encompass grade, economic viability assessment, market development trends, production cost or any other related cost but provides only some comparative resource value. At the moment, the Estonian GA may be classified as marginal to sub-marginal economic quantity. Moreover, since a simple, environmentally-friendly and economic technology has yet to be developed for the co-extraction of most of the enriched elements from GA, its economic value remains theoretical.

5. Conclusions

The occurrence of the Middle Cambrian to Upper Ordovician organic-rich black shale deposits in an extensive area of Baltoscandia has been known for a long time. Alum shale as well as Estonian graptolite argillite (GA) contains remarkably high concentrations of trace metals such as U, Mo, V and Ni, but may also be locally enriched with REE, Cd, Au, Sb, As and Pt.

The total estimated area (by ArcGIS software) of the Estonian GA on the mainland and islands is about 12,210 km^2, with the corresponding argillite volume of about 31.92 billion m^3. The estimated eroded area between the West-Estonian islands is about 3,190 km^2 with the corresponding eroded material volume of 9.02 billion m^3. Thus, the calculated total volume of Estonian GA (on the mainland and in the eroded part in Western Estonia) extends up to 40,935 km^3. In order to calculate the tonnage of GA, the value of the specific gravity is needed. It is known [15] that the specific gravity of graptolite argillite varies to a great degree, mostly between 1.8 and 2.5 g/cm^3. Assuming an average GA specific gravity of 2.1 g/cm^3, the amount of GA is about 67 billion tonnes. The amount of possibly eroded/ dissolved material between the Estonian mainland and Hiiumaa Island is about 18.9 billion tonnes. This is an extremely large amount of material. Based on the extrapolated GA thickness and average metal contents in the

drill cores from the most westerly part of Estonia, Vormsi and Hiiumaa islands, the total amount of the uranium that has been eroded and redeposited/ dissolved reaches 1.798 million tonnes (at an average content of 95 grams per tonne), zinc (Zn) 22.716 million tonnes (average 1200 g/t), lead (Pb) 6.625 million tonnes (average 350 g/t), molybdenum (Mo) 4.448 million tonnes (average 235 g/t) and vanadium (V) 13.251 million tonnes (average 700 g/t).

The U, Zn and Mo tonnage is calculated in the cell of 400 m × 400 m (at the corresponding thickness of GA). These calculations allow us to provide a more realistic total amount of metals in the Estonian GA (based not just on an average concentration value). The calculated amount of U_3O_8 is about 6.68 million tonnes, ZnO is 20.58 million tonnes, and MoO_3 is 19.15 million tonnes. The highest studied element amounts (Fig. 5) show a somewhat similar pattern – Western Estonia has the highest potential, especially for U and Mo. However, there are also distinctions between those elements. For example, the Central Zone, where the enrichment is the lowest, still shows high amounts of Zn. However, since a simple, environmentally-friendly and economic technology has yet to be developed for the co-extraction of most of the enriched elements from GA, its economic value remains theoretical.

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REFERENCES

1. Andersson, A., Dahlman, B., Gee, D. G., Snäll, S. *The Scandinavian Alum Shales*. Sveriges Geologiska Undersöknin,. 1985, **56**, 1–50.
2. Henningsmoen, G. Cambro-Silurian deposits of the Oslo region. In: *Geology of Norway* (Holtedahl, O., ed.). Norges geologiske undersmkelse, 1960, **208**, 130–150.
3. Poulsen, V. Cambro-Silurian Stratigraphy of Bornholm. *Medd. Dansk Geol. Foren.*, 1966, **16**, 117–137.
4. Männil, R. *Evolution of the Baltic Basin during the Ordovician*. Valgus, Tallinn, 1966, 200 pp (in Russian).
5. Szymanski, B. The Tremadoc and Arenig sediments in the Bialowieza area. *Pr. Inst. Geol.,* 1973, **69**, 1–92 (in Polish).
6. Baturin, G. N., Ilyin, A. V. Comparative geochemistry of shell phosphorites and Dictyonema shales of the Baltic. *Geochem. Int.*, 2013, **51**(1), 23–32.
7. Loog, A., Petersell, V. The distribution of microelements in Tremadoc graptolitic argillite of Estonia. *Acta et Comm. Univer. Tartuensis,* Tartu, 1994, **972**, 57–75.

