UNKNOWN GRAPTOLITE ARGILLITE

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Extensive published literature and various presentations available in the Internet show that Estonian Graptolite Argillite is not much known among Europeans (or rest of the World).

According to the Earth's Crust Act of Estonia, mineral resources are clay, dolostone, gravel, lacustrine lime, mud, limestone, oil shale, peat, phosphate rock (phosphorite), and sand. As you see, the list does not include argillite, which has been considered as a „recource for the future".
It's often said that there are two types of oil shales in Baltic Basin: the Middle Ordovician shale named kukersite mined in the Estonia and St.Petersburg fields, and lower Ordovician shale named argillite.

The marine-type Estonian Graptolite Argillite ie GA (often named also dictyonema oil shale and dictyonema shale although argillite is not shale, i.e. metamorphosed clay, but just hardened clay) of an Early Ordovician age is a brown lithified claystone belonging to the formation of black shales of sapropelic origin[1]. The argillite correlates with the Ordovician Alum Shale of central and southern Sweden and belongs to the extensive formation of the Cambrian-Ordovician black shales extending from Lake Onega in the east to the Jutland Peninsula in the west. It occurs in most of northern Estonia on an area of about 11 000 km2 (that equals approx. quarter of the republic) and the estimated reserve is 65 billion tons.

Figure 1 Freehand drawing of argillite supplies in Estonia – deposit are marked with green line .

[1] R. VESKI; E. Palu, E. Investigation of Dictyonema oil shale and its natural and artificial transformation products by a vankrevelenogram *Oil Shale 2003* 20 (3): 265–281

The nick-name „dictyonema“ comes from ore fossils mistakenly named *Dictyonema flabelliforme,* since 1980'ies given fossils have been shown to be member of Rhabdinopora genus.

The thickness of GA decreases east- and southward, from 5–6 m in the western part of the klint until ultimately disappearing near Narva and in Central Estonia, respectively. Argillite lies at a depth of 10 to 90 m.

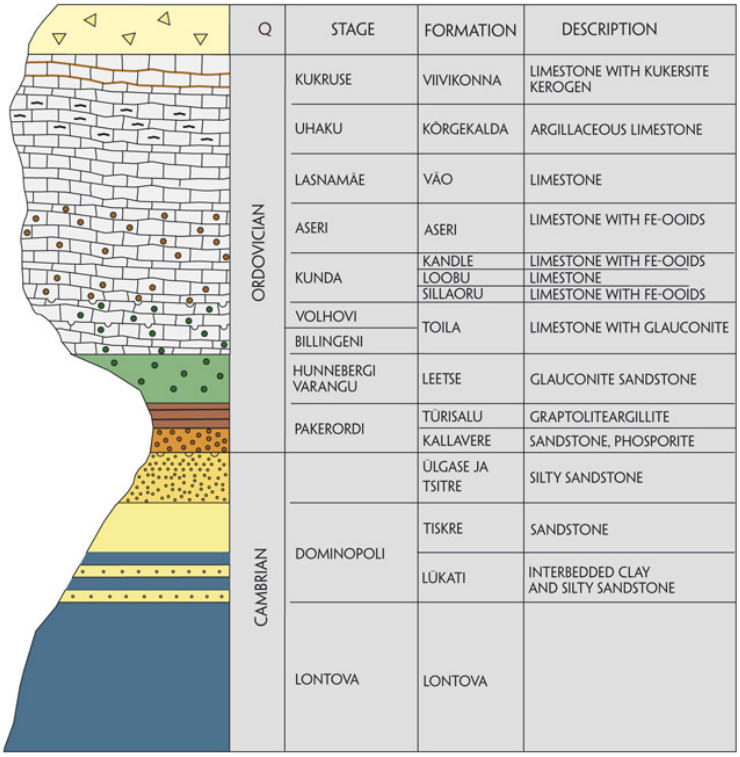

Figure 2 The layers in North Estonian Klint[2]

GA is poor in heating value (5-8 MJ/kg), oil yield (Fischer Assay) is 3-5 %, sulfur content 2-4 %. This has prevented its utilization for energy production and processing into oil[3].
GA contains 80 to 90% mineral matter and 10 to 22% (on average 15%) organic matter.

