

Review

Uranium and Thorium Resources of Estonia

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Abstract: We provide a compilation of geology of uranium and thorium potential resources in the Ordovician black shale (graptolite argillite), Cambrian–Ordovician shelly phosphorite and in the secondary resources (tailings) of Estonia. Historical and new geological, XRF and ICP-MS geochemical data and ArcGIS modeling results of elemental distribution and tonnages are presented. The Estonian black shale contains 5.666 million tons of U, 16.533 Mt Zn, 12.762 Mt Mo, 47.754 Mt V and 0.213–0.254 Mt of Th. The Estonian phosphate resources, altogether about 3 billion metric tons of phosphate ore, contain about 147,000 to 175,000 tons of U. Rare earth element concentrations in the phosphorite ore average at 1200–1500 ppm of Σ REE. Thorium can also be a possible co-product. The mining waste dump at the Maardu contains at least 3650 tons of U and 730 tons of Th. The Sillamäe radioactive waste depository contains about 1200 tons of U and 800 tons of Th. Due to the neighboring geological positions, as well as environmental constraints and mining technologies, the black shale and phosphorite can be treated as a complex multi-resource, possibly at the continental scale, which needs to be extracted together.

Keywords: uranium; thorium; black shale; graptolite argillite; phosphorite; resources; tailings

1. Introduction

There are no uranium or thorium deposits in the national registry of the Estonian mineral resources. This is partly because uranium has a very short history of usage and scientific studies, and partly because there are no major discoveries in Estonia of economically significant uranium deposits. At the same time, Estonia has had historical mining activity for uranium and beneficiation for many decades. After World War II, due to the atomic bomb “competition”, the Soviet Union started to look for uranium deposits. As the Estonian graptolite argillite—non-metamorphosed black shale—was known to host uranium, a mine and uranium beneficiation plant were built in a small town Sillamäe, north-eastern Estonia in 1948 (Figure 1). The plant operated as a Soviet top-secret facility until 1991. After Estonian independence, it was later privatized in 1997 and renamed “AS Silmet”. At the moment the plant produces rare metals, rare earth metals and their compounds, and is the most important REE producer in the European Union.

Uranium beneficiation in Sillamäe started in 1948. A total of 22.5 tons of elemental uranium was produced from about 271,575 tons of graptolite argillite from an underground mine near Sillamäe town [1]. Due to low uranium concentration and primitive technology, a large part of the uranium was left in solid waste. In 1952, the mining of Estonian graptolite argillite stopped and between 1950 and 1977 more than four million tons of the uranium ore was imported from Middle Asia and Eastern Europe, mostly from Czechoslovakia and East Germany. The estimated amount of elemental uranium produced from that resource was 25,000 tons.

In addition to graptolite argillite, underlying shelly phosphorites and some Precambrian granitoids may be of interest, however, limited data of the Estonian Paleoproterozoic rock makes it impossible to assess uranium and thorium resources at the moment in the Estonian crystalline basement.

It is well known that phosphates of sedimentary origin may have high concentrations of uranium. Estonian phosphorites, known as Obolus-sandstone or shelly phosphorite, and formed around 490 million years ago contain uranium in amounts of 10–70 ppm. Phosphorus-rich layers are formed in shallow water conditions, where shell-rich sand is accumulated. Estonia has the biggest phosphate reserves in Europe, however, not currently exploited. Phosphorite was mined in the Maardu deposit and adjacent areas from 1921–1991.

In addition, human-made secondary resources, such as tailings and excavated overburden can be the subject of research for uranium and thorium resource assessments. In this paper, we provide a compilation of geology of uranium and thorium in black shale, phosphorite and in the secondary resources of Estonia.

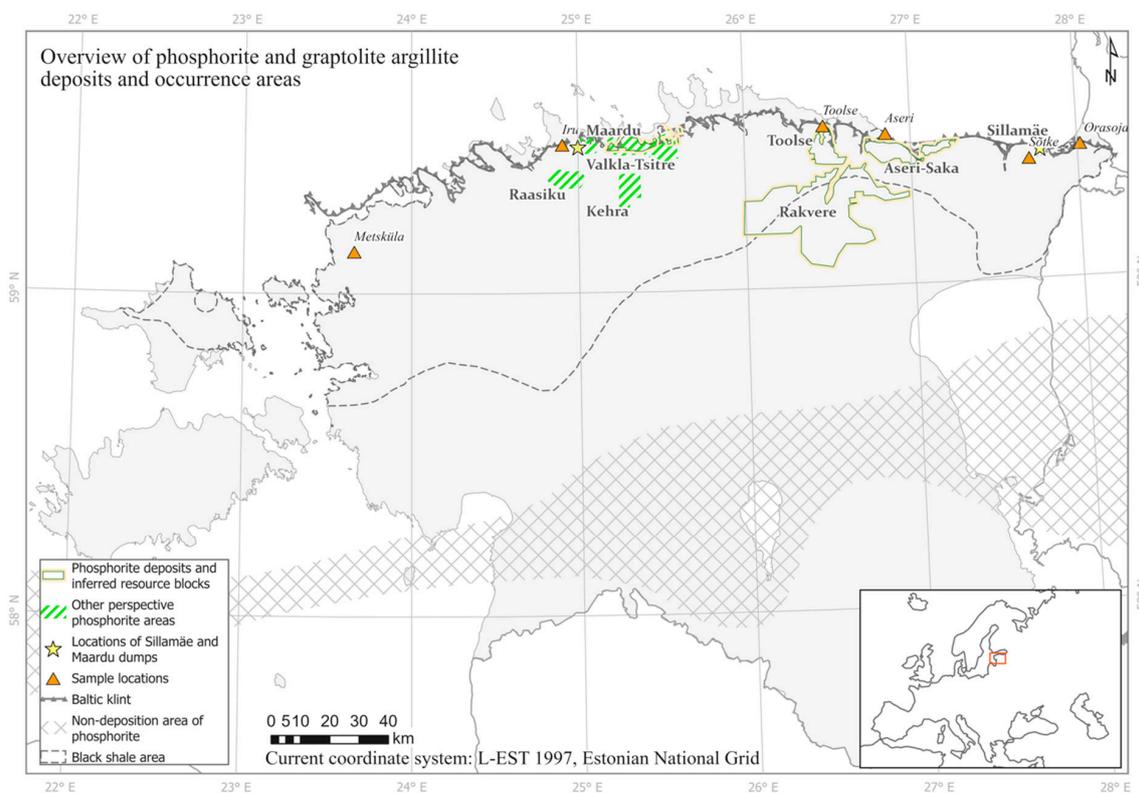


Figure 1. Overview of phosphorite and graptolite argillite (black shale) deposits, occurrence areas and other sites of interest.

2. Materials and Methods

Historical and new geological, XRF and ICP-MS geochemical data of the Estonian Ordovician black shale (graptolite argillite), Cambro-Ordovician shelly phosphorite and waste material (tailings) after uranium and phosphate production are combined in this overview (locations in Figure 1). Initial potential reserves for a limited number of elements have been calculated for graptolite argillite ([2] and this study) and phosphorites (this study). As initial data, the combined database of 468 drill cores (Estonian Geological Survey and Estonian Land Board database, see at www.maaamet.ee [3]) were used for graptolite argillite calculations.

Historical reports of phosphorite exploration typically contain relatively densely (vertically and laterally) populated data of P_2O_5 , Fe_2O_3 and MgO concentrations, while no information is given about secondary and trace elements; however, the exploration reports were often followed by a series of

works concerning the complex exploitation of phosphorite and rocks in its overburden. Those works contain a limited amount of vertically sampled phosphorite trace elements data (Σ REE, Y, U, Th, Sr, occasionally Mo, Pb, Ag, etc.). As much as the workflow can be followed, the analyses were made from the duplicate samples of the initial exploration campaigns. Uranium as well as Th were measured mostly either by X-ray fluorescence or less frequently by instrumental neutron activation methods. Quality was assured by inter-laboratory testing in up to four laboratories with both identical and different methods. A dataset containing 873 phosphorite trace element analyses was compiled for serving the purposes of current work [4–7]. Weighted average concentrations were calculated for 160 drilled locations, excluding occasional black shale interlayers.

The samples in Table 1 were recently analyzed in the ALS Geochemistry laboratory located in Outokumpu, Finland. Trace element composition is determined by ICP-MS after four acid digestion. Major element composition is determined by ICP-AES analyses after lithium borate fusion. All black shale samples were roasted before chemical treatment due to the high content of carbon and sulfur. Total organic carbon (TOC) content in black shale samples was determined by the LECO analyzer by infrared detection of CO₂ released from the combustion of the sample. Before infrared analyses, the samples were treated with HCl to remove carbonate carbon (inorganic carbon).

The dataset was used for calculating raster models of lateral U and Th distribution as well as hypothetical reserves by the same methods applied to the graptolite argillite (GA) dataset [2]. Specific gravities from original phosphorite resource estimations reports were applied in the calculations (2.12 g/cm³ and 2.26 g/cm³ for the Toolse and Rakvere deposits, respectively). One artificial data point was extrapolated in the southernmost part of the Rakvere deposit.

The historical data were compared with new data, although new data are only available for a limited number of samples. Recent, mostly unpublished trace element chemical analyses (XRF and ICP-MS) were used in the assessment of U and Th potential related to shelly phosphorites. The calculated amounts are preliminary and should be taken with precaution.

Uranium and thorium contents in secondary resources were assessed based on historical data ([8]; Sillamäe radioactive waste depository) or by a combination of historical and new geochemical analyses (Maardu overburden piles).

The ArcGIS software (Versions: ArcMap 10.7 and ArcGIS PRO 2.5 ***; Environmental Systems Research Institute, Inc.—ESRI, Redlands, CA, USA) was used for generating elemental distribution maps and computing resource volumes.

3. Results

According to the classification by International Atomic Energy Agency (2018) [9], the Estonian U-bearing rocks belong to several types: (1) the largest potential resource—Ordovician graptolite argillite belongs to Type 15.1—Black shale, Stratiform deposits; (2) Ordovician shelly phosphorites—Type 14.1 Phosphate, Organic Phosphorite; the third target—uranium and thorium potential in secondary resources—are not listed in the present (2018) Uranium Resources Classification system. There are two cases in Estonia where uranium-bearing rocks or material have been piled up as mining waste (overburden) or historical uranium processing tailings. As in several tailings in different countries, the uranium concentrations may be high, there is a potential need to update the Uranium Resources Classification to indicate this type of possible future resource as well.

3.1. Uranium and Thorium in Black Shales

Organic carbon-rich black shales have been studied regarding the industrial interest in a variety of metals, especially U, Mo, Zn, V, Ni, Cu, Cr, Co, Pb and Ag. These studies have shown a variety of metal sulfides in shales and suggested that sulfide minerals may be an integral part of the sediment diagenesis, e.g., [10–13].

