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BLACK SHALE OF ESTONIA: MOVING TOWARDS A FENNOSCANDIAN-BALTOSCANDIAN DATABASE

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The occurrences of Cambro-Ordovician organic-rich black shale and their metamorphosed Precambrian and Lower Palaeozoic analogues have been known in Fennoscandia for a long time. These rocks show high concentrations of U, Mo, V, Zn, Pb, Ni and other metals. For example, Estonian uranium reserves have been estimated at 6.6 million tons (U_3O_8). Apart from commercial interest, there are environmental aspects related to black shale. Early mining in Sweden and Estonia caused significant damage to environment. Black shale emanates radon, and the weathering of shale releases harmful elements into the soil and groundwater. As the Fennoscandian and Baltoscandian black shale provides a large lithological and geochemical variety of shale and meta-shale, there is need for a new and updated assessment and re-evaluation of this resource. Our proposal is to feed geological, geochemical and environmental information into the Fennoscandian-Baltoscandian Black Shale Database (FBSD) with browser-based visualization possibilities. The database gathers data on both Paleozoic and Precambrian rocks, and includes shale stratigraphy, resource, metal/element distribution, environmental impact assessment, soil and groundwater impact, etc. Some visualizations have been presented using Estonian graptolite argillites as an example.

K e y w o r d s: black shale, graptolite argillite, resource, Estonia, Fennoscandia, database.

А. Соесоо, С. Хаде. ЧЕРНЫЙ СЛАНЕЦ В ЭСТОНИИ: НА ПУТИ К СОЗДАНИЮ ФЕННОСКАНДИНАВСКО-БАЛТОСКАНДИНАВСКОЙ БАЗЫ ДАННЫХ

Проявления кембро-ордовикского обогащенного органическими веществами черного сланца и их метаморфизованные докембрийские и нижнепалеозойские аналоги давно известны в Фенноскандии. Для этих пород характерны высокие концентрации U, Mo, V, Zn, Pb, Ni и других металлов. К примеру, запасы урана в Эстонии оцениваются в 6,6 млн тонн (U_3O_8). Кроме коммерческого интереса с черным сланцем связаны и экологические проблемы. Ранняя добыча в Швеции и Эстонии нанесла серьезный вред окружающей среде. Черный сланец излучает радон, а при выветривании черного сланца высвобождаются вредные элементы, которые попадают в почву и грунтовые воды. Поскольку черный сланец Фенноскандии и Балтоскандии представляет собой сланцы и метасланцы с разнообразными литологическими и геохимическими характеристиками, необходимо уточнить его ресурсы. Мы предлагаем создать Базу данных по черному сланцу Фенноскандии-Балтоскандии с геологической, геохимической и экологической информацией. В эту базу данных заносятся данные по палеозойским и докембрийским породам, включая такие характеристики сланцев, как стратиграфия, ресурсы, распределение металлов/элементов, оценка воздействия на окружающую среду, влияние на почвы и грунтовые воды и т. д. Представлены некоторые визуализации на примере граптолитовых аргиллитов Эстонии.

К л ю ч е в ы е с л о в а: черный сланец, граптолитовый аргиллит, ресурсы, Эстония, Фенноскандия, база данных.

Introduction

Shale is usually a fine-grained sedimentary rock containing organic matter and silt- and clay-size mineral grains that have accumulated together. Shale is characterized by fissility – it breaks along thin laminae, parallel layering or bedding texture that is less than one centimeter in thickness. Black shale commonly forms in anoxic or low oxygen conditions and contains unoxidized carbon and iron sulfides such as pyrite. Minor amounts of authigenic carbonate minerals, either dispersed in cements or in concretions, are characteristic features of many black shale units. Most black shale is marine in nature and may have areal extents of thousands of square kilometers. It typically requires conditions that are conducive to the accumulation of large quantities of organic matter, as well as slow accumulation rates to prevent the dilution of the accumulating metals. Metals may be derived from seawater, either directly or via pre-concentration in planktonic organisms. Unusual circulation patterns and volcanic ash deposition may enhance metal enrichments. There is currently no consensus on the source of metals and the genesis of black shale. It is plausible that several sources and mechanisms may be responsible in different black shale formations. Black shale is common in many Palaeozoic and Mesozoic strata worldwide including Fennoscandia and Baltoscandia. Black shale commonly contains abundant heavy and other metals. Its units may have beds enriched in metals by factors much greater than 50 for Ag, for example, and greater than 10 for Mo [Krauskopf, 1955]. Such increased concentrations of Ag, Mo, Zn, Ni, Cu, Cr, V, and less commonly Co, Se, and U are conspicuous features of only some black shale [Vine and Tourtelot, 1970]. There are black shales that are quite enriched in uranium, for example, the Estonian graptolite argillites and Swedish Alum shale are the main future resource of uranium for Europe.

Black shale as a metal resource

Organic carbon-rich black shale has long been studied regarding the industrial interest in a variety of transition metals, especially Mo, Zn, Ni, Cu, Cr, V, Co, Pb, U, and Ag. These studies reveal a variety of metal sulfides in shale, and suggest that sulfide minerals are an integral part of the sediment diagenesis [e. g. Amstutz and Park, 1971; Vulimiri and Cheney, 1980; Hofmann, 1989; Schieber, 1991].

Besides these widespread, but low-grade metal deposits, shale is also host to some of the world's largest economic deposits of copper, lead, and zinc. For example, the Kupferschiefer in Central Europe is probably one of the most well-known occurrences. Mined since the Middle Ages, the mining in Germany continued until very recently [e.g. Jung and Knitschke, 1976], and still continues in Poland. Although generally very thin, the Upper Permian Kuperschiefer is a transgressive black shale deposit that extends from Poland to Britain and covers an area in excess of 600,000 km^2. Somewhat less extensive, and much less mined, black shale extends from the Syas River in Russia to Estonia, Sweden and to southern, central and northern Norway.