Ore deposit	OM composition, %					Heating value MJ/kg	Oil %
	C	H	N	O	S		
Oil Shale - Kukersiit	77,0	9,7	0,4	10,6	1,6	3,9	66
Graptolite Argillite	67,6	7,6	3,6	18,6	2,6	3,3	22-26
In Paldiski	72,8	7,4	2,6	17,2	?		
In Maardu	69,3	8,4	3,7	16,1	2,6		
In Ontika	58,3	5,3	2,4	34,4	?		

Table 1 Elemental composition of organics (OM), heating value and retorted oil from the OM (V.Petersell, 1992)

[2] North Estonian klint, webpage made by Ministry of Envirnment. http://www.klint.envir.ee/klint/eng/6.html
[3] M .KOEL "Estonian oil shale". *Oil Shale. A Scientific-Technical Journal* (Estonian Academy Publishers) (Extra 1999)

Element	Unit	Area				
		Western Estonia	Maardu	Toolse	Sillamäe	Ranstad*
OM	%	21,39	17,83	18,76		19.89
SiO_2	%	48,92	52,09	51,15		
Al_2O_3	%	13,09	13,09	9,76		12,47
Fe_2O_3	%	5,61	5,68	8,03	5,41	9,42
TiO_2	%	0,73	0,64	0,73	0,69	0,58
CaO	%	0,49	0,82	2,82	1,64	0,98
MgO	%	1,49	1,42	1,08	0,67	0,82
Na_2O	%	0,08	0,56	0,09	0,07	0,28
K_2O	%	7,89	7,74	5,72	6,93	4,82
P_2O_5	%	0,2	0,23	0,39		0,18
Ag	g/t	1,5	0,6	1,6	2,5	1,4
Au	g/t	0,08	0,2	0,04	0,08	
As	g/t	49	44	38	124	110
Cd	g/t	0,5	0,2	1,6	4,7	2,2
Cu	g/t	94	80	75	114	110
Mo	g/t	162	53	406	1100	340
Pb	g/t	130	98	120	400	140
Re	g/t	0,1	0,08	0,18		
Sb	g/t	11	6,4	34	37	5
Se	g/t	2,8	1,4	2,9	4,6	
Ta	g/t	2,7	2,9	2,4	2,5	
Tl	g/t	8,2	2,3	7,4	1,4	
U	g/t	86	36	162	450	300
V	g/t	724	350	1040	900	750

*Andersson, et al, 1985.

Table 2 Elements in Graptlite Argillite in different parts of Estonian deposit and in Alum Shale at Ranstad deposit (V.Petersell 2008)

The first attempts to make use of the argillite, first, as a fertilizer, were made already in the 19th century, but failed. In the northern coast of Estonia, near the islands of Pakri and in the Paldiski Bay, the argillite is covering the seabed. Waves are breaking off fractions from it, piling them up in beach ridges. The ore attracted attention also by its self-ignition. The first researcher to study this phenomenon was obviously August Mickwitz (1849 – 1910), who had studied in Tartu University and Zurich Polytechnic Institute. He has written in his notes that at the beginning of the 20th century (1909) the shale ignited in the Paldiski beach ridge and the town dwellers feared that it was a volcano[4].

[4] A. O. HASSELBATTAlbum Academicum der Kaiserlichen Universitat Dorpat. Dorpat, 1889, p. 626, (Nr. 8526).