Some black shales are significantly enriched by noble metals, occasionally coupled with Mo- and Ni-bearing shales. For instance, the Lower Cambrian black shales of southern China contain

up to hundreds of ppb's PGE's and gold in strata deposited as individual, metal-rich sulfide layers, commonly 2–15 cm in thickness [14]. A number of these metals in the Fennoscandian–Baltoscandian black shales may be of commercial interest. In many Precambrian terrains, metamorphosed sedimentary rocks, which were initially black shales, are known and also may provide future economic interest. As an example, the Talvivaara mine in Sotkamo, Finland (previously owned by Talvivaara Mining Company Plc, now by Terrafame) is using black shale for the production of nickel, cobalt and zinc. The estimated resource is over one billion tons of ore. Technologically, it is the first mining operation in the world collectively recovering NiCoCuZn(Mn)(U) by bioheap leaching polymetallic black shale. As a co-product, they recently started the extraction of uranium [15].

The occurrences of the Middle Cambrian to Late Ordovician organic-rich black shale deposits are known in an extensive area of Sweden (Alum shale; [16]), the Oslo region [17], Bornholm [18], Estonia (known as graptolite argillite or “Dictyonema shale” [19] and kukersite as proper oil shale), Poland [20] and northwest Russia [21]. The Swedish Alum shale, as well as Estonian graptolite argillite, contains remarkably high concentrations of trace metals such as U, Mo, V and Ni [22–25].

These black shale layers have been historically exploited for local uranium production in Sweden and Estonia. For example, in the Viken area, Sweden, Continental Precious Minerals Inc. has estimated the uranium resource to be 1.163 Billion lbs. of U_3O_8 (18 M lbs as indicated; 1.145 B lbs as an inferred resource) in Alum shale and a large number of other metals [26].

Kerogen in these black shales is of algal origin and the content of total organic carbon is mostly between 10–25 wt% [16]. The mineral matter of these black shales is dominated by clay minerals, illite–smectite and illite [22,27]. The high concentration of pyrite, which, together with kerogen, is thought to be the main carrier of some rare earth and other elements, is distinctive for black shale. The Alum shale and graptolite argillite form patches over extensive areas in the outskirts of the Baltica palaeocontinent [16]—Baltoscandia and Fennoscandia. A possible spatial continuity of those complexes is the graphitic phyllites that are found in the tectonically disrupted allochthonous and autochthonous Caledonian complexes in central and northern Sweden and Norway [28]. The metal-enriched phyllites exhibit similar geochemical signatures to the unmetamorphosed black shale of Baltoscandia [28]. These geochemical similarities may imply that organic-rich muds might have accumulated over a wide geographic area and probably under quite different depositional conditions—from shallow marine settings to continental slope environments. The black shales of Fennoscandia (Alum shale) and the graptolite argillite (GA) of Estonia can thus be treated as metal ore and a twofold energy source (including U, Th and hydrocarbons). This means that these rocks have, apart from scientific value, a significant economic value as well.

3.1.1. Estonian Black Shale—Graptolite Argillite

If we compare the Fennoscandian sedimentary and metamorphosed black shales and the Estonian graptolite argillite (GA), the stratigraphic characteristics and geological position of the Estonian GA are very simple (Figure 2). Early Ordovician, organic-rich marine metalliferous black shale–graptolite argillite lies beneath most of northern Estonia. It has been named “Dictyonema shale”, “Dictyonema argillite” or previously “alum shale”; however, the name “dictyonema” came from the benthonic root-bearing *Dictyonema flabelliforme*, which subsequently turned into planktonic nema-bearing *Rhabdinopora flabelliformis* [29]. More recently the term graptolite argillite is used in Estonia, while “Dictyonema shale” is still used in Russian literature.

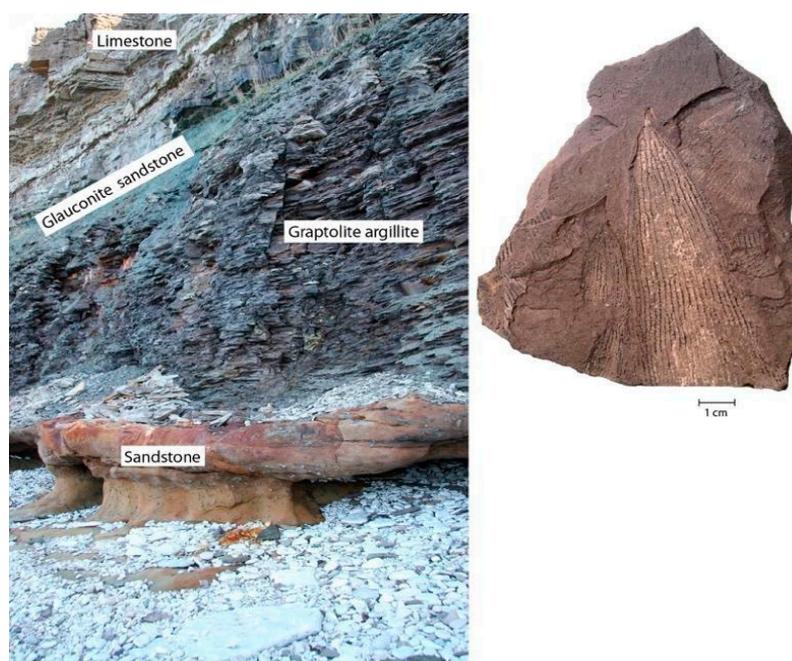


Figure 2. Cross-section of the northern Estonian klint at Cape Pakri (**left**). The thickness of the graptolite argillite is about 4.2 m, it is overlain with glauconite sandstone and limestone. Graptolite argillite shale with *Rhabdinopora flabelliformis* imprint (**right**).

The Estonian graptolite argillite is commonly fine-grained, unmetamorphosed, horizontally-lying and undisturbed, organic-rich (8–20%) lithified clay (Türisalu Formation), where the layers are usually 0.3 to 6 m thick. The graptolite argillite belongs to the group of black shales of sapropelic origin [2,23,24,30]. The Estonian GA crops out in many places in Northern Estonia, especially in the klint area and in several narrow river valleys (Figure 2). As the Estonian Lower Palaeozoic sedimentary section, as well as the Precambrian rocks, are inclined towards the south due to its geological position in the southern slope of Fennoscandian Shield [31], at its southwest end the GA layers lie at a depth of more than 250 m.

The Estonian GA is commonly characterized by high concentrations of U (up to 1200 ppm), Mo (1000 ppm), V (can be over 1600 ppm), Ni and several other heavy metals and is rich in N, S and O [2,22,23]. Examples of some major and trace element concentrations are shown in Table 1. These high concentrations of certain metals may be potentially useful and hazardous at the same time. In the Soviet Union, the GA was mined for uranium production at Sillamäe (see below, Section 3.3.). Between 1964 and 1991, approximately 73 million tons of graptolite argillite was mined and piled into waste heaps from a covering layer of phosphorite ore at Maardu, near Tallinn (see below, Section 3.3.).

Table 1. Major and trace elements of representative graptolite argillite samples. LOI—Loss on ignition. TOC—total organic carbon. Locations are indicated in Figure 1. Data: Geological Survey of Estonia.

Sample	Locality	Lat	Long	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	P ₂ O ₅	TiO ₂	K ₂ O	LOI	TOC
IRU-7A	Iru	59.460	24.91	49.00	14.35	5.69	0.86	0.33	1.35	0.89	8.53	17.7	7.60
RITA-1Y	Sõtke	59.37	27.71	38.5	7.81	4.06	0.81	13.9	1.2	0.46	4.84	13.8	5.98
RITA-4A	Sõtke	59.37	27.71	52.2	8.36	7.52	0.69	1.57	0.96	0.54	5.00	15.3	5.54
F-338-09	Metsküla	59.13	23.65	46.3	11.3	4.21	1.04	0.23	0.12	0.67	6.57	28.3	12.65
Sample	Locality	Lat	Long	V	Mo	Ni	Zn	Cd	Pb	Th	U	ΣREE	ΣREE + Y
IRU-7A	Iru	59.460	24.91	174	25	21	106	0.13	81	14.8	58.9	170	195
RITA-1Y	Sõtke	59.37	27.71	664	361	109	4010	30.9	205	10.3	206.0	218	271
RITA-4A	Sõtke	59.37	27.71	916	202	169	53	0.2	186	14.3	258.0	377	475
F-338-09	Metsküla	59.13	23.65	1240	170	168	47	0.12	85	13.5	121.5	207	236

While the reserves of Estonian graptolite argillite surpass those of Estonian kukersite (proper oil shale), it is of too poor quality for energy production at present. The GA calorific value ranges from 4.2–6.7 MJ/kg [22] and the Fischer Assay oil yield is 3–5% (for Estonian kukersite, it is about 30–47%, for example, [1]). The moisture content of fresh GA ranges from 11.9% to 12.5%, while the average composition of the combustible part is: C—67.6%, H—7.6%, O—18.5%, N—3.6% and S—2.6% [32]; however, considering that it is a low-grade oil source, its potential oil reserves are about 2.1 billion tons [1].

The specific gravity (bulk density) of Estonian GA varies between 1800 and 2500 kg/m³ [30]. The pyrite content of GA is highly variable, ranging from 0.5% to 9.0%, averaging between 2.4% and 6%. Pyrite commonly forms fine-crystalline disseminations or thin interlayers and concretions of different sizes. The diameter of the pyrite concretions is usually 1.5–3 cm. It needs to be noted that some concretions are complex in a structure containing small crystals of sphalerite, galenite and/or calcite. A higher degree of sulfide mineralization within the GA may be associated with the occurrence of silt interbeds. These interbeds may contain a higher amount of other authigenic compounds such as phosphates (mainly apatite as biogenic detritus and nodules), carbonates (calcite and dolomite as cement and concretions), baryte and glauconite [23]. The concentration of sulfur ranges between 2–6%, from which about 0.6–0.8% is composed of organic matter, ca. 0.3% is sulphatic and the remaining part is sulfidic sulfur [33].

3.1.2. Estonian Graptolite Argillite Resources

Most of the geological information on Estonian GA is obtained from basement mapping and different exploration projects, which were conducted by the Geological Survey of Estonia and its predecessor institutions, starting from the 1950s. The huge amount of information on the lithology and geochemistry of the GA was collected during the exploration of Estonia's phosphorite resources in the 1980s. The initial estimates of the total GA reserves in Estonia range from 60 [30] to 70 billion tons [1]; however, little is known about the previous calculation methods and the initial data (number of drill cores, etc.) that were used. Nevertheless, GA resource estimates were regularly reported in works dedicated to phosphorite exploration and its complex exploitation (Table 2), because GA was considered as a possible useful material in phosphorite overburden. In those works, resource estimates mostly were calculated by the panels method (blocking) [4].

The earliest partially preserved documentation of U resource estimates dates to 1944, when the information concerning radioactivity was checked and confirmed by geologists of the USSR's North-Western Geological Administration. The largest concentrations were recorded in the middle part of the deposit within the northeast of Estonia and the western part of St. Petersburg (Leningrad at the time). Uranium concentrations varied from tens to a few hundreds of ppm-s (80–750 ppm U). In addition to uranium in the shale, elevated molybdenum and vanadium contents were also recorded.