These occurrences of Middle Cambrian to Late Ordovician organic-rich black shale deposits in an extensive area of Sweden [Alum shale; Andersson et al., 1985], the Oslo region [Henningsmoen, 1960], Bornholm [Poulsen, 1966], Estonia (known as graptolite argillite or "Dictyonema shale" [Männil, 1966], and kukersite as proper oil shale), Poland [Szymariski, 1973] and northwest Russia [Baturin and Ilyin, 2013] have been known for a long time. The 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 REE, Cd, Au, Sb, As, Pt [Voolma et al., 2013; Hade and Soesoo, submitted]. The beds have historically been exploited for local uranium production in Sweden and Estonia. Kerogen in the black shale is of algal origin and the content of total organic carbon is mostly between 10–25 wt % [Andersson et al., 1985]. The mineral matter of the black shale is dominated by clay minerals, illite-smectite and illite [Pukkonen and Rammo, 1992; Lindgreen et al., 2000]. 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 [Andersson et al., 1985] – Baltoscandia and Fennoscandia. A possible spatial continuity of those complexes are the graphitic phyllites that are found in the tectonically disrupted allochtonous and autochtonous Caledonian complexes in central and northern Sweden and Norway [Sundblad and Gee, 1985]. The metal-enriched phyllites exhibit geochemical signatures similar to the unmetamorphosed black shale of Baltoscandia [Sundblad and Gee, 1985]. These geochemical similarities suggest that organic-rich mud might have accumulated over a wide geographic area and under fairly different depositional conditions – from pericratonic shallow marine settings to continental slope environments. The black shale of Fennoscandia and the graptolite argillite (GA) of Estonia can thus be treated as metal ore and a twofold energy source (including U and shale oil); the rocks have a high scientific and significant economic value.

There are many known Paleozoic black shale deposits in various basins. The Silurian Zn-Pb deposits of Howards Pass (Canada) are also located in graptolite shale and contain in excess of 100x106 metric tons of ore [Gustavson and Williams, 1981]. Devonian representatives are the well-known Zn-Pb deposits of Rammelsberg and Meggen in Germany and the Selwyn Basin Pb-Zn deposits in the Yukon Territory (Canada) [Gardner and Hutcheon, 1985].

Some black shale is significantly enriched by noble metals, sometimes coupled with Mo- and Ni-bearing shale. For example, the Lower Cambrian black shale of southern China contains up to several hundred ppb's PGE's and Au in strata deposited as individual, metal-rich sulfide layers, 2–15 cm thick [Grauch et al., 1991]. Some of these elements in the Fennoscandian-Baltoscandian black shale may be of commercial value. In many Precambrian terrains metamorphosed sedimentary rocks, which were initially black shale, are known and also provide great economic interest.

Major base metal deposits in shale also occur in the Proterozoic of Australia, North America, and Africa. In Africa, the most prominent and best known are the deposits of the Zambian Copper Belt [Fleischer et al., 1976]. In Australia, there are several Pb-Zn-Ag deposits hosted in Proterozoic shale, such as Mt. Isa, Hilton, McArthur River, and Lady Loretta [Gustavson and Williams, 1981]. In North America, the known shale-hosted mineral deposits of Proterozoic age include the White Pine copper deposit in Michigan and the Sullivan Pb-Zn deposit in British Columbia [Gustavson and Williams, 1981].

The Fennoscandian Shield provides several good examples of metamorphosed metal-rich black shale of the Precambrian age [Yudovich and Ketris, 1988; Arkimaa et al., 1999]. A few are in active mining operation, several in exploration stage and many waiting to be discovered and exploited. The Talvivaara mine in Finland, with more than one-billion-ton resource, has been in production since 2008, by Talvivaara Mining Company Plc, and is the first mining operation collectively recovering NiCoCuZn(Mn)(U) by bioheapleaching polymetallic black shale. In the Viken area, Sweden, Continental Precious Minerals Inc. has estimated the uranium resource to be 1.05 billion lbs. of U_3O_8 in Alum shale and large amount of other metals.

The Geological Survey of Finland has compiled a distribution map of Precambrian black shale in Finland, based on magnetic and apparent resistivity datasets [Arkimaa et al., 1999]. An extensive study of the Paleozoic Alum shale has previously been conducted in Sweden. The Geological Survey of Norway is compiling information about various aspects of black shale in the country. Russian scientists have also conducted drilling and studies of black shale (graptolite argillites) in the Leningrad oblast area. In Estonia, a compilation of existing and new geochemical studies has resulted in distribution maps of some elements and elemental resource calculation [see Hade and Soesoo, submitted; Voolma et al., 2013]. These results will be briefly presented here.

Apart from the commercial value of ore, there is another important aspect related to black shale – the environmental one. It has been known for a long time that the early mining in Sweden and Estonia has caused significant damage to environment and human health. However, mining is not the only cause of environmental impact. On or near the surface sedimentary black shale emanates radon, weathering of shale releases harmful elements into the soil and groundwater, and so on. It is only recently that we have started comprehending all the possible negative impacts related to this type of organic- and metal-rich shale. It is also important to note that metamorphosed Precambrian black shale also has an environmental impact – even if it is not mined. This sulfide-rich black shale weathers more easily and thus releases more harmful elements than most of types of rock in the Fennoscandian Shield. For example, a study of a small lake in a black shale area in Finland indicated that it has been acidified for 9,000 years already [Loukola-Ruskeeniemi et al., 1998].