8. Hints, R., Hade, S., Soesoo, A., Voolma, M. Depositional framework of the East Baltic Tremadocian marginal black shale revisited. *GFF*, 2014, (in press).
9. Lindgreen, H., Drits, V. A., Sakharov, B. A., Salyn, A. L., Wrang, P., Dainyak, L. G. Illite-smectite structural changes during metamorphism in black Cambrian Alum shales from the Baltic area. *Am. Mineral.*, 2000, **85**(9), 1223–1238.
10. Sundblad, K., Gee, D. G. Occurrence of a uraniferous-vanadiniferous graphitic phyllite in the Köli Nappes of the Stekenjokk area, central Swedish Caledonides. *GFF*, 1985, **106**, 269–274.
11. Heinsalu, H., Bednarczyk, W. Tremadoc of the East European Platform: lithofacies and palaeogeography. *Proc. Acad. Sci. Estonian SSR. Geology,* 1997, **46**(2), 59–74.
12. Leventhal, J. S. Comparative geochemistry of metals and rare earth elements from the Cambrian alum shale and kolm of Sweden. *Special Publication of the International Association of Sedimentologists*, 1990, **11**, 203–215.
13. Petersell, V., Mineyev, D., Loog, A. Mineralogy and geochemistry of obolus sandstones and dictyonema shale of North Estonia. *Acta et Comm. Univer. Tartuensis,* Tartu, 1981, **561**, 30–49 (in Russian).
14. Thickpenny, A. The sedimentology of the Swedish Alum Shales. In: *Fine Grained Sediments: Deep Water Processes and Environments* (Stow, D. A. W., Piper, D. J. W., eds.). Spec. Publ., Geol. Soc., Blackwell Scientific Publications, Oxford, 1984, **15**, 511–526.
15. Petersell, V. Dictyonema argillite. In: *Geology and Mineral Resources of Estonia* (Raukas, A., Teedumäe, A., eds.). Estonian Academy Publishers, Tallinn, 1997, 313–326.
16. Veski, R., Palu, V. Investigation of Dictyonema oil shale and its natural and artificial transformation products by a vankrevelenogram. *Oil Shale,* 2003, **20**(3), 265–281.
17. Erdtmann, B.-D. The planktonic nema-bearing *Rhabdinopora flabelliformis* (Eichwald, 1980) versus benthonic root-bearing *Dictyonema Hall*, 1952. *Proc. Acad. Sci. Estonian SSR. Geology,* 1986, **35**(3), 109–114 (in Russian).
18. Pukkonen, E. & Rammo, M. Distribution of Molybdenum and Uranium in the Tremadoc Graptolitic Argillite (Dictyonema Shale) of North-Western Estonia. *Bull. Geol. Surv. Estonia*, 1992, **2**(1), 3–15.
19. Soesoo, A., Hade, S. Metalliferous organic-rich shales of Baltoscandia – a future resource or environmental/ecological problem. *Archiv Euro Eco*, 2012, **2**(1), 11–14.
20. Voolma, M., Soesoo, A., Hade, S., Hints, R., Kallaste, T. Geochemical heterogeneity of Estonian graptolite argillite. *Oil Shale*, 2013, **30**(3), 377–401.
21. Lippmaa, E., Maremäe, E. Uranium production from the local Dictyonema shale in North-East Estonia. *Oil Shale*, 2000, **17**(4), 387–394.
22. Kleesment, A., Kurvits, T. Mineralogy of Tremadoc graptolitic argillites of North Estonia. *Oil Shale,* 1987, **4**(2), 130–138 (in Russian).
23. Loog, A., Petersell, V. Authigenic siliceous minerals in the Tremadoc graptolitic argillite of Estonia. *Proc. Est. Acad. Sci. Geol.*, 1995, **44**(1), 26–32.
24. Soesoo, A., Hade, S. Black shale of Estonia: moving towards a Fennoscandian-Baltoscandian database. *Transactions of Karelian Research Centre, Russian Academy of Science*, 2014 (in press).

25. Baukov, S. S. General characteristics of dictyonema shale. In: *Geology of Coal and Oil Shale Deposits of the USSR*, Nedra, Moscow, 1968, **11**, 145–148 (in Russian).
26. Sibson, R. A brief description of natural neighbor interpolation. In: *Interpreting Multivariate Data* (Barnett, V., ed.). John Wiley, Chichester, 1981, 21–36.
27. Wahba, G. *Spline Models for Observational Data*. Society for Industrial and Applied Mathematics, Philadelphia, 1990, 162 pp.
28. Cressie, N. A. C. *Statistics for Spatial Data*. John Wiley & Sons, New York, 1991, 900 pp.
29. Estonian National Balance of Natural Resources, Year 2012. Located http://geoportaal.maaamet.ee/docs/koondbilanss_2012.pdf?t=20130614161639.
30. Suuroja, K. *Baltic Klint in North Estonia as a symbol of Estonian nature*. Ministry of Environment, Tallinn, 2006, 224 pp.
31. Soesoo, A. Miidel, A. *North Estonian Klint*. GeoGuide Baltoscandia, Tallinn, 2007, 28 pp.
32. Overeem, I., Weltje, G. J., Bishop-Kay, C., Kroonenberg, S. B. The Late Cenozoic Eridanos delta system in the Southern North Sea Basin: a climate signal in sediment supply? *Basin Res.*, 2001, **13**(3), 293–312.
33. Rhebergen, F. Ordovician sponges (Porifera) and other silicifications from Baltica in Neogene and Pleistocene fluvial deposits of the Netherlands and northern Germany. *Est. J. Earth Sci.*, 2009, **58**(1), 24–37.

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