Since 1945, the Baltic Geological Expedition identified 14 deposits of low-grade uranium ore—Sillamäe (5464 t U, 260 ppm average U), Toila (7000 t U, 250 ppm average U), Aseri, Saka and others in the present-day Russian territory. The deposits were explored by boreholes along networks of 250 m × 250 m and 125 m × 125 m. A total resource of 72,000 t U was reported in the Baltic region. Alongside uranium exploration, a black shale enrichment technology was developed to produce uranium concentrates from the rock.

As mentioned briefly, the efforts of estimating GA resources and U contained within were almost uniquely associated with phosphorite exploration. The highest resources of U were attributed to GA in the overburden of Aseri deposit phosphorite (Table 2). Even though GA is wedging out in the territory of the Rakvere deposit, U resources were estimated in its northern parts where the higher U concentrations occur. A somewhat more independent GA exploration was finalized in 1989 when resources in western Estonia (highest shale thickness) were calculated with the focus on hydrocarbons, but also for U, V and Mo. The conditionally exploitable proportion of GA was evaluated based on a minimum resource thickness of 1.6 m, and a minimum calorific value of 1450 kcal/kg (~6.1 MJ) [34].

Very little data have been collected in the last three decades; the modern GIS-based methods now allow us to obtain better estimates of the total resource and visualize metal distribution.

In recent research, the verified database of 468 drill cores (database of the Estonian Geological Survey and Estonian Land Board, [3]) has been used as the initial data. The estimated area of the Estonian GA on the mainland and islands is 12,212.64 km², with a corresponding volume of 31,919,259,960 m³ [2]. For comparison, Estonian oil shale—kukersite—occupies an area of 2884 km², and its reserves (proven plus probable) are about 5 billion tons [35]. To calculate the total mass of the GA, the value of the specific gravity (density) is required. It is known [30] that the density of the graptolite argillite varies to a great degree, between 1800 and 2500 kg/m³. So, assuming an average density of 1800 kg/m³, the total mass of GA is about 57.45 billion tons, while in the case of 2500 kg/m³ the mass is 79.80 billion tons. Assuming the average density to be 2100 kg/m³, the total weight of GA is about 67 billion tons, which is in accordance with the earlier estimates of 60 to 70 billion tons.

Table 2. Some historical and modern GIS-based preliminary resource estimates of metals in graptolite argillite.

Area	Area (km ²)	Total Resource (Mt)	U (t)	V (t)	Mo (t)	Th (t)	Average U (ppm)	Reference
GIS-based total basin	12,212.64	67,000	5,665,600	-	12,761,600	-	-	[2]
	-	-	-	47,753,803	-	213,000–254,300 ¹	-	current
NW Estonia (total)	4540.6	42,830	4,216,000	28,123,000	7,860,000	-	103	[34]
NW Estonia (meeting criteria)	1607.5	10,651	1,176,000	7,260,000	2,444,000	-	116	<i>ib.</i>
Toolse	62.219	141.4	21,143	147,000	57,400	-	148	[36]
Aseri	162	-	72,800	521,500	193,300	-	162	[4]
Rakvere, incl.:	213	-	17,810	139,780	37,140	-	-	<i>ib.</i>
Assamalla	132	-	8910	98,900	25,150	-	73	<i>ib.</i>
Rägavere	40	-	2770	-	6230	-	187	<i>ib.</i>
Kabala	41	-	6130	40,880	5760	-	231	<i>ib.</i>
Total basin	-	64,000	6,800,000	58,200,000	11,500,000	-	-	[37]

¹ Depending on the area of calculation.

It should be noted, however, that in the eastern part of the GA basin there are frequent silty interlayers, resulting in a lower specific gravity of about 1850 kg/m³, which has also been the basis of deposit-specific calculations in Table 2 [4]. In the Toolse deposit, the average specific gravity of 1900 kg/m³ was applied [36]. For Western Estonia, the exploitable proportion of GA was based on a minimum resource thickness of 1.6 m, and a minimum calorific value of 1450 kcal/kg. The average specific gravity was 2080 kg/m³, but variations were considered in the calculations [34]. The distribution of several metals such as U, Zn, Mo and V in the GA has been modeled earlier [2]. The initial data were selected from the databases of the Geological Survey and the Estonian Land Board. It needs to be mentioned that the metal concentration data represents the average metal concentrations of the GA drill core. There are differences in metal distributions—the central and western regions of eastern Estonia show the highest concentrations for V and Mo, whereas V is also high in the southern region of the Eastern and central Estonia. Uranium shows the highest contents in the eastern part of Estonia, while in Western Estonia the concentrations show medium values, while the lowest values are typical for central Estonia (Figure 3).

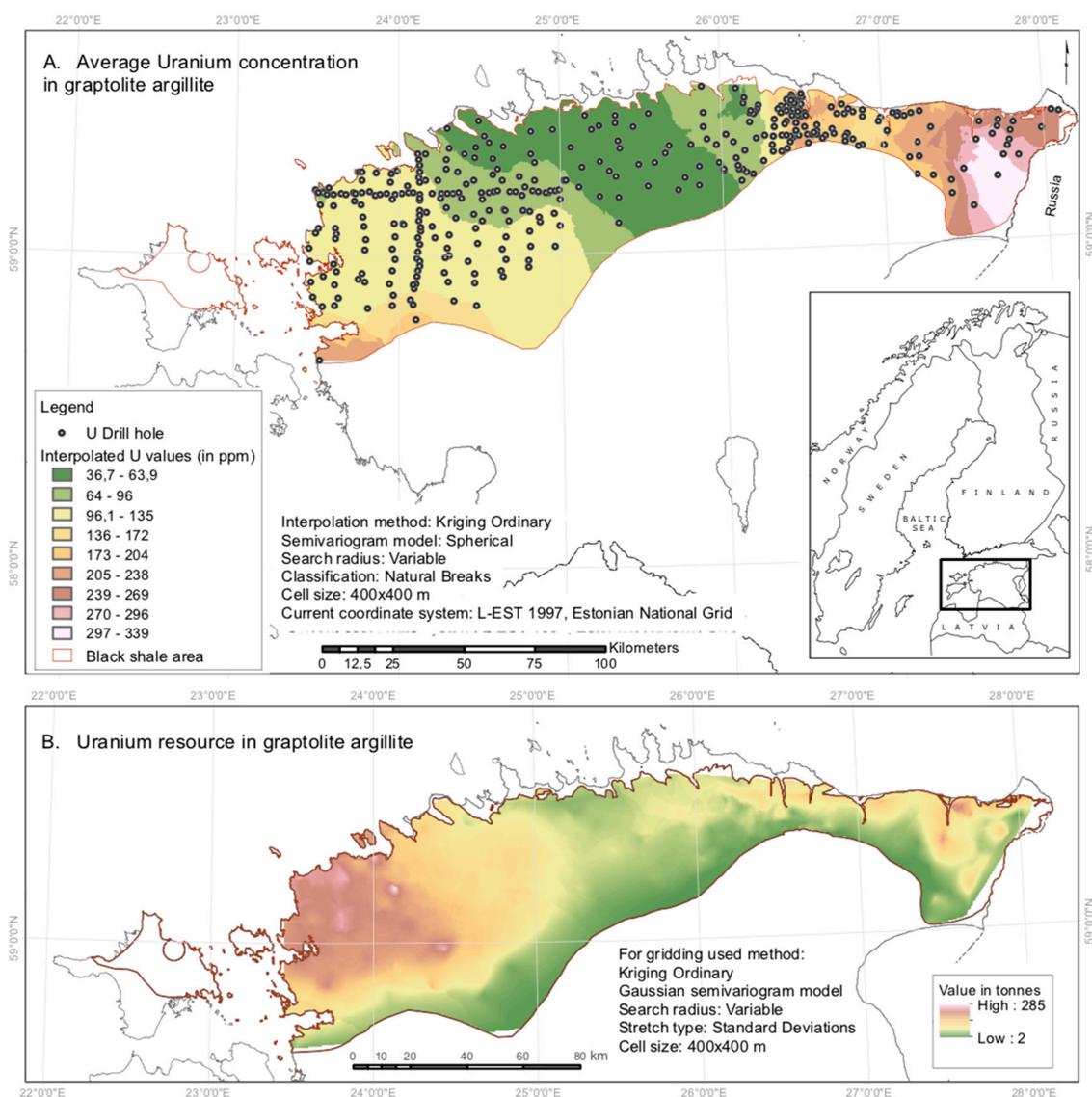


Figure 3. (A) Location map of the drill holes penetrating the graptolite argillite layers and the extent of the graptolite argillite. U tonnage model in the 400 to 400 m cell at the modeled thickness of the graptolite argillite. (B) Modeled uranium content in the Estonian GA based on calculated average drill core contents (data: Geological Survey of Estonia; www.maaamet.ee [3]).

Uranium distribution has not been modeled in the Estonian islands due to the small number of available analyses. It is also likely that the high concentrations in the southwest area may be an artefact of the model since there are only a few drill cores available but they show locally high contents of U. Based on these data, it can be concluded that the concentration of most of the metals (except Zn) is relatively low in central Estonia. It is also important to emphasize that the available geochemical data are relatively unevenly distributed across the area and the present geochemical generalization is informative but must be taken with caution. In addition, there are very little data on the southern margin of the GA area; however, we believe that due to its limited thickness of GA (less than 0.5 m), the calculated total elemental amounts have not much affected the calculations.

Concerning the shale standard values (PAAS and NASC), the Estonian GA is very rich in U and V. For instance, the average U concentration in the Saka section (267 ppm) is a hundred times higher than the corresponding values for NASC [23]. In the 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 (1190 ppm; [23]). 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, a correlation of P_2O_5 contents with other trace elements, such as U, was not detected. Nevertheless, it is well established that U is more enriched in the bottom of the black shale bed, at least in the western part of Estonia.

Recent ICP-MS geochemical data from 11 north-western Estonian drill cores were divided into upper and lower beds, which revealed a reverse trend with regard to U association with P_2O_5 and total organic carbon (TOC) [38]. Namely, the correlation of U and TOC is weakly positive in the upper bed and reverses to weakly negative in the lower bed (see Section 4, Discussion). The opposite was observed in the relation between P_2O_5 and U—their association becomes more relevant in the lower, U-enriched bed. Hierarchical clustering of dataset classifies U within the group of typical redox-sensitive elements such as Mo, Sb, V, Re as well as TOC, Ag, Pb and Te.

While average metal concentrations are very useful in dividing GA into “poor” and “rich” deposits, the total content of a certain metal depends on the thickness of the GA bed. To calculate the total amount of the metal on the square meters, the ESRI ArcGIS software was employed. As an example, the total tonnage of U in the Estonian GA is shown in Figure 3B. The presented model is based on: (1) the element grid which shows the element distribution, in ppm; (2) an interpolated grid of the GA thickness, in meters; (3) assumption of the average density 2100 kg/m^3 ; (4) since the element and thickness grids were calculated with the cell size of $400 \text{ m} \times 400 \text{ m}$, the same cell size was used for the calculation of the total amount of element.