Since the Fennoscandian Shield and Paleozoic Baltoscandia provide a large variety of black shale, with different genetic characteristics and metal, sulfur and carbon occurrences, and different environmental aspects, there is a need for a new and updated assessment and re-evaluation of this resource. Data should be gathered on both Paleozoic and Precambrian rocks and, at least, the following should be included: a) geographical/stratigraphical position and resource/reserve estimate, b) metal/element distribution, calorific value etc.; c) environmental and health impact assessment, soil and groundwater impact. The compiled data should be put in a database and visualized in geographical space, and made accessible to the public. Some black shale characteristics, in a format for the possible future database will be presented below, based on the Estonian graptolite argillite studies.

Overview of Estonian graptolite argillite (black shale)

Compared to the Fennoscandian sedimentary and metamorphic black shale, the geological position and stratigraphic characteristics of Estonian black shale are very simple. Therefore, Estonia may be a good example on which to base the future Fennoscandian-wide compilation.

Organic-rich Early Ordovician marine metalliferous black shale – graptolite argillite (GA) lies beneath most of northern Estonia (Fig. 1). Historically, it was called "Dictyonema shale", "Dictyonema argillite" or "alum shale." The word *dictyonema* came from the benthonic root-bearing *Dictyonema flabelliforme*, which subsequently turned into planktonic nema-bearing *Rhabdinopora flabelliformis* [Erdtmann, 1986]. Here the term graptolite argillite is used, while "Dictyonema shale" is still used in Russian literature.

The graptolite argillite is fine-grained, unmetamorphosed, (sub-)horizontally lying and undisturbed, organic-rich (8–20 %) lithified clay (Türisalu Formation), which is commonly 0.5 to 6 m thick and belongs to the group of black shale of sapropelic origin [Petersell, 1997; Voolma et al., 2013; Hade and Soesoo, submitted] (Fig 1, A). The graptolite argillite crops out in some places in Northern Estonia, in the klint area or in some narrow river valleys. Since the entire Estonian Lower Palaeozoic sedimentary section is inclined towards the south due to its geological position on the southern slope of Fennoscandian Shield [Soesoo et al., 2004], at the southwest end, the GA deposit lies at a depth of more than 250 meters (Fig. 1, B).

The Estonian GA is characterized by high to very high concentrations of U (up to 1200 ppm), Mo (1000 ppm), V (1600 ppm), Ni and other heavy metals, and is rich in N, S and O [Pukkonen and Rammo, 1992; Soesoo and Hade, 2012; Voolma et al., 2013]. High concentrations of certain elements may be potentially useful or hazardous. During the Soviet era, the GA was mined for uranium production at Sillamäe, in Northeast Estonia, between 1948 and 1952 [Veski and Palu, 2003]. A total of 22.5 tons of elemental uranium was produced from 272,000 tons of GA from an underground mine near Sillamäe. Between 1964 and 1991, approximately 73 million tons of GA was