In 1901 A.Peli, a physician from St.Petersburg, published a piece of information stating that the ore found in the Tsarskoye Selo is radioactive. Dmitri Mendeleyev, who also took up this topic, pointed out that the ground in the vicinity of St.Petersburg, dating back to the Silurian period, was radioactive and exercised a considerable influence on the growth of vegetation and the health of people.

In the early 1920s August Tammekann, who later on became a professor of geography in Tartu University, wrote rather detailed surveys on the former research work carried out in Estonia and the application possibilities for the GA – at that time mainly as a fuel or oil-production tests[5].

During the 1940ies an open mine for phosphorite was established just 14km from Tallinn and overlaying argillite was peeled and collected into dumps. As in contact with atmospheric oxygen and water, argillite is a subject of spontaneous ignition due to pyrite oxidation such open-air piles of argillite led to the release of radioactive substances and the emission of hazardous gases into the environment.

The formation of the US and the beginning of the atomic era turned a metal uranium pretty soon into the most significant strategic raw material. The nearest place to Moscow where geologists had reported to have found large quantities of uranium ore was in Northeast Estonia, and so the foundation of uranium processing facility was started in the Estonian town Sillamäe, situated on the southern coast of the Gulf of Finland, 172 km east of Tallinn and 25 km from the Russian border.

Following the classified Decree No. 1626-718cc/оп (cc/оп meaning top secret operative) of 27 July 1946 of the USSR Council of Ministers, the Head of the First Main Directorate of the USSR Ministry of Internal Affairs at the Council of Ministers issued a classified Decree No. 0282cc of 6 August 1946:

> to establish a diversified enterprise "Combine No. 7 " at Sillamae within the First Directorate of the same Main Directorate for the mining and industrial processing of the Baltic Dictyonema shale on the basis of the Glavgastopprom Oil Shale Processing Plant[6].

"Combine No. 7" was constructed by military construction units, mostly prisoners of the war and the assembly divisions of Glavpromstroi of the USSR Ministry of Internal Affairs, as ordered in the Appendix No. 2 of the Decree No. 0282cc/оп of 6 August 1946.

The first shaft of the argillite mine, situated alongside the planned uranium factory at Sillamäe, was sunk in December 1946. Deadline for the planned 400 tons daily ore capacity was 1 June 1947, when deliveries to the Narva pilot plant had to start. The mining conditions were near ideal a dry 1.15 m thick seam of argillite with 13 to 20 m of overlay.

Nevertheless, the planned production quotas were difficult to achieve in spite of the large workforce used at the building site (16,000 prisoners and convicts, and a 10,000 man forced labor unit). The workforce thus consisted of prisoners of war and criminal convicts (79%) and of soldiers serving various kinds of punishment (19%) with only 2% of free labor. Out of all these, 30% were in normal health, 60% weak and 10% very weak.

[5] A. TAMMEKANN, A. Eesti Diktuoneemakihi uurimine tema tekkimise, vanaduse, levimise ja majandusliku tahtsuse kohta. Tartu, 1924

[6] E. MAREMÄE Historical Survey of Nuclear Non-Proliferation in Estonia, 1946-1995; 2003

The Pilot Plant in Narva, founded by the Decree No. 0282cc/оп of 6 August 1946 was built round the clock from 27 November 1946 to 1 June 1947.The argillite beneficiation included crushing, sieving, classification through grading and flotation. A rotary kiln was used for thermal pretreatment and leaching could be carried out by column percolation. The end product was a concentrate of uranium salts produced through sulfuric acid or soda leaching of the as mined (unburnt) or burnt shale. The research laboratory was fairly well equipped for the mid-forties. It had all the necessary apparatus for spectral, luminescence and radiometric analysis. All operations were carried out without a waste depository, the workers and even most chemists were unaware of what they were doing (the word "uranium" was taboo) and the occupational safety was not applied.

Even though most of the USSR leading R&D centers participated in this effort, industrial uranium production from GA turned out to be both technologically possible, but at the same time economically untenable at this time.