These calculations provide more realistic total amounts for the elements in the Estonian GA (not just based on an average concentration value in ppm). The calculated total tonnage of U is about 5.6656 million tons (6.6796 million tons as U_3O_8).

The calculated Zink tonnage is 16.5330 million tons (20.5802 million tons as ZnO) and Mo is 12.7616 million tons (19.1462 million tons as MoO_3). The highest studied element amounts 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, in central Estonia, where the enrichment is the lowest for most elements, except Zn.

Presently, the calculation for thorium and vanadium, based on the cell of $400 \text{ m} \times 400 \text{ m}$, was conducted (for Th, see Figure 4). Vanadium concentrations (as drill core averages; 469 drill cores) commonly vary in between 190 and 1700 ppm, being in certain layers as high as 4500 ppm [5]. The calculated vanadium tonnage is 47.7538 million tons.

Thorium concentrations are analyzed in less than 100 drill cores, where the average varies between less than 1 and 17 ppm. As there are very few measurements of Th concentrations in western and eastern Estonia, the distribution and tonnage calculations can be provided only for the central part of Estonia (Figure 4). The concentrations of Th are higher in the southern part and the central part of the calculated area; however, this distribution model should be taken with care since the number of measurements in the southern part is very low. Depending on the area of the calculation, the Th tonnage is 213,000 to 254,300 tons (in Figure 4, the tonnage of Th is 213 thousand tons).

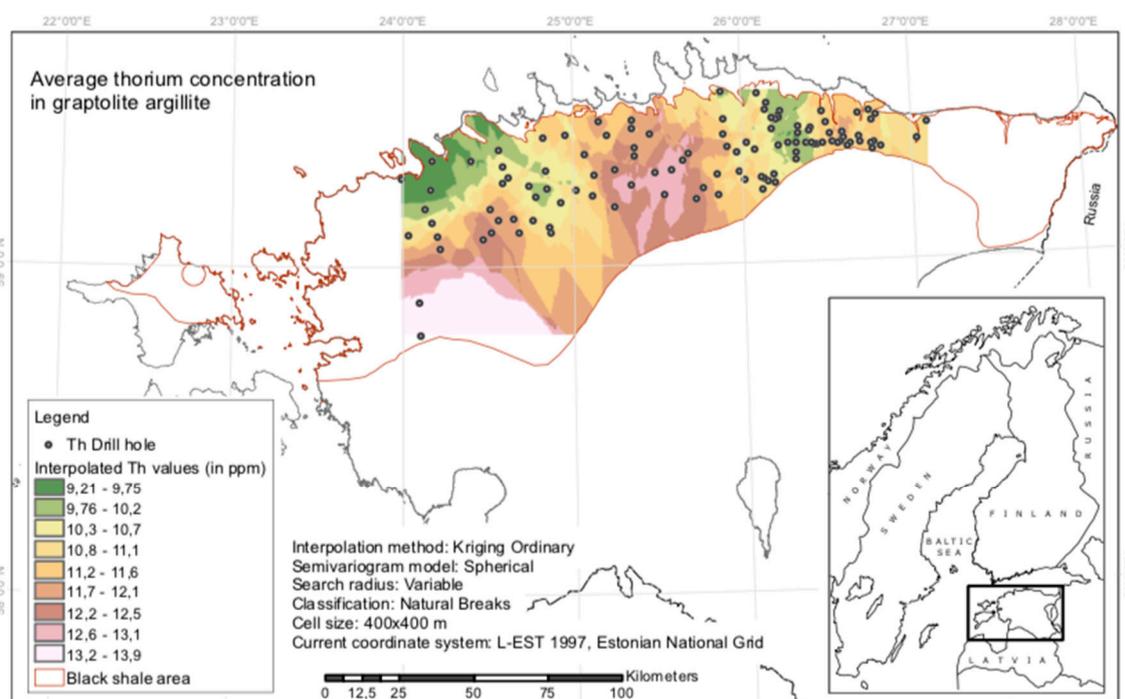


Figure 4. Location map of the drill holes with available thorium data of the graptolite argillite. The thorium distribution model was calculated using Kriging interpolation.

3.2. Uranium and Thorium in Cambro-Ordovician Shelly Phosphorites

It is well known that phosphates of sedimentary origin have higher concentrations of uranium (100–150 ppm U) and lower concentrations of thorium (20–35 ppm Th), whereas phosphates of magmatic or metamorphic origin have higher thorium (40–120 ppm Th) and lower uranium (25–35 ppm U; [9]). The world's largest phosphate deposits consist of marine phosphorite of continental shelf origin that may contain syn-sedimentary stratiform, disseminated uranium in fine-grained apatite. Historically, uranium has been recovered in the USA, Belgium and Israel as a by-product of phosphate production. For instance, in Florida, about 17,275 t of uranium was produced between 1978 and 2000 from eight production centers [9].

The US Geological Survey dataset of world phosphate mines, deposits and occurrences lists 1635 deposits, most of these marine phosphorites. As of 2015, only 57 phosphate deposits were listed in the UDEPO (World Distribution of Uranium Deposits) database, suggesting that uranium resources in phosphorites could be much more significant than previously thought [39].

Thus, phosphorites commonly contain very large uranium resources, albeit at a very low grade (<50–200 ppm U). World uranium resources in phosphorites are estimated at 15–20 million tons [9]. Well-known examples of this type of phosphorite deposits include districts in Florida and the Phosphoria Formation (USA) and the Gantour, Meskala and Oulad Abdoum Basins (Morocco). Other types of phosphorite deposits consist of organic phosphate, including sandy to argillaceous marine sediments enriched in fish and/or shell remains that are uraniferous. The Estonian phosphorites belong to this type of deposit where phosphorus, but also uranium and thorium, are associated with Cambrian–Ordovician brachiopod shells. Unfortunately, very little information about the Estonian phosphorites is available in international literature. The total resource is estimated at more than 800 million tons P_2O_5 [40] or 3 billion metric tons as phosphate ore [41]. The World's phosphate rock reserves are estimated at 70 billion tons [39]. According to the present knowledge, Estonia holds, in Europe, the largest unused sedimentary phosphate rock reserves.

The Estonian phosphorite is known as Obolus-sandstone (shelly phosphorite, [42]). It was formed approximately 488 million years ago and occurs in the Upper Cambrian and Lower Ordovician

boundary beds. In the Estonian basement, it is known as the Kallavere, Tsite, Ülgase and Petseri Formations. Phosphorus-rich layers were formed in shallow water conditions, where shell-rich sand is accumulated by the continuous displacement caused by waves and currents. This means that phosphorite was formed as separate zones, unlike oil shale, which covers the whole distribution area. Estonian phosphorite can be described as yellowish-light or dark-grey fine- or coarse-grained slightly cemented sandy deposit (Figure 5). Usually, it is weakly cemented or friable, strongly cemented phosphorites are less spread [42].

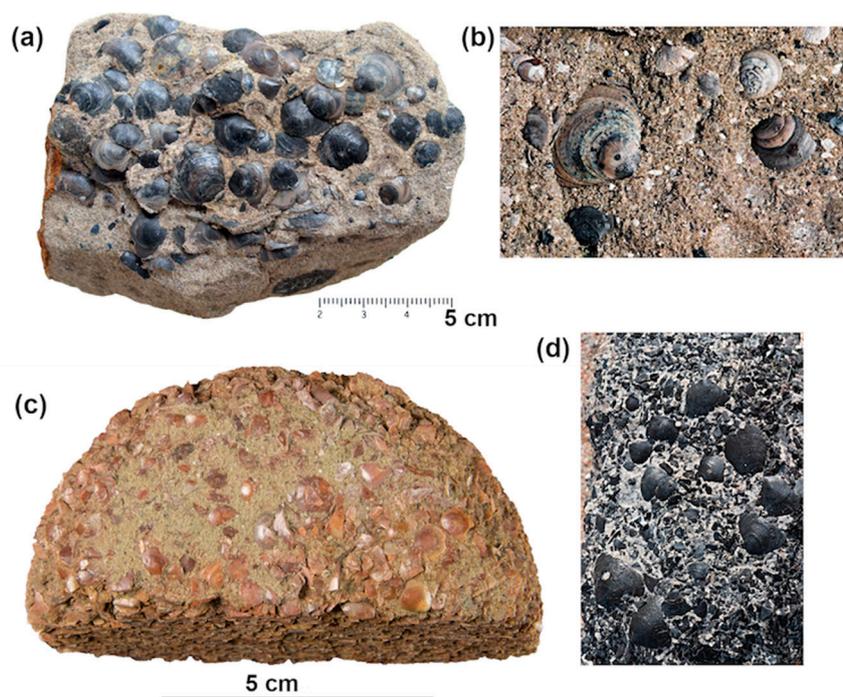


Figure 5. Varieties of Estonian sandstone-hosted shelly phosphorite. Photos: T. Saadre (a,c) H. Bauert (b,d), University of Tartu and Geological Survey of Estonia.

Estonian phosphorite contains 10.5–10.6% P_2O_5 , ca 16.0% CaO, 0.8% MgO, 0.5–0.7% Al_2O_3 , 1.8–1.9% Fe_2O_3 , 64.0–65.0% SiO_2 and F 0.8%. Phosphate rocks free from impurities contain 28.2–28.8% P_2O_5 , some studies show even higher P_2O_5 contents—about 33.6–35.5% [21]. The P_2O_5 content in the phosphorite layer is commonly in a range of 6–20%. Concentrations of major and minor components of some phosphorite samples are shown in Table 3.

Table 3. Major (wt%) and trace (ppm) elements of some phosphorite samples. LOI—Loss on ignition. Bdl—below detection limit. Data sourced from the FRAME project [43]. Locations are shown in Figure 1.