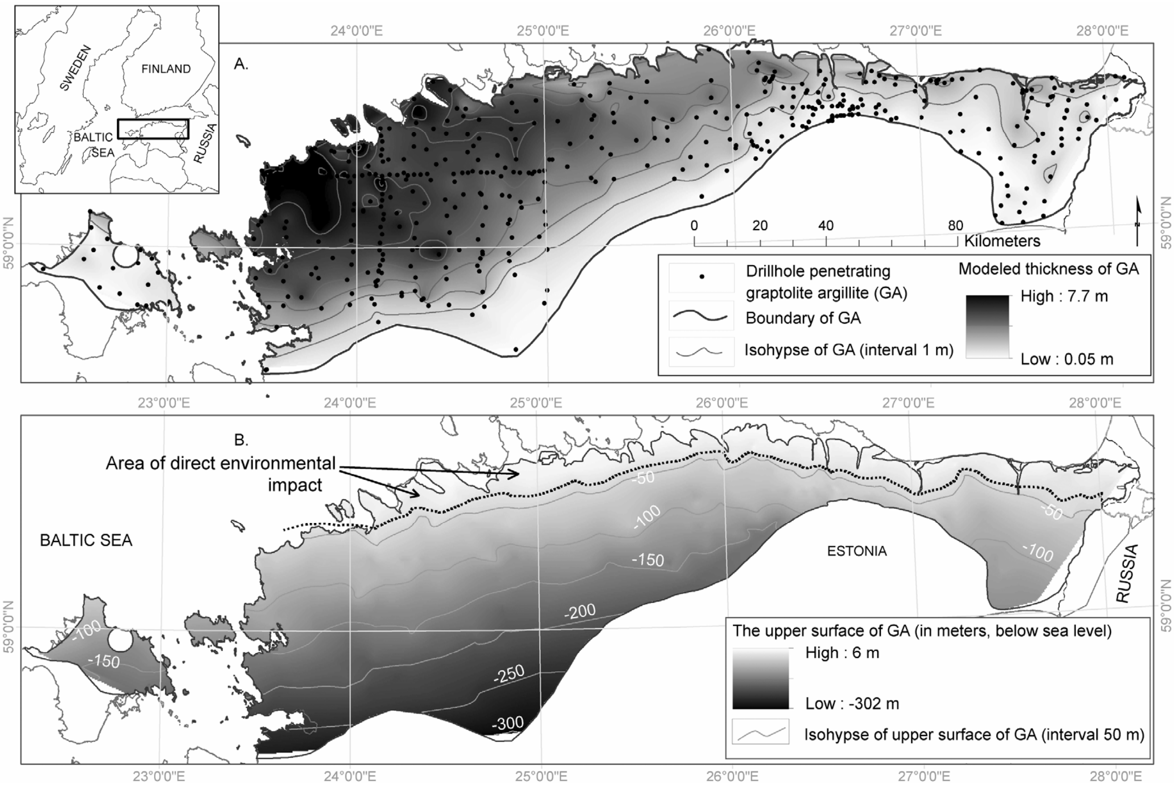

Fig. 1. A. Thickness map of the Estonian graptolite argillites and location of the drill holes penetrating argillite layers (black dots). The thickness of GA was modeled by ArcInfo 10.1, based on the studied drill holes. For creating the thickness grid, the Natural Neighbor interpolation method was used, and the grid cell size is 400 meters. B. The depth of graptolite argillite (upper surface). Due to the location in the southern margin of the Precambrian Fennoscandian Shield GA layer is dipping southwards following the regional trend. As GA crops out in Northern Estonia, direct environmental impacts result

mined from a covering layer of phosphorite ore at Maardu, near Tallinn. The GA was mixed up with other overlying deposits, such as carbonate rocks, sandstone, glauconite sandstone, and Quaternary sediments, and piled into waste heaps.

Although the reserves of GA surpass those of Estonian kukersite (oil shale), it is of a quality too poor for energy production. The GA calorific value ranges from 4.2–6.7 MJ/kg [Pukkonen and Rammo, 1992] and the Fischer Assay oil yield is 3–5 % (for Estonian kukersite, it is about 30–47 %, for example [Veski and Palu, 2003]). The moisture content of fresh GA ranges from 11.9 to 12.5 %, while average composition of the combustible part is: C – 67.6 %, H – 7.6 %, O – 18.5 %, N – 3.6 % and S – 2.6 % [Lippmaa and Maremäe, 2000]. However, considering it is a low-grade oil source, its potential oil reserves are about 2.1 billion tons [Veski and Palu, 2003]. The Fennoscandian black shale together with Estonian GA is considered to be a potential energy reserve for the future.

The specific gravity of Estonian GA mostly varies between 1800 and 2500 kg/m^3 [Petersell, 1997]. The content of pyrite in GA is also highly variable, ranging from 1.5 % to 9.0 %, but concentrated between 2.4 % and 6 %. Pyrite forms fine-crystalline disseminations, thin interlayers and concretions of different forms and sizes. The diameter of the concretions is usually 2–3 cm. Some concretions are complex in structure and contain crystals of galenite, sphalerite and calcite.

The mineral composition of GA is dominated by K-feldspar, quartz and clay minerals. In the lateral, as well as vertical, dimension, the contents of the major rock-forming minerals show slight, but pronounced variation patterns [Voolma et al., 2013]. It seems that a higher degree of sulphide mineralization within the GA is associated with the occurrence of silt interbeds. Those interbeds might also contain 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. Organic matter, constituting about 15 % to 20 % of the GA, is sapropelic in origin [Pukkonen and Rammo, 1992] and rich in N, S and O. The ratio of C and H in OM is about 9. The concentration of S ranges between 2–6 %, of which 0.6–0.8 % is comprised of organic matter, ca. 0.3 % is sulphatic, and the remaining part is sulphitic S [Petersell et al., 1981]. Based on previous geochemical exploration [Pukkonen and Rammo, 1992; Voolma et al., 2013], three geochemical zones have been distinguished in the Estonian GA – the Western, Central and Eastern zones. These zones differ mainly in the concentration of metals, but also in lithology.

Estonian graptolite argillite resources

Most of the geological information on the 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 when Estonia's phosphorite resources were prospected in the 1980s. The previous estimates of the graptolite argillite reserves in Estonia range from 60 [Petersell, 1997] to 70 billion tons [Veski and Palu, 2003] and little is known about the calculation methods and the initial data (number of drill cores, etc.) that were used. Although practically no new data have been added during the last two decades, the GIS-based methods now allow us to obtain better estimates of the total resource and metal distribution [see Hade and Soesoo, submitted]. The combined database of 468 drill cores [Estonian Geological Survey & Estonian Land Board database, see at www.maaamet.ee] has been used as the initial data. The estimated area of the Estonian GA on the mainland and islands is 12,212.64 km^2, with a corresponding volume of 31,919,259,960 m^3 [Hade and Soesoo, submitted]. For instance, Estonian oil shale – kukersite – occupies an area of 2.884 km^2, and its reserves (proven and probable) are about 5 billion tons [Kattai and Lokk, 1998]. In order to calculate the total weight of the GA, the value of the specific gravity (density) is required. It is known [Petersell, 1997] that the density of the graptolite argillite varies to a great degree, mostly between 1,800 and 2,500 kg/m^3. So, assuming an average density of 1,800 kg/m^3, the total mass of GA is about 57.45 billion tons, while in case of 2500 kg/m^3 the mass is 79.80 billion tons. Assuming the average density to be 2100 kg/m^3, the total weight of GA is about 67 billion tons, which is between the earlier estimates of 60 to 70 billion tons.