The decree of 27 July 1946 issued by the USSR Council of Ministers ordered twelve well-known research institutions of the Soviet Union to carry out extensive research on Estonian argillite. Unfortunately the results achieved by the institutes differed widely and did not meet the expectations at all. The most important objective, extraction of uranium from the shale into the final product was, instead of the expected 70 – 80% extraction, as follows:
All-Union Institute of Mineral Raw Materials – 20%,
Scientific Research Institute No. 9 – 44%,
All-Union Scientific Research Institute of Hydrometallurgy –57%.

A year later, the second directive of the First Main Directorate was issued on 7 May 1949. It stressed the importance of developing a new technology for efficient uranium extraction from the argillite and announced unheard of bonuses, up to one million roubles for the task. The best USSR equipment and new highly qualified staff were to be provided.

Version No.	Proposal	Uranium Extraction yield, %	Calculated factory cost of 1 t uranium, thousand roubles
1	Leaching of ore using the percolation method	49	724
2	Leaching of ore in heaps on special stands or in a quarry	42	900
3	Underground leaching of argillite	34	1,010
4	Combined scheme, where 70% of the ore goes to direct percolation and 30% for leaching after roasting	59	665

Table 3 Proposals of the Leningrad Tech Institute for processing Estonian argillite (Maremäe 2003)

Much better ore was soon found elsewhere in Soviet Union and local mining operations were discontinued as of 10 June 1952. Only a very limited production (30 to 35 tons per day) remained for research purposes. The total quantity of the GA mined in 1948 – 1952 was 271,500 tons. Uranium production from this shale was 22.4 tons of elemental uranium (while the final product was 40% concentrate) The mine itself was not destroyed, but conserved for optional further use. So it has remained to this day.

In 1960 – 1963 bacterial leaching experiments with the GA were carried out at Sillamäe Factory No 7. A 50% uranium yield was achieved in a large 2,000-ton concrete percolator with up to 25 mm crushed shale. In a two-year run (23 months) in open-air heaps, and the wooden percolators with shelves and added bacterial cultures, a 55% uranium yield was achieved with up to 25 mm crushed shale, but only 33% with larger up to 50 mm material and only 1% with 100 to 200 mm lumps (18 months run). These results proved to be unsatisfactory and further studies of this extremely polluting process were discontinued.

The financing of the pilot plant at Sillamäe was terminated in 1973 and work with the graptolite argillite ceased at about the same time. All attempts to achieve reasonably good uranium (and possibly also molybdenum and vanadium) yields by native or roasted/burned shale leaching have thus failed.

Starting from the late 80'es research related to GA possibilites was considered to be senseless and therefore investigations were minimum, sampling was prohibited due to political reasons. For more than 36 years, very large reserves of easily accessible ore (in places just surface overlay over rich phosphate deposits) have remained both untouched and tempting[7].

In 2010 an accredited metagenomics testing lab BiotaTec (formely known as BiotaP) started investigating bioleaching possibilities of argillite.
In 2014 given SME won and implemented a public procurement of Enterprize Estonia addressing the bioleaching possibilities of the GA.
More than 5 years long research aiming to more efficient bioleaching technology with two phase processing resulted with patent application in 2016.
In Fall 2016 BiotaTec complied a preliminary asessment for Ministry of Envirnment about the efficiency of bioleaching GA.
Company is currently continuing the development of more cost-efficient and environmentally friendly bioleaching technology for GA.

According to Estonian Environmental Ministry web-page, it is likely, that the need for electric power in the coming decades will trigger the need to go for the uranium and other rare metals concealed in argillite[8].

[7] E. LIPPMAA, E.MAREMÄE The beginnings of uranium production in Estonia. Oil Shale 20, 2003
[8] Estonian Rocks descriptions http://www.klint.envir.ee/klint/eng/6.html

Photo 1 Klint in Paldiski peninsula

Photo 2 Black argillite sheets in Paldiski coast