Sample	Locality	Lat	Long	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	P ₂ O ₅	LOI
ASERI	Aseri	59.469	26.850	21.78		1.80	0.17	5.37	34.80	0.47	19.21	15.97
IRU9	Iru	59.460	24.905	59.67	0.46	0.85	0.09	0.10	19.66	0.19	14.20	2.65
ORASOJA	Orasoja	59.410	28.018	47.35	0.15	1.58	0.06	0.24	25.25	0.20	18.98	3.37
SAKA1	Saka	59.442	27.214	86.81	0.49	0.45	0.02	0.23	5.35	0.07	3.74	1.57
TOOLSE2	Toolse	59.500	26.476	11.79	0.27	2.65	0.26	4.77	39.21	0.39	24.01	15.03
Sample	Locality	Lat	Long	V	Sr	Zn	Cd	Pb	Th	U	ΣREE	ΣREE + Y
ASERI	Aseri	59.469	26.850	55	1843	4	0.02	9.0	2.2	28.9	769	1023
IRU9	Iru	59.460	24.905	23	1409	110	0.12	16.2	12.8	15.7	1005	1401
ORASOJA	Orasoja	59.410	28.018	34	1825	5	0.00	23.2	4.9	62.1	1191	1506
SAKA1	Saka	59.442	27.214	33	358	bdl	0.00	14.8	4.8	11.7	402	534
TOOLSE2	Toolse	59.500	26.476	33	2193	10	0.12	21.0	5.4	32.6	1298	1584

In the vertical sections, there are no universally definitive trends in the distribution of U (Figure 6), although certain co-variability with P₂O₅ is noted, as is also implied from the biplot of U and P₂O₅ of the historical dataset (Figure 7). In the Toolse deposit, the richest phosphorite beds are the lowest and higher enrichment of U can occur there. In the Rakvere deposit, there appears to be a two-layered phosphorite accumulation, which is not currently defined in the resource models and is treated as a single layer. Generally, the highest P₂O₅ concentrations are noted in the upper part of the ore layer [40]. The same trend is at least partly observed in the distribution of U concentrations. The content of U in phosphorite is about an order of magnitude lower than in the overlying black shale.

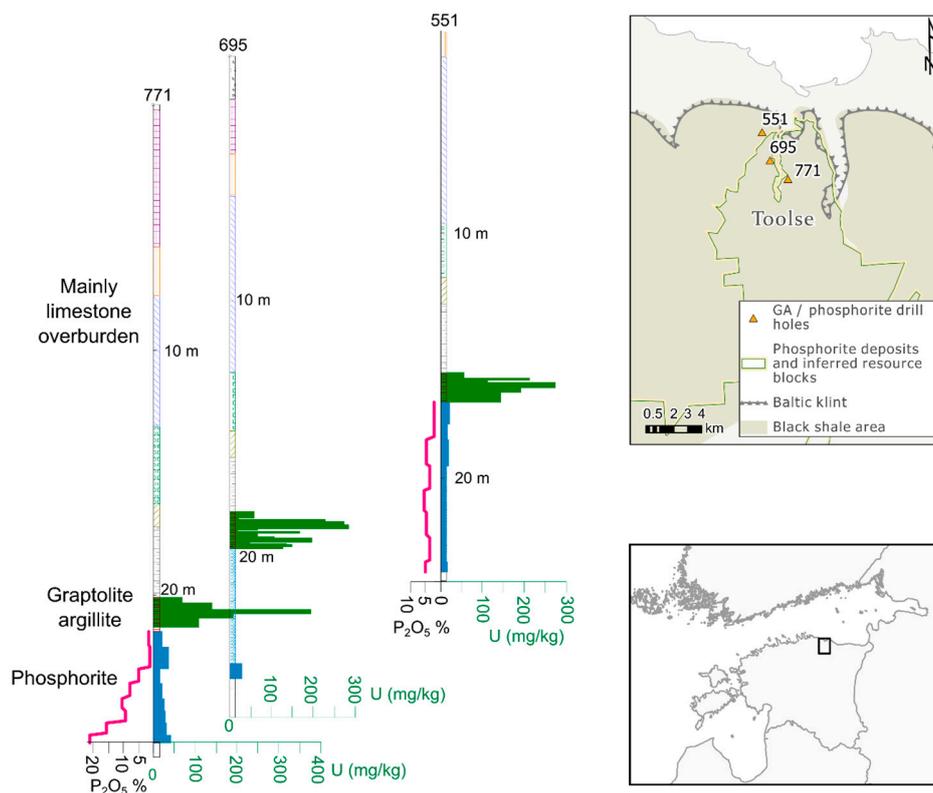


Figure 6. Examples of downhole variations of U concentrations to P₂O₅ concentration based on drill cores located in the Toolse deposit area. The cores form a south–northerly cross-section. Profiles are depicted vertically and horizontally in scale.

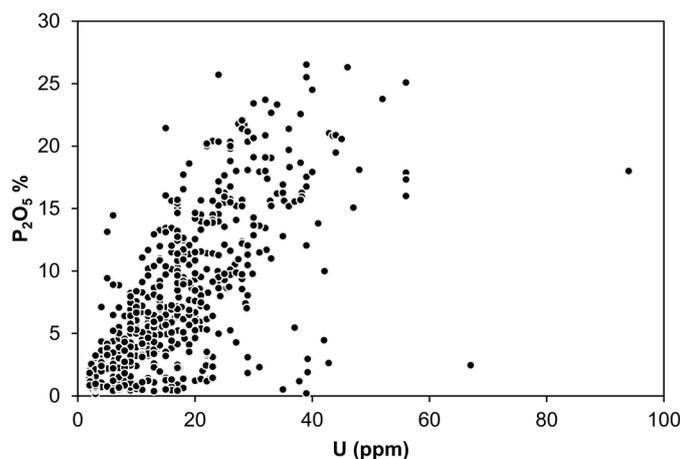


Figure 7. Biplot of P₂O₅ versus U in Estonian phosphorites based on the digitized historical dataset.

The regional overview of average U contents reflects the areas, where phosphorite deposits are located (Figure 8). There are occurrences of phosphorite in the western part of the country, but they are of very low grade, and this is also reflected in the lower concentrations of U (~5–15 ppm). The three easternmost data points are somewhat biased, because in those cases, only single very rich phosphorite samples were analyzed.

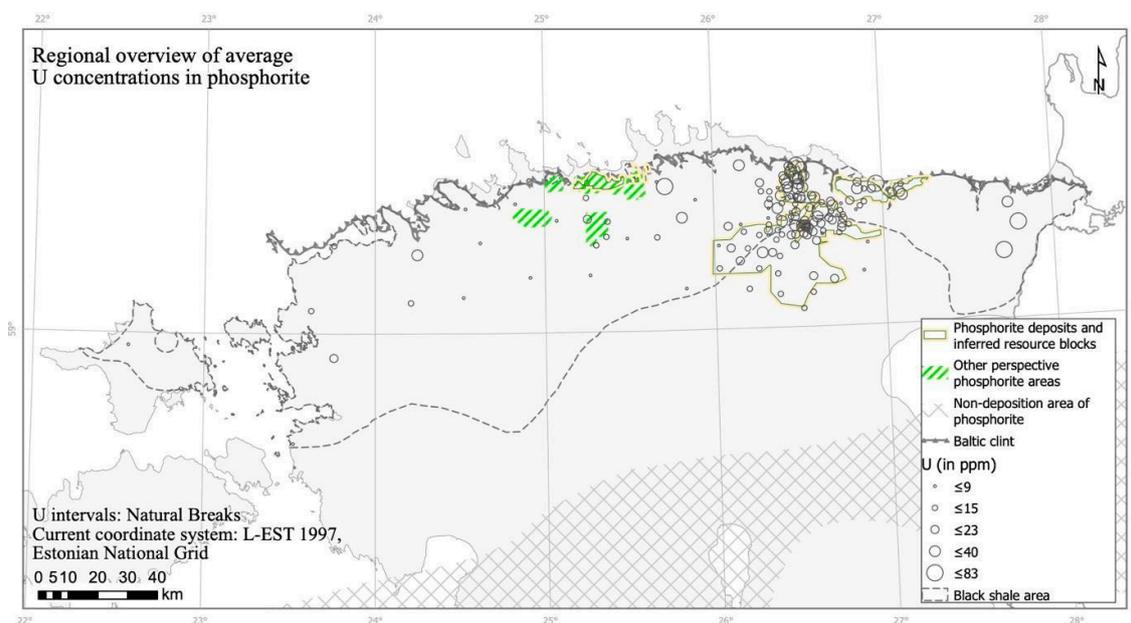


Figure 8. Regional overview of U concentrations in Northern Estonia.

There appears to be a trend that the northernmost phosphorite deposits area is the most enriched in U (~25–50 ppm; Figure 9). There are only a few locations where U concentration exceeds 25 ppm, which are in the middle and southern parts of the phosphorite occurrence area (Rakvere deposit). The mean concentrations of U are 24 ± 6 ppm and 15 ± 4 ppm in the Toolse and Rakvere deposits, respectively. The overall weighted average across all Estonian phosphorite samples is 16 ± 11 ppm, implying a high variability, but generally a low amount of U. The formerly shown errors are given as one standard deviation. Perspective resource estimates associated with phosphorite are given in Table 4, and an extended overview in Appendix A.

Table 4. Resources of U (t) in phosphorite deposits. Note that the contour defining the Toolse deposit is different in historical works and the current national registry of the Estonian mineral resources. Refer to Appendix A for an extended overview of resource estimates.

Deposit	[4]	[6]	This Study
Toolse	8300	5599	-
Toolse, current extent	-	-	14,368
Aseri	5300	-	-
Southern Maardu	27,400	-	-
Rakvere, including fields:	134,300	-	146,989
Rägavere	37,600	-	-
Western locality	14,000	-	-
Assamalla	29,700	-	-
South-Eastern locality	22,900	-	-
Kabala, including:	30,100	-	-
Western Kabala	18,100	-	-
TOTAL	175,300	-	-

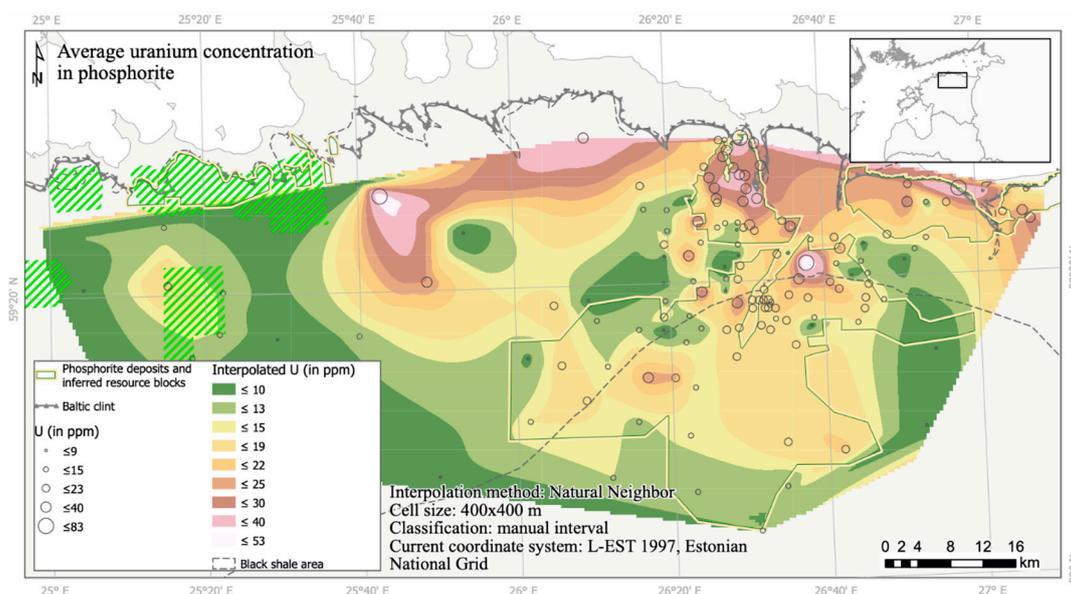


Figure 9. The distribution model of U in the main phosphorite deposit areas based on the historical data.