Metals in Estonian graptolite argillite

The vertical and lateral geochemical heterogeneity in the GA has not been well understood, especially the scale of the heterogeneity and specific distribution pattern of the elements. Recently, a study on vertical geochemical heterogeneity based on two cross-sections has shown distinctive differences between the eastern and western part of the GA [Voolma et al., 2013]. The previous geochemical explorations revealed that the studied sequences demonstrate pronounced vertical variations in U, V, Mo, Zn and other element concentrations. The common distinctive feature

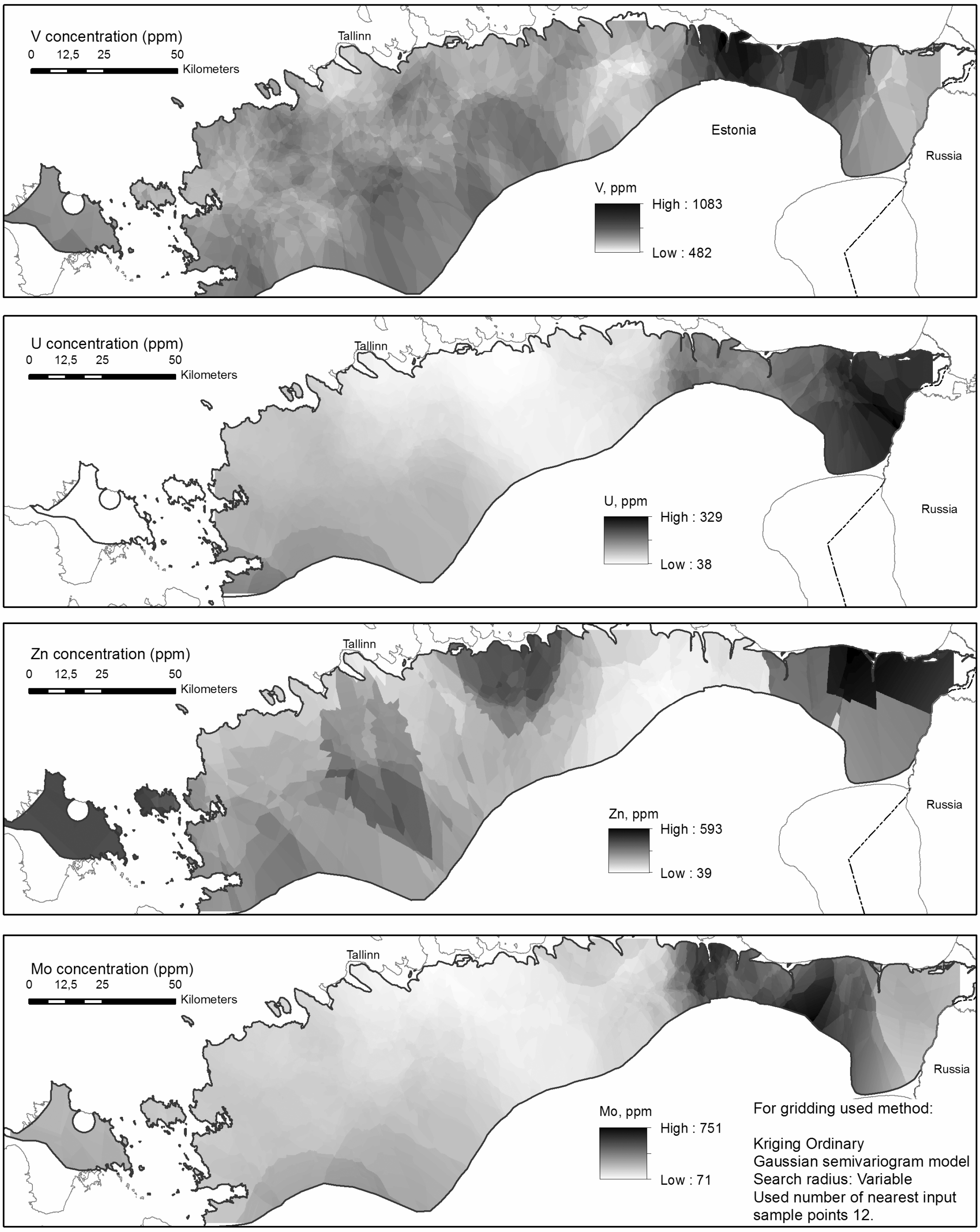

Fig. 2. Vanadium, uranium, zinc and molybdenum concentrations in the Estonian GA (in ppm) as modeled using calculated average drill core analyses. The element concentration surface was modeled with the Ordinary Kriging interpolation method using Gaussian semivariogram model (ESRI ArcInfo). Due to a small number of drill cores, U concentrations were not modeled for the western Estonian islands

of the sections is the occurrence of highest concentrations of the elements in the lower half of the section.

The distribution of U, Zn, Mo and V in the Estonian GA has been modeled and shown in Figure 2. The initial data were selected from the databases of the Geological Survey of Estonia and the Institute of Geology at TUT. These elemental concentration data represent the average concentrations in the 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 easternmost part of Estonia, while in Western Estonia the concentrations show medium values and the lowest values are characteristic of the Central Zone (Fig. 2). U distribution has not been modeled in the Estonian islands due to the small number of