Thorium seems to possess a similar trend—being more concentrated in the northernmost part of the phosphorite deposits area (Figure 10). Yet, this indication is very speculative because there are too few data points situated in the Rakvere deposit area. It can be mentioned here that the northernmost part of the Toolse deposit also yields comparatively higher total rare earth element (REE) concentrations.

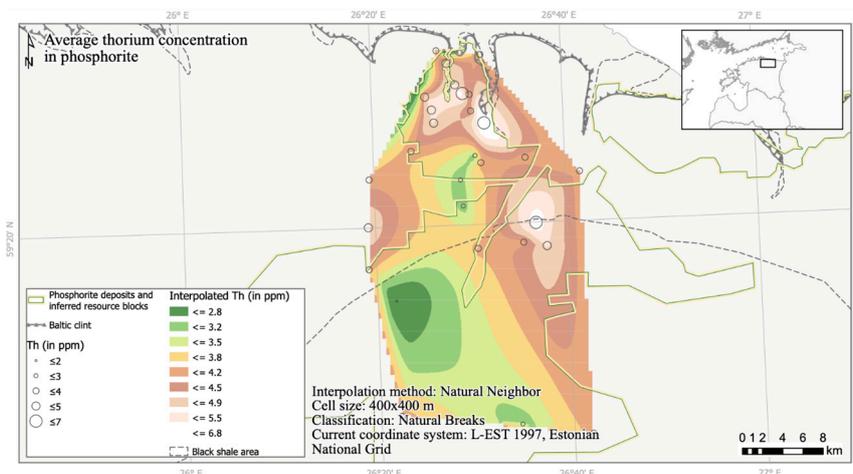


Figure 10. The distribution model of Th in the main phosphorite deposit areas.

Recent studies have shown relatively enriched but variable concentrations of REEs in single phosphate shells. For instance, La in a single shell ranges from 50 to 550 ppm, Ce—40–1200 ppm, Pr—4–170 ppm, Nd—20–800 ppm, Sm—3–180 ppm and Gd—4–135 ppm [44]. The total REEs can reach 3000 ppm; however, on average they range between 1000 and 2000 ppm. At the moment the Estonian phosphorites cannot be regarded as an economic REE source, but considering REEs as a co-product of phosphorus production, it may economically be feasible. Considering the possibility that these resources will be developed for phosphorus (and REE) production, it is important to focus also on uranium and thorium; however, the contents of U and Th are quite low to provide economical interest but high enough in environmental meaning. The new analyses show that uranium content in the ore ranges between 2 and 91 ppm (52 samples), whereas in single shells it ranges between 0.5 to 159 ppm

(41 samples; Figure 11). Thorium content in ore ranges between 1 to 15 ppm and in shells 0.5–48 ppm. It needs to be emphasized that in both single shells and ore, uranium and thorium contents are spatially very heterogeneous.

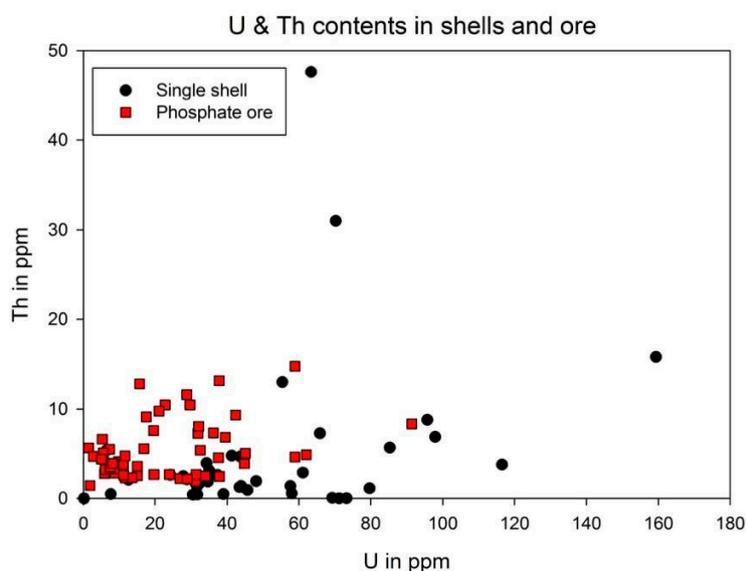


Figure 11. Concentrations of U and Th in single brachiopod shells and in brachiopod sandstone–phosphorite ore as analyzed by ICP-MS. Unpublished data from the University of Tartu and Tallinn University of Technology.

Considering that future possible mining operations will have an annual production of 5 Mt tons of ore with average U and Th contents as shown in Table 5, the total uranium content reaches above 120 tons and thorium reaches above 27 tons. It would be interesting to add that total REE contents for this annual mining amount will be 720 tons at $\Sigma\text{REE} = 1200$ ppm, or 900 tons at $\Sigma\text{REE} = 1500$ ppm.

Table 5. Minimum, maximum, average and standard deviation of U and Th contents in analyzed brachiopod shells and phosphate ore. As an example, U and Th contents for mining activity with different annual amounts have been calculated as a possible co-product.

Single Shell or Ore	Single Shell	Single Shell	Ore	Ore
Value	Uranium (ppm)	Thorium (ppm)	Uranium (ppm)	Thorium (ppm)
No. Analyses	41	41	52	52
MIN	0.2	0.0	1.5	1.5
MAX	159.3	47.6	91.4	14.8
AVERAGE	50.2	4.9	24.3	5.4
STD DEVIATION	30.8	8.8	18.2	3.3
Annual Mining, Ore (t)	Single Shell	Single Shell	U (kg)	Th (kg)
5,000,000	-	-	121,659	27,108
10,000,000	-	-	243,317	54,216

3.3. Secondary Uranium and Thorium Resources

There are two cases in Estonia where mining waste rock and processing tailings may provide a target for future studies of uranium and thorium resources: (1) piled up overburden during the phosphorite mining in Maardu, northern Estonia and (2) the Sillamäe radioactive waste depository in north-eastern Estonia (Figure 1).

3.3.1. Graptolite Argillite Overburden Dumps in Maardu

During the opencast mining of phosphorite in 1964–1991, some tens of millions of tons of graptolite argillite were mined from the covering layer of phosphorite ore at Maardu town, near Tallinn. As an overburden, graptolite argillite was mixed up with other overlying rocks, including carbonate rocks (limestone), sandstone, glauconite sandstone and Quaternary sediments. The material was concentrated into large waste dumps. For example, in 1989, opencast mining at Maardu was carried out on more than 6 km² [45]. The mining and processing stopped in 1991. At present, the waste dumps at Maardu contain about 73 million tons of graptolite argillite [45,46].

The average uranium contents in graptolite argillite sections in this area vary between 42 to 60 ppm, with the highest values of 300–450 ppm in some sub-layers. If taking an average of 50 ppm uranium in the waste dump, the total uranium content can be as high as 3650 tons. There are only a few thorium analyses in the area ranging from 5 to 14 ppm. The total thorium content, averaging to 10 ppm, in the waste dumps is then 730 tons. These values are not high if considering the waste as a natural rock; however, these dumps are an environmental concern.

Under normal weathering conditions, the graptolite argillite is easily oxidized, and spontaneous combustion can happen. In some places at Maardu, the temperatures in the heap occasionally exceeded 500 °C [45]. It has been noticed that spontaneous combustion can occur in heaps that are both a few months as well as over 30 years old leading to the conclusion that some old heaps can still be dangerous. These processes lead to an annual leaching of 1500 tons of mineral matter per square kilometer of a waste dump and the wastewater being discharged into the Maardu lake nearby [47]. The graptolite argillite is also a major source for radon (Rn) in northern Estonia. Very high radon concentrations up to 10,000 Bq/m³ have been recorded at some natural outcrops. This means that it is necessary to deal with these dumps in the near future. As graptolite argillite, apart from U, is also very enriched in several other metals (see above), one possible scenario is to extract most of the commodity metals, including uranium. A complex metal extraction may be the key to an economically feasible rehabilitation of these dumps.

3.3.2. The Radioactive Waste Depository in Sillamäe, Northeastern Estonia

The Soviet Union started uranium mining and production in the top-secret industrial town of Sillamäe, north-eastern Estonia in 1947. From 1947 to 1952, about 270,000 tons of graptolite argillite was mined from an area of 5 hectares at the coastal cliff at Türsamäe, near Sillamäe. The uranium beneficiation plant in Sillamäe was established in 1948 and about 22.5 tons of elemental uranium was produced from Estonian graptolite argillite.

The technology was primitive and provided only about 50% U recovery, as a result, a large part of the uranium was left in the solid waste. This production was found to be inefficient and the factory switched to other raw materials in 1950, but the uranium beneficiation process was stopped completely only in 1989 [48].

From 1971 to 1989, pre-processed uranium ore was imported. The estimated amount of elementary uranium in the U₃O₈ concentrate produced was 74,000 tons. Additionally, from 1982 to 1989, 1350 tons of UO₂, containing 40–80% uranium, was imported to Estonia. In 1970, the processing of loparite, obtained from the Kola Peninsula, commenced. Loparite has high concentrations of tantalum, niobium and other metals, but also yielding uranium and thorium. It also contains rare earth metals, which were left in the waste at the beginning of the processing. Vast amounts of different ore and concentrates ended up as waste rock that was collected in the waste depository near Sillamäe, close to the coast of the Gulf of Finland.

After uranium processing ceased in Estonian in 1989, industrial activity at Sillamäe experienced a significant decline throughout the 1990s. Finally, the Sillamäe plant was privatized in 1997 to form a company “AS Silmet”, which continued to produce rare metals (tantalum, niobium) and rare earth metal products. The plant—now named Neo Performance Materials Silmet AS—remains the top world producer of niobium and tantalum products including hydroxides, oxides, various grades of metal,

metal hydrides, metal powders and NbNi alloy. Among rare earth element products are lanthanum, cerium, praseodymium, neodymium and samarium–europium–gadolinium carbonates, oxides, metals, chloride and nitrate solutions.

It has been estimated that the Sillamäe radioactive waste depository contains about 4–6 million tons of uranium processing residuals, 1.5 million tons of oil–shale ash and waste from processing about 140,000 tons of loparite [8]. Calculations show that the remediated depository contains 1200 tons of uranium, 800 tons of thorium and 4.4×10^{15} Bq (1.2×10^5 Ci) of naturally occurring radionuclides (decay products of U and Th) of which about 3×10^{14} Bq (7000 Ci) is ^{226}Ra [8].