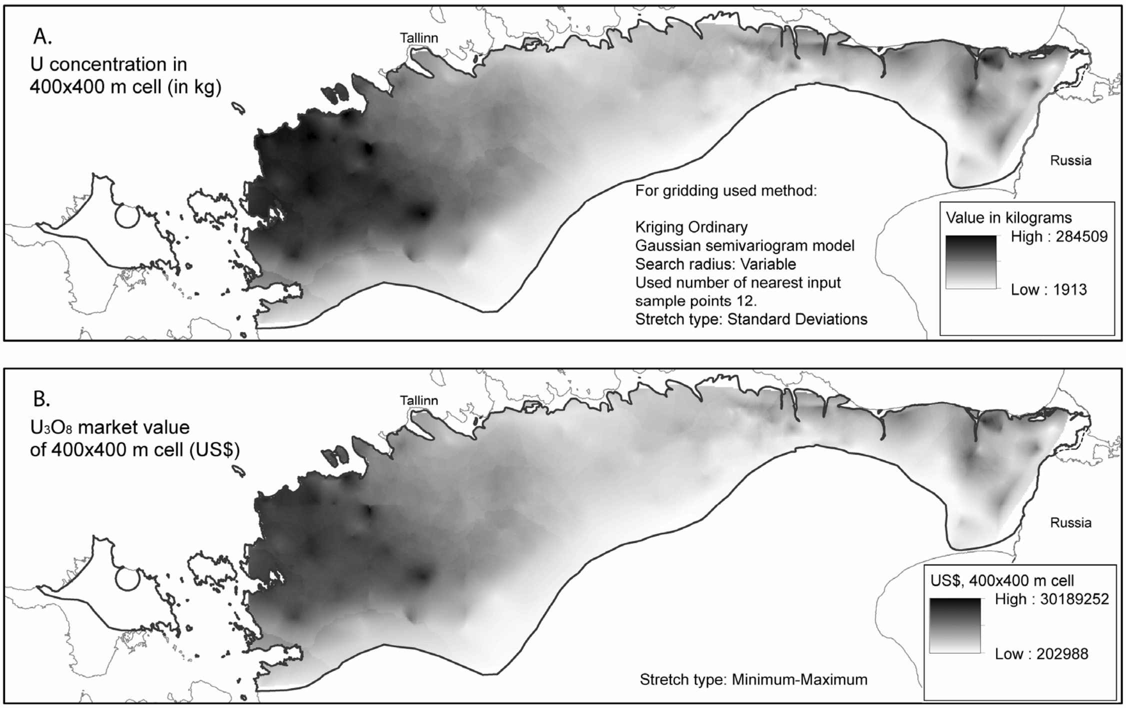

Fig. 3. A. Modeled uranium total concentrations (tonnage) in a cell of 400 m x 400 m at the thickness of the graptolite argillite. The specific gravity of GA is set at 2100 kg/m^3. Note that the highest total uranium tonnage is observed in Western Estonia (up to 285 ton per cell), while elemental concentrations in ppm are the highest in Eastern Estonia. B. The market value of uranium oxide (U_3O_8) in a cell as calculated at 90 US$ per kilogram

analyses. The high concentrations in the southwest 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 are relatively unevenly distributed across the area and the present geochemical generalization is informative, but 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 [Voolma et al., 2013]. 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 (1,190 ppm [Voolma et al., 2013]). In general, the U content of GA shows quite a strong positive correlation with the organic matter content, most likely indicating early fixation via metal-organic complexes. At the same time, no correlation of P_2O_5 with other enriched trace elements, such as U was detected.

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. As an example, the total concentration (tonnage) of uranium in the Estonian GA is shown in Figure 3. This calculation is based: 1) on the element/metal grid which shows the element distribution in ppm (e. g. Fig. 2 for U); 2) on an interpolated grid of the GA thickness, in meters; 3) by assuming the average density of the GA to be 2,100 kg/m^3; 4) since the element/metal and thickness grids were calculated with the cell size of 400 x 400 meters, the same cell size was used for the calculation of the total amount of element/metal.

The results of U tonnage (A) and market values (B) within the cell of 400 m x 400 m (at the thickness of GA in the area) are shown in Figure 3. These calculations allow for the provision of a more realistic total amount for the metal in the Estonian GA (not just based on an average concentration value in ppm). The calculated total weight of U is about 5.6656 million tons (6.6796 million tons as U_3O_8). Similarly, the calculations for some other elements are provided in the paper by Hade and Soesoo [submitted 05/2013]. Zn is as high as 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, the Central Zone, where the enrichment is the lowest, still shows high amounts of Zn. The market value of these metals is high: about US$ 460 billion for the uranium, US$ 30 billion for the zinc and about US$ 350 billion for the molybdenum, considering the average market prices in April 2013. However, since a simple, environment-friendly and economical technology has yet to be developed for the co-extraction of most of the enriched elements from GA, its economic value remains theoretical.

Health and environmental impact

Sedimentary, unmetamorphosed black shale has historically been used in Sweden and Estonia. In Sweden, the Cambrian and Lower Ordovician Alum shale has been known for more than 350 years. Mining the shale for alum began in 1630s in Skene. The Alum shale was also recognized as a source of fossil energy and, toward the end of the 1800s, attempts were made to extract and refine hydrocarbons [Andersson et al., 1985]. Before and during World War II, Alum shale was retorted for its oil, but production ceased in 1966 owing to the availability of cheaper supplies of crude petroleum. During this period, about 50 million tons of shale were mined at Kinnekulle and Närke in Sweden.

For uranium production, a pilot plant built at Kvarntorp, Sweden, produced more than 62 tons of uranium between 1950 and 1961. A small uranium mill was constructed at Ranstad and went on-stream in 1965. The plant operated at reduced capacity for 3 years producing about 300 tons of yellowcake. The Alum shale was also burned with limestone to manufacture "breeze blocks," a lightweight porous building block that was widely used in the Swedish construction industry. Production stopped when it was realized that the blocks were radioactive and emitted unacceptably high amounts of radon.

Just after World War II, due to the atomic bomb “competition”, the Soviet Union started looking for uranium deposits. The nearest place where geologists found large quantities of uranium ore (graptolite argillite) was in Northeast Estonia and the first Soviet uranium processing facility was started in a small town called Sillamäe. The plant operated as a top-secret Soviet institution until 1991.

In addition, graptolite argillite is also a co-product of phosphorite mining in Estonia, so the Maardu area near Tallinn is among the most polluted regions in Estonia [Jüriado et al., 2012]. During the opencast mining of phosphorite, radioactive GA with average uranium content of 50 to 130 ppm, and a maximum of 300–450 ppm, was deposited in waste dumps. It should be mentioned that the phosphorite in Estonia lies directly below the GA. In 1989, opencast mining at Maardu was carried out on more than 6 km^2. The mining and processing was discontinued in 1991. Today, waste hills in Maardu contain about 73 million tons of GA, which contains, with a minimum content of 30 ppm U, totally as much as 2.19 million kg of U [Jüriado et al., 2012]. This waste leaches into the surface water and groundwater.

Under normal weathering conditions GA is easily oxidizing, and spontaneous combustion can occur. In some places, for example at Maardu waste hills, in northern Estonia, the temperatures in the heap occasionally exceeded 500 °C. It is interesting to note that spontaneous combustion can occur in heaps that are a few months or over 20 years old, which leads us to the conclusion that some old heaps can still be dangerous. These processes lead to an annual leaching of 1,500 tons of mineral matter per square kilometer of a waste dump and the waste water being discharged into Lake Maardu. In 1990, at the average temperature of the heap, an estimated 520.3×10^3 tons of oxygen was spent on oxidizing the rocks buried in the heap. The amount of gases emitted from burning shale was estimated as SO_2 – 10^4 tons and CO_2 – 73.3×10^3 tons [Pihlak, 2009]. The effluent of the Maardu opencast mine and processing plant, which was directed into Muuga Bay (Gulf of Finland) delivered up to 20.18 million m^3 of water with varying levels of polluting elements each year. The amount of dissolved minerals delivered into the sea was estimated at up to 38.4×10^3 tons annually [Pihlak, 2009; Jüriado et al., 2012].

GA, if lying on or near the surface, is also a major source for radon (Rn) in Estonia and elsewhere. Very high radon concentrations of up to 10 000 Bq/m^3 have been recorded at some natural outcrops of GA in the North Estonian Klint. Radon is a highly radioactive and carcinogenic element causing mutations, especially lung cancer.

In spite of the fact that the impact of black shale on a nation’s health and biological environment is well recognized, little is being done to quantify these impacts in a real and reliable way. Moreover, only a small number of measures are being taken to avoid direct contamination of soil and groundwater and direct and indirect influences on the local people. Sometimes, contaminated black shale industrial areas are used as a political instrument in decision-making or for someone's commercial interest. In many cases, those decisions bring no real environmental improvement results.

There are areas in Estonia, Sweden and elsewhere in Fennoscandia where black shale forms the surfaces where humans live and conduct their everyday activities, thus directly influencing health and well-being. For example, there are a number of towns in northern Estonia which are located in the area where graptolite argillite crops out, including the capital Tallinn, Paldiski, Kunda, Aseri and others. In Sweden, in the focus for the current interest in Alum shale mining is the Östersund area, where people have historically lived on the top of black shale. These influences need to be quantified and measures taken to minimize negative health and environmental impacts. However, as nations depend on mining and metal/electronics industries, the need for new resources cannot be neglected and a balance must be achieved between the nation's sustainable economic development, exploitation of black shale resources and public health. A new, modern, science-based revision of black shale resources and related environments across Estonia – NW Russia – Sweden – Finland – Norway would definitely foster a better understanding of the problem, and help to create an industrially and environmentally sound expert model of the Fennoscandian and Baltoscandian black shale potential.

Moving towards a Fennoscandian-Baltoscandian Black Shale Database

Creating regional, large-scale, across-border databases is not uncommon in geology. Geological maps are the best and oldest form of such information compilation, which extend across political borders and continents. An initiative group on the Fennoscandia Metallogenic Map and Database, which involves specialists from the geological surveys and other organizations in Finland, Norway, Russia and Sweden, has been active for more than a decade. The work has resulted in well-compiled, cross-border database and a digital map (see http://en.gtk.fi/informationservices/databases/fodd/index.html).

The Fennoscandian Ore Deposit Database (FODD) is a comprehensive numerical database that includes the metallic mines, deposits and significant occurrences in Fennoscandian Shield, which could be part of the geological information compilation and standardization, and be very useful for future metal ore discoveries. The first FODD metallogenic map was published in 2009. An updated version will be available in August 2013. This database contains information on about 1,700 (June, 2013) mines, deposits and significant occurrences in Fennoscandia. The map contains 168 major metallogenic areas, of which 46 are completely or partly in Finland, 40 in Norway, 41 in Russia, and 41 in Sweden. The map includes 24 areas that cross international border (http://en.gtk.fi/informationservices). The database and map contain information on the location, mining history, tonnage and commodity grades, with comments on data quality, geological setting, age, ore mineralogy, and types of mineralization, as well as genetic models and the primary sources of data.

This range of information is also important in "mapping" black shale. Our proposal is to compile the geological, geochemical and environmental information into the Fennoscandian-Baltoscandian Black Shale Database (FBSD) with browser-based visualization possibilities for thematic maps (Fig. 4).

1. The database should include both sedimentary and metamorphosed black shale from the Precambrian and Lower Paleozoic ages. There will be some overlapping with FODD data concerning some Precambrian ores which had formerly been black shale. However, compiling Fennoscandian Precambrian and Paleozoic black shale data according to a common standard may even add some understanding of sulphide ore geology, and especially environmental conditions.

2. The data structure should include: a) location; b) geological setting and structure, body/deposit size; c) age; d) major and trace element geochemistry, calorific values; e) ore mineralogy, style of mineralization; f) tonnage and commodity grades with a comment on data quality; g) genetic models; h) groundwater and surface geology/soil and hydro-geological parameters; i) data on biological environment/harmful element assessment; j) infrastructure and population density; k) data source and l) mining history (Fig. 4).

3. The database should have GIS-based, easily browserable thematic layers allowing for the assessment of specific impacts as well as metal/element concentrations, additional resource (oil, gas, etc.) potential assessment and more.