4. Discussion

4.1. Metals in Graptolite Argillite

The vertical and lateral geochemical heterogeneity in the Estonian graptolite argillite (GA) has not been well understood, particularly the scale of the heterogeneity and specific distribution patterns of elements. Recently, a study on vertical geochemical heterogeneity based on two cross-sections has shown distinctive differences between the eastern and western parts of the GA [23]. The previous geochemical explorations revealed that the studied sequences demonstrate pronounced vertical variations in U, V, Mo, Zn and other element concentrations. A common distinctive feature of the sections is the occurrence of the highest concentrations of the elements in the lower half of the section.

Trace metal enrichment in black shales is mostly explained by two alternative theories: (1) syn-sedimentary sequestration of metals under oxygen-deficient conditions from marine water, e.g., [49,50] or (2) flushing the sediments by metal-enriched syngenetic brines or contemporaneous exhalation of such brines into marine basin, e.g., references [51–53]; however, these theories are challenged by works that underline the influence of source rocks and particulate precursor material on the final character of metal enrichment in black shales, or the crucial role of diagenetic redistribution processes induced by late diagenetic brines. Johnson et al. [54] proposed, based on complex stable isotope and pyrite geochemical data, that the preeminent source of metals in black shales globally could be terrigenous rocks after all, but their hypothesis brings in the possibility that very high oxygenation of the atmosphere promoted substantial oxidation of terrigenous material that in turn released metals into oceans. If true, these re-occurring events must have taken place together with widespread, but timely constrained (global) marine anoxia, which allowed the fixation of (redox-sensitive) metals into black shale sediments.

In general, U-Mo-V-Pb-(Co) enriched trace metal association with sporadically elevated concentrations of some other trace elements were detected in GA from Saka (east) and Pakri (west) sections (Table 2) and in regional EW and NS profiles (Figure 12). The U-enriched bottom part of GA can be well followed in the western part of the country, whereas in the east, where the most important phosphorite deposits are situated, its distribution becomes more heterogeneous.

Most of the highly enriched trace metals in GA as well as other abundant trace elements, like As, Sb, Ni, Cu and Re, belong to the group of the redox-sensitive and/or stable sulfide-forming metals and might undergo considerable partitioning in marine geochemical and biogeochemical cycles. As indicated by the studies of trace elements in modern marine environments e.g., [55–57], the redox-sensitive elements mostly occur as soluble species under oxidizing conditions. Under the oxygen-depleted conditions, however, the redox-sensitive elements typically are present via insoluble species (metal-organic complexes, sulfides, metal oxyhydrates, etc.) and thus tend to sequester into sediments. The whole metal trapping process is strongly linked with organic matter breakdown and sulfate reduction processes, which inhibit the crystallization of sulfides.

Based on comparative studies of trace element accumulation in modern and ancient organic-rich sediments (e.g., [23,58,59]) it has been suggested that oxygen availability in the sedimentary environment could have had major control over the development of enriched trace metal associations in different black shales.

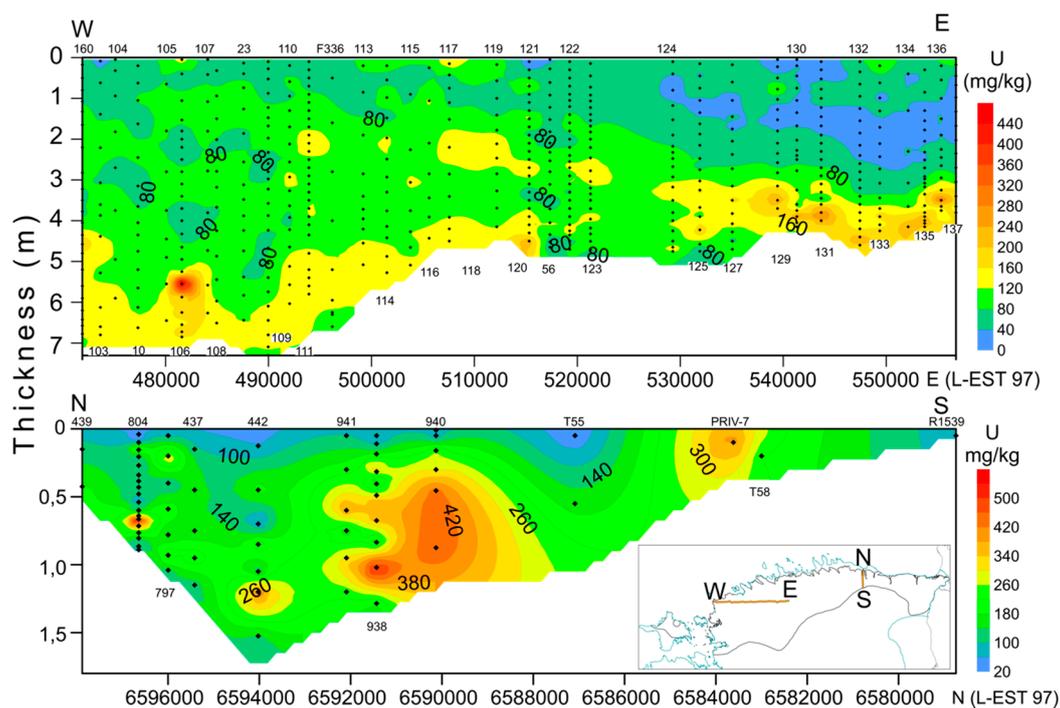


Figure 12. West–East and North–South geochemical profiles across the graptolite argillite area of Estonia. Dots indicate samples. Note the large heterogeneity of uranium concentrations.

In general, the dominance of common marine redox-sensitive elements among enriched metals in GA favors syngenetic enrichment as the major process of trace metal sequestration. On the other hand, the remarkably high concentration of enriched elements in GA and the lack of clear spatial covariance patterns imply that element sequestration solely from seawater due to Eh gradients is likely an insufficient model for explaining the observed large-scale trace metal heterogeneity in GA [23]. The common distinctive feature of sections is the occurrence of the highest concentrations of enriched elements in the lower half of the complex; however, the considered trace metals do not show linear covariance patterns and the maximum (and minimum) enrichment intervals of different enriched components mostly do not overlap. In the case of the Pakri GA sequence, one can separate about 1.3 m thick lower part, which is enriched with some trace metals like Mo, U and Sb, and also contains more organic matter as indicated by higher LOI 500 °C values.

While Mo gradually decreases towards the upper part of the Pakri sequence, U and V contents are somewhat more erratic. Box plots as well as distribution histograms in Figure 13 clearly show that U, V, Mo and TOC are always more concentrated in the lower part of the north-western Estonian GA bed. The thinner GA complex from Saka, which on average contains more Mo, U and V than the Pakri GA, is also characterized by the larger variance of those elements. In Saka samples, no clear vertical distribution trends of Mo and U can be followed, the concentrations fluctuate in a large scale and very high values alternate with low ones.

These results agree with the observation that V, U and Mo content in black shales typically correlates with the abundance of organic matter (Figure 13), likely indicating early fixation via metal–organic complexes. Previous studies have suggested that ~30% of the uranium in GA is associated with organic matter, 30% with phosphate, another ~30% with clay phases and about 6% with pyrite [60]; however, recent microanalyses have revealed a mainly bimodal distribution of U only between organic matrix and phosphate phases, while adsorption onto organic matter is assumed the primary occurrence form [61].

Bimodal character of U occurrence is also reflected in bulk geochemistry, whereas the association of U with TOC is stronger in the upper GA bed and association with P, on the other hand, is stronger in

the lower bed (Figure 13). The correlation coefficient is somewhat biased from the occasional distinctly high P concentrations, but the simultaneously occurring highest U values (>200 ppm U) are again speaking in the favor of phosphate-associated U in the lower GA bed. Generally, the relationship of U is the highest with Mo (U-Mo biplot in Figure 13), quantified by a correlation coefficient of 0.83 in the upper GA bed.

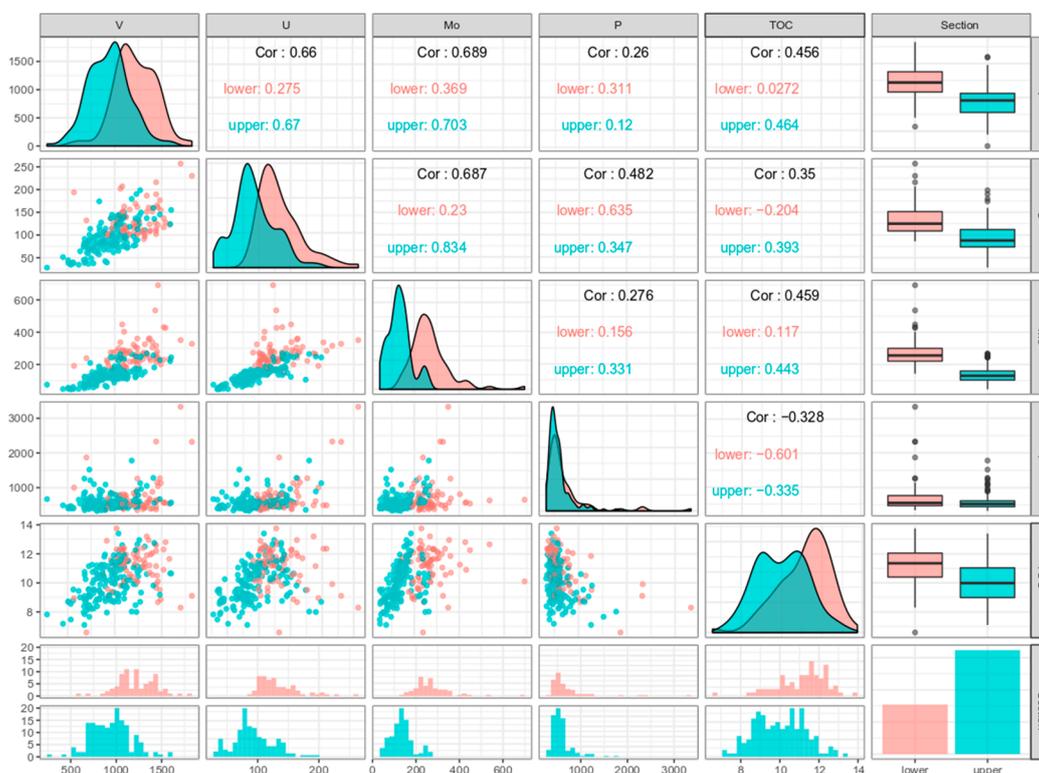


Figure 13. Associations of U in black shale with other redox-sensitive elements, P and total organic carbon (TOC). The division is made between the upper and lower bed. Based on core material originating from NW Estonia, no of observations 239 [38].

Complex research on GA geochemistry and pyrite trace elements by laser ablation ICP-MS in Pakri outcrop (western Estonia) revealed that Th is mostly associated with pyrite and again, is most abundant in pyrite of the lower part of GA, averaging at about 200 ppm Th. Simultaneously, the variance of Th concentrations is the highest in the lowest section. Thorium is thus clearly enriched in pyrite compared to bulk rock [54,62]. Since pyrite formation seems to be mainly associated with bacterial sulfate reduction (negative $\delta^{34}\text{S}$), Th could also be captured from the seawater during pyrite formation; but again, the high variance of this metal concentration remains unanswered.