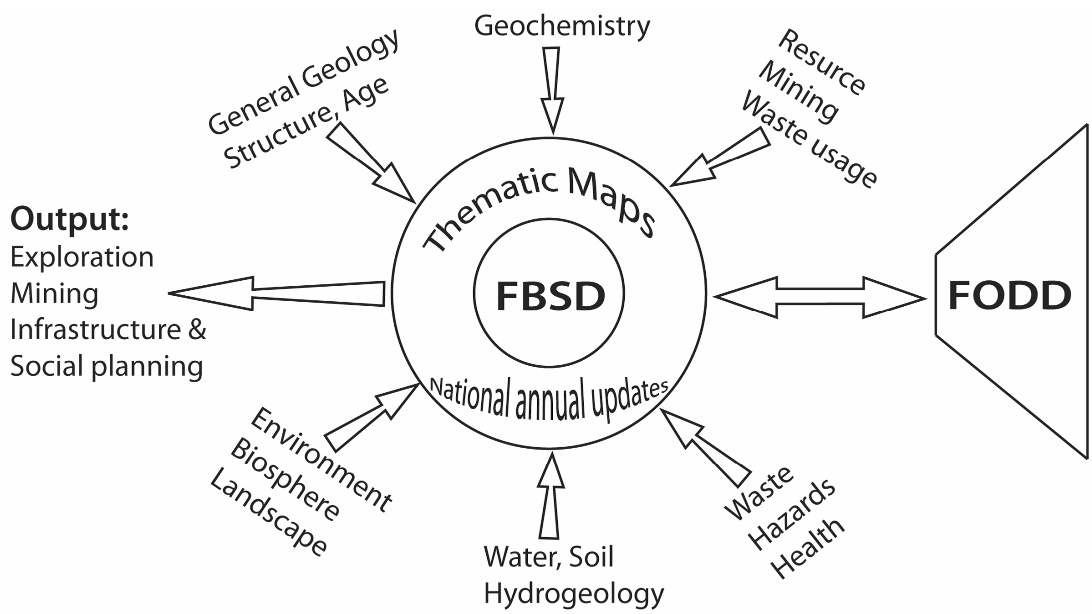

Fig. 4. A possible database (FBSD) structure, inputs and outputs of the Fennoscandian – Baltoscandian black shales database. Tight interaction with the Fennoscandian Ore Deposit Database (FODD) is envisaged

This database can then be used by a number of specialists and officials including mineral explorers and local government decision-makers for preparing environmental impact assessments, as well as in infrastructure and social development planning. This information is also very useful for public health monitoring and development.

As far as the mineral resource part is concerned, the European Commission already took steps to improve the long-term availability of raw materials through the implementation of the Raw Material Initiative in 2008. The Initiative lists fourteen economically important metals and minerals labeled as critical, that are subject to a higher risk of supply interruption (e.g. REE, PGE, Co, etc.). As some of these metals have been concentrated in black shale, black shale too could be under consideration as a source of some of the EU's critical metals in near future. Thus, the FBSD initiative could fulfill several requirements at the EU and national levels including resource, environment, public health and economy policies.

Conclusions

The occurrence of Middle Cambrian to Late 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), contain 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. So do the Precambrian metamorphic analogues of shale in Fennoscandia, some of which are being actively mined. Apart from the commercial interest in ore, there is an environmental aspect related to black shale. Mining in Sweden and Estonia has caused significant damage to the environment. Close or near-surface black shale emanates radon; weathering of shale releases harmful elements into the soil and groundwater. Some metamorphosed Precambrian black shale has an environmental impact, even without being mined. Since the Fennoscandian and Baltoscandian black shale provides a large lithological and geochemical variety of shale and meta-shale, with different genetic characteristics and metal, sulfur and carbon occurrences, and different environmental aspects, there is need for a new and updated assessment and re-evaluation of this resource.

Based on the principal structure of FODD initiative (The Fennoscandian Ore Deposit Database), our proposal is to compile cross-border (Norway, Sweden, Finland, Estonia, Russia) geological, geochemical and environmental information on black shale into the Fennoscandian-Baltoscandian Black Shale Database (FBSD) with browser-based visualization possibilities that enable the creation of thematic maps.

The FBSD database should include both sedimentary and metamorphosed black shale of the Precambrian and Lower Paleozoic age. The data structure should include: a) location; b) geological setting and structure, body/deposit size; c) age; d) major and trace element geochemistry, calorific values; e) ore mineralogy, style of mineralization; f) tonnage and commodity grades with a comment on data quality; g) genetic models; h) groundwater and surface geology/soil and hydro-geological parameters; i) data on biological environment/harmful element assessment; j) infrastructure and population density; k) data source; l) mining history. Most importantly, the database should have a GIS-based, simple, browser-accessed module in order to select information and allow for the visualized assessment of specific parameters (e.g. distribution of element X) and impacts (release of hazardous element Y into soil) as well as social, medical and environmental impact assessments.

Some geological information, as well as thematic maps (black shale thickness and depth, elemental distribution, metal market value and reserve), have been presented using the Estonian graptolite argillite as an example. The total estimated area of Estonian GA on the mainland and islands is about 12,212.64 km^2, with corresponding argillite volume of about 31,919,259,960 m^3. Assuming an average GA density of 2,100 kg/m^3, the total weight of GA is about 67 billion tons. The calculated weight of U_3O_8 is about 6.6796 million tons; ZnO is 20.5802 million tons; and MoO_3 is 19.1462 million tons. The market value of these metals is high: about € 460 billion for the uranium, € 30 billion for the zinc and about € 350 billion for the molybdenum at the average market prices in April 2013. However, since a simple, environment-friendly and economical 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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