The organic-rich black shale, from which Estonian graptolite argillite is just a part of, is covering a large area of Baltoscandia and Fennoscandia (Figure 14). It was formed in proximal settings of Baltic Palaeobasin in Early Ordovician in times when Baltica was located around 40–50 degrees at southern latitudes [63,64]. On the regional scale, these black shales form a patchy, but vast Middle Cambrian–Lower Ordovician black shale belt in the Baltoscandian region stretching east–west from Lake Onega to the Jutland peninsula. Originally it has accumulated in a large exceptionally flat-floored epeiric sea, which has now been tectonically disturbed, especially in the northern sections (Figure 14). Even the black shale in Sweden (known as Alum Shale) has historically been used mostly for uranium production, there are rising commercial interests in other metals. As the resource is vast in tonnage and geographical scale, the black shales should be considered as a possible future resource for several metals, apart from uranium. Thus, the Estonian graptolite argillite together with the Swedish Alum Shale may be the largest European reserve for uranium.

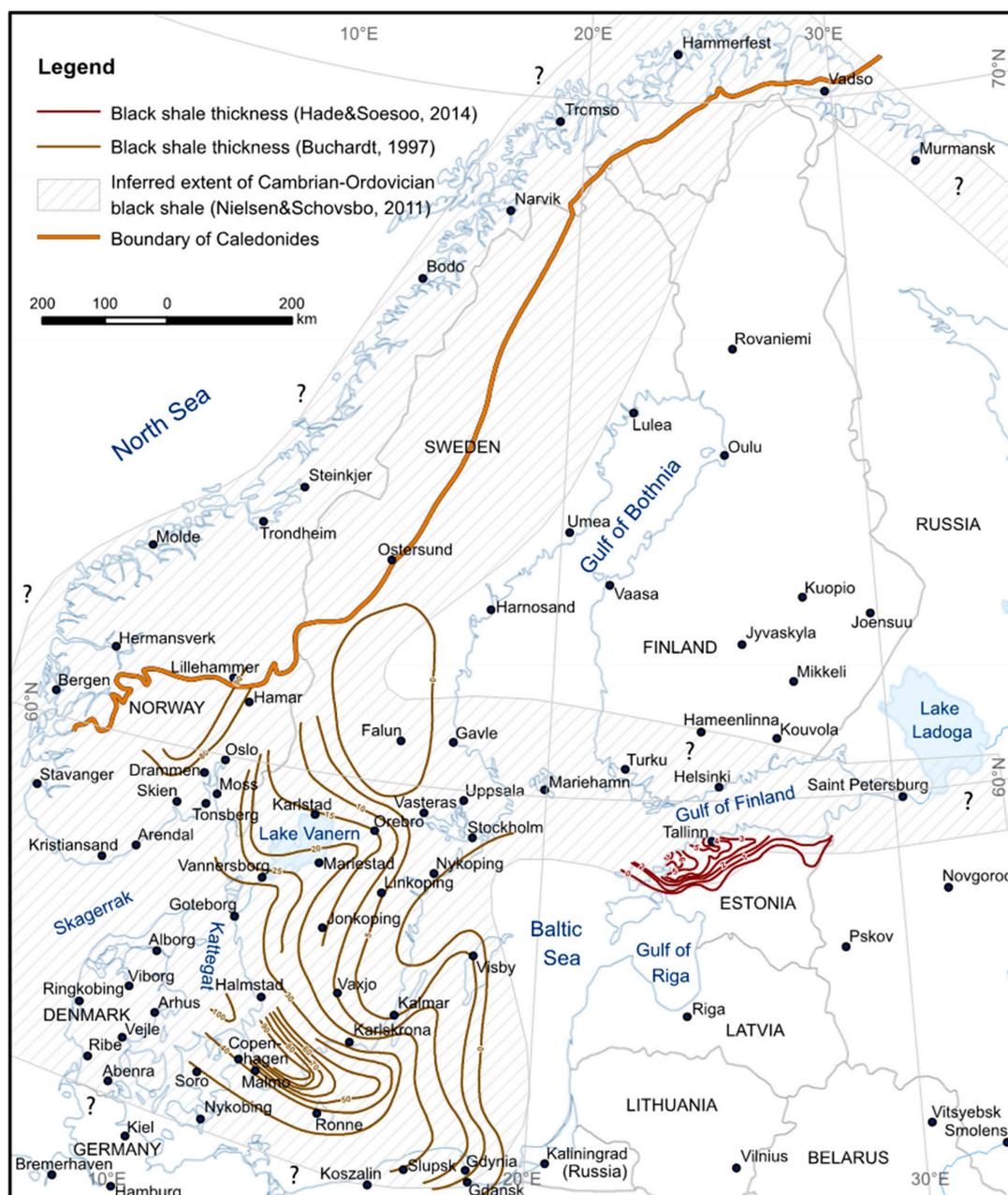


Figure 14. The extent of Cambrian–Ordovician black shale (Alum shale, graptolite argillite and Dictyonema shale) in Fennoscandia and Baltoscandia [2,65,66].

4.2. Metals in Phosphorite

The Estonian phosphorite is a European-scale phosphorus reserve. At the same time, high REE enrichment makes it attractive for REE production, which in turn will put a focus on a number of environmentally hazardous elements, including uranium and thorium. Even if Estonian sedimentary phosphorite has low concentrations of U and Th, its processing might concentrate radionuclides into main or by-products depending on the chosen technological flowsheet, and therefore might result in the generation of Technologically Enhanced Naturally Occurring Radioactive Materials (TENORM). It would be beneficial to consider the extraction of U along with phosphate products as this would leave behind less environmentally hazardous by-products. It is likely, if the decision is made to utilize the Estonian phosphate ore, uranium and thorium cannot be dumped into the waste piles, instead they would be extracted as co-products.

The presently determined variability of REE and U in the Estonian phosphorites cannot easily be explained. As the recent lingulates are commonly not rich in trace elements, including uranium and REEs (below or a few ppm), later processes will be a likely cause for the metal enrichment in the phosphorites. According to the current understanding, the high and very heterogeneous concentrations of metals are the result of post-depositional diagenetic processes; however, geological processes and other conditions (pH, Eh, etc.) need further detailed studies. Although the phosphate raw ore beneficiation (separating shells from sandstone) and phosphorous extraction are technologically feasible, the technology for REE and uranium extraction in parallel with the phosphorous acid production needs further technological developments. From the perspective of creating marketable by-products from phosphorite trace constituents, the northern part of the Toolse deposit seems to be attractive due to relatively higher contents of U as well as total REEs compared to the Rakvere deposit; however, the total resources of U and REEs seem to be greater in the Rakvere deposit and its individual blocks as phosphorite bed is thicker in there.

Relying on the vast phosphorite reserves in Estonia, the critical nature of both the phosphorus and REEs for the European economy and security, it may be a worthwhile opportunity to develop these resources into production at the European scale. It is important to note that due to the neighboring geological positions in cross-section of the black shale and phosphorite, the future mining activity can be complex. There are no easy extraction technologies that can be applied on only one of those resources separately. Both the graptolite argillite and phosphorite need to be treated as a complex multi-resource.

5. Conclusions

Regarding uranium and thorium, three possible rock types/resources can be in focus in Estonia: Ordovician black shales, Cambrian–Ordovician phosphorites and two sites with secondary resources (tailings). Due to the neighboring geological positions the black shale and phosphorite can be treated as a complex multi-resource, possibly at the continental scale. Because of mining technologies and environmental concerns, these resources can be most likely mined simultaneously.

About 60 billion tons of Estonian black shale contain 5.666 million tons of U, 16.533 million tons of Zn, 12.762 million tons of Mo, 47.754 million tons of V and at least 0.213 million tons of Th.

Estonian phosphate resources are estimated to be more than 800 million tons of P₂O₅ or 3 billion metric tons as phosphate ore. The phosphorite contains in large quantities rare earth elements, in smaller quantities uranium and thorium. Perspective uranium resources associated with phosphorite are calculated to be in between 147,000 to 175,000 tons. Considering future possible mining operations with an annual production of 5 Mt tons of ore—about 120 tons of uranium and 27 tons of thorium could be extracted as a co-product together with 720 to 900 tons of total REEs.

The mining waste dump at the Maardu town contains at least 3650 tons of U and 730 tons of Th. The Sillamäe radioactive waste depository contains about 1200 tons of U and 800 tons of Th.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

Table A1. Phosphorite (P₂O₅ in Mt) and associated element resources in different Estonian deposits. Adapted from reference [4].

Reserve Type	Reserves of P ₂ O ₅ (Mt)					Element Ratios					Resources of Minor Components, Mt				
	Proven	Probable	Inferred P ₂ O ₅ (Mt)	Sum of reserves and inferred resource P ₂ O ₅ (Mt)	Average concentration of P ₂ O ₅	F/P ₂ O ₅	Sr/P ₂ O ₅	TR ₂ O ₃ /P ₂ O ₅	Y ₂ O ₃ /P ₂ O ₅	U/P ₂ O ₅	F	Sr	TR ₂ O ₃	Y ₂ O ₃	U
Toolse	27.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Toolse	-	14.2	-	41.5	10.4	0.093	0.0138	0.007	0.00178	0.0002	3.86	0.573	0.29	0.074	0.0083
Aseri	22.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Aseri	-	4.5	-	26.9	8.7	0.093	0.0138	0.007	0.00178	0.0002	2.502	0.371	0.188	0.048	0.0053
Southern Maardu	-	-	137	137	8.7	0.081	0.0138	0.007	0.00178	0.0002	11.097	1.891	0.959	0.244	0.0274
Rakvere, including:	-	-	-	675	-	-	-	-	-	-	68.946	9.295	3.408	0.846	0.1343
(a) Rägavere	188.1	-	-	188.1	9.4	0.093	0.0138	0.007	0.00178	0.0002	17.493	2.596	1.317	0.335	0.0376
(b) Western locality	-	-	69.8	69.8	7.9	0.093	0.0138	0.007	0.00178	0.0002	6.491	0.963	0.489	0.124	0.014
(c) Assamalla	-	-	185.7	185.7	9.6	0.087	0.0111	0.0031	0.00075	0.00016	16.156	2.061	0.576	0.139	0.0297
(d) South-Eastern locality	-	-	143	143	8.5	0.087	0.0111	0.0031	0.00075	0.00016	12.441	1.587	0.443	0.107	0.0229
(e) Kabala, including:	188.1	-	-	188.1	12.3	0.087	0.0111	0.0031	0.00075	0.00016	16.265	2.088	0.583	0.141	0.0301
Western Kabala	113	-	-	113	14	0.087	0.0111	0.031	0.00075	0.00016	9.831	1.254	0.35	0.085	0.0181
Total	-	-	-	675	-	-	-	-	-	-	86.405	12.127	4.845	1.212	0.1753

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